



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



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ABSTRACT

This work provides accurate experimental (p , ρ , T) values for three binary mixtures of methane with helium: (0.95 (amount-of-substance fraction) CH_4 + 0.05 He) and (0.90 CH_4 + 0.10 He) at temperatures of (240, 250, and 260) K and (0.50 CH_4 + 0.50 He) from (240 to 400) K. This work is a continuation of a previous one which reported accurate experimental (p , ρ , T) values for the (0.95 CH_4 + 0.05 He) and the (0.90 CH_4 + 0.10 He) binary mixtures over the temperature range from (250 to 400) K. All density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at pressures up to 20 MPa. Experimental values were compared with the corresponding densities calculated from the GERG-2008 and the AGA8-DC92 equations of state, respectively. Deviations from the GERG-2008 are much larger than from the AGA8-DC92 (up to -6.5%). These deviations increase with decreasing temperature, with increasing pressure, and with increasing helium fraction. In contrast, deviations from the AGA8-DC92 are within the 0.5% band. The experimental values were also used to calculate the second and the third virial coefficients, $B(T, x)$ and $C(T, x)$, as well as the second interaction virial coefficient $B_{12}(T)$ for this mixture.

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1. Introduction

The GERG-2008 equation of state [1] was established as ISO standard (ISO 20765-2) for the calculation of thermodynamic properties of natural gases [2]. The equation satisfies the demand on the accuracy in the calculation of thermodynamic properties in the entire fluid region for 21 natural gas components. Experimental values for these pure components and for 210 binary combinations of these components were considered for the development of the GERG-2008 equation of state. The quality and the availability of experimental values limit the achievable accuracy of multi-parametric equations of state, such as the GERG-2008. For those binary mixtures for which enough accurate experimental values were available, binary specific departure functions or a generalized departure function were developed. However, most of the binary systems were taken into account by using adjusted reducing functions for density and temperature, due to the lack of experimental values for these binary mixtures. Formally, GERG-2008 should be adequate for any mixture consisting of an arbitrary combination of the 21 considered components.

However, there are some mixtures for which the equation does not yield a satisfactory property description. A major reason is the lack of accurate measurements to establish the corresponding specific departure function. This is the case for the binary mixture (methane + helium), where no departure function was established yet. In fact, the GERG-2008 report considers binary mixtures containing helium as one of the binary mixtures proposed to develop a generalized departure function in the future [1]. Due to its unique characteristics, helium displays various important medical, scientific and industrial applications and the global demand for helium is increasing. In practice, helium is extracted from certain natural gas fields with helium contents above 0.3 mol-% [3].

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

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calculated from the GERG-2008 and the AGA8-DC92 [4] equations of state.

This work is a continuation of a previous one which reported accurate experimental (p , ρ , T) values for (0.95 CH₄ + 0.05 He) and the (0.90 CH₄ + 0.10 He) binary mixtures over the temperature range from (250 to 400) K [5]. In that work, large deviations of the experimental density from the GERG-2008 were perceived, especially at lower temperatures and with increasing helium content. For that reason, it was decided to extend the experimental study for the same mixtures to even lower temperatures (240 K) and to a new mixture with higher helium content (0.50 CH₄ + 0.50 He). A new refrigerated-heating circulator was installed in the laboratory to extend the temperature range of the single-sinker densimeter. This new device allows measuring (p , ρ , T) values down to a minimum temperature of 240 K.

Moreover, the second interaction virial coefficients $B_{12}(T)$ for the (CH₄ + He) binary mixture at temperatures from (240 to 400) K were also estimated from the new experimental values presented in this paper and the experimental values presented in the previous publication [5].

To achieve the highest accuracy in composition, the three binary mixtures were prepared following the gravimetric method.

2. Experimental

2.1. Mixture preparation

The (CH₄ + He) binary mixtures were prepared by the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM) in Berlin, Germany, according to the ISO 6142 [6]. The mixtures were supplied in aluminum cylinders of 10 dm³. Table 1 shows the composition and the expanded uncertainty ($k = 2$) of the mixtures. Table 2 shows the purity, supplier, molar mass, and critical parameters of pure compounds methane and helium. All substances were used without further purification.

The procedure of mixture preparation is described in the previous study [5].

After preparation, the samples of (0.95 CH₄ + 0.05 He) and (0.90 CH₄ + 0.10 He) were validated by gas chromatography (GC) against samples of similar composition following the single-point exact-match calibration according to ISO/DIS 12963 [7]. The corresponding details are also given in that paper [5]. The GC analysis for the (0.50 CH₄ + 0.50 He) mixture was not performed due to the fact that the helium content was higher than the validated limit of the method used. However, it was possible to validate its composition indirectly from the results for the two other mixtures as these results were in concordance.

2.2. Equipment description

The single-sinker densimeter was developed by Brachthäuser et al. [8] and further improved by Klimeck et al. [9] in the 1990s. The measuring technique is based on the application of the Archimedes' principle which ensures high accuracy. The magnetic

Table 2

Purity, supplier, molar mass, and critical parameters of the individual components of the (CH₄ + He) mixtures studied.

Components	Purity/mol-%	Supplier	M/g·mol ⁻¹	Critical parameters	
				T _c /K	P _c /MPa
Methane	≥99.9995	Linde ^a	16.043 ^b	190.564 ^b	4.599 ^b
Helium	≥99.9999	Linde ^a	4.003 ^c	5.195 ^c	0.228 ^c

^a Linde AG, Unterschleißheim, Germany.

^b Setzmann and Wagner [23].

^c Ortiz-Vega et al. [24].

suspension coupling system allows measuring the buoyancy force on the sinker without any contact between the sinker and the high-accuracy microbalance. This allows accurate density measurements of fluids over wide temperature and pressure ranges [10]. The single-sinker densimeter used in this work was especially designed for density measurements of pure gases and gaseous mixtures and has been previously described in detail by Chamorro et al. [11] and further improved by Mondéjar et al. [12].

The sinker used in this experiment was a silicon cylinder with a mass of 61.59181 ± 0.00016 g and a volume of 26.444 ± 0.003 cm³ ($k = 2$), measured at 293.05 K and 0.101134 MPa.

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

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

where the difference between the sinker weight in vacuum m_{S0} and the sinker apparent weight 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 m³, which is accurately known as a function of temperature and pressure [12].

A new ultra-low temperature refrigerated-heating circulator Julabo FP51-SL (Julabo GmbH, Seelbach, Germany) was installed to control the temperature inside the measuring cell. This new equipment allows measuring (p , ρ , T) values at temperatures as low as 240 K (instead 250 K). In addition, the temperature stability inside the measuring cell with this new thermostatic bath is better than with the old one, particularly at low temperatures. The temperature of the fluid inside the measuring cell is determined by two platinum resistance thermometers (S1059PJ5X6, Minco Products, Inc., Minneapolis MN, USA) connected to an AC comparator resistance bridge (F700, Automatic Systems Laboratories, Redhill, England). The pressure is measured by two Digiquartz transducers (2300A-101 and 43KR-HHT-101, Paroscientific Inc., Redmond WA, USA) which are used for pressures up to 2 MPa and for pressures between (2 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 the final density results. There are two main effects that must be evaluated: the force transmission error (FTE) due to the magnetic coupling and

Table 1

Composition of the studied (CH₄ + He) binary mixtures.

Component	(0.95 CH ₄ + 0.05 He) BAM n°: 8036-150126		(0.90 CH ₄ + 0.10 He) BAM n°: 8069-150127		(0.50 CH ₄ + 0.50 He) BAM n°: 8092-141020	
	x _i (mol-%)	U(x _i) (k = 2) (mol-%)	x _i (mol-%)	U(x _i) (k = 2) (mol-%)	x _i (mol-%)	U(x _i) (k = 2) (mol-%)
Methane	95.0015	0.0092	89.9933	0.0083	49.2592	0.0051
Helium	4.9985	0.0014	10.0067	0.0017	50.7408	0.0058

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