

# Accurate Experimental ( $p$ , $\rho$ , $T$ ) Data for the Introduction of Hydrogen into the Natural Gas Grid (II): Thermodynamic Characterization of the Methane–Hydrogen Binary System from 240 to 350 K and Pressures up to 20 MPa

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## Abstract

Most of the experimental density data of the binary system methane–hydrogen available at the time of the development of the equation of state for natural gases and related mixtures, GERG-2008, at temperatures above 270 K were limited to hydrogen contents higher than 0.20 (amount-of-substance fraction). On the contrary, for mixtures with hydrogen contents lower than 0.20, experimental data were limited to temperatures below 270 K. This work intends to close the gap and provides accurate experimental ( $p$ ,  $\rho$ ,  $T$ ) data for three binary mixtures of methane and hydrogen: (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>), (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>), and (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>), at temperatures of (240, 250, 260, 275, 300, 325, and 350) K, thus extending the range of available experimental data to higher temperatures for mixtures with hydrogen contents lower than 0.20, and, accordingly, to lower temperatures for mixtures with hydrogen contents higher than 0.20. The density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at pressures up to 20 MPa. Experimental data were compared to the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state, respectively. The experimental data are within the uncertainty of both equations of state, except at the lower temperatures of 240 and 250 K and pressures over 14 MPa for the mixtures with a hydrogen content of 0.05 and 0.10, respectively. The virial coefficients  $B(T, x)$  and  $C(T, x)$ , as well as the second interaction virial coefficient  $B_{12}(T)$  for the methane–hydrogen binary system, were also calculated from the experimental data set at temperatures from (240 to 350) K using the virial equation of state.

Keywords: methane; hydrogen; natural gas; density; single-sinker densimeter; virial coefficients.

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## 1. Introduction

In recent years, hydrogen is being pursued as a sustainable energy carrier. The addition of hydrogen produced from renewable energy sources, such as biomass, solar or wind power, to natural gas, could significantly reduce greenhouse gas emissions.<sup>1</sup> Therefore, blending hydrogen into natural gas pipelines could path the way to a sustainable, reliable, and cost-effective future energy. The GERG-2008 equation of state (EoS)<sup>2</sup> currently serves as the ISO standard (ISO 20765-2) for the calculation of thermodynamic properties of natural gases.<sup>3</sup> The GERG-2008 EoS basically was developed from consolidated experimental data of binary combinations of the 21 constituting components. Consequently, the quality and the availability of experimental data both determine and limit the achievable accuracy of any GERG-2008 calculations. For the binary system (methane–hydrogen), a binary specified departure function was developed. However, most of the experimental density data of this particular binary system available at the time of the development of the GERG-2008 EoS were limited to temperatures above 270 K for mixtures with hydrogen contents higher than 0.20 (amount-of-substance fraction) and, accordingly, temperatures below 270 K for mixtures with hydrogen contents lower than 0.20.

This work provides accurate experimental ( $p$ ,  $\rho$ ,  $T$ ) data for three methane and hydrogen binary mixtures with nominal compositions of (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>), (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>), and (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>). Density measurements were performed by means of a single-sinker densimeter with magnetic suspension coupling at temperatures from (240 to 350) K and pressures up to 20 MPa. The experimental data were compared to the corresponding densities calculated from the GERG-2008 and the AGA8-DC92<sup>4</sup> EoS. Additionally, the second and the third virial coefficients,  $B(T, x)$  and  $C(T, x)$ , and the second interaction virial coefficients  $B_{12}(T)$  for the (CH<sub>4</sub> + H<sub>2</sub>) binary mixture were also determined at temperatures ranging from (240 to 350) K.

To achieve the highest accuracy in composition, the three binary mixtures were prepared according to a gravimetric method,<sup>5</sup> a method that qualifies for the production of reference materials.

This work is part of a research project aimed to obtain accurate experimental ( $p$ ,  $\rho$ ,  $T$ ) data for the development and improvement of models that favor the introduction of hydrogen into the natural gas grid.

The current research is a continuation of a previous work<sup>6</sup> consisting on the thermodynamic characterization of the nitrogen–hydrogen binary system.

## 2. Experimental

### 2.1. Mixture preparation

Three ( $\text{CH}_4 + \text{H}_2$ ) 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 6142-1.<sup>5</sup>

Purity, supplier, molar mass, and critical parameters of the pure compounds (obtained from the reference equations of state for methane<sup>7</sup> and hydrogen<sup>8</sup>) are given in Table 1. Table 2 shows the cylinder identifiers, composition and the corresponding expanded uncertainty ( $k = 2$ ) of the mixtures. The prepared mixtures were supplied in aluminum cylinders of a volume of 10 dm<sup>3</sup>. Methane and hydrogen were used without further purification, but information on impurities from the specification was considered in the mixture preparation.

The preparation of the mixtures was carried out as follows: In a first step, the equimolar mixture of (0.50  $\text{CH}_4 + 0.50 \text{H}_2$ ) was prepared introducing pure hydrogen followed by pure methane into an evacuated recipient cylinder. Hydrogen goes first, because the throttling process produces heating at room temperature. The mass of gas added was controlled by pressure difference between the cylinder which contains the pure compound and the recipient cylinder, thus avoiding the use of a compressor which could have introduced further impurities. The exact mass of the gas added was determined after each filling step using a high-precision mechanical balance (Volland model HCE 25, Volland Corp., New Rochelle NY, USA, weighing range: 25 kg, readability: 2.5 mg).

The other two binary mixtures were subsequently prepared by diluting a predefined amount of the (0.50  $\text{CH}_4 + 0.50 \text{H}_2$ ) parent mixture with a known amount of methane, following an analogous procedure as above. The three mixtures were homogenized by subsequent heating and rolling and had a pressure of approximately 14 MPa each.

Prior to density determination, the cylinders were validated at BAM by gas chromatography following the same procedure as described in a previous document<sup>6</sup>. Hydrogen was analyzed on a channel with nitrogen

as carrier gas; methane was analyzed on a different channel with helium as carrier gas. The samples of (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>) and (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>) were validated, but the composition of the equimolar mixture fell outside the operational range of the GC device. A successful validation of the diluted mixture, however, was regarded as a proof of accuracy of the equimolar mixture. The results of the GC analysis and the corresponding (gravimetric) composition of the binary mixtures used for validation can be found in Table 3.

## 2.2. Equipment description

The ( $p$ ,  $\rho$ ,  $T$ ) data were measured using a single-sinker densimeter with magnetic suspension coupling especially designed for density measurements of pure gases and gaseous mixtures. Details of the equipment have been previously described by Chamorro *et al.*<sup>9</sup> Further improvements were done by Mondéjar *et al.*<sup>10</sup> This method, originally developed by Brachthäuser *et al.*<sup>11</sup> and improved by Klimeck *et al.*<sup>12</sup>, operates on the Archimedes' principle. A magnetic suspension coupling system allows the determination of the buoyancy force on a sinker immersed in the gas so that accurate density measurements of fluids over wide temperature and pressure ranges can be obtained.<sup>13</sup> The sinker used in this work was cylindrical and made of silicon with a 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  $T = 293.05$  K and  $p = 1.01134$  bar. Two calibrated masses made of tantalum and titanium are used for reducing the 'nonlinearity effect' of the electronic balance and to improve the accuracy of the measurements. They have different masses but approximately the same volume (4.9 cm<sup>3</sup>). The difference in weight between both masses is similar to that of the sinker. This load compensation system allows operating the balance near to its zero point while making the air buoyancy effect negligible. The two masses were provided by Rubotherm GmbH, Bochum, Germany, and their individual masses and volumes were accurately determined at the Mass Division of the Spanish National Metrology Institute (*Centro Español de Metrología*, CEM).<sup>14</sup> A detailed description of the measurement procedure in single-sinker densimeters, especially the way the load compensation system is used and the final expression to obtain the density of the fluid, is presented by Mondéjar *et al.*<sup>10</sup>, McLinden<sup>15</sup>, and Richter *et al.*<sup>16</sup> In a simplified way, it can be said that the density of the fluid can be calculated from Eq. (1):

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

where the difference between the result of weighing the sinker in vacuum,  $m_{s0}$ , and the result of weighing the sinker in the pressurized fluid,  $m_{sf}$ , is related to the buoyancy force that is exerted on the sinker and it is determined using a high-precision microbalance (Mettler Toledo XPE205DR, Mettler Toledo GmbH, Gießen, Germany, weighing range: 81 g, extended weighing range: 220 g, readability: 0.01 mg, readability in extended weighing range: 0.1 mg).  $V_s(T, p)$  is the volume of the sinker immersed in the fluid, whose dependence with temperature and pressure is accurately known.<sup>10</sup>

The temperature inside the measuring cell is determined by means of two platinum resistance thermometers (S1059PJ5X6, Minco Products, Inc., Minneapolis MN, USA). A very accurate measurement of temperature is achieved using an AC comparator resistance bridge (F700, Automatic Systems Laboratories, Redhill, England) connected to the Pt thermometers and a reference resistance. The pressure inside the cell is recorded by two pressure transducers which cover different pressures ranges: a Paroscientific 2500A-101 for pressures from (0 to 3) MPa and a Paroscientific 43KR-HHT-101 (Paroscientific Inc., Redmond WA, USA) for pressures up to 20 MPa.

The single-sinker densimeter is capable of very accurate fluid density measurements over a wide range of temperatures and pressures. Corrections due to two effects should be considered: a) the force transmission error (FTE) due to the magnetic coupling<sup>17</sup> and b) the adsorption of gas molecules on the cell and sinker surfaces.<sup>18</sup> The FTE can be split into two terms: the apparatus effect and the fluid-specific effect. The apparatus effect can be annulled by determining the sinker mass in vacuum after each isotherm measurement. The fluid-specific effect depends on the magnetic behavior of the measured gas. The magnetic susceptibilities ( $\chi$ ) of the three (CH<sub>4</sub> + H<sub>2</sub>) binary mixtures studied in this work were estimated by using the additive law proposed by Bitter.<sup>19</sup> The estimated values were  $\chi_{5\%} = -8.62 \times 10^{-9}$  for the (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>) mixture,  $\chi_{10\%} = -8.18 \times 10^{-9}$  for the (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>), and  $\chi_{50\%} = -4.61 \times 10^{-9}$  for the (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>) mixtures. According to the literature, the fluid-specific effect is negligible compared to the apparatus effect, except for strongly paramagnetic fluids.<sup>17</sup> The fluid-specific effect depends also on the density of the sinker. The relative errors in density are larger with a sinker of high density. The silicon sinker used in this work has a relatively low density ( $\rho_{\text{Si}} = 2329 \text{ kg} \cdot \text{m}^{-3}$ ) compared to that of titanium ( $\rho_{\text{Ti}} = 4506 \text{ kg} \cdot \text{m}^{-3}$ ) or tantalum

( $\rho_{\text{Ta}} = 16670 \text{ kg}\cdot\text{m}^{-3}$ ) sinkers. Since the values of magnetic susceptibility of the studied ( $\text{CH}_4 + \text{H}_2$ ) mixtures are low (three orders of magnitude lower than oxygen,  $\chi_{\text{O}_2} = 1.78 \times 10^{-6}$ ), and the density of the sinker is relatively low, a correction due to the fluid-specific effect was not considered in these measurements.

Sorption effects inside the measuring cell may cause errors up to 0.1 % in density.<sup>18</sup> In order to minimize this effect, the measuring cell is evacuated and flushed several times with fresh mixture before each isotherm is measured, as recommended by Richter and Kleinrahm.<sup>18</sup> The residence time of the mixture in the cell is never longer than 40 hours. Specific sorption test for this particular mixture were performed in the same way that they were made for previous works.<sup>20</sup> Continuous density measurements on the same state point were recorded over 48 hours. The results showed that the difference observed in the trend of the relative deviation in density from the GERG-2008 EoS between the first and the last measurement are one order of magnitude lower than the density uncertainty. A measurement with fresh mixture executed immediately afterwards, for the same temperature and pressure, repeated also the density value with a deviation of one order of magnitude lower than the density uncertainty. Therefore, residual errors due to sorption effects are not appreciable with the experimental technique, and it should be considered that they are already included in the measurement uncertainty of the density and in the uncertainty in composition.

### 2.3. Experimental procedure

Experimental ( $p, \rho, T$ ) data for the three ( $\text{CH}_4 + \text{H}_2$ ) binary mixtures were obtained at temperatures of (240, 250, 260, 275, 300, 325, and 350) K and pressures up to 20 MPa. In the course of a measurement, the pressure was reduced in 1 MPa steps from (20 to 1) MPa for each isotherm. 30 repeated measurements were recorded for each point. The true sinker mass  $m_{\text{S0}}$  was measured at the end of each isotherm to detect any misalignment suffered by the magnetic suspension coupling during the measurement. Thus, the apparatus effect of the force transmission error (FTE) is compensated for.

The experimental method was validated before and after the measurements of the ( $\text{CH}_4 + \text{H}_2$ ) mixtures, using nitrogen as reference fluid over the entire operational range of the apparatus. These results were compared to the densities calculated from the reference equation of state for nitrogen by Span *et al.*<sup>21</sup> The relative deviations of the experimental densities agreed with those calculated from the literature data as the relative deviations lie within a  $\pm 0.02$  % band, with an absolute average deviation (*AAD*) of 0.007 %.

## 2.4. Uncertainty of the measurements

A detailed analysis of the uncertainties of the measurements involved in this experimental procedure was reported in a previous work.<sup>10</sup> The expanded uncertainty in temperature ( $k = 2$ ) is less than 4 mK. The pressure uncertainty depends on the range and it is given by Eq. (2) and Eq. (3) for the (3 to 20) MPa and (0 to 3) MPa transducers, respectively. The expanded uncertainty ( $k = 2$ ) in pressure is in both cases less than 0.005 MPa.

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

$$U(p)/\text{MPa} = 60 \cdot 10^{-6} \cdot p/\text{MPa} + 1.7 \cdot 10^{-3} \quad (3)$$

Uncertainty in density was evaluated from Eq. (1) using the law of propagation of uncertainties according to the Guide to the Expression of Uncertainty in Measurement (GUM).<sup>22</sup> Contributions to uncertainty in density are true sinker mass  $m_{S0}$ , apparent sinker mass in fluid  $m_{SF}$ , and uncertainty of the sinker volume,  $V_S(T, p)$ . The uncertainties of the apparent sinker masses were calculated taking into account the calibration, resolution, repeatability, and drift of the balance as sources of uncertainty. Due to thermal expansion and pressure distortion effects, the sinker volume is a function of temperature and pressure. The expanded uncertainty ( $k = 2$ ) in density  $\rho$  ( $\text{kg} \cdot \text{m}^{-3}$ ) is expressed as a function of density by Eq. (4).

$$U(\rho)/\text{kg} \cdot \text{m}^{-3} = 1.1 \cdot 10^{-4} \cdot \rho/\text{kg} \cdot \text{m}^{-3} + 2.3 \cdot 10^{-2} \quad (4)$$

To calculate the overall expanded uncertainty in density  $U_T(\rho)$  ( $k = 2$ ), the uncertainties of density, temperature, pressure, and composition of the mixture must be included, as 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 component in the mixture. Partial derivatives were calculated from the GERG-2008 EoS by using the software REFPROP.<sup>23</sup>

Table 4 displays a summary of the uncertainty contributions of density, temperature, pressure, and composition to the overall uncertainty in density for the three studied ( $\text{CH}_4 + \text{H}_2$ ) binary mixtures.



### 3. Experimental results

Tables 5, 6, and 7 show the 391 experimental ( $p$ ,  $\rho$ ,  $T$ ) data measured for the three ( $\text{CH}_4 + \text{H}_2$ ) binary mixtures during this work. The temperature, pressure, and density of each measured point were calculated as the arithmetic mean of ten consecutive measurements. Tables 5, 6, and 7 also show the expanded uncertainty in density  $U(\rho_{\text{exp}})$  ( $k = 2$ ), calculated by Eq. (4) and expressed in absolute density units and as percentage of the measured density.

Experimental data were compared to the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state. Relative deviations also go with Tables 5, 6, and 7 and are shown in Figures 1 to 6.

The virial coefficients for the three ( $\text{CH}_4 + \text{H}_2$ ) mixtures were calculated by fitting the experimental data to the virial equation of state (VEoS), as discussed below.

### 4. Discussion of the results

#### 4.1. Relative deviation of the experimental data from the reference equations of state

Figures 1 and 2 show the relative deviations for the (0.95  $\text{CH}_4 + 0.05 \text{H}_2$ ) mixture from the GERG-2008 and AGA8-DC92 EoS, respectively. In the same way, Figures 3 and 4 show the deviations for the (0.90  $\text{CH}_4 + 0.10 \text{H}_2$ ) mixture and Figures 5 and 6 for the (0.50  $\text{CH}_4 + 0.50 \text{H}_2$ ) mixture.

The uncertainty of the GERG-2008 EoS in the gas-phase region over the temperature range from (250 to 450) K and at pressures up to 35 MPa amounts to 0.1 % in density.<sup>2</sup> The relative deviations observed in the studied mixtures remain within this uncertainty value, except in the mixtures with a  $\text{H}_2$ -content of 0.05 and 0.10 at temperatures of (240 and 250) K and pressures above 14 MPa. The largest deviations of both mixtures were  $-0.141$  % and  $-0.221$  %, respectively. For the mixtures with a higher hydrogen content (0.10 and 0.50), it can be observed in Figures 3 to 6 that relative deviations do not approximate to zero at low pressures, as should be expected in the ideal gas limit. It is worth to mention that the densities of these experimental points, for mixtures with high hydrogen content at low pressures, are as low as  $3.1 \text{ kg}\cdot\text{m}^{-3}$ , so that a small absolute deviation of the experimental density from the density calculated from the equation of state is amplified when shown as a relative deviation. Anyway, these relative deviations are not significant

since the relative uncertainty in experimental density is several times larger than the relative deviation itself, and the absolute deviations of experimental densities does approximate to zero at low pressures.

Regarding the AGA8-DC92 EoS, the relative deviations of experimental data from this EoS are very similar to the deviations from GERG-2008 EoS for the three studied mixtures.

Table 8 presents the statistical parameters of the relative deviation of the experimental data from the densities given by the GERG-2008 and AGA8-DC92 EoS. *AAD* is the average absolute deviation defined by Eq. (6), which indicates either a systematic or random difference between the data and the EoS; *Bias* is the average deviation defined by Eq. (7), which quantifies the average deviation of the data set; *RMS* refers to the root mean square defined by Eq. (8) and provides another indication of the systematic or random dispersion of the data from the EoS, and *MaxD* represents the maximum relative deviation in the considered data set. When all four statistical parameters are close to zero, data sets are accurately represented by the engaged equation of state.

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

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

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

The *AAD* of experimental data from the densities given by the GERG-2008 EoS is only 0.033 for the (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>) mixture, 0.053 for the (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>) mixture, and 0.035 for the (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>) mixture. The maximum relative deviation is -0.221 % for the (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>) mixture, but only 0.102 % for the (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>) mixture. The corresponding parameters from using the AGA8-DC92 EoS display a similar pattern for these statistical parameters.

These statistical parameters are also calculated for a selection of mixtures with similar compositions found in the literature.<sup>24-27</sup> The data provided by Jaeschke *et al.*<sup>24</sup> for a mixture with a hydrogen content of 0.50 have an *AAD* from the GERG-2008 EoS as low as 0.015, with a maximum relative deviation of only -0.104 %. These values are comparable to the statistical parameters obtained for the mixture presented in this work

with a similar composition. The data provided by Jett *et al.*<sup>25</sup> for a mixture with a hydrogen content of 0.05 have an *AAD* from GERG-2008 EoS of 0.430 and the corresponding maximum relative deviation is above -5 %. These values are quite different to the statistical values obtained for the mixture presented in this work with a similar composition, but these experiments were done in a low-temperature range between (154 and 273) K. Finally, the data provided by Magee *et al.*<sup>26</sup> for a mixture with a hydrogen content of 0.20 and by Mihara *et al.*<sup>27</sup> for a mixture with a hydrogen content of 0.45 display an *AAD* of 0.287 and 0.134 respectively, with maximum relative deviations of -0.709 % and -0.469 %.

#### 4.2. Virial coefficients

The virial coefficients for the three (CH<sub>4</sub> + H<sub>2</sub>) mixtures were calculated by fitting the experimental data to the virial equation of state (VEoS).

$$Z = \frac{pM}{\rho RT} = \sum_{k=1}^N \left( \frac{B_k}{M^k} \right) \cdot \rho^k \quad (9)$$

where  $Z$  is the compressibility factor,  $p$  is the pressure,  $M$  is the molar mass,  $R$  is the universal gas constant (8.31446 J·K<sup>-1</sup>·mol<sup>-1</sup>),  $T$  is the temperature,  $\rho$  is the density, and  $B_k$  are the virial coefficients, which have a physical meaning related to the interaction between groups of molecules, with  $B_1 = 1$ .  $N$  is the number of terms of the equation.

The method proposed by Cristancho *et al.*<sup>28</sup> was used to determine the number of terms at which the VEoS must be truncated for processing the virial coefficients for the three (CH<sub>4</sub> + H<sub>2</sub>) binary mixtures. A characteristic of this method is that the number of terms to be fitted depends on the maximum experimental pressure,  $p_{\max}$ , of the experimental dataset used for the adjustment.

The procedure, described in detail in a previous work,<sup>29</sup> consists of two consecutive fits. The first fit determines the number of virial coefficients,  $N$ , needed for the best representation of the experimental data, and the maximum pressure,  $p_{\max}$ , for which the fit gives a satisfying result. This is done through the determination of the apparent molar mass  $M$  of the mixture as a parameter of the VEoS. The second fit calculates the values of the corresponding virial coefficients. Both fits were executed by using a least-squares fitting method implemented in MATLAB software.<sup>30</sup>

The first fit was run at temperatures of (250, 300, and 350) K, obtaining similar results for each mixture. These results show that the fit is only effective for pressures below  $p_{max} = 11$  MPa and that three virial coefficients ( $N = 3$ ) are sufficient for the three studied mixtures.

The second fit to estimate the virial coefficients indicated by the results of the first fit was performed using the molar mass values from the gravimetric preparation of each mixture for each isotherm. A normal random distribution term based on the estimated uncertainties for temperature, pressure and density was included into the fitting process with a coverage interval of 95 %. This distribution was performed according to the Monte Carlo method as proposed by the GUM.<sup>22</sup> Table 9 displays the estimated results for the second  $B(T, x)$  and third  $C(T, x)$  virial coefficients with their corresponding uncertainties.

The methane-hydrogen second interaction virial coefficient  $B_{12}(T)$  was also estimated from  $B(T, x)$  using the mixing rule expressed in Eq. (10). Virial coefficients of pure methane ( $B_{11}$ ) and pure hydrogen ( $B_{22}$ ) were obtained from reference equations of state of methane<sup>7</sup> and hydrogen<sup>8</sup> at the corresponding temperatures using REFPROP.<sup>23</sup> The corresponding uncertainty was estimated by applying the uncertainty propagation law. The results are also shown in Table 9.

$$B(T, x) = x_1^2 B_{11}(T) + 2x_1 x_2 B_{12}(T) + x_2^2 B_{22}(T) \quad (10)$$

The estimated values for  $B_{12}(T)$  are compared to those calculated from the GERG-2008 EoS in Figure 7. As it can be observed, the second interaction virial coefficients do not depend significantly on composition which is expected, as, according to the theory,  $B_{12}(T)$  only depends on temperature. Considering the uncertainty estimated for  $B_{12}(T)$ , the values calculated from the experimental data agree with that.

Figure 8 shows  $B_{12}(T)$  as a function of temperature. The average of the calculated  $B_{12}(T)$  values for the system ( $\text{CH}_4 + \text{H}_2$ ) was also compared to those data reported by other authors<sup>27,31,32</sup> at temperatures from (220 to 350) K.

Experimental densities are very well represented by the virial equation of state using these adjusted coefficients. The average absolute deviation (*AAD*) is 0.005, 0.007, and 0.026, for the mixtures with a hydrogen content of 0.05, 0.10, and 0.50, respectively. Similarly, the average deviation (*Bias*) is -0.001,

0.002, and 0.025; the root mean square (*RMS*) is 0.007, 0.012, and 0.031; and finally, the maximum relative deviation (*MaxD*) is 0.018 %, 0.052 %, and 0.083 %. These results refer only to pressures below 11 MPa, which is the maximum pressure of the experimental data used to fit the virial coefficients. These values may also be compared to the corresponding statistical parameters of the relative deviation of the experimental data from the densities given by the GERG-2008 and AGA8-DC92 EoS, presented in Table 8.

## 5. Conclusions

New ( $p$ ,  $\rho$ ,  $T$ ) high-precision experimental data for three binary mixtures of methane and hydrogen, with nominal compositions of (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>), (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>), and (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>) at temperatures between (240 and 350) K and pressures up to 20 MPa, are reported. The experimental device used was a single-sinker densimeter with magnetic suspension coupling. The mixtures were prepared gravimetrically at the Federal Institute for Materials Research and Testing (BAM) in Berlin, Germany.

The new experimental data extend the current ranges of available data for the methane and hydrogen system at temperatures above 270 K for mixtures with a hydrogen content lower than 0.20, and, accordingly, at temperatures below 270 K for mixtures with a hydrogen content higher than 0.20.

The new experimental data were compared to the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 EoS, resulting in relative deviations within the  $\pm 0.1$  % band, which is the estimated uncertainty value of both equations at the temperature and pressure ranges evaluated, except for the mixtures with a hydrogen content of 0.05 and 0.10 at temperatures of (240 and 250) K and pressures above 14 MPa.

Further, the second  $B(T, x)$  and the third  $C(T, x)$  virial coefficients of each mixture as well as the second interaction virial coefficient  $B_{12}(T)$  for the (CH<sub>4</sub> + H<sub>2</sub>) binary system were estimated from the experimental data set at the temperature range investigated, together with the corresponding uncertainties. Experimental densities are also very well represented by the virial equation of state using these adjusted coefficients.

The experimental data presented in this paper for the mixture with a hydrogen content of 0.50 are very similar to the previous data given by Jaeschke *et al.*<sup>24</sup> for a mixture of similar composition. Both sets of data are compatible in the temperature range in which they overlap, namely from (270 to 350) K. The data presented in this paper extend the temperature range to (240, 250 and 260) K.

On the contrast, for the mixture with a hydrogen content of 0.05, the data obtained in this work have significant differences with the data provided by Jett *et al.*<sup>25</sup> for the same composition, as can be seen by the statistical parameters of the comparison with the GERG-2008 and AGA8-DC92 EoS. The data only overlap for temperatures between (240 and 273) K. The data presented in this work extend the temperature range up to 350 K.

Regarding the mixture with a hydrogen content of 0.10, there are no published data available for comparison.

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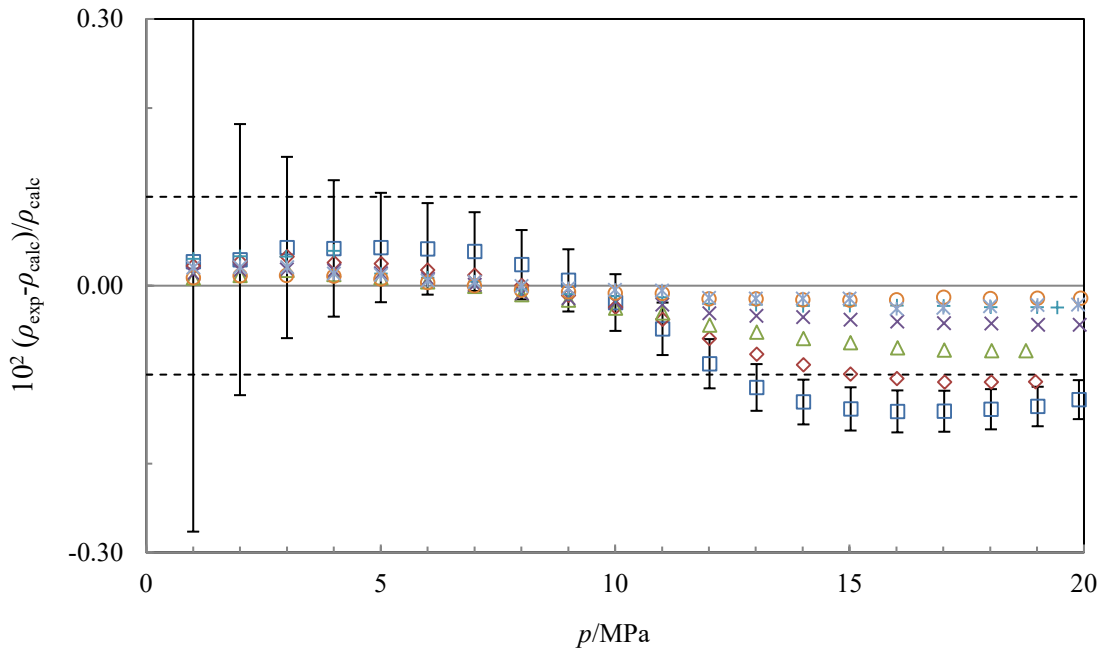
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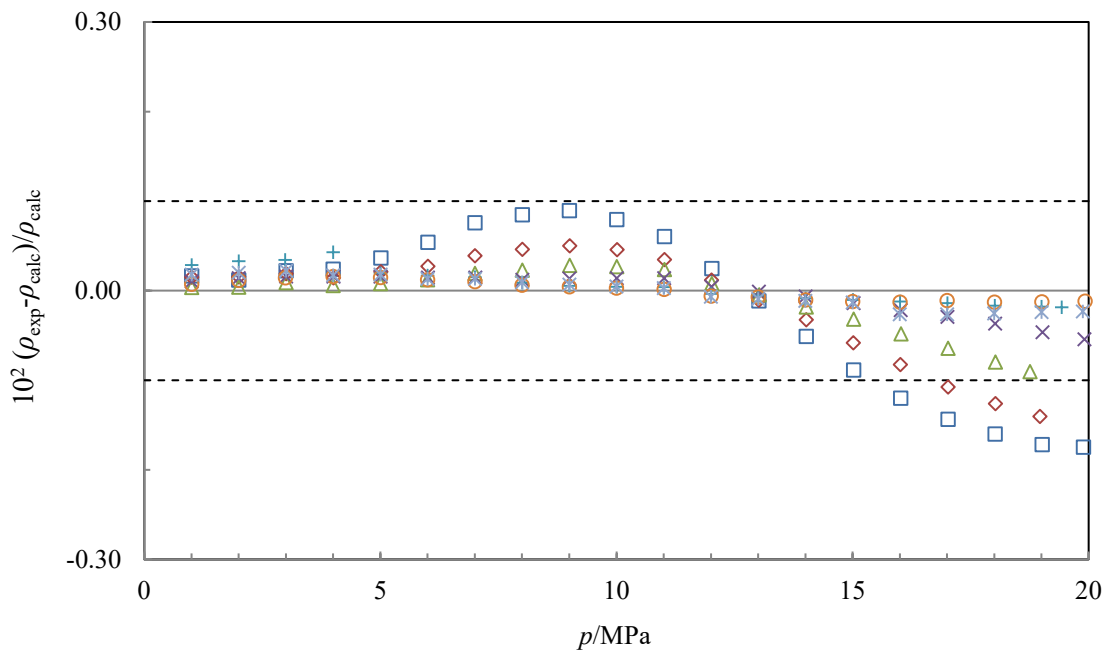
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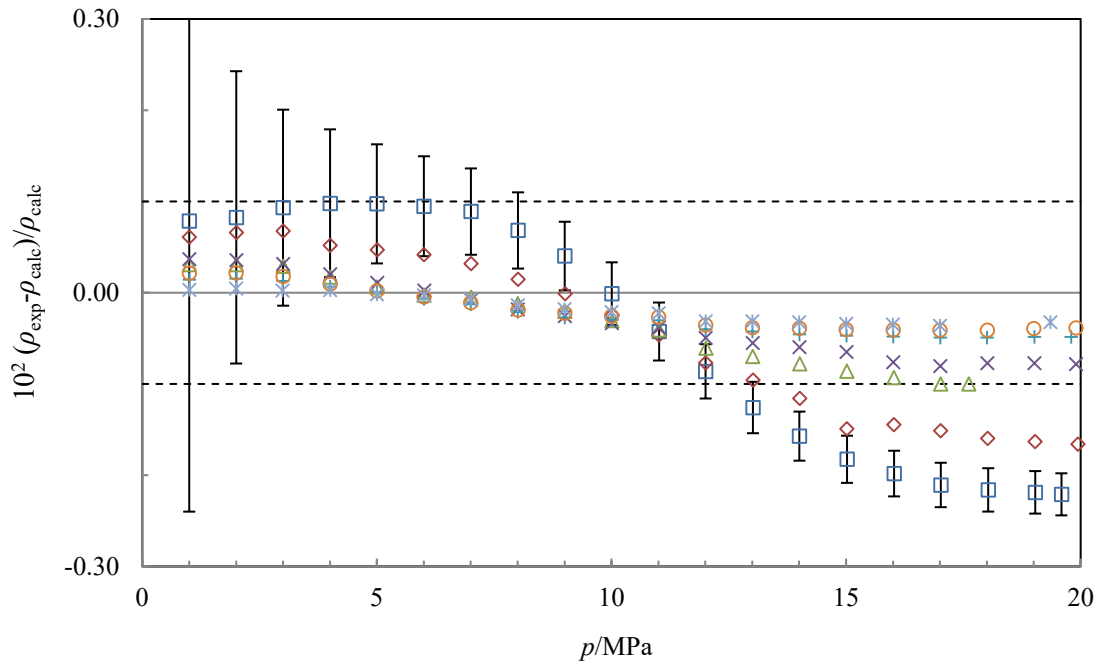
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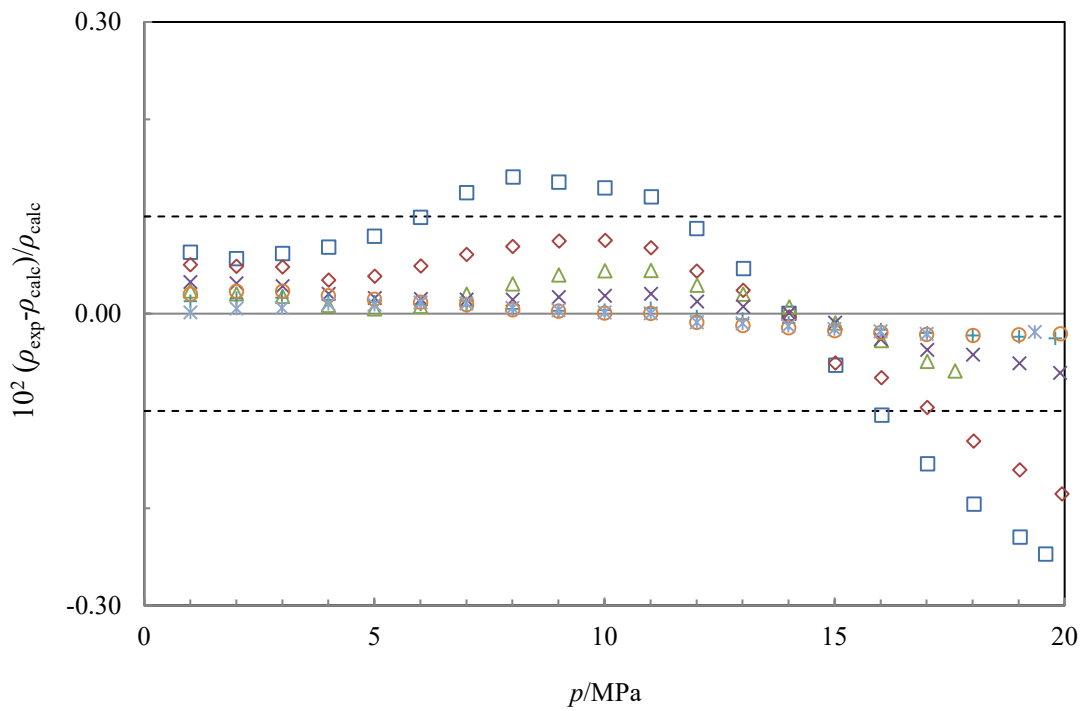
**Figure 1.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.94991009 CH<sub>4</sub> + 0.05008573 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 equation of state  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $+$   $T = 300$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. Error bars on the 240 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq. (4). The dashed line represents the intrinsic uncertainty of the GERG-2008 EoS.



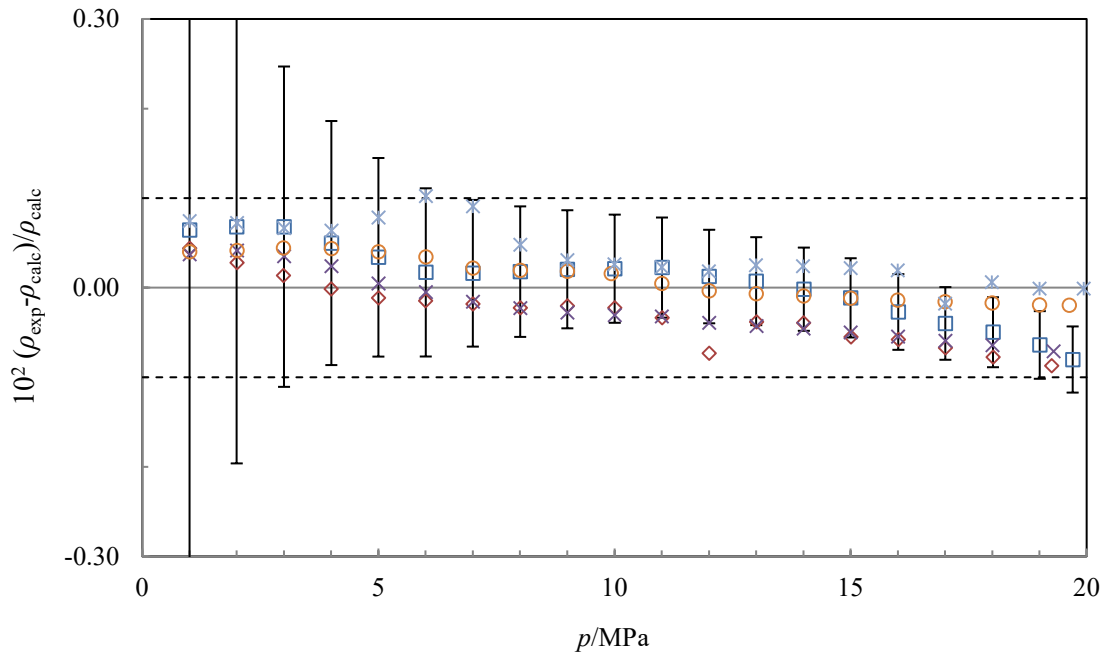
**Figure 2.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.94991009 CH<sub>4</sub> + 0.05008573 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $+$   $T = 300$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. The dashed line represents the intrinsic uncertainty of the AGA8-DC92 EoS.



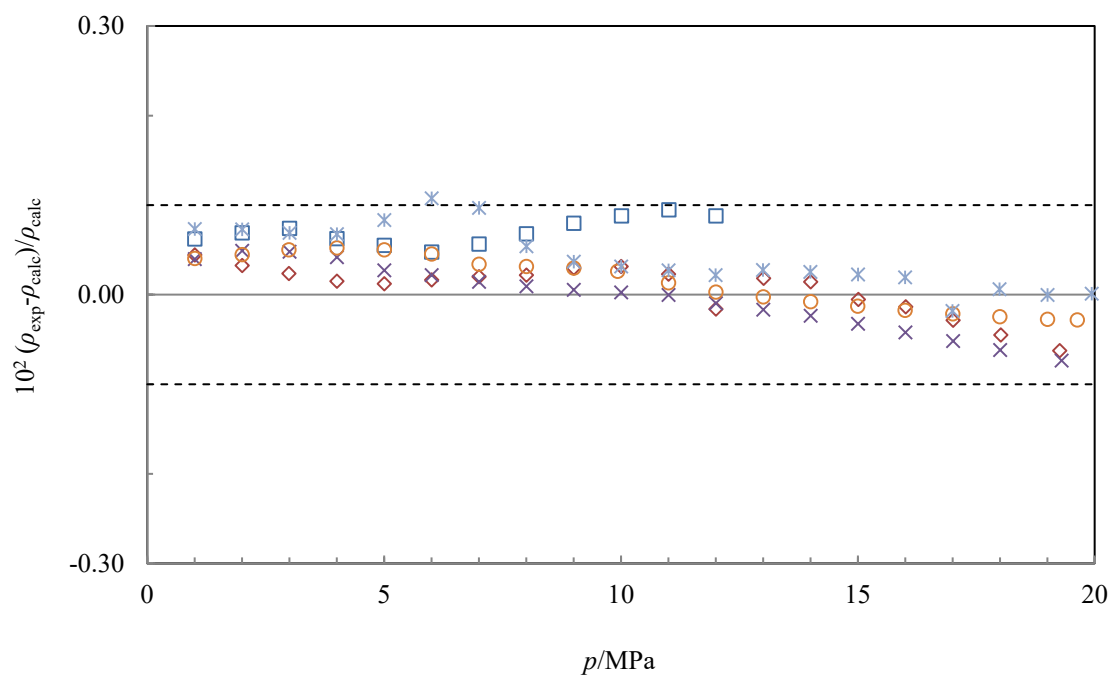
**Figure 3.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.90003135 CH<sub>4</sub> + 0.09996463 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 EoS  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $+$   $T = 300$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. Error bars on the 240 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq. (4). The dashed line represents the intrinsic uncertainty of the GERG-2008 EoS.



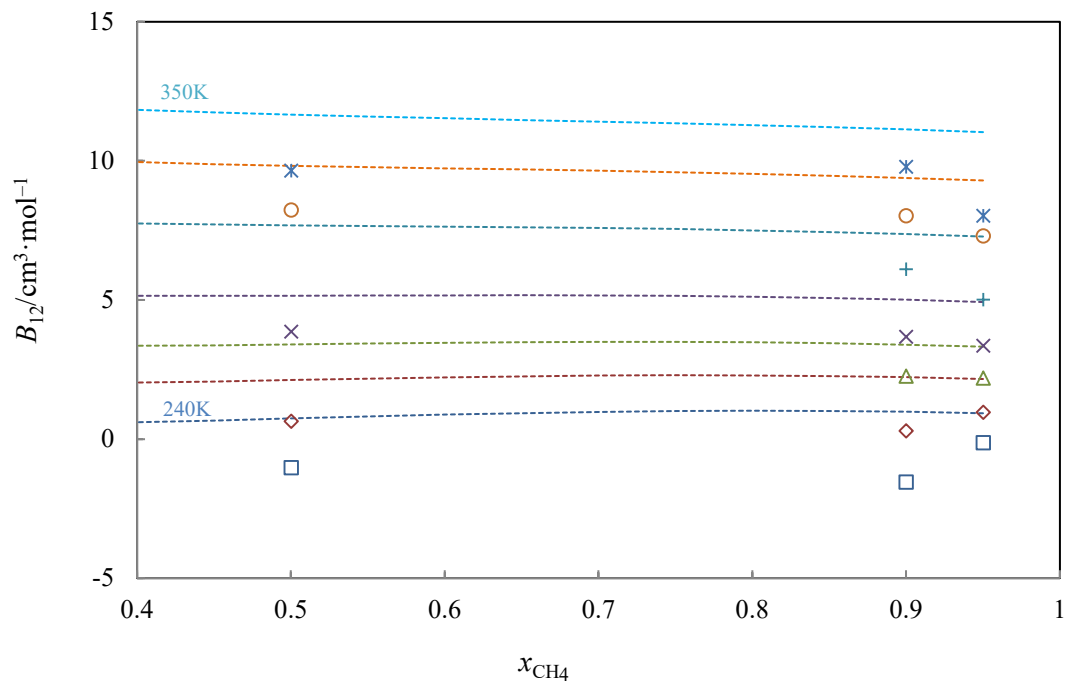
**Figure 4.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.90003135 CH<sub>4</sub> + 0.09996463 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $+$   $T = 300$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. The dashed line represents the intrinsic uncertainty of the AGA8-DC92 EoS.



**Figure 5.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.49967868 CH<sub>4</sub> + 0.50031867 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the GERG-2008 equation of state  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. Error bars on the 240 K isotherm indicate the expanded uncertainty ( $k = 2$ ) of the experimental density data calculated with Eq. (4). The dashed line represents the intrinsic uncertainty of the GERG-2008 EoS.

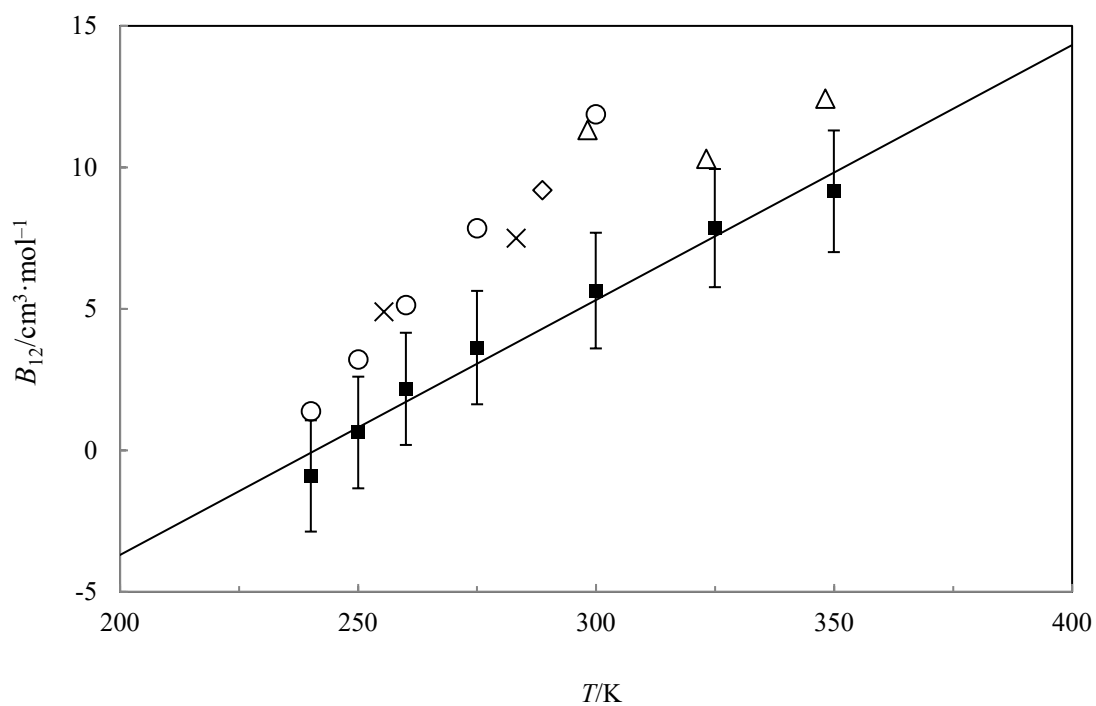


**Figure 6.** Relative deviations in density of experimental ( $p, \rho, T$ ) data of the (0.49967868 CH<sub>4</sub> + 0.50031867 H<sub>2</sub>) mixture  $\rho_{\text{exp}}$  from density values calculated from the AGA8-DC92 equation of state  $\rho_{\text{calc}}$  versus pressure:  $\square$   $T = 240$  K;  $\diamond$   $T = 250$  K;  $\triangle$   $T = 260$  K;  $\times$   $T = 275$  K;  $\circ$   $T = 325$  K;  $*$   $T = 350$  K. The dashed line represents the intrinsic uncertainty of the AGA8-DC92 EoS.



**Figure 7.** Second interaction virial coefficient  $B_{12}(T)$  for the  $(\text{CH}_4 + \text{H}_2)$  binary system estimated from the experimental data. □  $T = 240 \text{ K}$ ; ◇  $T = 250 \text{ K}$ ; △  $T = 260 \text{ K}$ ; ×  $T = 275 \text{ K}$ ; +  $T = 300 \text{ K}$ ; ○  $T = 325 \text{ K}$ ; \*  $T = 350 \text{ K}$ . The dashed lines represent the  $B_{12}(T)$  values estimated from the GERG-2008 EoS at different temperatures.





**Figure 8.** The second interaction virial coefficient  $B_{12}(T)$  for the (CH<sub>4</sub> + H<sub>2</sub>) binary mixture: ■ This work; ○ GERG-2008 EoS<sup>2</sup>; △ Mihara *et al.*<sup>27</sup>; × Mueller *et al.*<sup>31</sup>; ◇ Mason and Eakin<sup>32</sup>. Error bars indicate the expanded uncertainty ( $k = 2$ ) of the estimated  $B_{12}(T)$  value. The solid line represents the linear fit to experimental data of this work.  $B_{12}(T)/\text{cm}^3 \cdot \text{mol}^{-1} = 0.09 \cdot T/\text{K} - 21.71$ .

**Table 1.** Purity, Supplier, Molar Mass, and Critical Parameters of the Constituting Components of the Studied (CH<sub>4</sub> + H<sub>2</sub>) Mixtures.

components	purity	supplier	$M / \text{g}\cdot\text{mol}^{-1}$	critical parameters	
				$T_c / \text{K}$	$p_c / \text{MPa}$
methane	$\geq 99.9995$ mol-%	Linde <sup>a</sup>	16.043 <sup>b</sup>	190.564 <sup>b</sup>	4.599 <sup>b</sup>
hydrogen	$\geq 99.9999$ mol-%	Linde <sup>a</sup>	2.016 <sup>c</sup>	33.145 <sup>c</sup>	1.296 <sup>c</sup>

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

<sup>b</sup> Setzmann and Wagner<sup>7</sup>

<sup>c</sup> Leachman *et al.*<sup>8</sup>

**Table 2.** Composition of the Studied (CH<sub>4</sub> + H<sub>2</sub>) Binary Mixtures Including Information on Impurities from the Supplier.

component	(0.95 CH <sub>4</sub> + 0.05 H <sub>2</sub> )		(0.90 CH <sub>4</sub> + 0.10 H <sub>2</sub> )		(0.50 CH <sub>4</sub> + 0.50 H <sub>2</sub> )	
	BAM no.: 96054 988-160628		BAM no.: 96054 989-160621		BAM no.: 96054 990-160614	
	$x_i /$ (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> )	$x_i /$ (10 <sup>-2</sup> mol·mol <sup>-1</sup> )	$U(x_i) (k = 2) /$ (10 <sup>-2</sup> mol·mol <sup>-1</sup> )
methane	94.991009	0.002066	90.003135	0.002065	49.967868	0.001574
hydrogen	5.008573	0.001800	9.996463	0.002783	50.031867	0.012279
nitrogen	0.000193	0.000208	0.000185	0.000187	0.000125	0.000119
carbon dioxide	0.000210	0.000119	0.000199	0.000106	0.000115	0.000066
oxygen	0.000013	0.000013	0.000014	0.000012	0.000019	0.000016
ethane	0.000003	0.000002	0.000003	0.000001	0.000001	0.000001
carbon monoxide	0.000001	0.000001	0.000001	0.000001	0.000005	0.000006

**Table 3.** Results of the GC Analysis and Relative Deviation between Gravimetric Composition and GC Analysis for the (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>) and the (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>) Binary Mixtures.

component	(0.95 CH <sub>4</sub> + 0.05 H <sub>2</sub> ) BAM no.: 96054 988-160628			(0.90 CH <sub>4</sub> + 0.10 H <sub>2</sub> ) BAM no.: 96054 989-160621		
	concentration		relative deviation between gravimetric preparation and GC analysis	concentration		relative deviation between gravimetric preparation and GC analysis
	$x_i /$ (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	94.9814	0.0763	-0.010	89.9905	0.0866	-0.014
hydrogen	5.0055	0.0061	-0.062	10.0032	0.0180	0.067
	validation mixture BAM no.: 96054 982-160704			validation mixture BAM no.: 8016-150209		
methane	94.996093	0.003577		89.992034	0.002249	
hydrogen	5.003489	0.001767		10.007564	0.003505	
nitrogen	0.000193	0.000152		0.000185	0.000198	
carbon dioxide	0.000210	0.000087		0.000199	0.000113	
oxygen	0.000013	0.000010		0.000014	0.000013	
ethane	0.000003	0.000001		0.000003	0.000002	
carbon monoxide	0.000001	0.000001		0.000001	0.000001	
				Validation mixture BAM no.: 8017-140819		
methane				89.981632	0.002158	
hydrogen				10.017967	0.003520	
nitrogen				0.000185	0.000199	
carbon dioxide				0.000199	0.000113	

oxygen	0.000014	0.000013
ethane	0.000003	0.000002
carbon monoxide	0.000001	0.000001

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**Table 4.** Contributions to the Expanded Overall Uncertainty in Density  $U_T(\rho_{\text{exp}})$  ( $k = 2$ ) for the Three Studied ( $\text{CH}_4 + \text{H}_2$ ) Binary Mixtures in the Temperature Range from (240 to 350) K.

source of uncertainty	units	contribution ( $k = 2$ )	estimation in density ( $k = 2$ )	
			$\text{kg}\cdot\text{m}^{-3}$	%
(0.95 $\text{CH}_4$ + 0.05 $\text{H}_2$ )				
temperature $T$	K	0.004	< 0.008	< 0.005
pressure $p$	MPa	0.005	< 0.064	(0.006 - 0.19)
density $\rho$	$\text{kg}\cdot\text{m}^{-3}$	(0.024 - 0.054)	(0.024 - 0.054)	(0.006 - 0.30)
composition $x_i$	$\text{mol}\cdot\text{mol}^{-1}$	< 0.0004	< 0.140	< 0.086
overall uncertainty $U_T(\rho_{\text{exp}})$			(0.024 - 0.155)	(0.059 - 0.55)
(0.90 $\text{CH}_4$ + 0.10 $\text{H}_2$ )				
temperature $T$	K	0.004	< 0.007	< 0.004
pressure $p$	MPa	0.005	< 0.056	(0.006 - 0.19)
density $\rho$	$\text{kg}\cdot\text{m}^{-3}$	(0.024 - 0.052)	(0.024 - 0.046)	(0.021 - 0.32)
composition $x_i$	$\text{mol}\cdot\text{mol}^{-1}$	< 0.0004	< 0.032	< 0.020
overall uncertainty $U_T(\rho_{\text{exp}})$			(0.024 - 0.072)	(0.033 - 0.57)
(0.50 $\text{CH}_4$ + 0.50 $\text{H}_2$ )				
temperature $T$	K	0.004	< 0.002	< 0.002
pressure $p$	MPa	0.005	< 0.021	(0.006 - 0.18)
density $\rho$	$\text{kg}\cdot\text{m}^{-3}$	(0.024 - 0.038)	(0.024 - 0.034)	(0.006 - 0.52)
composition $x_i$	$\text{mol}\cdot\text{mol}^{-1}$	< 0.0004	< 0.029	< 0.031
overall uncertainty $U_T(\rho_{\text{exp}})$			(0.024 - 0.052)	(0.039 - 0.56)

**Table 5.** Experimental ( $p$ ,  $\rho$ ,  $T$ ) Measurements for the (0.95 CH<sub>4</sub> + 0.05 H<sub>2</sub>) Mixture, Absolute and Relative Expanded Uncertainty in Density ( $k = 2$ )  $U(\rho_{\text{exp}})$  and Relative Deviations from the GERG-2008 and AGA8-DC92 EoS; where  $T$  is the Temperature (ITS-90),  $p$  the Pressure,  $\rho_{\text{exp}}$  the Experimental Density, and  $\rho_{\text{GERG}}$  and  $\rho_{\text{AGA}}$  the Densities Calculated ( $\rho_{\text{calc}}$ , cf. Figures 1 and 2) from the GERG-2008 and the AGA8-DC92 EoS.

$T/\text{K}^a$	$p/\text{MPa}^a$	$\rho_{\text{exp}}/\text{kg}\cdot\text{m}^{-3}$	$U(\rho_{\text{exp}}) / \text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$\frac{10^2 U(\rho_{\text{exp}})}{\rho_{\text{exp}}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{GERG}}) / \rho_{\text{GERG}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{AGA}}) / \rho_{\text{AGA}}$
240.075	19.891	220.394	0.048	0.022	-0.128	-0.175
240.075	19.013	214.425	0.048	0.022	-0.136	-0.172
240.075	18.016	207.026	0.047	0.023	-0.139	-0.160
240.075	17.021	198.870	0.046	0.023	-0.141	-0.144
240.075	16.020	189.762	0.045	0.024	-0.141	-0.120
240.074	15.021	179.661	0.044	0.024	-0.139	-0.089
240.074	14.016	168.365	0.042	0.025	-0.131	-0.051
240.074	13.016	155.953	0.041	0.026	-0.114	-0.011
240.075	12.014	142.433	0.039	0.028	-0.088	0.025
240.075	11.011	128.048	0.038	0.030	-0.048	0.060
240.076	10.007	113.159	0.036	0.032	-0.019	0.079
240.076	9.003	98.317	0.034	0.035	0.006	0.089
240.077	8.004	84.026	0.033	0.039	0.024	0.085
240.077	7.002	70.478	0.031	0.044	0.038	0.076
240.077	6.000	57.870	0.030	0.051	0.041	0.054
240.077	5.004	46.287	0.028	0.062	0.043	0.036
240.077	3.999	35.505	0.027	0.077	0.042	0.024
240.077	3.000	25.620	0.026	0.102	0.043	0.022
240.078	1.998	16.447	0.025	0.152	0.029	0.012
240.077	0.999	7.937	0.024	0.304	0.027	0.016
250.047	18.962	196.737	0.046	0.023	-0.108	-0.140
250.048	18.020	189.342	0.045	0.024	-0.108	-0.126
250.048	17.022	180.830	0.044	0.024	-0.108	-0.107
250.047	16.007	171.395	0.043	0.025	-0.104	-0.082
250.048	15.015	161.379	0.042	0.026	-0.099	-0.058
250.047	14.017	150.503	0.040	0.027	-0.089	-0.032
250.047	13.015	138.840	0.039	0.028	-0.077	-0.011
250.048	12.009	126.528	0.038	0.030	-0.059	0.012
250.046	11.012	113.948	0.036	0.032	-0.038	0.035
250.046	10.007	101.135	0.035	0.034	-0.024	0.046
250.045	9.006	88.515	0.033	0.038	-0.011	0.050
250.046	8.002	76.259	0.032	0.042	0.001	0.046

250.044	7.002	64.575	0.031	0.047	0.012	0.039
250.044	6.001	53.515	0.029	0.055	0.018	0.027
250.043	5.005	43.167	0.028	0.065	0.025	0.021
250.043	4.006	33.422	0.027	0.081	0.026	0.014
250.043	3.002	24.252	0.026	0.107	0.033	0.019
250.043	1.999	15.652	0.025	0.160	0.027	0.015
250.043	0.999	7.587	0.024	0.317	0.022	0.015
260.041	18.756	179.616	0.044	0.024	-0.073	-0.090
260.042	18.026	173.779	0.043	0.025	-0.073	-0.080
260.040	17.019	165.220	0.042	0.025	-0.072	-0.064
260.040	16.023	156.169	0.041	0.026	-0.070	-0.048
260.041	15.018	146.448	0.040	0.027	-0.064	-0.032
260.040	14.016	136.214	0.039	0.028	-0.059	-0.018
260.040	13.017	125.550	0.038	0.030	-0.052	-0.005
260.040	12.013	114.514	0.036	0.032	-0.044	0.008
260.040	11.011	103.316	0.035	0.034	-0.031	0.024
260.040	10.006	92.073	0.034	0.037	-0.025	0.027
260.041	9.006	81.038	0.032	0.040	-0.016	0.028
260.040	8.003	70.258	0.031	0.044	-0.010	0.023
260.039	7.002	59.886	0.030	0.050	-0.001	0.019
260.041	5.999	49.941	0.029	0.058	0.004	0.012
260.040	5.000	40.497	0.028	0.069	0.009	0.008
260.039	3.999	31.515	0.027	0.085	0.012	0.006
260.040	2.999	23.006	0.026	0.112	0.017	0.009
260.040	1.999	14.926	0.025	0.167	0.012	0.004
260.041	0.999	7.267	0.024	0.331	0.009	0.004
275.015	19.909	168.440	0.042	0.025	-0.044	-0.054
275.015	19.020	161.966	0.042	0.026	-0.044	-0.046
275.016	18.019	154.292	0.041	0.026	-0.043	-0.037
275.015	17.010	146.150	0.040	0.027	-0.042	-0.029
275.015	16.016	137.753	0.039	0.028	-0.040	-0.022
275.015	15.018	128.986	0.038	0.029	-0.038	-0.014
275.014	14.006	119.787	0.037	0.031	-0.035	-0.006
275.015	13.011	110.507	0.036	0.032	-0.034	-0.001
275.013	12.009	101.013	0.035	0.034	-0.031	0.004
275.013	11.005	91.455	0.034	0.037	-0.021	0.014
275.015	10.006	81.955	0.033	0.040	-0.019	0.014
275.015	9.003	72.540	0.031	0.043	-0.014	0.014
275.014	8.003	63.333	0.030	0.048	-0.009	0.012
275.013	7.005	54.384	0.029	0.054	0.001	0.015
275.014	6.005	45.691	0.028	0.062	0.008	0.015



275.013	5.002	37.281	0.027	0.074	0.014	0.016
275.013	4.002	29.206	0.027	0.091	0.017	0.016
275.014	2.997	21.412	0.026	0.120	0.019	0.016
275.012	1.999	13.980	0.025	0.177	0.017	0.014
275.012	0.999	6.842	0.024	0.350	0.013	0.010
299.960	19.426	140.030	0.039	0.028	-0.024	-0.019
299.959	18.999	137.175	0.039	0.028	-0.024	-0.018
299.960	18.007	130.371	0.038	0.029	-0.024	-0.017
299.959	17.007	123.312	0.037	0.030	-0.023	-0.014
299.959	16.005	116.045	0.036	0.031	-0.022	-0.012
299.958	15.004	108.622	0.036	0.033	-0.022	-0.010
299.958	14.006	101.077	0.035	0.034	-0.023	-0.009
299.959	13.003	93.405	0.034	0.036	-0.021	-0.005
299.958	12.003	85.693	0.033	0.038	-0.020	-0.004
299.957	11.001	77.955	0.032	0.041	-0.013	0.004
299.957	10.004	70.258	0.031	0.044	-0.012	0.004
299.957	9.003	62.590	0.030	0.048	-0.009	0.005
299.957	8.001	55.012	0.029	0.054	-0.004	0.009
299.958	7.000	47.554	0.029	0.060	0.005	0.015
299.959	6.000	40.236	0.028	0.069	0.009	0.017
299.957	4.999	33.078	0.027	0.082	0.014	0.019
299.958	3.999	26.096	0.026	0.100	0.039	0.043
299.958	2.983	19.180	0.025	0.132	0.033	0.035
299.958	2.000	12.675	0.025	0.194	0.033	0.033
299.956	0.999	6.241	0.024	0.383	0.030	0.029
324.963	19.924	125.148	0.037	0.030	-0.014	-0.012
324.964	19.004	119.703	0.037	0.031	-0.014	-0.012
324.964	18.000	113.635	0.036	0.032	-0.014	-0.013
324.966	17.001	107.464	0.035	0.033	-0.013	-0.011
324.965	16.003	101.187	0.035	0.034	-0.016	-0.013
324.963	15.003	94.801	0.034	0.036	-0.016	-0.012
324.964	14.001	88.324	0.033	0.038	-0.016	-0.010
324.966	13.002	81.811	0.033	0.040	-0.015	-0.007
324.966	12.002	75.249	0.032	0.042	-0.015	-0.006
324.966	11.004	68.681	0.031	0.045	-0.009	0.002
324.966	10.000	62.076	0.030	0.049	-0.008	0.003
324.965	9.001	55.531	0.030	0.053	-0.007	0.004
324.966	7.999	49.004	0.029	0.059	-0.005	0.006
324.966	6.999	42.544	0.028	0.066	< 0.001	0.010
324.966	5.999	36.165	0.027	0.076	0.004	0.012
324.966	4.999	29.867	0.027	0.089	0.008	0.015

324.966	3.998	23.665	0.026	0.109	0.011	0.016
324.967	2.985	17.488	0.025	0.144	0.012	0.014
324.966	1.999	11.594	0.025	0.212	0.011	0.012
324.967	0.999	5.733	0.024	0.416	0.009	0.007
349.951	19.873	111.352	0.036	0.032	-0.021	-0.023
349.950	19.002	106.734	0.035	0.033	-0.022	-0.024
349.950	17.998	101.317	0.035	0.034	-0.023	-0.025
349.950	16.998	95.842	0.034	0.036	-0.025	-0.026
349.950	15.998	90.284	0.033	0.037	-0.026	-0.026
349.950	14.997	84.669	0.033	0.039	-0.015	-0.013
349.949	13.998	78.993	0.032	0.041	-0.014	-0.011
349.949	12.998	73.267	0.032	0.043	-0.014	-0.009
349.948	11.997	67.507	0.031	0.046	-0.014	-0.007
349.949	10.999	61.741	0.030	0.049	-0.005	0.003
349.949	9.996	55.938	0.030	0.053	-0.005	0.005
349.950	8.997	50.163	0.029	0.058	-0.003	0.007
349.950	7.998	44.399	0.028	0.064	< 0.001	0.009
349.949	7.000	38.671	0.028	0.071	0.004	0.013
349.950	5.998	32.957	0.027	0.082	0.006	0.013
349.949	4.999	27.309	0.026	0.096	0.012	0.018
349.949	4.000	21.712	0.026	0.118	0.014	0.017
349.949	2.999	16.173	0.025	0.155	0.021	0.022
349.949	1.999	10.702	0.024	0.228	0.021	0.020
349.949	0.999	5.309	0.024	0.448	0.020	0.018

<sup>a</sup> Expanded uncertainties ( $k = 2$ ) in temperature and pressure are  $U(T) = 0.004$  K and  $U(p) = 0.005$  MPa, respectively.

**Table 6.** Experimental ( $p$ ,  $\rho$ ,  $T$ ) Measurements for the (0.90 CH<sub>4</sub> + 0.10 H<sub>2</sub>) Mixture, Absolute and Relative Expanded Uncertainty in Density ( $k = 2$ )  $U(\rho_{\text{exp}})$  and Relative Deviations from the GERG-2008 and AGA8-DC92 EoS; where  $T$  is the Temperature (ITS-90),  $p$  the Pressure,  $\rho_{\text{exp}}$  the Experimental Density, and  $\rho_{\text{GERG}}$  and  $\rho_{\text{AGA}}$  the Densities Calculated ( $\rho_{\text{calc}}$ , cf. Figures 3 and 4) from the GERG-2008 and the AGA8-DC92 EoS.

$T/\text{K}^a$	$p/\text{MPa}^a$	$\rho_{\text{exp}}/\text{kg}\cdot\text{m}^{-3}$	$U(\rho_{\text{exp}})$ / $\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2$ $U(\rho_{\text{exp}})$ / $\rho_{\text{exp}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{GERG}})/\rho_{\text{GERG}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{AGA}})/\rho_{\text{AGA}}$
240.072	19.589	199.054	0.046	0.023	-0.221	-0.247
240.073	19.032	195.115	0.045	0.023	-0.219	-0.230
240.074	18.030	187.542	0.045	0.024	-0.216	-0.196
240.075	17.018	179.188	0.044	0.024	-0.211	-0.154
240.078	16.024	170.250	0.043	0.025	-0.198	-0.104
240.078	15.020	160.417	0.041	0.026	-0.183	-0.053
240.079	14.006	149.671	0.040	0.027	-0.157	0.000
240.079	13.016	138.410	0.039	0.028	-0.126	0.047
240.080	12.006	126.282	0.038	0.030	-0.086	0.088
240.078	11.012	113.893	0.036	0.032	-0.043	0.120
240.077	10.004	101.131	0.035	0.034	-0.001	0.129
240.077	9.004	88.565	0.033	0.038	0.040	0.135
240.077	8.008	76.371	0.032	0.042	0.068	0.141
240.075	7.005	64.620	0.031	0.047	0.089	0.124
240.075	6.003	53.504	0.029	0.055	0.095	0.099
240.074	5.001	43.067	0.028	0.065	0.097	0.080
240.074	4.001	33.300	0.027	0.081	0.098	0.069
240.075	3.001	24.162	0.026	0.107	0.093	0.062
240.073	1.999	15.591	0.025	0.160	0.083	0.057
240.072	0.999	7.556	0.024	0.318	0.079	0.063
250.046	19.940	186.044	0.044	0.024	-0.166	-0.185
250.047	19.023	179.463	0.044	0.024	-0.163	-0.161
250.048	18.018	171.725	0.043	0.025	-0.160	-0.131
250.046	17.011	163.416	0.042	0.026	-0.151	-0.096
250.046	16.018	154.622	0.041	0.026	-0.145	-0.066
250.047	15.015	145.138	0.040	0.027	-0.149	-0.051
250.047	14.014	135.178	0.039	0.029	-0.116	-0.003
250.047	13.012	124.698	0.037	0.030	-0.096	0.024
250.046	12.006	113.812	0.036	0.032	-0.077	0.044
250.045	11.010	102.827	0.035	0.034	-0.046	0.068
250.044	10.014	91.789	0.034	0.037	-0.024	0.075
250.043	9.011	80.795	0.032	0.040	-0.001	0.075

250.042	8.004	70.009	0.031	0.045	0.015	0.069
250.044	7.002	59.655	0.030	0.050	0.032	0.061
250.045	6.004	49.775	0.029	0.058	0.042	0.049
250.045	5.002	40.328	0.028	0.069	0.047	0.039
250.042	4.000	31.364	0.027	0.085	0.052	0.035
250.044	3.000	22.884	0.026	0.113	0.068	0.048
250.047	1.999	14.843	0.025	0.168	0.066	0.049
250.049	1.000	7.230	0.024	0.332	0.061	0.050
260.048	17.614	154.980	0.041	0.026	-0.100	-0.059
260.046	17.013	150.096	0.040	0.027	-0.100	-0.049
260.050	16.016	141.654	0.039	0.028	-0.093	-0.028
260.046	15.017	132.774	0.038	0.029	-0.086	-0.009
260.045	14.013	123.483	0.037	0.030	-0.078	0.007
260.047	13.009	113.883	0.036	0.032	-0.070	0.020
260.045	12.009	104.112	0.035	0.034	-0.061	0.029
260.044	11.008	94.232	0.034	0.036	-0.041	0.045
260.044	10.006	84.334	0.033	0.039	-0.031	0.044
260.044	9.004	74.538	0.032	0.043	-0.021	0.040
260.044	8.003	64.951	0.031	0.047	-0.012	0.031
260.043	7.001	55.622	0.030	0.053	-0.005	0.020
260.044	6.001	46.626	0.029	0.061	-0.002	0.008
260.047	5.000	37.974	0.028	0.072	0.006	0.005
260.045	4.000	29.682	0.027	0.090	0.017	0.008
260.042	3.001	21.762	0.026	0.118	0.029	0.018
260.043	2.000	14.169	0.025	0.175	0.031	0.020
260.041	1.000	6.927	0.024	0.346	0.031	0.024
275.016	19.897	154.661	0.041	0.026	-0.078	-0.061
275.016	19.012	148.567	0.040	0.027	-0.077	-0.051
275.015	18.006	141.344	0.039	0.028	-0.077	-0.042
275.014	17.009	133.878	0.038	0.029	-0.080	-0.037
275.013	16.003	126.067	0.038	0.030	-0.076	-0.026
275.013	15.008	118.086	0.037	0.031	-0.065	-0.009
275.014	14.006	109.837	0.036	0.033	-0.060	0.001
275.013	13.009	101.458	0.035	0.034	-0.055	0.007
275.015	12.007	92.928	0.034	0.036	-0.049	0.012
275.014	11.006	84.369	0.033	0.039	-0.038	0.021
275.013	10.005	75.811	0.032	0.042	-0.033	0.019
275.012	9.002	67.322	0.031	0.046	-0.026	0.017
275.013	8.002	58.973	0.030	0.051	-0.018	0.014
275.010	7.005	50.825	0.029	0.057	-0.008	0.015
275.009	6.005	42.849	0.028	0.066	0.002	0.015

275.009	5.005	35.103	0.027	0.077	0.011	0.016
275.010	4.001	27.568	0.026	0.096	0.020	0.021
275.008	3.001	20.304	0.026	0.126	0.031	0.028
275.007	2.001	13.293	0.025	0.186	0.036	0.031
275.006	1.000	6.522	0.024	0.367	0.037	0.033
299.956	19.795	131.987	0.038	0.029	-0.048	-0.025
299.956	19.011	127.134	0.038	0.030	-0.048	-0.024
299.956	18.003	120.727	0.037	0.031	-0.049	-0.022
299.956	17.007	114.233	0.036	0.032	-0.049	-0.020
299.955	16.003	107.531	0.035	0.033	-0.048	-0.016
299.956	15.005	100.739	0.035	0.034	-0.047	-0.013
299.956	14.003	93.813	0.034	0.036	-0.046	-0.010
299.957	13.002	86.810	0.033	0.038	-0.043	-0.006
299.957	12.002	79.763	0.032	0.040	-0.040	-0.003
299.958	11.003	72.706	0.031	0.043	-0.030	0.006
299.959	10.003	65.636	0.031	0.047	-0.030	0.004
299.958	9.002	58.590	0.030	0.051	-0.027	0.003
299.957	8.001	51.609	0.029	0.056	-0.021	0.005
299.957	6.999	44.708	0.028	0.063	-0.013	0.008
299.957	5.999	37.914	0.028	0.073	-0.007	0.010
299.956	4.999	31.243	0.027	0.086	0.001	0.012
299.955	3.999	24.698	0.026	0.105	0.007	0.014
299.958	2.990	18.241	0.025	0.139	0.013	0.017
299.956	1.999	12.047	0.025	0.204	0.015	0.016
299.957	0.999	5.941	0.024	0.402	0.015	0.013
324.962	19.902	116.626	0.036	0.031	-0.039	-0.021
324.965	19.001	111.659	0.036	0.032	-0.039	-0.022
324.963	18.006	106.065	0.035	0.033	-0.041	-0.022
324.963	16.999	100.301	0.035	0.035	-0.041	-0.021
324.963	16.001	94.491	0.034	0.036	-0.041	-0.019
324.963	15.000	88.578	0.033	0.038	-0.040	-0.017
324.964	14.003	82.625	0.033	0.039	-0.039	-0.014
324.963	13.002	76.592	0.032	0.042	-0.038	-0.012
324.963	12.003	70.531	0.031	0.044	-0.036	-0.009
324.964	11.001	64.438	0.031	0.047	-0.027	< 0.001
324.964	10.000	58.331	0.030	0.051	-0.026	0.001
324.964	9.000	52.245	0.029	0.056	-0.023	0.003
324.963	8.004	46.209	0.028	0.062	-0.019	0.004
324.963	6.999	40.162	0.028	0.069	-0.011	0.009
324.963	6.000	34.198	0.027	0.079	-0.005	0.012
324.963	4.999	28.286	0.026	0.093	0.002	0.015

324.964	4.000	22.453	0.026	0.115	0.009	0.018
324.964	2.999	16.700	0.025	0.150	0.018	0.023
324.964	1.999	11.036	0.024	0.222	0.022	0.023
324.965	0.999	5.467	0.024	0.436	0.021	0.020
349.952	19.350	101.832	0.035	0.034	-0.032	-0.019
349.952	17.000	89.954	0.033	0.037	-0.036	-0.021
349.951	15.997	84.764	0.033	0.039	-0.035	-0.018
349.950	14.998	79.534	0.032	0.041	-0.034	-0.016
349.952	13.994	74.229	0.032	0.043	-0.032	-0.012
349.951	13.000	68.930	0.031	0.045	-0.031	-0.010
349.951	12.003	63.582	0.030	0.048	-0.031	-0.009
349.950	11.000	58.181	0.030	0.051	-0.022	< 0.001
349.950	10.000	52.782	0.029	0.055	-0.021	0.002
349.951	8.997	47.361	0.029	0.060	-0.018	0.004
349.950	7.999	41.970	0.028	0.067	-0.014	0.006
349.950	6.998	36.584	0.027	0.075	-0.007	0.011
349.951	5.998	31.226	0.027	0.086	-0.003	0.012
349.950	4.999	25.902	0.026	0.101	-0.002	0.009
349.949	3.999	20.614	0.026	0.124	0.003	0.010
349.950	2.985	15.301	0.025	0.163	0.002	0.006
349.949	1.999	10.188	0.024	0.239	0.005	0.005
349.950	0.999	5.061	0.024	0.470	0.003	0.001

<sup>a</sup> Expanded uncertainties ( $k = 2$ ) in temperature and pressure are  $U(T) = 0.004$  K and  $U(p) = 0.005$  MPa, respectively.

**Table 7.** Experimental ( $p$ ,  $\rho$ ,  $T$ ) Measurements for the (0.50 CH<sub>4</sub> + 0.50 H<sub>2</sub>) Mixture, Absolute and Relative Expanded Uncertainty in Density ( $k = 2$ )  $U(\rho_{\text{exp}})$  and Relative Deviations from the GERG-2008 and AGA8-DC92 EoS; where  $T$  is the Temperature (ITS-90),  $p$  the Pressure,  $\rho_{\text{exp}}$  the Experimental Density, and  $\rho_{\text{GERG}}$  and  $\rho_{\text{AGA}}$  the Densities Calculated ( $\rho_{\text{calc}}$ , cf. Figures 5 and 6) from the GERG-2008 and the AGA8-DC92 EoS.

$T/\text{K}^a$	$p/\text{MPa}^a$	$\rho_{\text{exp}}/\text{kg}\cdot\text{m}^{-3}$	$U(\rho_{\text{exp}})$ / $\text{kg}\cdot\text{m}^{-3}$ ( $k = 2$ )	$10^2$ $U(\rho_{\text{exp}})$ / $\rho_{\text{exp}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{GERG}})/\rho_{\text{GERG}}$	$10^2 (\rho_{\text{exp}} - \rho_{\text{AGA}})/\rho_{\text{AGA}}$
240.067	19.703	90.858	0.034	0.037	-0.080	-0.040
240.069	19.008	88.009	0.033	0.038	-0.064	-0.018
240.071	18.016	83.857	0.033	0.039	-0.050	< 0.001
240.070	17.008	79.535	0.032	0.041	-0.040	< 0.001
240.069	16.013	75.179	0.032	0.042	-0.027	< 0.001
240.068	15.002	70.674	0.031	0.044	-0.011	< 0.001
240.069	14.011	66.173	0.031	0.046	-0.002	< 0.001
240.069	13.003	61.522	0.030	0.049	0.007	< 0.001
240.069	12.005	56.857	0.030	0.052	0.012	0.088
240.069	11.006	52.137	0.029	0.056	0.022	0.095
240.069	10.006	47.368	0.029	0.060	0.021	0.088
240.069	9.002	42.553	0.028	0.066	0.021	0.080
240.069	8.003	37.747	0.028	0.073	0.018	0.068
240.069	7.000	32.918	0.027	0.082	0.016	0.057
240.070	6.003	28.124	0.026	0.094	0.017	0.048
240.070	5.000	23.326	0.026	0.111	0.034	0.055
240.070	4.003	18.584	0.025	0.136	0.050	0.063
240.073	3.002	13.857	0.025	0.179	0.068	0.074
240.071	2.000	9.174	0.024	0.264	0.068	0.069
240.069	1.000	4.558	0.024	0.520	0.064	0.062
250.040	19.258	84.340	0.033	0.039	-0.087	-0.063
250.041	18.013	79.385	0.032	0.041	-0.077	-0.045
250.040	17.008	75.293	0.032	0.042	-0.067	-0.028
250.040	16.007	71.140	0.031	0.044	-0.058	-0.013
250.040	15.009	66.921	0.031	0.046	-0.055	-0.005
250.039	14.003	62.615	0.030	0.048	-0.039	0.015
250.037	13.005	58.270	0.030	0.051	-0.038	0.018
250.037	12.004	53.836	0.029	0.054	-0.073	-0.016
250.036	11.004	49.405	0.029	0.058	-0.034	0.023
250.036	10.001	44.910	0.028	0.063	-0.022	0.032
250.038	9.002	40.398	0.028	0.069	-0.020	0.030
250.034	8.002	35.861	0.027	0.076	-0.023	0.022

250.035	7.001	31.315	0.027	0.085	-0.018	0.020
250.036	5.999	26.765	0.026	0.098	-0.015	0.016
250.035	5.000	22.235	0.026	0.116	-0.011	0.012
250.035	4.000	17.721	0.025	0.142	-0.001	0.015
250.034	2.990	13.190	0.025	0.187	0.014	0.024
250.029	2.000	8.784	0.024	0.276	0.028	0.033
250.032	1.001	4.372	0.024	0.542	0.044	0.044
260.033	19.113	79.651	0.032	0.041	-0.065	-0.053
260.033	18.006	75.418	0.032	0.042	-0.085	-0.068
260.034	17.009	71.570	0.031	0.044	-0.051	-0.029
260.034	16.009	67.621	0.031	0.046	-0.047	-0.019
260.032	15.005	63.583	0.030	0.048	-0.061	-0.028
260.033	14.009	59.544	0.030	0.050	-0.037	0.001
260.033	13.002	55.387	0.030	0.053	-0.044	-0.002
260.031	12.008	51.246	0.029	0.057	-0.031	0.013
260.033	11.002	47.008	0.029	0.061	-0.026	0.019
260.031	10.005	42.775	0.028	0.066	-0.026	0.019
260.029	9.003	38.489	0.028	0.072	-0.027	0.015
260.031	8.000	34.185	0.027	0.079	-0.022	0.017
260.030	7.000	29.878	0.027	0.089	-0.020	0.015
260.030	6.003	25.579	0.026	0.102	-0.016	0.014
260.029	5.000	21.260	0.026	0.121	-0.008	0.016
260.029	4.002	16.974	0.025	0.148	0.016	0.034
260.030	3.002	12.694	0.025	0.194	0.034	0.046
260.030	1.977	8.330	0.024	0.290	0.060	0.066
260.031	1.002	4.206	0.024	0.563	0.088	0.090
275.007	19.297	74.901	0.032	0.042	-0.071	-0.073
275.006	18.001	70.294	0.031	0.044	-0.064	-0.062
275.006	17.006	66.693	0.031	0.046	-0.059	-0.052
275.006	16.005	63.009	0.030	0.048	-0.055	-0.042
275.007	15.000	59.259	0.030	0.051	-0.050	-0.032
275.007	14.003	55.493	0.030	0.053	-0.046	-0.024
275.005	13.004	51.668	0.029	0.056	-0.043	-0.017
275.005	12.001	47.790	0.029	0.060	-0.039	-0.009
275.006	11.001	43.883	0.028	0.064	-0.032	< 0.001
275.005	10.000	39.943	0.028	0.069	-0.031	0.002
275.005	9.003	35.989	0.027	0.076	-0.028	0.005
275.004	8.001	31.996	0.027	0.084	-0.023	0.009
275.004	7.001	27.997	0.026	0.094	-0.016	0.014
275.004	6.001	23.987	0.026	0.108	-0.005	0.022
275.003	5.001	19.969	0.025	0.128	0.005	0.027



275.003	4.001	15.957	0.025	0.157	0.024	0.042
275.003	3.002	11.950	0.025	0.206	0.035	0.048
275.003	2.001	7.947	0.024	0.303	0.041	0.049
275.002	1.001	3.964	0.024	0.597	0.037	0.040
324.957	19.631	62.562	0.030	0.048	-0.020	-0.028
324.957	19.002	60.728	0.030	0.050	-0.019	-0.027
324.958	17.994	57.761	0.030	0.052	-0.017	-0.024
324.959	16.999	54.795	0.029	0.054	-0.016	-0.021
324.959	15.999	51.775	0.029	0.056	-0.014	-0.018
324.958	14.998	48.720	0.029	0.059	-0.012	-0.013
324.958	14.000	45.642	0.028	0.062	-0.009	-0.008
324.958	12.999	42.522	0.028	0.066	-0.007	-0.003
324.960	12.002	39.381	0.028	0.070	-0.003	0.003
324.959	11.000	36.202	0.027	0.075	0.005	0.013
324.961	9.926	32.763	0.027	0.082	0.016	0.026
324.961	8.999	29.768	0.027	0.089	0.018	0.030
324.960	8.002	26.528	0.026	0.099	0.019	0.031
324.959	7.000	23.250	0.026	0.111	0.022	0.034
324.959	6.001	19.966	0.025	0.128	0.034	0.046
324.960	5.001	16.663	0.025	0.151	0.040	0.050
324.960	4.001	13.346	0.025	0.185	0.044	0.052
324.960	2.987	9.973	0.024	0.244	0.044	0.050
324.961	2.003	6.689	0.024	0.358	0.042	0.045
324.961	1.002	3.349	0.024	0.704	0.040	0.041
349.950	19.933	58.441	0.030	0.051	-0.001	0.001
349.948	19.002	55.940	0.030	0.053	-0.001	< 0.001
349.947	17.989	53.192	0.029	0.055	0.006	0.006
349.948	16.997	50.454	0.029	0.057	-0.018	-0.018
349.947	15.998	47.697	0.029	0.060	0.019	0.019
349.948	15.001	44.896	0.028	0.063	0.022	0.023
349.947	13.993	42.035	0.028	0.067	0.024	0.026
349.948	12.996	39.178	0.028	0.071	0.025	0.028
349.946	11.995	36.281	0.027	0.075	0.018	0.022
349.946	11.001	33.381	0.027	0.081	0.023	0.027
349.947	9.999	30.433	0.027	0.088	0.026	0.031
349.946	9.000	27.473	0.026	0.096	0.031	0.037
349.947	8.001	24.491	0.026	0.106	0.048	0.054
349.947	7.001	21.490	0.026	0.119	0.091	0.097
349.947	6.002	18.469	0.025	0.137	0.102	0.108
349.947	5.003	15.420	0.025	0.162	0.079	0.083
349.947	4.004	12.364	0.025	0.199	0.064	0.068

349.947	3.002	9.284	0.024	0.261	0.067	0.069
349.948	2.004	6.207	0.024	0.385	0.072	0.073
349.947	1.003	3.109	0.024	0.758	0.074	0.073

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<sup>a</sup> Expanded uncertainties ( $k = 2$ ) in temperature and pressure are  $U(T) = 0.004$  K and  $U(p) = 0.005$  MPa, respectively.

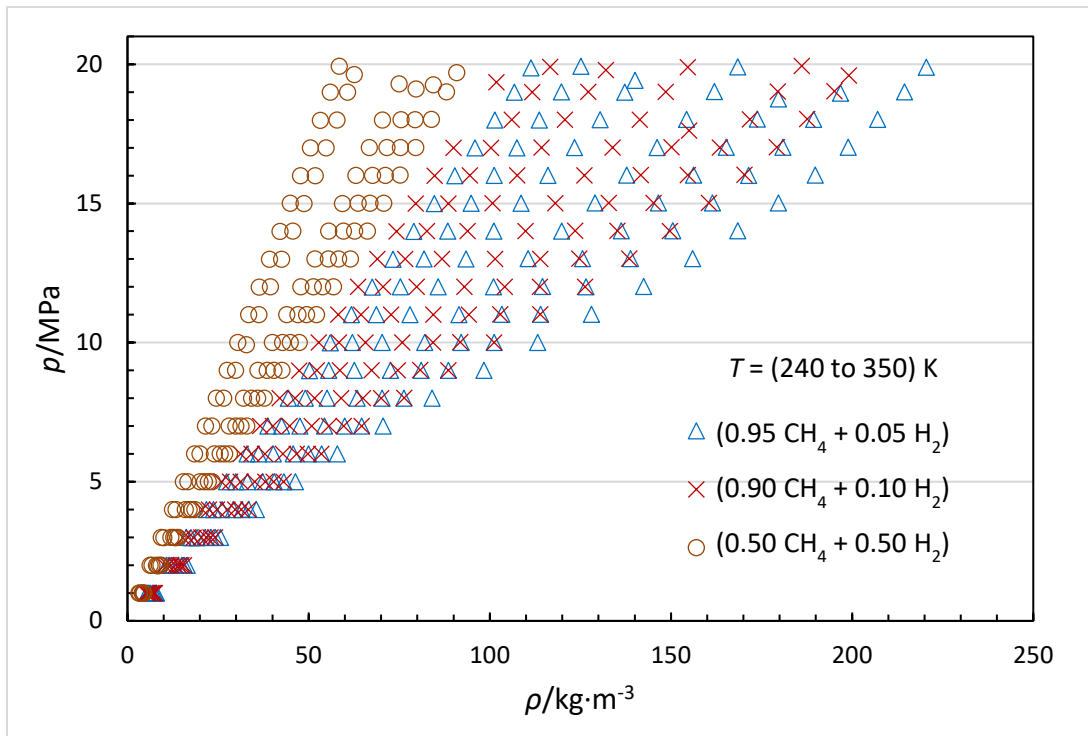
**Table 8.** Statistical Parameters of the Data Set with Respect to the GERG-2008 and AGA8-DC92 EoS for the (CH<sub>4</sub> + H<sub>2</sub>) Mixtures and Literature Comparison.

$(p, \rho, T)$ data	$x(\text{H}_2)$	covered ranges		$N$	experimental vs. GERG-2008				experimental vs. AGA8-DC92			
		$T/\text{K}$	$p/\text{MPa}$		$AAD$	$Bias$	$RMS$	$MaxD/\%$	$AAD$	$Bias$	$RMS$	$MaxD/\%$
this work (2018)	0.05	240 - 350	1 - 20	138	0.033	-0.020	0.048	-0.141	0.030	-0.005	0.046	-0.175
this work (2018)	0.10	240 - 350	1 - 20	136	0.053	-0.031	0.073	-0.221	0.038	0.002	0.060	-0.247
this work (2018)	0.50	240 - 350	1 - 20	117	0.035	-0.002	0.042	0.102	0.034	0.018	0.042	0.108
Jaeschke <i>et al.</i> <sup>24</sup> (1997)	0.50	270 - 350	0.5 - 28.9	126	0.015	-0.004	0.022	-0.104	0.019	0.006	0.026	-0.106
Jett <i>et al.</i> <sup>25</sup> (1994)	0.05	154 - 273	2.2 - 68.2	110	0.430	0.023	0.867	-5.133	-	-	-	-
Magee <i>et al.</i> <sup>26</sup> (1985)	0.20	273 - 300	3.5 - 58.2	135	0.287	-0.261	0.312	-0.709	0.217	-0.178	0.251	-0.651
Mihara <i>et al.</i> <sup>27</sup> (1977)	0.45	323 - 348	0.4 - 8.7	30	0.134	-0.134	0.186	-0.469	0.130	-0.130	0.179	-0.453

**Table 9.** Least-Squares Fit Results for the Three (CH<sub>4</sub> + H<sub>2</sub>) Mixtures. Virial Coefficients ( $B$ ,  $C$ , and  $D$ ) and the Second Interaction Virial Coefficient ( $B_{12}$ ) with the Corresponding Expanded Uncertainties.

$T/\text{K}^a$	$B/$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$U(B)/$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$C/$ $\text{cm}^6 \cdot \text{mol}^{-2}$	$U(C)/$ $\text{cm}^6 \cdot \text{mol}^{-2}$	$B_{12}/$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$U(B_{12})/$ $\text{cm}^3 \cdot \text{mol}^{-1}$
(0.95 CH <sub>4</sub> + 0.05 H <sub>2</sub> )						
240.076	-64.77	0.13	2892	18	-0.1	1.1
250.046	-59.12	0.16	2758	25	1.0	1.1
260.040	-53.96	0.19	2635	32	2.3	1.1
275.014	-47.14	0.25	2485	48	3.4	1.2
299.958	-37.59	0.33	2287	73	5.0	1.2
324.965	-29.68	0.41	2120	100	7.3	1.2
349.949	-23.22	0.49	2020	140	8.0	1.2
(0.90 CH <sub>4</sub> + 0.10 H <sub>2</sub> )						
240.076	-58.31	0.16	2690	23	-1.6	1.1
250.045	-53.00	0.19	2559	30	0.3	1.1
260.045	-48.13	0.21	2432	37	2.2	1.1
275.012	-41.84	0.26	2299	51	3.7	1.2
299.957	-32.96	0.36	2112	83	6.1	1.2
324.963	-25.71	0.44	1970	110	8.0	1.2
349.950	-19.65	0.52	1860	150	9.8	1.2
(0.50 CH <sub>4</sub> + 0.50 H <sub>2</sub> )						
240.080	-15.19	0.27	1275	45	-1.0	1.2
250.038	-12.74	0.28	1233	51	0.6	1.2
260.031	-10.56	0.32	1189	60	2.1	1.2
274.994	-7.70	0.37	1148	75	3.9	1.2
324.951	-0.54	0.50	1080	130	8.2	1.2

<sup>a</sup>  $T$  is the average temperature of each isotherm.



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