Density Measurements of (Methane + Propane) Mixtures at Temperatures between (256 and 422) K and Pressures from (24 to 35) MPa

Armand Karimi,¹ Thomas J. Hughes,¹ Markus Richter² and Eric F. May^{1,*}

¹ Fluid Science and Resources Division, School of Mechanical and Chemical Engineering, The University of Western Australia, Crawley, Western Australia 6009, Australia

² Thermodynamics, Ruhr-University Bochum, D-44780, Bochum, Germany

ABSTRACT

High accuracy equations of state (EOS) are crucial to industrial applications such as natural gas custody transfer and the development of gas processing facilities. The GERG-2008 EOS, which is the ISO Standard for calculating the equilibrium properties of natural gas mixtures, has a stated relative uncertainty in density of 0.1 % over the temperature range from (250 to 450) K at pressures up to 35 MPa. However, for the crucial (methane + propane) binary system, most of the density data sets used in the development of the GERG EOS that extend to pressures above 20 MPa, have root mean square relative density deviations of (0.4 to 0.8) % and maximum relative deviations of up to approximately 3 %. In this work, a single-sinker magnetic-suspension densimeter adapted from a commercial sorption apparatus was used to measure the density of two (methane + propane) mixtures along four isotherms at $T = (256, 310, 366, \text{ and } 422)$ K over the pressure range from (24 to 35) MPa. The binary mixtures were prepared gravimetrically with methane mole fractions of 0.9472 and 0.8924, respectively. The titanium sinker's volume ($V \approx 3.17 \text{ cm}^3$) was determined at each temperature as a function of pressure using pure methane and the reference equation of state for this pure fluid, which has a relative standard uncertainty of 0.03 %. The relative combined expanded uncertainty ($k = 2$) in mixture density measurements ranged from (0.11 to 0.24)%, including the uncertainty in composition. The measured binary mixture densities had relative deviations from those calculated with the GERG-2008 EOS of less than 0.14 %. When considered together with other recently measured high-accuracy density data for this binary system, these results help prioritize the nature of future improvements needed for the EOS.

KEYWORDS

binary gas mixture, density measurements, magnetic-suspension balance, methane, propane

1. INTRODUCTION

Hall and co-workers have a long and successful history of measuring and developing models to predict the density and phase behaviour¹⁻¹⁵ of fluid mixtures, with the broad aim of advancing industry's ability to produce, process and transport them safely and efficiently. A broad variety of experimental techniques for determining fluid densities, including Burnett apparatus,¹ isochoric cells,¹⁵ pycnometers⁷ and most recently magnetic-suspension densimeters,² have been used to deliver the data needed to characterise the thermodynamic behaviour of many important systems over a wide range of conditions. Hall and co-workers have also made important contributions to science and engineering by using such data to develop both technical equations used by industry^{4,5,14} and fundamental models describing intermolecular interactions.^{6,13} Along these lines, this paper reports accurate density measurements of a gas mixture with importance to industry, in a range of high-pressure conditions where the few data that do exist have comparatively large uncertainties. The new data acquired are then used to test the industry standard model for natural gas property prediction to help assess its suitability for use designing and developing the next generation of higher pressure natural gas fields.^{16,17}

The Groupe Européen de Recherches Gazières (GERG)-2008 EOS¹⁸ is the International Organization for Standardization (ISO) standard¹⁹ for the calculation of natural gas thermodynamic properties. Like most EOS used to describe hydrocarbon systems, this reference model for the properties of natural gas mixtures containing up to 21 components is based on accurate property descriptions of (i) each pure fluid and (ii) the constituent binary mixtures as a function of temperature, pressure and composition. The most important binary mixtures when developing a model capable of describing natural gas are those involving the most dominant component methane, and these are the systems that have been measured most extensively. Within the framework of the GERG-2008 EOS, binary interactions are accounted for through composition dependent reducing functions, which facilitate mixing of the pure fluid EOS at equivalent reduced temperatures and densities, and if sufficient data exist, binary departure functions that account for non-ideal contributions. However, only fifteen of the binary mixtures described by the GERG-2008 EOS have been sufficiently well-characterized to enable development of a reliable binary departure function. Furthermore, for many of those binaries described by a departure function, there are often regions of temperature, pressure or composition where the quality of the data

available is inadequate and/or there are significant inconsistencies between literature data sets. Recently, Rowland et al.²⁰ have shown how new, reference quality thermodynamic property measurements for the methane + butane binary²¹ that resolve discrepancies between literature data sets can enable the development of improved binary interaction parameters and departure functions for use within the GERG-2008 EOS.

In this work, the density of two methane + propane mixtures in the dense gas phase was investigated, as part of an ongoing program commissioned by the Gas Processors Association to improve the ability to predict the thermophysical properties of hydrocarbon mixtures at temperatures between (200 and 450) K and pressures to 35 MPa.²² In particular, while the methane + propane binary is reasonably well-studied at pressures below 20 MPa, the few literature data sets containing data measured at higher pressures exhibit significant discrepancies in the dense phase region. This is illustrated in Figure 1 where the relative deviations between experimental densities (tabulated in the NIST ThermoData Engine²³) and those calculated with the GERG-2008 EOS are shown as a function of density. It is clear that the deviations grow significantly at densities greater than 100 kg·m⁻³ with relative deviations ranging between about -3 % and 2.5 %. Despite these inconsistencies, all but one of the literature data sets shown in Figure 1 were used in the development of the GERG-2008 EOS because of no others were available at these conditions. The accurate data of Richter and McLinden²⁴ measured in 2014 are also shown in Figure 1, as these indicate that the accuracy of densities predicted with the GERG-2008 EOS decreases significantly for high propane fractions (greater than 0.5 mole fraction), even at densities lower than 100 kg·m⁻³.

The density data of Reamer and Sage²⁵ in the dense phase region were measured using a stainless steel vessel of known volume that was charged with propane from a weighing bomb and methane from a calibrated isochoric reservoir. The volume of hydrocarbons in the vessel could be reduced by injecting mercury. The relative uncertainty in the density of the measurements of Reamer and Sage²⁵ was estimated to be between (0.17 and 0.25) %, which appears somewhat optimistic given the degree of scatter illustrated in Figure 1. The density measurements of Huang et al.²⁶ were conducted by displacing known volumes of pure methane and propane from precision bore pumps into a mixing chamber of known volume. The masses of pure methane and propane added were calculated from literature density data available at the time. Huang et al. did not estimate an

uncertainty but they observed a reproducibility in their density measurements of 0.8 %, which appears consistent with Figure 1. Arai and Kobayashi's measurements²⁷ were made using an isochoric technique where the mixture was weighed into an isochoric cell. The uncertainty of these measurements was not stated by the authors and no estimate is available from the NIST ThermoData Engine.²³ From Figure 1 the scatter of the data is large indicating an uncertainty on the order of (1 to 2) %.

There are several possible approaches to the measurement of fluid densities, including those used by Hall and co-workers,¹⁻¹⁵ techniques based on vibrating tubes²⁸ or wires,²⁹ and methods based on the measurement of refractive index or dielectric permittivity.³⁰ Each technique has strengths and limitations and several factors influence the choice of method including the nature of the sample (e.g., volume, phase, toxicity), the uncertainty required, and the operating environment. For measurements of many high pressure gases, the magnetic-suspension densimeter (MSD) approach developed by Wagner and Kleinrahm⁴⁰ has established itself as the most accurate method available. The approach is based on the Archimedes' principle: the fluid density is determined by measuring the combination of the gravity and buoyancy forces acting on a sinker of known mass and volume immersed in that fluid. One key advantage of the technique is the contactless force transmission enabled by the magnetic coupling system that enables the immersed sinker to be weighed over wide ranges of pressure and temperature using a precision balance operating at ambient conditions. This experimental technique enabled Wagner and Kleinrahm's group to systematically measure the density of many different pure fluids with unprecedented uncertainties, which in turn provided the foundations for the development of reference EOS for these systems and, to a lesser extent, their mixtures.³²⁻³⁴ However, at the time of the GERG-2008 EOS development, few MSD density data were available for relevant binary mixtures at pressures above 20 MPa.

Recently, Yang et al.³⁵ have described how magnetic-suspension densimeters have been optimized for wide variety of applications, and MSDs are increasingly being used to study pure fluids or mixtures at pressures up to 35 MPa as demonstrated by the groups of Hall,¹¹ Chamorro,³⁶ Wagner,^{37,38} and Wang.³⁵ In this work, we report density measurements made with an MSD for two binary mixtures of $x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8$ with $x = 0.9472 \pm 0.0001$ and $x = 0.8924 \pm 0.0001$ along

four isotherms $T = (256.10, 310.93, 366.48, 422.04)$ K and pressures between (24 and 35) MPa. The p, T phase envelopes for these mixtures calculated using the GERG-2008 EOS are shown in Figure 2, together with the location of the measurement conditions.

2. EXPERIMENTAL SECTION

The apparatus employed in the present work was a commercial magnetic-suspension balance developed primarily for sorption analysis (type: IsoSORP, Rubotherm, Germany). The apparatus was modified in a way similar to that described by May et al.³⁹ for the purpose of mixture density measurements: the basket assembly that normally holds the adsorbent sample was removed and replaced with a single titanium sinker as shown in Figure 3. However, unlike the modifications made in May et al.,³⁹ only a single titanium sinker ($m_s \approx 14.37$ g, $V_s \approx 3.17$ cm³, $\rho_s \approx 4.53$ g·cm⁻³) was used to determine gas densities because (i) the commercial microbalance used here (WXS series of Mettler, weighing range: 20 g with a resolution of 1 µg) provided significantly improved sensitivity, and (ii) the density measurements were not made at conditions close to the dew point curves of the mixtures. In addition, two further modifications to the commercial sorption MSB system were implemented to enable measurements over a wider range of temperature, as discussed below.

The principle of the density measurement has been described in detail by many authors including Wagner and Kleinrahm,⁴⁰ McLinden,⁴¹ and, in the context of measurements at pressures above 20 MPa, by Hall and co-workers,^{3,10-12} so only a brief description is given here. To measure density, the sinker immersed in the fluid under study was weighed by the microbalance in conjunction with a magnetic-suspension coupling. The main components of the coupling system were two magnets, one on each side of the pressure vessel's wall. The top magnet (electromagnet) was connected to the balance via a hook on the underside of the balance while the bottom (permanent) magnet was suspended inside the measuring cell and could be connected to the sinker by means of a sinker-coupling rod. A stable suspension position was realized by a PID control circuit. The pressure vessel wall between the two magnets was non-magnetic to a first approximation; however, small variations in the magnetic-transmission force with suspension position were taken into account by determination of the sinker volume with a reference fluid as discussed below.

The magnetic-suspension coupling of the present apparatus allows generally three stable suspension positions. However, for the measurements reported here, only two positions were required, which are illustrated in Figure 3. In the zero-point position (ZP), the sinker sits on its deposit screw, and the permanent magnet is suspended at its farthest distance from the top magnet without being coupled to the sinker. In the measuring position (MP), the permanent magnet is gently moved to a higher vertical position and lifts the sinker so that it can be weighed with the balance. We followed the weighing procedure described by Richter et al.⁴² the sinker was coupled and decoupled from the balance several times for each measurement. Usually, the sinker was moved from ZP to MP ten times to yield 20 weighing values, allowing an average value to be calculated with reduced uncertainty. The balance was tared only once at the beginning of the sequence (balance reading: 0.000000 g) so that the small drift of the balance reading when in the ZP could be taken into account by subtracting it from the balance reading when in the MP. In this way, we could compensate for the zero-point drift of the balance. The ten sinker weighings took approximately 15 minutes. The fluid density was then determined by

$$\rho(T, p) = \frac{m_{S,vac}^*(T) - m_{S,fluid}^*(T, p)}{V_s(T, p)} \cdot \left(1 - \frac{\rho_{ambient}}{\rho_{St}}\right), \quad (1)$$

where $m_{S,vac}^*(T)$ is the average of the weighing values obtained for the sinker inside the evacuated measuring cell at the temperature T , and $m_{S,fluid}^*(T, p)$ is the average of the weighing values obtained for the sinker immersed in the fluid of unknown density at the temperature T and the pressure p . The sinker volume

$$V_s(T, p) = V_{S,0}(T) \cdot (1 - \beta_T \cdot p) \quad (2)$$

at the temperature T and the pressure p was determined by weighing the sinker in pure methane (mole fraction purity 0.99995) along each isotherm of interest over the relevant pressure range. The results were used to fit $V_{S,0}(T)$ and β_T for each isotherm (see section 5).

The last factor in eq 1 refers to the buoyancy correction as the electronic weighing range of the balance was calibrated by means of the balance's internal calibration masses made of stainless steel ($\rho_{\text{st}} = 8000 \text{ kg}\cdot\text{m}^{-3}$). The balance housing was filled either with (static) air or, for measurements at $T = 256 \text{ K}$, with a small continuous flow of ambient pressure argon. Thus, ρ_{ambient} in eq 1 was either set equal to the density of air or of argon. Flushing of the balance housing with argon was necessary to prevent water vapor from the air condensing on the electromagnet of the suspension coupling inside the central tube connecting the balance housing with the coupling housing. The implementation of this argon flushing procedure was one of the extra modifications to the commercial sorption MSB apparatus required to achieve the extended range of operating temperature.

The force transmission error,³⁵ which is an unavoidable systematic error of the magnetic-suspension coupling, was not analyzed specifically for the present measurements. Instead, this error was reduced to a second order effect, by determination of the sinker volume with pure methane. Moreover, since methane is the main component (mole fraction approximately > 0.8) of the two investigated mixtures, the fluid-specific part of the force transmission error would not be significantly different for pure methane and the binary mixtures. In future work it may be possible to achieve smaller uncertainties with the present apparatus than reported here through the implementation of refinements similar to those described elsewhere.⁴¹

The temperature of the measuring cell was controlled by a bath thermostat (type: FP ME50, Julabo, Germany) circulating heat transfer fluid through two separate thermostating jackets around the measuring cell and the coupling housing. The original insulation material provided for the thermostating jackets was replaced, and the high-pressure gas transfer lines were covered, with tight-fit EPT/EPDM insulation sheets and hoses of Armacell to improve temperature uniformity and regulation. Another important modification was implemented to facilitate a stable balance operation at measurement temperatures near and above 400 K . An additional cooling coil was wrapped around the top of the central tube connecting the balance housing (underneath the balance plate) with the coupling housing (that might be at high temperature). A separate thermostat was used to circulate cooling water through this coil to keep the balance housing at a constant temperature close to ambient.

The temperature inside the measuring cell was monitored with a 100 Ω platinum resistance thermometer (PRT). This PRT was calibrated on ITS-90 prior to the measurements by comparison to a reference thermometry chain consisting of a standard platinum resistance thermometer (SPRT) and a thermometry bridge (type: CTR5000, ASL/WIKA, Germany). The reference thermometry chain was calibrated by Deutscher Kalibrierdienst (DKD) with a reported standard uncertainty of 5 mK ($k = 1$). For the present measurements, we estimate the uncertainty in temperature (incl. self-heating of the PRT, heat dissipation of the test leads, temperature oscillations over time, gradients along the measuring cell wall etc.) to be 300 mK ($k = 1.73$). Pressures were measured using a vibrating quartz-crystal-type transmitter (type: 9000-6K-101, Paroscientific, U.S.A.); the manufacturer specifies an uncertainty ($k = 1.73$) of 0.01 % of the transmitter's maximum pressure, which was $p_{\max} = 41$ MPa.

3. MATERIALS AND PROCEDURES

The gas-mixtures were prepared gravimetrically in stainless steels gas cylinders with an internal volume of 12 L (Faber, Italy). The components of the gas mixtures are described in Table 1; they were used as received, no further purification or gas analysis were carried out. Prior to the sample preparation, the cylinder was briefly evacuated, then filled with nitrogen (mole fraction purity of 0.9999) to a pressure of 5 MPa and left overnight. This was done to dilute the residues of the previous filling and to trigger desorption of impurities adsorbed onto the internal surfaces of the gas cylinder. The cylinder was then evacuated to a pressure below 50 Pa and purged with propane. This procedure was repeated three times. After the final evacuation a couple of hours were allowed for thermal equilibration before the cylinder was weighed with a simple balance (resolution: 0.1 g) and subsequently filled with propane to the desired pressure. It was placed aside overnight to allow the cylinder to re-equilibrate to room temperature and was then weighed the next morning. The cylinder was then filled with the second gas (methane) to obtain the desired mixture composition. A further day was allowed to ensure the cylinder containing the (methane + propane) mixture had returned to room temperature before the final weighing was carried out. During the density measurements, which lasted several weeks, the bottom of the cylinder was heated to induce convective flows inside the cylinder that facilitate mixing. The compositions and uncertainties as well as the molar mass of the prepared mixtures are given in Table 2.

For each isotherm along which mixture measurements were carried out, the sinker volume was determined beforehand and/or afterwards by weighing the sinker in pure methane (mole fraction purity 0.99995) at the same temperature and over nearly the same pressure range as for the mixture measurements. To conduct measurements along an isotherm, the measuring cell was evacuated for 3 hours, and then the cell was filled with the gas sample under study to the highest required pressure. As suggested by Richter and Kleinrahm,⁴³ at each (T, p) state point, the measuring cell was flushed at constant pressure and temperature with fresh gas at a sufficient flow rate and time to ensure the gas volume inside the measuring cell was exchanged several times. Enough time (at least 3 hours) was allowed for the system to equilibrate before the density measurements commenced. Two or three replicate measurements were conducted at each (T, p) state point.

4. MEASUREMENT UNCERTAINTY

The combined uncertainty of the density measurement was calculated according to the “Guide to the Expression of Uncertainty in Measurement” (GUM).³¹ Assuming that the input quantities are not correlated, the combined standard uncertainty ($k = 1$) in density for the present measurements can be calculated as

$$u_c(\rho(T, p, x)) = \sqrt{u(\rho)^2 + \left[\left(\frac{\partial \rho}{\partial p} \right)_T u(p) \right]^2 + \left[\left(\frac{\partial \rho}{\partial T} \right)_p u(T) \right]^2 + \left[\frac{\Delta \rho}{\Delta x_{C_3H_8}} u(x_{C_3H_8}) \right]^2}. \quad (3)$$

Eq 3 includes the uncertainty contributions from the measurements of density, pressure and temperature as well as the from the mixture composition. As recently described by Richter et al.⁴² for a single-sinker densimeter, the standard uncertainty in density $u(\rho)$ arises from several individual contributions, e.g., from weighing the sinker in the fluid under study and in the evacuated measuring cell, from the uncertainty of the analytical balance, from the volume determination of the sinker and, in addition, from the force transmission error (FTE) of the magnetic suspension coupling. In this work, the uncertainty of the sinker volume determination was the dominant contribution to $u(\rho)$. As we will further discuss in section 5, the sinker volume was determined by weighing it in pure methane at different temperatures and pressures (as well as in the evacuated measuring cell at the same temperatures) and using calculated density values from

the reference equation of state (EOS) for methane of Setzmann and Wagner⁴⁵. Thus, for the uncertainty in sinker volume, the contributing uncertainties associated with the sinker weighings in methane and in the evacuated measuring cell, as well as the uncertainty of the EOS which is reported to be 0.03 %, were all taken into account. Based on the afore mentioned input quantities, the relative expanded ($k = 2$) uncertainty in density was estimated conservatively to be $u(\rho)/\rho = 0.038$ %.

The partial derivatives of density in eq 3 (sensitivity coefficients according to GUM) were calculated with the GERG-2008 EOS as implemented in the NIST REFPROP database of Lemmon et al.⁴⁴ The standard uncertainties in pressure $u(p)$ and temperature $u(T)$ were estimated according to section 2 to be 0.0024 MPa and 0.17 K, respectively. For gas mixtures, the contribution of the uncertainty in mixture composition can be accounted for using the method described in detail by Richter and McLinden.²⁴ However, this approach of fitting a virial equation to the isothermal data to estimate the molar mass of the mixture in the limit of zero density was not viable in the present case because the measurements were carried out only at high pressures between (24 and 35) MPa. Therefore, we used a simplified version of the method presented by Richter et al.,⁴² which was originally reported for measurements on liquid mixtures. With this method, a possible distortion of the composition due to sorption effects is not considered. However, such effects are expected to be negligible in this work as the measurements were carried out at a substantial distance from the dew line (see Figure 2). To calculate the last term in eq 3, $u(\text{C}_3\text{H}_8)$ was taken from Table 3. In general, for all of our measurements on the binary mixtures, the relative combined expanded uncertainty ($k = 2$) ranged from (0.11 to 0.24) %.

5. RESULTS

Figure 4 illustrates the results of the density measurements with pure methane following our adjustment of the sinker volume at each temperature to force agreement with the equation of state densities. In the top panel, we present the data in a density versus pressure plot, and in the bottom panel, relative deviations of the densities derived from weighing the sinker in pure methane from values calculated with the reference EOS for methane of Setzmann and Wagner⁴⁵ (once the sinker

volume was optimized to minimize those deviations) are plotted versus pressure. Overall, 39 data points were determined for methane along the four isotherms (several points were repeated at nearly the same temperature and pressure). For each point, the volume of the sinker $V_s(T, p)$ was calculated from eq 1 using density values from the reference equation of state. The calculated sinker volumes for each isotherm were regressed to eq 2 by a least squares fit to determine the parameters $V_{s,0}(T)$ and β_T . These best-fit parameters were then used in eqs 1 and 2 to calculate the density of methane for comparison with the reference equation of state, and the deviations are shown in the bottom panel of Figure 4. The maximum and root mean square values of the relative deviations shown in the bottom panel of Figure 4 are 0.03 % and 0.009 %, respectively, both of which are within the stated uncertainty of the reference equation of state for methane (0.03 %). Although they should not be considered as measurements of methane's density owing to our adjustment of the sinker volume to force agreement with the equation of state, tabulated values of the methane densities calculated from weighing the sinker in pure methane are listed in the Supporting Information.

Mixture measurements were carried out along the same isotherms and in the same pressure range as for pure methane (cf. Figure 2). The numerical values of the measured densities of both (methane + propane) mixtures are listed in Table 3, and the results are plotted for each isotherm in Figure 5. For both (methane + propane) mixtures and all four isotherms, the comparison of our experimental densities with the GERG-2008 equation of state reveal relative deviations of less than 0.14 %, and in all cases the relative deviations are smaller than the estimated state point uncertainties of our measurements. The root mean square relative deviation is 0.09 %, which is comparable with the reported uncertainty of the GERG-2008 EOS (0.1 %). For both mixtures, the relative deviations only exceed 0.1 % at densities greater than $255 \text{ kg}\cdot\text{m}^{-3}$, which occurs for all data measured at $T = 256 \text{ K}$ for both mixtures and also at $T = 309 \text{ K}$ above $p = 31 \text{ MPa}$ for the mixture richer in propane.

Figure 6 shows the relative deviations of our new (methane + propane) density data and those of literature data for binary mixtures with methane mole fractions larger than 0.74 from values calculated with the GERG-2008 EOS. It appears from this figure that the density data of RuhrGas⁴⁶ and Gasunie⁴⁶, which collectively have a root mean square relative deviation of 0.024 %, were particularly important in the development of the EOS. Two common features of these data sets are their pressure range ($p < 12$ MPa), and their low propane mole fractions (0.0401 to 0.0702), which constrains them to densities $\rho \leq 100$ kg·m⁻³. The data of May et al.³⁹, which were also used in the EOS development, were measured over a similar range of pressure but with a larger range of propane fractions (0.0670, 0.1581 and 0.2069). Similarly to the RuhrGas⁴⁶ and Gasunie⁴⁶ data sets, the leanest mixture measured by May et al.³⁹ had a root mean square relative deviation of 0.04 % from the GERG EOS, which is smaller than the estimated experimental relative uncertainty of their data of approximately (0.06 to 0.23) %. However, for the two mixtures measured by May et al. with larger propane fractions, the root mean square relative deviations increase to 0.15 % and 0.27 %, respectively. Nevertheless, since these latter two deviations are roughly comparable with the estimated uncertainty of the measurements of those richer mixtures, which was approximately (0.05 to 0.11) %, it is plausible that this did not indicate any problems with the model's composition dependence during the development of the EOS.

However, the 2014 data of Richter and McLinden²⁴, who used a two-sinker magnetic-suspension densimeter to systematically investigate the impact of increasing propane fraction with very high accuracy, reveal this trend unambiguously. Their relative combined expanded uncertainty in density ranged from 0.032 % at the highest densities measured to 0.17 % at $\rho = 1.66$ kg·m⁻³. The root mean square relative deviations of their data for (methane + propane) mixtures with propane fractions of 0.25023, 0.49312, and 0.73421 are 0.09 %, 0.29 %, and 0.49 %, respectively; these are relatively large considering that the data have a maximum pressure of 6 MPa. Figure 1 shows that for the two mixtures richer in propane, the relative deviations of the data systematically become increasingly negative with increasing density and exceed -1.3 %. Figure 6 shows a reasonable consistency between their data for a binary mixture with a propane fraction of 0.26579 and those of May et al.³⁹ for binary mixtures with propane fractions of 0.1581 and 0.2069. These results establish clearly the need for an improved description of the reducing and/or departure

functions used in the GERG-2008 EOS for methane + propane, with further discussion on this point given in reference 24.

The new data reported in this work help to resolve the question raised by the large scatter apparent in Figure 1 regarding the performance of the GERG-2008 EOS for methane + propane in the dense gas region with $\rho > 100 \text{ kg}\cdot\text{m}^{-3}$. At the time of the equation's development, only three density data sets were available for this region, each of which might have experimental uncertainties of order 1 %. In this context it is somewhat remarkable that the mixture densities measured in this work up to nearly $350 \text{ kg}\cdot\text{m}^{-3}$ are consistent within experimental uncertainty with those predicted using the GERG-2008 EOS. This may reflect that the deviations of the data of Reamer et al.²⁵ from the EOS are approximately opposite in sign and similar in magnitude to the deviations of the data of Arai and Kobayashi²⁷. It also possibly reflects the robustness of the EOS functional form for the description of the dense gas region.

6. CONCLUSION

A commercial magnetic-suspension balance for sorption analysis was adapted for use as a single-sinker densimeter to measure the density of two (methane + propane) mixtures along each of four isotherms at approximately $T = (256, 310, 366, \text{ and } 422) \text{ K}$ over the pressure range from (24 to 35) MPa. Several modifications to the commercial apparatus were made to enable the apparatus to operate over this temperature range. The binary gas-mixtures were prepared gravimetrically, and had methane mole fractions of 0.9472 and 0.8924. The measurements were carried out in the dense gas region at a substantial distance from each mixture's dew point curve, so sorption effects could be considered negligible. The sinker volume and its variation with pressure were determined for each isotherm by weighing the sinker in pure methane. For all measurements on the binary mixtures, the relative combined expanded uncertainty ($k = 2$) ranged from 0.11 % at the highest temperature to 0.24 % at the lowest temperature.

The new mixture density data resolve discrepancies of around (2 to 3) % between existing data sets in the literature at similar conditions. Remarkably, the new data have relative deviations from the GERG-2008 equation of state of less than 0.14 % given that at the time of its development the EOS was regressed to the discrepant literature data sets above. Together with the density data of

Richter and McLinden²⁴ published in 2014, these results help identify how future efforts to improve the description of the methane + propane binary should be focused: namely, for this binary, modelers should prioritize improving the equations' dependence on propane mole fraction ahead of refining its description of the high pressure dense gas region.

AUTHOR INFORMATION

Corresponding Author

*Email: eric.may@uwa.edu.au, Tel.: +61 8 6488 2954

Funding Sources

This work was supported by the Gas Processors Association and the Australian Research Council's Linkage Program (LP130101018).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors thank the GPA and Australian Research Council for funding this work, Craig Grimm and David Amm for helping to maintain the apparatus and the University of Western Australia's (UWA) Institute of Advanced Studies for supporting the visit of Markus Richter to UWA.

Figure 1. Relative deviations of selected literature density data, ρ , for $x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8$ mixtures from values, ρ_{GERG} , calculated with the GERG-2008 equation of state:¹⁸ $\square$, Reamer and Sage²⁵ [$x = 0.9$, $310 < T/\text{K} < 511$, $12 < p/\text{MPa} < 69$]; red $*$, Huang et al.²⁶ [$x = 0.753$, $T = (273, 311) \text{ K}$, $13 < p/\text{MPa} < 35$]; blue $+$, Arai and Kobayashi²⁷ ($x = 0.9464$, $212 < T/\text{K} < 327$, $6.5 < p/\text{MPa} < 65$); blue $\times$, Gasunie⁴⁶ [$x = (0.9502, 0.9599)$, $279 < T/\text{K} < 309$, $3.7 < p/\text{MPa} < 6.4$]; green Δ , Ruhr gas⁴⁶ (optical interferometry) [$x = 0.9298$, $280 < T/\text{K} < 330$, $0.3 < p/\text{MPa} < 12$]; red Δ , Ruhr gas⁴⁶ (Burnett apparatus) [$x = 0.9298$, $T = 313 \text{ K}$, $0.3 < p/\text{MPa} < 11$]; purple $\circ$, May et al.³⁹ [$x = 0.9330$, $290 \leq T/\text{K} \leq 313$, $0.9 < p / \text{MPa} < 7.9$]; green $\circ$, May et al.³⁹ [$x = 0.8419$, $278 \leq T/\text{K} \leq 313$, $2.1 < p / \text{MPa} < 9.5$]; black $\circ$, May et al.³⁹ [$x = 0.7931$, $284 < T/\text{K} < 294$, $1.9 < p / \text{MPa} \leq 10$]; black $\diamond$, Richter and McLinden²⁴ [$x = 0.74977$, $248 \leq T/\text{K} \leq 373$, $0.3 \leq p/\text{MPa} \leq 6$]; green $\diamond$, Richter and McLinden²⁴ [$x = 0.50688$, $248 \leq T/\text{K} \leq 373$, $0.1 < p/\text{MPa} < 2$]; purple $\diamond$, Richter and McLinden²⁴

$[x = 0.26579, 248 \leq T/\text{K} \leq 373, 0.1 \leq p/\text{MPa} < 1.4]$. Only the data of Richter and McLinden²⁴ were not included in the development of the GERG-2008 EOS.

Figure 2. Calculated p , T phase envelopes for $x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8$ mixtures using the GERG-2008 equation of state¹⁸ and density measurement p , T conditions: red –, phase envelope for $x = 0.9472$; black –, phase envelope for $x = 0.8924$; the filled circles indicate the calculated critical point of each mixture; black $\times$, density measurement p , T conditions for $x = 0.9472$ mixture, red $+$, density measurement p , T conditions for $x = 0.8924$ mixture.

Figure 3. A schematic of the magnetic suspension balance densimeter and the two possible sinker positions. (a) Zero-position: the sinker is sitting on the deposit screw. (b) Measuring position: The permanent magnet lifts the sinker.

Figure 4. a) Pure methane densities measured in this work for sinker volume calibration. The tabulated data are presented in the Supporting Information. b) Relative deviations of pure methane densities (ρ) measured from reference equation of state (Setzmann and Wagner⁴⁵) densities (ρ_{EOS}), following calibration of the sinker volume at each temperature: $\square$, $T = 256.1 \text{ K}$; $+$, $T = 311 \text{ K}$; $\circ$, $T = 366.4 \text{ K}$; Δ , $T = 421.5 \text{ K}$. The relative deviations of pure methane densities (ρ) calculated using the shortened EOS for methane implemented in the GERG -2008 EOS from the reference equation of state of Setzmann and Wagner⁴⁵ (ρ_{EOS}) are also shown : ---, $T = 256.1 \text{ K}$; ..., $T = 421.5 \text{ K}$.

Figure 5. Measured densities, ρ , of the binary mixtures compared with the density of pure methane measured at the same temperature, together with relative deviations of the measured mixture

densities from the GERG-2008 EOS¹⁸ (ρ_{GERG}) along each isotherm. $\circ$, 0.9472 methane + 0.0528 propane mixture; Δ , 0.8924 methane + 0.1076 propane; $\blacksquare$, pure methane.

Figure 6. Relative deviations of selected literature density data, ρ , for $x\text{CH}_4 + (1-x)\text{C}_3\text{H}_8$ mixtures with $x > 0.74$ from values, ρ_{GERG} , calculated with the GERG-2008 equation of state:¹⁸ black $\bullet$, this work ($x = 0.9472$, $256 < T/\text{K} < 422$, $22 < p/\text{MPa} < 35$); red $\bullet$, this work ($x = 0.8924$, $256 < T/\text{K} < 422$, $23 < p/\text{MPa} < 35$); $\square$, Reamer and Sage²⁵ [$x = 0.9$, $310 < T/\text{K} < 511$, $12 < p/\text{MPa} < 69$]; red $*$, Huang et al.²⁶ [$x = 0.753$, $T = (273, 311) \text{ K}$, $13 < p/\text{MPa} < 35$]; blue $+$, Arai and Kobayashi²⁷ [$x = 0.9464$, $212 < T/\text{K} < 327$, $6.5 < p/\text{MPa} < 65$]; blue $\times$, Gasunie⁴⁶ [$x = (0.9502, 0.9599)$, $279 < T/\text{K} < 309$, $3.7 < p/\text{MPa} < 6.4$]; green Δ , Ruhr gas⁴⁶ (optical interferometry) [$x = 0.9298$, $280 < T/\text{K} < 330$, $0.3 < p/\text{MPa} < 12$]; red Δ , Ruhr gas⁴⁶ (Burnett apparatus) [$x = 0.9298$, $T = 313 \text{ K}$, $0.3 < p/\text{MPa} < 11$]; purple $\circ$, May et al.³⁹ [$x = 0.9330$, $290 \leq T/\text{K} \leq 313$, $0.9 < p / \text{MPa} < 7.9$]; green $\circ$, May et al.³⁹ [$x = 0.8419$, $278 \leq T/\text{K} \leq 313$, $2.1 < p / \text{MPa} < 9.5$]; black $\circ$, May et al.³⁹ [$x = 0.7931$, $284 < T/\text{K} < 294$, $1.9 < p / \text{MPa} \leq 10$]; black $\diamond$, Richter and McLinden²⁴ [$x = 0.74977$, $248 \leq T/\text{K} \leq 373$, $0.3 \leq p/\text{MPa} \leq 6$].

Table 1. Sample information.

chemical name	source	purification method	mole fraction purity
methane	Air Liquide	none	0.99995
propane	Air Liquide	none	0.9999

Table 2. Compositions and standard uncertainties (from gravimetry) of the prepared methane + propane mixtures.

	0.9472 CH ₄ + 0.0528 C ₃ H ₈		0.8924 CH ₄ + 0.1076 C ₃ H ₈	
	Amount	Uncertainty ^a	Amount	Uncertainty ^a
Moles of propane /mol	2.4515	0.0035	4.6346	0.0037
Moles of methane /mol	44.007	0.011	38.441	0.011
Moles of mixture /mol	46.459	0.012	43.075	0.011
Mole fraction of methane	0.9472	0.0001	0.8924	0.0001
Mole fraction of propane	0.05278	0.0001	0.1076	0.0001
Average molar weight /g·mol ⁻¹	17.5231	0.0020	19.0611	0.0023

^a These include the uncertainties due to weighing, impurities of gases and dead volume of valves.

Table 3 - Experimental density data and relative combined expanded ($k = 2$) uncertainties^a for the dense gas phase mixtures of methane + propane containing methane mole fractions of 0.9472 and 0.8924, together with their relative deviations from values calculated with the GERG-2008¹⁸ equation of state.

0.9472 methane + 0.0528 propane					0.8924 methane + 0.1076 propane				
T/K	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$100 (\rho - \rho_{\text{GERG}}) / \rho_{\text{GERG}}$	$100 U(\rho)/\rho$	T/K	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$100 (\rho - \rho_{\text{GERG}}) / \rho_{\text{GERG}}$	$100 U(\rho)/\rho$
256.10	34.790	305.13	0.14	0.15	256.21	34.785	331.89	0.12	0.13
256.08	34.782	305.07	0.12	0.15	256.21	34.766	331.87	0.12	0.13
256.05	30.715	293.25	0.13	0.17	256.18	31.147	322.21	0.11	0.15
256.05	30.717	293.28	0.14	0.17	256.20	31.084	322.04	0.12	0.15
255.98	27.954	283.87	0.13	0.18	256.22	28.086	312.72	0.12	0.16
255.96	27.952	283.84	0.11	0.18	256.22	28.065	312.68	0.12	0.16
256.00	25.850	275.51	0.10	0.20	256.24	26.025	305.45	0.12	0.18
256.01	25.854	275.52	0.10	0.20	256.21	26.021	305.48	0.12	0.18
255.99	23.936	267.07	0.11	0.21	256.21	24.012	297.50	0.12	0.19
255.97	23.939	267.09	0.11	0.21	256.24	24.004	297.39	0.11	0.19
255.98	21.976	257.11	0.12	0.24	309.42	34.880	270.34	0.11	0.15
255.96	21.979	257.16	0.12	0.24	309.25	31.028	255.66	0.11	0.16
311.00	34.522	242.27	0.01	0.15	309.24	31.031	255.61	0.08	0.16
311.06	34.790	243.21	0.02	0.15	309.25	28.004	241.88	0.09	0.18
311.05	30.918	227.93	0.04	0.17	309.29	28.018	241.90	0.09	0.18
311.04	30.914	227.92	0.04	0.17	309.16	26.102	232.17	0.10	0.19
311.04	27.860	213.84	0.06	0.18	309.17	26.097	232.15	0.10	0.19
311.06	27.854	213.79	0.06	0.18	367.80	34.716	215.64	0.04	0.13
311.08	25.989	204.11	0.07	0.19	367.77	34.715	215.72	0.08	0.13
311.05	25.971	204.02	0.06	0.19	366.36	30.973	200.86	0.07	0.14
311.05	23.863	191.97	0.09	0.20	366.34	30.963	200.84	0.07	0.14
311.04	23.866	191.99	0.08	0.20	366.24	28.061	187.06	0.08	0.15
311.07	24.045	193.05	0.09	0.20	366.24	28.085	187.16	0.07	0.15

366.40	34.566	195.80	0.10	0.14	365.85	25.963	176.42	0.09	0.16
366.39	34.564	195.79	0.10	0.14	365.83	25.963	176.42	0.08	0.16
366.32	30.932	180.96	0.09	0.14	366.16	23.804	164.05	0.09	0.16
366.31	30.931	180.97	0.10	0.14	366.20	23.816	164.10	0.09	0.16
366.35	28.053	167.89	0.08	0.15	421.90	34.972	181.45	0.07	0.11
366.36	28.052	167.87	0.07	0.15	421.94	34.955	181.39	0.09	0.11
366.46	26.000	157.80	0.07	0.15	421.89	30.827	164.82	0.07	0.12
366.47	26.003	157.81	0.07	0.15	421.88	30.808	164.75	0.08	0.12
366.48	24.052	147.71	0.05	0.16	421.78	27.956	152.32	0.06	0.12
366.48	24.052	147.71	0.04	0.16	421.77	27.951	152.30	0.06	0.12
421.52	34.606	163.74	0.07	0.12	421.62	26.103	143.85	0.07	0.12
421.52	34.605	163.75	0.08	0.12	421.61	26.095	143.81	0.07	0.12
421.54	30.990	150.13	0.06	0.12	421.43	23.987	133.76	0.09	0.13
421.54	30.989	150.13	0.07	0.12	421.45	23.987	133.73	0.08	0.13
421.46	27.834	137.39	0.05	0.12					
421.44	27.830	137.38	0.05	0.12					
421.46	25.835	128.88	0.06	0.12					
421.47	25.833	128.86	0.05	0.12					
421.47	23.902	120.35	0.07	0.12					
421.48	23.902	120.33	0.07	0.12					

^a Expanded uncertainties U for temperature T and pressure p are $U(p)/p = 1 \cdot 10^{-4}$ ($k = 1.73$), and $U(T) = 0.3$ K ($k = 1.73$)

REFERENCES

- (1) Blancett, A. L.; Hall, K. R.; Canfield, F. B. Isotherms for the He-Ar System at 50°C, 0°C and -50°C up to 700 atm. *Physica* **1970**, *47*, 75-91.
- (2) Cristancho, D. E.; Mantilla, I. D.; Ejaz, S.; Hall, K. R.; Atilhan, M.; Iglesia-Silva, G. A. Accurate $P\rho T$ Data for Methane from (300 to 450) K up to 180 MPa. *J. Chem. Eng. Data* **2010**, *55*, 826-829.
- (3) Cristancho, D. E.; Mantilla, I. D.; Ejaz, S.; Hall, K. R.; Atilhan, M.; Iglesias-Silva, G. A. Accurate $P\rho T$ Data for Ethane from (298 to 450) K up to 200 MPa. *J. Chem. Eng. Data* **2010**, *55*, 2746-2749.
- (4) Hall, K. R.; Iglesias-Silva, G. A.; Mansoori, G. A. Quadratic Mixing Rules for Equations of State: Origins and Relationships to the Virial Expansion. *Fluid Phase Equilib.* **1993**, *91*, 67-76.
- (5) Hall, K. R.; Yarborough, L. A New Equation of State for Z-factor Calculations. *Oil Gas J.* **1973**, *71*, 82-92.
- (6) Holste, J. C.; Young, J. G.; Eubank, P. T.; Hall, K. R. Interaction Second Virial Coefficients and Binary Interaction Parameters for the CO₂ □ C₂H₆ Systems Between 250 and 300 K. *AIChE J.* **1982**, *28*, 807-812.
- (7) Hwang, C. A.; Simon, P. P.; Hou, H.; Hall, K. R.; Holste, J. C.; Marsh, K. N. Burnett and Pycnometric (p, V_m, T) Measurements for Natural Gas Mixtures. *The Journal of Chemical Thermodynamics* **1997**, *29*, 1455-1472.
- (8) Lau, W. R.; Hwang, C. A.; Brugge, H. B.; Iglesias-Silva, G. A.; Duarte-Garza, H. A.; Rogers, W. J.; Hall, K. R.; Holste, J. C.; Gammon, B. E.; Marsh, K. N. A Continuously Weighed Pycnometer for Measuring Fluid Properties. *J. Chem. Eng. Data* **1997**, *42*, 738-744.
- (9) Patil, P. E., S.; Atilhan, M.; Cristancho, D.; Holste, J.C.; Hall, K.R. Accurate Density Measurements for a 91% Methane Natural Gas-Like Mixture. *J. Chem. Thermodyn.* **2007**, *39*, 1157-1163.
- (10) Atilhan, M.; Ejaz, S.; Zhou, J.; Cristancho, D.; Mantilla, I.; Holste, J.; Hall, K. R. Characterization of Deepwater Natural Gas Samples. Part 1: 78 % Methane Mixture with Heavy Components. *J. Chem. Eng. Data* **2010**, *55*, 4907-4911.
- (11) Atilhan, M.; Aparicio, S.; Ejaz, S.; Cristancho, D.; Mantilla, I.; Hall, K. R. p - ρ - T Behavior of Three Lean Synthetic Natural Gas Mixtures Using a Magnetic Suspension Densimeter and Isochoric Apparatus from (250 to 450) K with Pressures up to 150 MPa: Part II. *J. Chem. Eng. Data* **2011**, *56*, 3766-3774.
- (12) Atilhan, M.; Aparicio, S.; Ejaz, S.; Cristancho, D.; Hall, K. R. $P\rho T$ Behavior of a Lean Synthetic Natural Gas Mixture Using Magnetic Suspension Densimeters and an Isochoric Apparatus: Part I. *J. Chem. Eng. Data* **2011**, *56*, 212-221.
- (13) McGregor, D. R.; Holste, J. C.; Eubank, P. T.; Marsh, K. N.; Hall, K. R.; Schouten, J. An Interaction Model for Third Virial Coefficients which Provides Simplified Equations for Mixtures. *Fluid Phase Equilib.* **1987**, *35*, 153-164.
- (14) Vogl, W. F.; Hall, K. R. Generalized Temperature Dependence of the Redlich-Kwong Constants. *AIChE J.* **1970**, *16*, 1103-1104.
- (15) Zhou, J.; Patil, P.; Ejaz, S.; Atilhan, M.; Holste, J. C.; Hall, K. R. (p, V_m, T) and Phase Equilibrium Measurements for a Natural Gas-Like Mixture using an Automated Isochoric Apparatus. *The Journal of Chemical Thermodynamics* **2006**, *38*, 1489-1494.

- (16) Goodwin, A. R. H. The Future of Oil and Gas Fossil Fuels. In *Future Energy: Improved, Sustainable and Clean Options for our Planet*; 1st ed.; Letcher, T. M., Ed.; Elsevier: Oxford, UK, 2008; pp 3-24.
- (17) Nasrifar, K. B., O. Predicting Natural Gas Dew Points from 15 Equations of States. *Energy Fuels* **2005**, *19*, 561-572.
- (18) Kunz, O.; Wagner, W. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. *J. Chem. Eng. Data* **2012**, *57*, 3032-3091.
- (19) *ISO 20765-2:2015 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, Switzerland, 2015.
- (20) Rowland, D.; Hughes, T. J.; May, E. F. Extending the GERG-2008 Equation of State: Improved Departure Function and Interaction Parameters for (Methane + Butane). *J. Chem. Thermodyn.* **2016**, *97*, 206-213.
- (21) May, E. F.; Guo, J. Y.; Oakley, J. H.; Hughes, T. J.; Graham, B. F.; Marsh, K. N.; Huang, S. H. Reference Quality Vapor–Liquid Equilibrium Data for the Binary Systems Methane + Ethane, + Propane, + Butane, and + 2-Methylpropane, at Temperatures from (203 to 273) K and Pressures to 9 MPa. *J. Chem. Eng. Data* **2015**, *60*, 3606-3620.
- (22) Stanwix, P. L.; Locke, C. R.; Hughes, T. J.; Johns, M. L.; Goodwin, A. R. H.; Marsh, K. N.; May, E. F. Viscosity of $\{x\text{CH}_4 + (1 - x)\text{C}_3\text{H}_8\}$ with $x = 0.949$ for Temperatures between (200 and 423) K and Pressures between (10 and 31) MPa. *J. Chem. Eng. Data* **2015**, *60*, 118-123.
- (23) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C. D.; Kazakov, A. F.; Magee, J. W.; Abdulagatov, I. M.; Kroenlein, K.; Diaz-Tovar, C. A.; Kang, J. W.; Rafiqul ThermoData Engine (TDE) Version 7.0 (Pure Compounds, Binary Mixtures, Ternary Mixtures and Chemical Reactions) NIST Standard Reference Database #103b. Thermodynamics Research Center (TRC), Thermophysical Properties Division, National Institute of Standards and Technology: Boulder, CO, 2011.
- (24) Richter, M.; McLinden, M. O. Vapor-Phase (p, ρ, T, x) Behavior and Virial Coefficients for the (Methane + Propane) System. *J. Chem. Eng. Data* **2014**, *59*, 4151-4164.
- (25) Reamer, H. H. S., B. H.; Lacey, W. N. Phase Equilibria in Hydrocarbon Systems: Volumetric and Phase Behavior of the Methane-Propane System. *Ind. Eng. Chem.* **1950**, *42*, 534-539.
- (26) Huang, E. T. S.; Swift, G. W.; Kurata, F. Viscosities and Densities of Methane-Propane Mixtures at Low Temperatures and High Pressures. *AIChE J.* **1967**, *13*, 846-850.
- (27) Arai, K.; Kobayashi, R. Measurement of Isochoric P - V - T Behavior of a Nominal 95-Mol.-%-Methane-5-Mol.-%-Propane Mixture from Near-Ambient to Cryogenic Temperatures. *Adv. Cryog. Eng.* **1980**, *25*, 640-653.
- (28) May, E. F.; Tay, W. J.; Nania, M.; Aleji, A.; Al-Ghafri, S.; Martin Trusler, J. P. Physical Apparatus Parameters and Model for Vibrating Tube Densimeters at Pressures to 140 MPa and Temperatures to 473 K. *Rev. Sci. Instrum.* **2014**, *85*, 095111.
- (29) Ciotta, F.; Trusler, J. P. M. Improved Understanding of Vibrating-Wire Viscometer–Densimeters. *J. Chem. Eng. Data* **2010**, *55*, 2195-2201.
- (30) Moldover, M. R.; Marsh, K. N.; Barthel, J.; Buchner, R. Chapter 9. Relative Permittivity and Refractive Index. In *Measurement of the Thermodynamic Properties of Single*

- Phases*; Goodwin, A. R. H., Marsh, K. N., Wakeham, W. A., Eds.; Experimental Thermodynamics, Elsevier: Amsterdam, The Netherlands, 2003.
- (31) Kleinrahm, R.; Wagner, W. *Entwicklung und Aufbau einer Dichtemeßanlage zur Messung der Siede- und Taudichten reiner fluider Stoffe auf der gesamten Phasengrenzkurve*. Fortschr.-Ber. VDI-Z.; Düsseldorf, Germany, 1984; Vol. 92.
 - (32) Kleinrahm, R. W., W. Measurement and Correlation of the Equilibrium Liquid and Vapour Densities and the Vapour Pressure Along the Coexistence Curve of Methane. . *J. Chem. Thermodyn.* **1986**, *18*, 739-760.
 - (33) Klimeck, J.; Kleinrahm, R.; Wagner, W. Measurements of the (p,ρ,T) Relation of Methane and Carbon Dioxide in the Temperature Range 240 K to 520 K at Pressures up to 30 MPa using a New Accurate Single-Sinker Densimeter. *The Journal of Chemical Thermodynamics* **2001**, *33*, 251-267.
 - (34) Klimeck, J.; Kleinrahm, R.; Wagner, W. An Accurate Single- Sinker Densimeter and Measurements of the (p,ρ,T) Relation of Argon and Nitrogen in the Temperature Range from (235 to 520) K at Pressures up to 30 MPa. *J. Chem. Thermodyn.* **1998**, *30*, 1571-1588.
 - (35) Yang, X.; Richter, M.; Wang, Z.; Li, Z. Density Measurements on Binary Mixtures (Nitrogen + Carbon Dioxide and Argon + Carbon Dioxide) at Temperatures from (298.15 to 423.15) K with Pressures from (11 to 31) MPa using a Single-Sinker Densimeter. *The Journal of Chemical Thermodynamics* **2015**, *91*, 17-29.
 - (36) Mondéjar, M. E.; Segovia, J. J.; Chamorro, C. R. Improvement of the Measurement Uncertainty of a High Accuracy Single Sinker Densimeter via Setup Modifications Based on a State Point Uncertainty Analysis. *Measurement* **2011**, *44*, 1768-1780.
 - (37) Claus, P.; Kleinrahm, R.; Wagner, W. Measurements of the (p,ρ,T) Relation of Ethylene, Ethane, and Sulphur Hexafluoride in the Temperature Range from 235 K to 520 K at Pressures up to 30 MPa using an Accurate Single-Sinker Densimeter. *The Journal of Chemical Thermodynamics* **2003**, *35*, 159-175.
 - (38) Sommer, D.; Kleinrahm, R.; Span, R.; Wagner, W. Measurement and Correlation of the (p,ρ,T) Relation of Liquid Cyclohexane, Toluene, and Ethanol in the Temperature Range from 233.15 K to 473.15 K at Pressures up to 30 MPa for use as Density Reference Liquids. *The Journal of Chemical Thermodynamics* **2011**, *43*, 117-132.
 - (39) May, E.; Miller, R.; Shan, Z. Densities and Dew Points of Vapor Mixtures of Methane + Propane and Methane + Propane + Hexane Using a Dual-Sinker Densimeter. *J. Chem. Eng. Data* **2001**, *46*, 1160-1166.
 - (40) Wagner, W. K., R. Densimeters for Very Accurate Density Measurements of Fluids over Large Ranges of Temperature, Pressure. *Metrologia* **2004**, *41*, S24-S39.
 - (41) McLinden, M. O. Chapter 2 – Experimental Techniques 1 (Direct Methods). In *Volume Properties: Liquids, Solutions and Vapours*; Wilhelm, E., Letcher, T. M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2014.
 - (42) Richter, M.; Kleinrahm, R.; Lentner, R.; Span, R. Development of a Special Single-Sinker Densimeter for Cryogenic Liquid Mixtures and First Results for a Liquefied Natural Gas (LNG). *J. Chem. Thermodyn.* **2016**, *93*, 205-221.
 - (43) Richter, M.; Kleinrahm, R. Influence of Adsorption and Desorption on Accurate Density Measurements of Gas Mixtures. *The Journal of Chemical Thermodynamics* **2014**, *74*, 58-66.

- (44) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP*, 9.1; National Institute of Standards and Technology: Gaithersburg, MD, 2013.
- (45) Setzmann, U.; 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* **1991**, 20, 1061-1151.
- (46) Jaeschke, M. H., A. E. GERG Technical Monograph 4: The GERG Databank of High Accuracy Compressibility Factor Measurements. *Verein Deutscher Ingenieure: Düsseldorf, Germany*, **1990**.

SUPPORTING INFORMATION

Density Measurements of (Methane + Propane) Mixtures at Temperatures between (256 and 422) K and Pressures from (24 to 35) MPa

Armand Karimi,¹ Thomas J. Hughes,¹ Markus Richter² and Eric F. May^{1,*}

1. Fluid Science and Resources Division, School of Mechanical and Chemical Engineering,
The University of Western Australia, Crawley, Western Australia 6009, Australia

2. Thermodynamics, Ruhr-University Bochum, D-44780, Bochum, Germany

Corresponding author

*E-mail: Eric.May@uwa.edu.au. Fax: +61 8 6488 1024

Table S1 - Experimental density measurements of methane in the dense gas phase and relative combined expanded ($k=2$) uncertainties as well their relative deviations from values calculated with the reference equation of state of Setzman and Wagner⁴⁵ (ρ_{EOS}) state. For each isotherm, the density values reported were determined from eqs (1) and (2) by adjusting the parameters $V_{\text{S},0}$ and β_{T} in eq (2) to force agreement with the value of ρ_{EOS} calculated from the measured temperature and pressure.

Pure methane				
T/K	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$	$100 (\rho - \rho_{\text{EOS}}) / \rho_{\text{EOS}}$	$100 U(\rho)/\rho$
256.08	34.726	276.454	0.008	0.14
256.10	34.727	276.416	0.000	0.14
256.14	31.113	265.214	-0.014	0.15
256.14	31.114	265.205	-0.016	0.15
256.12	28.067	254.208	-0.016	0.17
256.10	28.067	254.250	-0.011	0.17
256.18	26.026	245.639	-0.006	0.18
256.19	26.033	245.691	0.009	0.18
256.15	24.108	236.590	-0.013	0.20
256.15	24.102	236.589	-0.004	0.20
256.11	22.048	225.495	0.001	0.22
256.11	22.046	225.474	-0.001	0.22
311.01	30.647	202.8331	-0.048	0.15
311.08	30.625	202.6727	-0.003	0.15
311.06	28.020	190.8825	0.000	0.16
311.04	28.016	190.8809	-0.003	0.16
311.03	25.970	180.6636	0.001	0.16
311.05	25.972	180.6587	0.001	0.16
311.04	24.035	170.1313	0.008	0.17
311.03	24.032	170.1215	0.004	0.17
311.06	20.937	151.4131	-0.005	0.18
311.06	20.917	151.2871	-0.004	0.18

366.48	34.665	176.318	-0.019	0.12
366.47	34.663	176.310	-0.005	0.12
366.49	30.975	162.155	-0.003	0.12
366.48	27.934	149.492	0.030	0.12
366.47	25.760	139.701	0.002	0.13
366.47	25.760	139.700	0.004	0.13
366.46	23.928	131.056	-0.007	0.13
366.46	23.927	131.045	-0.009	0.13
421.49	34.704	148.339	0.003	0.10
421.48	34.696	148.323	0.005	0.10
421.64	30.979	135.371	0.004	0.10
421.63	30.974	135.349	-0.002	0.10
421.45	27.921	124.125	-0.011	0.10
421.48	27.925	124.131	-0.009	0.10
421.48	25.973	116.581	-0.005	0.10
421.47	25.968	116.570	-0.002	0.10
421.53	23.932	108.411	0.007	0.10
421.53	23.932	108.415	0.011	0.10