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

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**Abstract**

This work provides accurate experimental \((p, \rho, T)\) values for three binary mixtures of methane with helium: \((0.95 \text{ (amount-of-substance fraction) CH}_4 + 0.05 \text{ He})\) and \((0.90 \text{ CH}_4 + 0.10 \text{ He})\) at temperatures of \((240, 250, \text{ and } 260) \text{ K}\) and \((0.50 \text{ CH}_4 + 0.50 \text{ He})\) from \((240 \text{ to } 400) \text{ K}\). This work is a continuation of a previous one which reported accurate experimental \((p, \rho, T)\) values for the \((0.95 \text{ CH}_4 + 0.05 \text{ He})\) and the \((0.90 \text{ CH}_4 + 0.10 \text{ He})\) binary mixtures over the temperature range from \((250 \text{ to } 400) \text{ K}\). All density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at pressures up to \(20 \text{ MPa}\). 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.

**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 \((p, \rho, T)\) values for three methane and helium binary mixtures with \((0.95 \text{ (amount of substance fraction) CH}_4 + 0.05 \text{ He})\), \((0.90 \text{ CH}_4 + 0.10 \text{ He})\), and \((0.50 \text{ CH}_4 + 0.50 \text{ He})\). Density measurements were performed by using a single-sinker densimeter with magnetic suspension coupling at temperatures of \((240, 250, \text{ and } 260) \text{ K}\) and pressures up to \(20 \text{ MPa}\) for the \((0.95 \text{ CH}_4 + 0.05 \text{ He})\) and the \((0.90 \text{ CH}_4 + 0.10 \text{ He})\) mixtures and at temperatures from \((240 \text{ to } 400) \text{ K}\) and pressures up to \(20 \text{ MPa}\) for the \((0.50 \text{ CH}_4 + 0.50 \text{ He})\) mixture. Experimental values were compared with the corresponding densities.
calculated from the GERG-2008 and the AGA8-DC92 [4] equations
of state.

This work is a continuation of a previous one which reported
accurate experimental (p, ρ, T) 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 con-
tent. 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 pre-
sented 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, accord-
ing 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. The purity, supplier, molar mass, and critical parameters of the individual components of
the (CH₄ + He) mixtures studied.

<table>
<thead>
<tr>
<th>Component</th>
<th>Purity/mol-%</th>
<th>Supplier</th>
<th>M/g mol⁻¹</th>
<th>Critical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>≥ 99.9995</td>
<td>Lindē⁻</td>
<td>−</td>
<td>T/K</td>
</tr>
<tr>
<td>Helium</td>
<td>≥ 99.9999</td>
<td>Lindē⁻</td>
<td>4.003¹</td>
<td>P/MPa</td>
</tr>
</tbody>
</table>

¹ Linde AG, Unterschleißheim, Germany.

Table 2

<table>
<thead>
<tr>
<th>Components</th>
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² Setzmann and Wagner [23].
³ Ortiz-Vega et al. [24].

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 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
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 mea-
surements of fluids over wide temperature and pressure ranges
[10]. The single-sinker densimeter installed in this work was especially
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The measuring technique is based on the application of the
Archimedes' principle which ensures high accuracy. The magnetic

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.
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