Application of a two-sinker densimeter for phase-equilibrium measurements: A new technique for the detection of dew points and measurements on the (methane + propane) system¹

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Abstract

We explore a novel method for determining the dew-point density and dew-point pressure of fluid mixtures and compare it to traditional methods. The (p , ρ , T , x) behavior of three (methane + propane) mixtures was investigated with a two-sinker magnetic suspension densimeter over the temperature range of (248.15 to 293.15) K; the measurements extended from low pressures into the two-phase region. The compositions of the gravimetrically prepared mixtures were (0.74977, 0.50688, and 0.26579) mole fraction methane. We analyzed isothermal data by: (1) a “traditional” analysis of the intersection of a virial fit of the (p vs. ρ) data in the single-phase region with a linear fit of the data in the two-phase region; and (2) an analysis of the adsorbed mass on the sinker surfaces. We compared these to a traditional isochoric experiment. We conclude that the “adsorbed mass” analysis of an isothermal experiment provides an accurate determination of the dew-point temperature, pressure, and density. However, a two-sinker densimeter is required.

Keywords: adsorption; dew point; gas density; measurement; methane; propane

1. Introduction

To understand the phase behavior of fluid mixtures and to develop models that precisely describe the phase boundary between liquid and vapor, accurate experimental data are essential.

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Such models are of increasing importance for research and industry, *e.g.*, in the fields of natural gas processing and carbon capture and storage (CCS). With regard to experimental data, the dew line, separating the homogeneous vapor region from the heterogeneous two-phase region, is very difficult to determine accurately. The resulting lack of accurate values is an impediment to the improvement of mixture models.

A number of experimental techniques has been applied to determine dew points of fluid mixtures. These can be divided into two broad categories: (1) methods that detect the presence of condensate, such as chilled mirrors [1]-[2], other optical methods [3] and the magnetic-suspension balance [4] or (2) methods that detect a change in slope of one measured quantity versus another, such as the isochoric technique [5]-[6], quartz crystal microbalances [7]-[8] microwave re-entrant cavities [9]-[10] and the acoustic spherical resonator [11]-[12]. For many of these techniques, the accuracy is unfortunately rather poor. Compared to properties for mixtures in the homogeneous vapor region, which can achieve nearly the accuracy of the corresponding properties for pure fluids, the experimental uncertainty for properties on the saturation line (*e.g.*, dew-point pressures) can be much higher. Moreover, accurate data for dew-point densities of fluid mixtures are virtually nonexistent. A significant contribution to the uncertainty arises from the uncertainty in the mixture composition; most authors used an analytic method, which involved taking samples for a composition measurement (often by gas chromatography). A minority of authors used a synthetic method with gravimetrically prepared mixtures. While the synthetic approach can yield good results with careful calibration of the composition-analysis method, the synthetic approach is generally more accurate.

A notable example of careful investigation of the dew point available in the literature is the work of May *et al.* [4], who conducted accurate (p , ρ , T) measurements with gas mixtures when approaching and crossing the dew line, thus, locating the dew-point pressure and density. They used a modified commercial magnetic-suspension balance with three stable suspension positions. Two sinkers could be weighed in different suspension positions within the fluid of interest. For investigations at dew-point conditions, measurements were carried out along isochores. Measurements began at a temperature above the expected dew point and went into the two-phase region with decreasing temperature. In contrast to the original two-sinker densimeter technique of Kleinrahm and Wagner [13], [14], the bottom sinker could not be weighed separately, and this limited the accuracy of their results. Nevertheless, they detected the presence of condensate in a quantitative manner, rather than merely detecting a change in slope. They prepared their mixture samples gravimetrically (*i.e.*, using a “synthetic method”).

Against this background, the major objective of the present work was to investigate a new technique for the accurate determination of dew-point pressures and dew-point densities of binary mixtures. Binary mixtures were chosen because state-of-the-art models for multicomponent mixtures (for example, the GERG-2008 equation of state for natural gas of Kunz and Wagner [15]) are only fitted in terms of the constituent binary pairs. The instrument utilized was the highly accurate two-sinker densimeter of the National Institute of Standards and Technology (NIST)[16]. We selected the binary system (methane + propane) because the two-phase region fits well within the operating temperature and pressure range of the densimeter. Moreover, this system is of industrial importance so that resulting data would be useful for improving mixture models. The vapor-phase (p , ρ , T , x) behavior and virial coefficients of three (methane + propane) mixtures were reported by us previously [17].

The two-sinker density measurement method, as developed by Kleinrahm and Wagner [13], [14], is the most accurate technique to determine densities of fluids in the gas phase. Thus, we assumed that this technique would also be suitable for the determination of mixture dew-point densities. We build on the work of May *et al.* [4], but also extend it in several ways; in particular, we carry out measurements along isotherms, and we will argue that this gives more information and lower uncertainties compared to an isochoric method. Furthermore, our “true” two-sinker instrument allows microgram-level detection of condensate.

In this work, the densimeter was utilized with sinkers that were optimized for accurate density measurements. The intention of this paper is to explore different methods to approach the dew line and to determine dew-point pressures as well as dew-point densities of three (methane + propane) mixtures. An additional novel method is suggested which is a modification of the two-sinker technique. However, this is the topic of a companion paper [18].

2. Experimental

2.1. Apparatus Description

The present measurements utilized a two-sinker densimeter with a magnetic suspension coupling. This type of instrument applies the Archimedes (buoyancy) principle to provide an absolute determination of the density. This general type of instrument is described by Wagner and Kleinrahm [14], and our instrument is described in detail by McLinden and Lösch-Will [16]. Briefly, two sinkers of nearly the same mass and same surface area, but very different volumes (ratio ≈ 3.7), were each weighed with a high-precision balance while they were immersed in a fluid of unknown density. The fluid density ρ is given by

$$r = \frac{(m_1 - m_2) - (W_1 - W_2)}{(V_1 - V_2)}, \quad (1)$$

where m and V are the sinker mass and volume, W is the balance reading, and the subscripts refer to the two sinkers. Each sinker had a mass of approximately 60 g; one was made of tantalum (which we designate as sinker 1, $V_1 \approx 3.6 \text{ cm}^3$) and the other of titanium (sinker 2, $V_2 \approx 13.3 \text{ cm}^3$). The surface area of each sinker was approximately 41.5 cm^2 . A magnetic suspension coupling transmitted the gravity and buoyancy forces on the sinkers to the balance, thus isolating the fluid sample from the balance. Two additional calibration masses (designated as “tare” and “cal”), which were placed directly on the balance pan, were also weighed as part of each density determination. In comparison with other buoyancy techniques, the main advantage of the two-sinker method, as developed by Kleinrahm and Wagner [13] is that systematic errors in the weighing and from other sources approximately cancel. Moreover, the two-sinker technique leads to lower uncertainties for measurements at low densities compared to a single-sinker instrument.

2.2. Analysis of Sorption/Condensation

Equation (1) must be expanded to account for perturbations to the magnetic suspension coupling due to the magnetic effects of the measuring cell and of the fluid being measured, *i.e.*, to account for the so-called “force-transmission error;” this analysis is presented by McLinden *et al.* [19]. Briefly, they wrote out equations listing all of the forces for each of the four weighings required for a density determination (*i.e.*, the two sinkers and the two calibration masses). This yielded a system of four equations that were solved for the four unknowns of fluid density ρ_{fluid} , a balance calibration factor α , a parameter β related to the balance tare (*i.e.*, the magnets and other elements of the system that are suspended from the balance for all the weighings), and a parameter ϕ that characterizes the efficiency of the magnetic suspension coupling. The difference of the value of ϕ from 1 indicates the magnitude of the force transmission error. This analysis yields the fluid density

$$r_{\text{fluid}} = \left[(m_1 - m_2) - \frac{(W_1 - W_2)}{af} \right] / (V_1 - V_2). \quad (2)$$

where the balance calibration factor and coupling parameter are given by

$$a = \frac{W_{\text{cal}} - W_{\text{tare}}}{(m_{\text{cal}} - m_{\text{tare}}) - r_{\text{air}}(V_{\text{cal}} - V_{\text{tare}})} \quad \text{and} \quad (3)$$

$$f = \frac{(W_1/a) - b}{m_1 - r_{\text{fluid}} V_1} , \quad (4)$$

and the tare parameter is

$$b = \frac{W_{\text{cal}}}{a} - (m_{\text{cal}} - r_{\text{air}} V_{\text{cal}}) . \quad (5)$$

The subscripts “cal” and “tare” refer to the calibration masses, and ρ_{air} is the density of the gas under the balance hood. Note that equation (2) reduces to equation (1) when $\alpha = 1$ and $\phi = 1$. Equations (2 to 5) yield the fluid density, including an accounting of the force-transmission error, in terms of directly measured quantities.

A key assumption in the analysis of McLinden *et al.* [19] was that all quantities were constant over the time necessary to complete the weighings for a density determination, which was about 12 minutes. In addition, the sinker masses were assumed to be constant and equal to the values determined prior to their installation in the densimeter. For measurements in homogenous liquid or gaseous states, these assumption apply. But for measurements near the dew line, sorption onto the surface of the sinkers can affect the effective sinker masses, and inside the two-phase region, condensation of sample onto one or both sinkers will change the effective sinker masses. Thus, the above equations must be modified.

As in the original analysis of McLinden *et al.* [19], the weighings of the sinkers and calibration masses can be written as

$$W_1 = a [f \{m_1 - r_{\text{fluid}} V_1\} + b] , \quad (6)$$

$$W_2 = a [f \{m_2 - r_{\text{fluid}} V_2\} + b] , \quad (7)$$

$$W_{\text{cal}} = a [m_{\text{cal}} - r_{\text{air}} V_{\text{cal}} + b] , \text{ and} \quad (8)$$

$$W_{\text{tare}} = a [m_{\text{tare}} - r_{\text{air}} V_{\text{tare}} + b] , \quad (9)$$

where the parameters α and β are as defined above. However, now we will solve for the sinker masses in terms of the other variables:

$$m_1^{\text{c}} = m_1 + dm_{1,\text{sorp}} = \frac{W_1/a + r_{\text{fluid}} V_1 - b}{f} , \quad (10)$$

$$m_2^{\text{c}} = m_2 + dm_{2,\text{sorp}} = \frac{W_2/a + r_{\text{fluid}}V_2 - b}{f}, \quad (11)$$

where the prime indicates that the mass may be different from the original determination because of adsorbed material present on the sinker, *i.e.*, $\delta m_{1,\text{sorp}}$ or $\delta m_{2,\text{sorp}}$:

$$dm_{1,\text{sorp}} = \frac{W_1/a + r_{\text{fluid}}V_1 - b}{f} - m_1 \text{ and} \quad (12)$$

$$dm_{2,\text{sorp}} = \frac{W_2/a + r_{\text{fluid}}V_2 - b}{f} - m_2. \quad (13)$$

Depending on the different surface characteristics of the two sinkers and any temperature gradients in the measuring cell, varying amounts of sample will adsorb or condense on each of the sinkers. Taking the difference of Eqs 12 and 13 yields a measure of the adsorbed mass:

$$\Delta m_{\text{sorption}} = (dm_{2,\text{sorp}} - dm_{1,\text{sorp}}) = \frac{W_2 - W_1}{af} + r_{\text{fluid}}(V_1 - V_2) + (m_1 - m_2). \quad (14)$$

Note that $\Delta m_{\text{sorption}}$ is not the mass of material adsorbed onto sinker 2, but rather the mass of material adsorbed onto sinker 2 minus that adsorbed onto sinker 1. It is not possible to solve for $\delta m_{1,\text{sorp}}$ and $\delta m_{2,\text{sorp}}$ separately because the remaining equations would not be sufficient to solve for the fluid density.

Equation (14) gives a quantitative estimate of sorption effects, but at the expense of “using” one of the four available equations, *i.e.*, equations (6 – 9). The parameters α and β “use” two additional equations, leaving only one equation, but two unknowns: ρ_{fluid} and ϕ . This is the situation one has with a single-sinker densimeter, and we apply the analysis of McLinden *et al.* [19] for that type of instrument. That analysis demonstrated that the coupling factor can be divided into apparatus and fluid-specific contributions; ϕ_0 is the value of ϕ in vacuum and is the apparatus contribution. Furthermore, ϕ is related to the fluid density and the specific magnetic susceptibility of the fluid χ_s so that

$$f = f_0 + \varepsilon_r \frac{C_s}{C_{s0}} \frac{r_{\text{fluid}}}{r_0}, \quad (15)$$

where $\rho_0 = 1000 \text{ kg}\cdot\text{m}^{-3}$ and $\chi_{s0} = 10^{-8} \text{ m}^3\cdot\text{kg}^{-1}$ are reducing constants and ε_p is an apparatus-specific constant. For a single-sinker densimeter ε_p must be determined by a tedious calibration involving measurements with different sinkers installed at different times. For our two-sinker densimeter, however, ε_p can be determined from measurements in the homogeneous vapor

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5 region, including measurements made along an isotherm just prior to entering the two-phase
6 region. The value of χ_s is calculated as the mole-fraction-weighted average of the molar pure-
7 fluid susceptibilities given by [20]; the specific susceptibility is obtained by dividing by the
8 molar mass of the mixture. The value of ϕ_0 is determined by weighing made with the measuring
9 cell under vacuum; in any event, this test is carried out regularly to check for possible
10 contamination of the sinkers and to reset the zero of the pressure transducers.
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15 The result is that we have obtained a quantitative measure of sorption/condensation effects,
16 which is a very sensitive indicator of the onset of condensation, as will be discussed in section 3.
17 However this has come at the expense of effectively changing our two-sinker densimeter to a
18 single-sinker instrument. In other words, one of the sinkers serves as the “density sinker” and the
19 other serves as a “sorption sinker.”
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23 *2.3. Preparation of the Sample Mixtures*

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26 The gas mixtures were prepared gravimetrically. The components are described in table 1. We
27 used the materials as received, but we did confirm their purity with our own analysis. The
28 compositions of the three prepared mixtures are given in table 2. The maxcondentherm for the
29 three mixtures ranged from 292.1 K to 346.6 K. They were prepared in aluminum gas cylinders
30 of approximately 10 L internal volume. The sample mass was determined by a double
31 substitution weighing design as described by Harris and Torres [21], with a nearly identical
32 “tare” or reference cylinder serving as the main substitution mass. Further details are provided by
33 Richter and McLinden [17].
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40 The three sample cylinders were loaded to pressures corresponding to the dew-point pressure at
41 $T = 293.15$ K, which were $p = 6$ MPa for the (0.74977 methane + 0.25023 propane) mixture,
42 $p = 1.9$ MPa for the (0.50688 methane + 0.49312 propane) mixture, and $p = 1.2$ MPa for the
43 (0.26579 methane + 0.73421 propane) mixture. There may have been a small amount of liquid in
44 the sample cylinders after filling, but they were heated continuously to $T > 313$ K for the
45 duration of the testing to ensure that only single-phase vapor was present. Due to sorption
46 effects, the composition of the sample in the measuring cell could be different from that
47 calculated from the sample masses loaded into the sample cylinder. This is discussed in section
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54 *2.4. Experimental Procedures*

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57 The vapor-phase densities of the (methane + propane) system was previously studied by Richter
58 and McLinden [17], and a subset of their data is analyzed here. Reference [17] reports
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measurements along 27 isotherms for the three mixtures. Of those, 16 were entirely in the homogenous vapor region. The remaining 11 isotherms extended into the two-phase region and are analyzed here. (The two-phase values were not reported by Richter and McLinden [17] and are included here in the Supplementary Data.) In addition to the measurements along isotherms, two pseudo-isochores were also measured for the (0.26579 methane + 0.73421 propane) mixture.

Measurements were carried out along isotherms at $T = (248.15, 273.15, \text{ and } 293.15)$ K for each of the three mixtures; except that $T = 293.15$ K was above the maxcondentherm for the (0.74977 methane + 0.25023 propane) mixture. Each isotherm started at a low pressure well within the homogeneous vapor region; the pressure was increased in steps of (0.1 to 0.2) MPa by cycling a pair of pneumatically controlled valves that trapped a volume of sample between them. After an equilibration time of 30 min., three replicate density determinations were made. As the dew-point pressure was approached, the pressure was increased in smaller steps by cycling the pneumatic valves a single time. The isotherm was terminated when the data indicated that the system had entered the two-phase region.

The standard procedure between measurements on the different isotherms was to evacuate the measuring cell for (10 to 30) min. This was followed by a purging cycle consisting of filling the measuring cell to approximately 50% of the dew-point pressure; this sample remained inside the cell for 2 min; the cell was then evacuated for 2 min; this routine was repeated three times before filling in the sample for the next isotherm. For several of the isotherms, however, the measuring cell was evacuated for several hours between fillings.

For the isochoric experiments the measuring cell was equilibrated at a temperature approximately 2 K above the target dew-point temperature; it was then filled to a pressure approximately 1 % above the expected dew-point pressure at the target temperature. Additional equilibration time was allowed, and then the electrical heating to the measuring cell and shields was turned off, and the temperature subsequently decreased at the rate of approximately $0.25 \text{ K} \cdot \text{h}^{-1}$. A density determination was carried out every 30 min until the data indicated that the system had entered the two-phase region.

3. Results

3.1. Analysis of (p, ρ, T, x) Data Along Isotherms

The isothermal data will be analyzed in multiple ways. The basic approach is to fit a simple function (*e.g.*, a linear or a quadratic equation) to the data points in the single-phase and two-phase regions; the dew point is given by the intersection. Figure 1 shows the results for the

isotherm at $T = 273.149$ K, with a composition of (0.26579 methane + 0.73421 propane), which is typical for our results. For the plot of pressure versus density (figure 1a), the vapor-phase data are well fitted by a quadratic function, which is equivalent to a virial expansion truncated at the second virial coefficient. There is a discontinuity in slope at the dew point, and the two-phase values are fitted reasonably well by a straight line. The intersection of these fits yields a dew-point density of $12.026 \text{ kg}\cdot\text{m}^{-3}$.

A plot of $\Delta m_{\text{sorption}}$ versus density (figure 1b) shows a very small ($< 0.03 \text{ mg}$), nearly constant value of $\Delta m_{\text{sorption}}$ in the single-phase region. Upon entering the two-phase region, there is a dramatic change in slope. The dew-point density given by this intersection is $12.003 \text{ kg}\cdot\text{m}^{-3}$. The effect is very clear despite the small magnitude of $\Delta m_{\text{sorption}}$ (less than 0.6 mg). The negative values of $\Delta m_{\text{sorption}}$ indicate that more sample collected on sinker 1 (the tantalum sinker, which is located at the top of the measuring cell) compared to sinker 2 (the titanium sinker, which is located below the tantalum sinker at the bottom of the cell). This result may be due to temperature gradients in the measuring cell: for operation at sub-ambient temperatures, cooling is applied to the top of the cell, and thus, the top of the cell was cooler than the bottom. The greater adsorption on the tantalum sinker could also be the result of different surface characteristics for the two sinkers. The original sinkers in this densimeter were both gold plated, as described by McLinden and Lösch-Will [16]. Those sinkers have been replaced by tantalum and titanium sinkers of a “monolithic” design that were milled from solid bar stock (as opposed to the original sinkers, which had “lifting pins” that were welded into the main body of the sinkers). The new sinkers were polished to a similar surface roughness, but they were not plated. The effect of the different metals on adsorption effects will be the subject of future work.

All of the densities plotted in the figures and reported in the Supporting Data (including those labeled as “two-phase” or “transition”) were measured for the vapor phase; however, they do not necessarily represent the actual state of the vapor sample in the measuring cell. The sinker masses and volumes are affected by the adsorbed/condensed sample that has collected on the sinkers. The composition of the vapor-phase composition is affected by sample condensing not only onto the surfaces of the sinkers but also on the walls of the measuring cell. The changing composition is largely responsible for the increased slope of the two-phase data observed in the plot of pressure versus density (Fig 1a). But, in this work, we extrapolate the two-phase data to the dew point where the effects of the condensed mass and the changing composition vanish.

Similar data for the isotherm at $T = 248.151$ K, with a composition of (0.50688 methane + 0.49312 propane), are plotted versus pressure in figure 2a. The results are very similar to those shown in figure 1b, except that the data in the two-phase region show a larger scatter. This may

be due to two factors. At the low pressures measured for this isotherm, the pressure transducer is at the lower portion of its range and its relative resolution is lower. Also the uncertainty in pressure due to hydrostatic head effects is proportionally larger compared to pressures in the homogeneous vapor region. (This effect is discussed further in section 4.1.) By comparison, the data plotted versus density, figure 2b, show less scatter. For these reasons, it may be preferable to find the dew-point density by the intersection of the $\Delta m_{\text{sorption}}$ versus density data (figure 2b) and calculate the dew-point pressure by extrapolating the virial fit of the data in the single-phase region to the dew-point density. The three replicates for the (0.50688 methane + 0.49312 propane) mixture at $T = 273.15$ K, for example, show less variation when the p_{dew} is calculated by evaluating the virial fit of single-phase vapor data at ρ_{dew} compared to the $\Delta m_{\text{sorption}}$ versus p analysis (total variations of 0.90 % and 2.03 %, respectively).

The analysis methods shown in figures 1 and 2 show a distinct change in slope at the dew point, and the dew points calculated from each of them are nearly the same. A case where the analysis of $\Delta m_{\text{sorption}}$ is clearly better than the “traditional” analysis of pressure versus density is shown in figure 3, for the isotherm at $T = 293.147$ K for the (0.50688 methane + 0.49312 propane) mixture. Here only a small range of pressure was measured in the two-phase region, and the two-phase points in the pressure versus density plot (figure 3a) show only a very small deviation from the single-phase virial fit. The $\Delta m_{\text{sorption}}$ versus density plot (figure 3b), on the other hand, clearly shows the transition to the two-phase region. It would have been difficult to correctly identify the two-phase points in the absence of the $\Delta m_{\text{sorption}}$ data.

The dew-point densities and pressures resulting from the different methods of analysis are given in table 3 for the “traditional analysis” of the 11 (methane + propane) isotherms. Table 4 gives the results for the analysis based on $\Delta m_{\text{sorption}}$. A comparison of these results with the GERG model is given in table 3 (for the “traditional analysis”) and in table 4 and figure 4 (for the “sorption analysis”), where we give the relative deviation in the dew point

$$D_{g,\text{dew}} = 100 \frac{(g_{\text{dew,exp}} - g_{\text{dew,GERG}})}{g_{\text{dew,GERG}}}, \quad (16)$$

where γ is either dew-point pressure or density. There is a clear systematic trend observed in figure 4; the deviations become increasingly negative as the dew-point density increases. (The same trend applies to increasing temperature. Since we measured at the same temperatures for each mixture, we plot the deviations versus density to better separate the isotherms on the plot.) There is better agreement with the GERG model for the (0.74977 methane + 0.25023 propane) mixture compared to the mixtures with higher propane contents. Richter and McLinden [17]

observed the same trend for the single-phase vapor densities. Detailed data for each of the measured (p , ρ , T , x) points are given in the Supplementary Data.

3.2. Analysis of (p , ρ , T , x) Data Along Quasi-Isochores

The results for the isochoric experiment for the (0.26579 methane + 0.73421 propane) mixture at a density of approximately $12.1 \text{ kg}\cdot\text{m}^{-3}$ are shown in figure 5. The “traditional” analysis of pressure versus temperature (figure 5a) shows a distinct change in slope at the dew point ($T_{\text{dew}} = 273.409 \text{ K}$, $p_{\text{dew}} = 0.6722 \text{ MPa}$). But in contrast to typical isochoric experiments, which are carried out in a simple closed vessel, we were measuring density continuously as the measuring cell was cooled. A plot of the pressure versus density (figure 5b) shows a distinct transition region (plotted as Δ) between the homogenous vapor phase (plotted as $\circ$) and the two-phase region (plotted as $+$). We postulate that this transition region corresponds to “capillary condensation,” which is also known as “precondensation;” the exploration of this region is the subject of a companion paper [18].

The density for this “isochoric” experiment is seen to vary (figure 5b). It increased very slightly (relative variation of less than 0.04 %) as the temperature decreased in the homogeneous vapor phase. This is due to contraction of the measuring cell with decreasing temperature and pressure and to migration of sample between the measuring cell and the pressure transducer, which was located outside the measuring cell, and which was thermostatted at $T = 313 \text{ K}$. In the two-phase region, however, the density decreased a total of 1.52 % as the cell cooled from $T = 273.378 \text{ K}$ to $T = 272.765 \text{ K}$. Here, the less-volatile propane preferentially condensed out, leaving the vapor phase enriched in the less-dense methane. The total variation in $\Delta m_{\text{sorption}}$ for the isochoric experiment was less than 0.050 mg; this was much less than in the isothermal experiments, and so it was not feasible to carry out the $\Delta m_{\text{sorption}}$ analysis, as was done for the isothermal experiments. The small magnitude of $\Delta m_{\text{sorption}}$ may be the result of the way the isochoric experiment was carried out. The temperature was continuously decreasing due to heat loss from the measuring cell; thus, the cell cooled faster than the sample inside it. Sample would thus adsorb/condense on the walls of the measuring cell rather than on the sinkers, which were the slowest to cool down.

The dew-point densities and pressures are given in table 5 for the two isochores measured. A comparison of these results with the GERG equation of state is given in table 5 and figure 4. The deviations for the isochoric experiments are in close agreement with the isothermal experiments at similar temperatures. Detailed information for each of the measured (p , ρ , T , x) points are given in the Supplementary Data.

3.3. Comparison to Literature Data

Kunz *et al.* [22] provide a comprehensive review of the literature data for the (methane + propane) system existing as of 2004. Dr. Eric Lemmon of NIST [23] made his database of mixture data available to us, and it included five additional sources not referenced by Kunz *et al.* (these were Kalra and Robinson [24], Powers *et al.* [25], Cutler [26] Roof and Baron [27], and Stoeckli and Stateley [28]). The only recent source was that of May *et al.* [29] In total, there are 21 literature sources with 787 data points at saturation; these cover the full range of composition and temperatures spanning nearly the full range from the triple point to critical point of propane (85.5 K to 369.9 K). Most of the sources report VLE (typically (p, T, x) or (p, T, x, y)) data, and in figure 6, we plot deviations in the saturation pressure (either bubble-point pressure or dew-point pressure, depending on what was reported). Although the data are wide-ranging, the distinct observation from figure 6 is that the scatter in the data (both between data sets and, often, within sets) is quite large; the average RMS deviation between the data and the GERG model is 4.1%. This figure shows that the present data are well inside the “cloud” of literature data.

May *et al.* [29] recently reported careful (p, T, x, y) measurements on the (methane + propane) system and also evaluated the literature data and recommended the “best” literature data sets, which were those of Webster and Kidnay [30] and Price and Kobayashi [31]. These recommended sets, along with the present data and those of May *et al.* [29] are plotted in black and red in figure 6; there is much better internal consistency between these sets compared to the literature data overall.

Three sources report dew-point densities, and these data are compared to the GERG model in figure 7. In this figure, we plot the difference between the experimental dew-point temperature and the T_{dew} calculated from the GERG model as a function of the composition. We plot ΔT_{dew} rather than $\Delta \rho_{\text{dew}}$ because a significant fraction of the literature data are either near the maxcondentherm (where a small difference in temperature results in a large difference in dew-point density) or in the retrograde-condensation region (where there are two solutions for $\rho_{\text{dew}}(T)$). The data of Sage *et al.* [32] and Reamer *et al.* [33], from 1934 and 1950, respectively, show very large deviations, ranging from -21.2 K to 9.3 K. Both of these sources used an isochoric method combined with a graphical analysis to interpolate the raw experimental results. The more recent (2001) data from May *et al.* [4] show much smaller deviations of 0.71 K to 0.94 K in T_{dew} . The deviations in our current data range from -0.05 K to 1.60 K. This figure illustrates both the scarcity of dew-point density data for mixtures, and the large scatter in many of the literature sources.

The most meaningful comparison of our current data with the literature data for dew-point density is for our measurement on the (0.74977 methane + 0.25023 propane) mixture at $T = 273.152$ K, which has $\Delta T_{\text{dew}} = 0.40$ K. This compares to the results of May *et al.* [4] on a (0.7931 methane + 0.2069 propane) mixture at $T = (284.6 \pm 0.2)$ K, which has $\Delta T_{\text{dew}} = 0.71$ K. The difference is slightly outside the mutual uncertainties, but the two points are at slightly different compositions and temperatures.

There are additional data sets that report densities in the homogeneous vapor phase for the (methane + propane) system. These were compared to the single-phase portion of the present data in Richter and McLinden [17]. The scatter observed for the vapor-phase densities (*i.e.*, figure 7 in [17]) was somewhat smaller than that seen here in figure 6. There was, however, generally good consistency between the sets reporting the interaction second virial coefficient B_{12} (see figure 9 in [17]), which further highlights the difficulties of measurements at the dew point compared to single-phase states.

Considering the literature data presented in figures 6 and 7, we conclude that the GERG model fitted the data as well as was possible given the large scatter in the data.

4. Uncertainty Analysis

The uncertainty sources include the temperature, pressure, density, and composition. For measurements in single-phase states, these have been discussed in previous publications and are summarized in sections 4.1 through 4.3. The dew point was determined by the intersection of single-phase and two-phase data, and the uncertainties in the dew-point density and dew-point pressure involve additional terms, which are discussed in section 4.4.

4.1 Uncertainty in temperature, density, and pressure

McLinden and Lösch-Will [16] provide an analysis of uncertainties for gas-phase measurements, and McLinden and Splett [34] provide a further detailed uncertainty analysis for this instrument. Those results are summarized here. The standard uncertainty in the density was

$$\frac{u(r)}{\text{kg} \cdot \text{m}^{-3}} = \left[\{16\}^2 + \{0.20|(T / \text{K} - 293)|\}^2 + \{0.63p / \text{MPa}\}^2 \right]^{0.5} \frac{10^{-6} r}{\text{kg} \cdot \text{m}^{-3}} + 0.0010, \quad (17)$$

where the term in brackets is from the uncertainties in the volumes of the two sinkers, and the final, constant term includes all other uncertainties. We added to this uncertainty the standard deviations actually observed in the multiple balance readings made over the 12 minutes

necessary to complete a single density determination. For the present work, the uncertainty in the density measurement itself (for single-phase states) was a maximum of $0.0077 \text{ kg}\cdot\text{m}^{-3}$; the largest relative uncertainty was 0.10 % at the lowest measured density, $\rho = 1.66 \text{ kg}\cdot\text{m}^{-3}$. The uncertainties in two-phase states were higher because of sample condensing onto the sinkers.

The SPRT used to measure the temperature of the mixture was calibrated in our laboratory on ITS-90 from $T = (83 \text{ to } 505) \text{ K}$ by use of fixed-point cells. The standard uncertainty of the temperature, including the uncertainty in the fixed-point cells, drift in the SPRT and in the standard resistor, and any temperature gradients, is 3 mK. Oscillations over time were separately accounted for and were 1 mK or less. This temperature uncertainty impacts gas densities at the level of approximately 0.0010 %.

For the isochoric experiments, the temperature of the measuring cell was continuously decreasing. This resulted in greatly increased temperature gradients across the cell compared to the isothermal experiments. This effect was estimated to increase the standard temperature uncertainty to 0.050 K.

The uncertainty of the pressure measurement arises from three sources: (1) the calibration of the transducers, (2) the repeatability and temporal drift of the transducers, and (3) the uncertainty in the hydrostatic head correction. The pressure transducers were calibrated with a gas-operated piston gauge. This calibration was done *in situ* by connecting the piston gauge to the sample port of the filling and pressure manifold. We estimated the standard uncertainty due to the calibration and drift of the transducers to be $(20 \times 10^{-6} \cdot p + 0.025 \text{ kPa})$ for the low-range transducer ($p_{\text{max}} = 2.7 \text{ MPa}$) and $(20 \times 10^{-6} \cdot p + 0.06 \text{ kPa})$ for the mid-range transducer ($p_{\text{max}} = 6.9 \text{ MPa}$). The complete data tables in the Supplementary Data of this paper indicate which transducer was used for a given measurement.

Because we are concerned here primarily with pressures near the dew point, the uncertainty due to the hydrostatic head correction is substantially larger than is usually the case for this instrument. The connecting line from the measuring cell to the pressure transducer exited at the bottom of the measuring cell and was in contact with the isothermal shield (which was maintained at a temperature 1 K lower than the cell temperature) before connecting with the pressure manifold, which was maintained at $T = 313 \text{ K}$. Because of this arrangement, it is likely that liquid was present in a portion of the pressure line, but the location of the liquid-vapor interface was uncertain. We estimate the standard uncertainty in the hydrostatic head correction corresponds to a 5 cm height of liquid in equilibrium with the vapor in the measuring cell, corresponding to a maximum pressure uncertainty of 0.24 kPa.

The combined standard uncertainty in pressure is

$$u_c(p) = \left\{ u^2(p_{\text{transducer}}) + [S(p)]^2 + [u(h)g(r_{\text{liq}} - r_{\text{vap}})]^2 \right\}^{1/2}, \quad (18)$$

The first term on the right-hand side represents the uncertainty due to the pressure transducer, $\sigma(p)$ is the standard deviation of the replicate pressure readings taken over the 12 minutes of a density determination, g is the local acceleration of gravity, ρ_{liq} and ρ_{vap} are the liquid and vapor sample densities in the pressure line (as calculated with the GERG EOS), and $u(h)$ is the uncertainty in the height of the liquid/vapor interface (*i.e.*, 5 cm). The combined standard uncertainty in pressure ranged from (0.05 to 2.0) kPa for the present measurements.

4.2 Uncertainty in composition arising from mixture preparation

For a gas mixture, a considerable fraction of the overall density uncertainty is due to uncertainty in the composition. To first order, the molar density of a vapor mixture is constant for a given T , p , and x , or equivalently, the mass density is proportional to the molar mass, so that the uncertainty in density due to uncertainties in the composition is proportional to the uncertainty in M , the molar mass of the mixture. The uncertainty in M due to uncertainties in the gravimetric preparation is given by

$$u(M_{\text{grav}}) = \left\{ \sum_{j=1}^n \left[\frac{\sum_{i=1}^n \frac{m_i}{M_i} - \left(\sum_{i=1}^n m_i \right) / M_j}{\left(\sum_{i=1}^n \frac{m_i}{M_i} \right)^2} u(m_j) \right]^2 \right\}^{0.5}, \quad (19)$$

where the M_i are the molar masses of the components, and the m_i represents the mass of each of the components loaded into the sample cylinder. With an uncertainty of 0.010 g for each of the component masses, $u(M_{\text{grav}})$ ranged from (0.00016 to 0.00185) g·mol⁻¹ for the mixtures studied here. A derivation of equation (19) is presented in the Supporting Information of Richter and McLinden [17]. The uncertainty in M for a binary mixture can be converted to an equivalent uncertainty in the composition $u(x)$ by

$$u(x) = \frac{u(M)}{(M_1 - M_2)}. \quad (20)$$

This analysis is exact for ideal gases, and it is a good approximation for real gases at low pressures. In any event, it is adequate for assigning uncertainties, which are inherently approximate.

Given the very high purity of our starting materials, the uncertainty in M_i due to impurities in the components was negligible. The standard uncertainty due to the uncertainties in the atomic masses of carbon (from fossil fuels) and hydrogen (Wieser *et al.* [35]) was approximately $0.0003 \text{ g}\cdot\text{mol}^{-1}$.

4.3 Uncertainty in composition arising from sorption effects

A further source of uncertainty in the composition arose from sorption of sample onto the sinkers, the inner walls of the measuring cell, sample cylinder, filling lines, etc. In other words, the composition in the measuring cell was not necessarily a simple ratio of the component masses loaded into the sample cylinder. The virial analysis of the data by Richter and McLinden [17] provides an independent estimate of M . We take the root-mean-square (RMS) average of the difference between the M from the gravimetric preparation M_{grav} and that determined from the virial analysis M_{virial} to be the standard uncertainty in M arising from sorption effects. This uncertainty is $0.0052 \text{ g}\cdot\text{mol}^{-1}$ (or 0.0114 % to 0.0226 % of M or 0.00019 mole fraction), which is 2.8 to 32 times larger than the effect from the gravimetric preparation of the mixture.

The density uncertainty arising from the composition uncertainty (both mixture preparation and sorption effects) is thus

$$u(r(x)) = r \times \frac{1}{M} \left[u(M_{\text{grav}})^2 + u(M)_{\text{atomic weights}}^2 + u(M)_{\text{sorption}}^2 \right]^{0.5}. \quad (21)$$

4.4 Uncertainty in dew point arising from data analysis

The dew point is calculated by the intersection of two curves fitted to the data. Uncertainties result from (1) the assignment of a given data point to either the function fitted to the homogeneous vapor-phase data or the two-phase function and (2) the scatter in the data and the resulting uncertainty in the fitted coefficients. The assignment of a data point to either the “single-phase” or “two-phase” function was, in most cases, quite obvious. For points very near the dew point, however, the assignment can significantly affect the fit of the function(s) and, thus, the calculated dew point. We first fitted the data that were obviously in each of the regions and obtained the goodness-of-fit statistic, R^2 ; the “transition” points were then added one-by-one. If the R^2 statistic remained essentially constant, the point was retained; if, on the other hand, the R^2 changed significantly, that point was tested with the function for the other phase, or, in a few

cases, omitted entirely from the analysis. (Out of a total of 469 density measurements along the 11 isotherms, 24 were thus assigned to the “transition” region.)

The single-phase and two-phase functions were fitted simultaneously to a point-slope form with the intersection point being a common parameter to both functions. This was done as an orthogonal distance regression using the ODRPACK routines of Boggs *et al.* [36] ODRPACK returned a standard deviation for each of the fitted parameters, including the intersection point, and this was taken as the uncertainty in the intersection. The relative standard uncertainty from this effect ranged from 0.01 % to 1.20 %, making it the most significant source of uncertainty in the dew-point densities and pressures for most of the points measured.

4.5 Combined state-point uncertainty

For purposes of comparing (p, ρ, T, x) measurements to a model, it is customary to assume that the temperature, pressure, and composition are known exactly, and to lump all uncertainties into a single value for the density, a so-called state-point uncertainty. This combined expanded uncertainty ($k = 2$) for the density in the homogeneous vapor phase, including all effects, is given by:

$$U_c(r) = 2 \cdot \left\{ \left[u(r) \right]^2 + \left[\left(\frac{\partial r}{\partial p} \right)_T u(p) \right]^2 + \left[\left(\frac{\partial r}{\partial T} \right)_p u(T) \right]^2 + \left[\frac{r}{M} u(M) \right]^2 \right\}^{0.5}, \quad (22)$$

where the u are the individual standard uncertainties, and the derivatives are calculated from the GERG equation. This value is tabulated in the Supplementary Data for each measured point. The relative combined expanded state-point uncertainty in density ranged from 0.035 % at the highest densities measured to 0.21 % at the lowest measured density $\rho = 1.66 \text{ kg}\cdot\text{m}^{-3}$ (which was an absolute uncertainty of $0.0035 \text{ kg}\cdot\text{m}^{-3}$).

The combined expanded state-point uncertainty ($k = 2$) for the dew-point density also includes the variation of the dew-point density with temperature and composition and the uncertainty arising from the intersection of the single-phase and two-phase data:

$$U_C(r_{\text{dew}}) = 2 \cdot \left\{ \left[u_C(r) \right]^2 + \left[\left(\frac{\partial r_{\text{dew}}}{\partial T} \right)_{\text{sat}} u(T) \right]^2 \right. \\ \left. + \left[\left(\frac{\partial r_{\text{dew}}}{\partial x} \right)_{\text{sat}} u(x) \right]^2 + \left[u(r_{\text{intersection}}) \right]^2 \right\}^{0.5}, \quad (23)$$

where $u_C(\rho)$ is one-half of the expanded combined uncertainty in density (given by Eq 22), the derivatives of the dew-point density with respect to temperature and composition were numerically evaluated along the saturation (*i.e.*, dew) line from the GERG equation, and the uncertainty in the intersection is the term discussed in section 4.4.

The combined expanded state-point uncertainty ($k = 2$) for the dew-point pressure is given by an expression analogous to Eq 23:

$$U_C(p_{\text{dew}}) = 2 \cdot \left\{ \left[u(p) \right]^2 + \left[\left(\frac{\partial p_{\text{dew}}}{\partial T} \right)_{\text{sat}} u(T) \right]^2 \right. \\ \left. + \left[\left(\frac{\partial p_{\text{dew}}}{\partial x} \right)_{\text{sat}} u(x) \right]^2 + \left[u(p_{\text{intersection}}) \right]^2 \right\}^{0.5}. \quad (24)$$

When the dew-point pressure is computed from a virial fit of the vapor-phase data evaluated at the dew-point density, the combined expanded state-point uncertainty ($k = 2$) for the dew-point pressure is

$$U_C(p_{\text{dew}}) = 2 \cdot \left\{ \left[\left(\frac{\partial p}{\partial r} \right)_{\text{dew point}} u_C(r_{\text{dew}}) \right]^2 + \left[u(p_{\text{virial}}) \right]^2 \right\}^{0.5}, \quad (25)$$

where $u(p_{\text{virial}})$ is the standard uncertainty in the virial fit, which we take as the RMS deviation given by Richter and McLinden [17]. The derivative of pressure with respect to density is evaluated in the vapor phase very close to the dew line. In this case, the uncertainty in the dew-point pressure is primarily a function of the uncertainty in the dew-point density.

5. Discussion and conclusions

The (p, ρ, T, x) behavior of three (methane + propane) mixtures was investigated with the NIST two-sinker densimeter over the temperature range of (248.15 to 293.15) K; the measurements extended from low pressures into the two-phase region. These data were analyzed in several different ways. For the isothermal experiments, the measurements started at a low pressure, well

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5 inside the single-phase vapor region, and the pressure was incremented to a final pressure several
6 percent above the dew-point pressure; the dew point was indicated by an abrupt change in slope.
7 The “traditional” analysis of plotting (pressure versus density) as well as the novel method of
8 plotting (adsorbed mass versus density) gave consistent results. The uncertainties for the
9 adsorbed mass analysis were lower in most cases. A further, significant advantage of the
10 (adsorbed mass versus density) analysis was that the dew point was quite distinct, even when the
11 measurements extended only slightly into the two-phase region.
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16 A similar analysis plotting adsorbed mass versus pressure resulted in larger scatter and
17 uncertainties in the two-phase data because of increased uncertainty in the pressure
18 measurement. Thus, we recommend that the dew-point pressure be calculated from extrapolating
19 a virial fit of the single-phase vapor (p vs. ρ) data to the dew-point density. This effect was
20 largely a consequence of the configuration of the pressure measuring system in our instrument,
21 and it could be avoided in an instrument optimized for dew-point measurements by heating the
22 pressure line and pressure transducer such that condensation would not occur in the pressure
23 system.
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30 An isochoric experiment, in which a fixed quantity of sample was slowly cooled from slightly
31 above to slightly below the dew-point temperature, was also carried out. This experiment yielded
32 results consistent with the isothermal experiments. The uncertainties arose primarily because of
33 the continuously changing temperature. In contrast with the “traditional” isochoric experiment,
34 which is conducted in a simple closed vessel, we continuously measured the density in our
35 experiment and, thus, also obtained the dew-point density. The isochoric experiment required (18
36 to 48) hours to carry out, or about the same total time as a complete isothermal series, but it
37 yielded only the dew-point data. In contrast, the isothermal experiment also yielded single-phase
38 vapor (p , ρ , T , x) data. Thus, the isothermal experiment is preferred.
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46 We carried out a detailed uncertainty analysis for our measurements, including a consideration of
47 the uncertainties arising from sorption effects on the mixture composition. These effects are not
48 typically considered in literature sources of dew-point data, and this may be responsible for a
49 portion of the large scatter observed in the literature data.
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53 This work has demonstrated that the analysis of sorption/condensation effects is a useful
54 technique for the detection of dew points. It provides a quantitative measure of the
55 adsorbed/condensed mass on the sinker surfaces, not just a change in slope, as is typical with
56 many traditional dew-point measurement techniques. The uncertainties in the dew points
57 determined with this technique were often, but not always, lower than traditional techniques; the
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5 cases with larger uncertainties corresponded to isotherms that extended only slightly into the
6 two-phase region. With more experience, we will be able to obtain consistently the lower
7 uncertainties. We considered only binary systems in this work, which are the simplest. May *et al.*
8 [4], for example, measured both binary and ternary systems and found that the dew point was
9 less distinct for the ternary. We will be investigating multi-component mixtures with our new
10 method in the near future.
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15 Finally, we note that our instrument was not optimal for detecting adsorption onto the sinkers; in
16 particular, our sinkers had approximately equal surface areas and a similar surface finish—
17 details specifically intended to “cancel out” sorption effects, as discussed by Kleinrahm and
18 Wagner [13] in the description of their original two-sinker densimeter. This suggests that a
19 densimeter with two sinkers of the same mass and same material (and thus the same volume), but
20 having very different surface areas and/or surface finishes, could better detect sorption
21 phenomena. Such a modification is the topic of a companion paper [18].
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Table 1. Sample information.

Chemical Name	Source	Initial Purity/ mole fraction	Purification Method	Final Purity/ mole fraction	Analysis Method
methane	Matheson	0.99999	none	0.99999	GC/MS ^a
propane	Scott	0.99999	none	0.99999	GC/MS

^aGas chromatography/mass spectrometry

Table 2. Gravimetric compositions (mole fraction) and average molar mass of the studied mixtures.

Component	Mole fraction mixture		
	(75/25)	(50/50)	(27/73)
Methane	0.74977	0.50688	0.26579
Propane	0.25023	0.49312	0.73421
<i>M</i> /g·mol ^{−1}	23.0623	29.8761	36.6393

Table 3. Summary of dew-point densities and pressures ρ_{dew} and p_{dew} from the isothermal experiments evaluated by the “traditional” intersection of pressure versus density, relative combined expanded uncertainties ($k = 2$); and relative deviations to the GERG model of Kunz and Wagner [15] $\Delta_{\rho,\text{dew}}$ and $\Delta_{p,\text{dew}}$; the standard uncertainty in temperature was 3 mK.

T /K	p versus ρ					
	ρ_{dew} /kg·m ⁻³	p_{dew} /MPa	$U_C(\rho_{\text{dew}})$ /%	$U_C(p_{\text{dew}})$ /%	$\Delta_{\rho,\text{dew}}$ /%	$\Delta_{p,\text{dew}}$ /%
$x_{\text{methane}} = 0.26579$; $u(x) = 0.00020$						
248.152	5.309	0.2821	0.22	0.34	-0.09	0.02
273.149	12.027	0.6685	0.10	0.24	-1.23	-0.48
273.149	12.026	0.6684	0.16	0.68	-1.24	-0.49
293.146	21.457	1.2049	0.09	0.31	-2.41	-0.99
$x_{\text{methane}} = 0.50688$; $u(x) = 0.00019$						
248.151	6.627	0.4324	0.80	1.52	-0.34	-0.03
273.148	15.266	1.0410	0.11	0.12	-2.88	-2.06
273.149	15.322	1.0445	0.14	0.24	-2.52	-1.73
273.149	15.226	1.0387	0.16	0.34	-3.14	-2.28
293.147	28.360	1.9440	0.10	0.12	-5.36	-3.69
$x_{\text{methane}} = 0.74977$; $u(x) = 0.00019$						
248.161	10.590	0.8861	0.49	0.50	-2.61	-2.30
273.152	27.730	2.3666	0.42	0.41	-4.13	-3.40

Table 4. Summary of dew-point densities and pressures ρ_{dew} and p_{dew} from the isothermal experiments evaluated by the intersection of the adsorbed mass $\Delta m_{\text{sorption}}$ versus (p or ρ); relative deviations to the GERG model of Kunz and Wagner [15] $\Delta_{\rho,\text{dew}}$ and $\Delta_{p,\text{dew}}$; and relative combined expanded uncertainties ($k = 2$), $U_C(\rho_{\text{dew}})$ and $U_C(p_{\text{dew}})$; the standard uncertainty in temperature was 3 mK.

T K	$\Delta m_{\text{sorption}}$ versus p			$\Delta m_{\text{sorption}}$ versus ρ					
	p_{dew} /MPa	$U_C(p_{\text{dew}})$ /%	$\Delta_{p,\text{dew}}$ /%	ρ_{dew} /kg·m ⁻³	p_{dew}^* /MPa	$U_C(\rho_{\text{dew}})$ /%	$U_C(p_{\text{dew}})$ /%	$\Delta_{\rho,\text{dew}}$ /%	$\Delta_{p,\text{dew}}$ /%
$x_{\text{methane}} = 0.26579$; $u(x) = 0.00020$									
248.152	0.2799	2.40	-0.76	5.273	0.2803	0.83	0.83	-0.95	-0.61
273.149	0.6649	0.62	-1.01	12.008	0.6676	0.13	0.14	-1.39	-0.61
273.149	0.6638	0.65	-1.18	12.003	0.6674	0.11	0.12	-1.43	-0.64
293.146	1.2046	0.80	-1.01	21.393	1.1974	0.76	0.76	-2.70	-1.60
$x_{\text{methane}} = 0.50688$; $u(x) = 0.00019$									
248.151	0.4236	2.06	-2.06	6.552	0.4277	0.97	0.97	-1.46	-1.11
273.148	1.0553	0.72	-0.71	15.375	1.0477	0.11	0.12	-2.18	-1.43
273.149	1.0369	0.82	-2.45	15.239	1.0395	0.38	0.38	-3.05	-2.20
273.149	1.0584	0.46	-0.42	15.425	1.0476	0.13	0.14	-1.87	-1.44
293.147	1.9504	0.21	-3.32	28.420	1.9275	0.08	0.09	-5.16	-4.50
$x_{\text{methane}} = 0.74977$; $u(x) = 0.00019$									
248.161	0.9132	0.29	0.69	10.873	0.9080	0.19	0.20	0.00	0.12
273.152	2.4320	0.29	-0.73	28.441	2.4186	0.25	0.25	-1.67	-1.27

* p_{dew} calculated by evaluating virial expansion (fitted to homogeneous vapor-phase data) at $\rho = \rho_{\text{dew}}$

Table 5. Summary of dew-point temperatures, pressures and densities T_{dew} , p_{dew} and ρ_{dew} , from the isochoric experiments on the methane/propane mixture with a composition of (0.26579 methane + 0.73421 propane); relative combined expanded uncertainties $U_C(p_{\text{dew}})$ and $U_C(\rho_{\text{dew}})$; and relative deviations to the GERG model of Kunz and Wagner [15] $\Delta_{\rho,\text{dew}}$ and $\Delta_{p,\text{dew}}$; the dew points were evaluated from the “traditional” intersection of temperature T versus pressure p and by the intersection of pressure versus density ρ ; the standard uncertainty in the composition was 0.00020 mol frac.

T versus p					p versus ρ					
$T_{\square\square\square}$ K	p_{dew} /MPa	$U_C(T_{\text{dew}})$ /K	$U_C(p_{\text{dew}})$ /%	$\Delta_{p,\text{dew}}$ /%	p_{dew} /MPa	ρ_{dew} /kg·m ⁻³	$U_C(\rho_{\text{dew}})$ /%	$U_C(p_{\text{dew}})$ /%	$\Delta_{p,\text{dew}}$ /%	$\Delta_{\rho,\text{dew}}$ /%
273.409	0.6722	0.100	0.33	-0.74	0.6720	12.086	0.31	0.32	-1.54	-0.77
293.815	1.2225	0.103	0.29	-1.41	1.2224	21.750	0.30	0.29	-2.95	-1.41

Figure 1. Results for the isotherm at $T = 273.149$ K, with a composition of (0.26579 methane + 0.73421 propane); (a) the “traditional” plot of pressure versus density; (b) adsorbed mass versus density; $\circ$, single-phase data; $\times$, two-phase data; the lines are fitted to the data in each region.

Figure 2. Results for the isotherm at $T = 248.151$ K, with a composition of (0.50688 methane + 0.49312 propane), with the adsorbed mass plotted versus pressure (a) and versus density (b); $\circ$, single-phase data; $\times$, two-phase data; the lines are fitted to the data in each region.

Figure 3. Results for the isotherm at $T = 293.147$ K for the (0.50688 methane + 0.49312 propane) mixture; (a) the dew point is difficult to detect in the “traditional” plot of pressure versus density; (b) the dew point is easily identified in the plot of adsorbed mass versus density; $\circ$, single-phase data; $\times$, two-phase data; the lines are fitted to the data in each region.

Figure 4. Relative deviations of experimental dew-point densities $\rho_{\text{dew,exp}}$ at $T = (248.15, 273.15 \text{ and } 293.15) \text{ K}$ from those calculated with the GERG-2008 equation of state of Kunz and Wagner [15]; $\circ$, isotherms measured on the (0.26579 methane + 0.73421 propane) mixture; $\times$, isotherms measured on the (0.50688 methane + 0.49312 propane) mixture; $\triangle$, isotherms measured on the (0.74977 methane + 0.25023 propane) mixture; $\boxtimes$ isochoric measurements on the (0.26579 methane + 0.73421 propane) mixture. The error bars show the relative combined expanded uncertainty ($k = 2$) in the measured dew-point densities.

Figure 5. Results for the isochoric measurements on the (0.26579 methane + 0.73421 propane) mixture; (a) a "traditional" plot of pressure versus temperature; (b) a plot of pressure versus density; $\circ$, single-phase data; $\triangle$, "precondensation" region; $+$, two-phase data; the lines are fitted to the data in each region.

Figure 6. Relative deviations of experimental saturation pressures p_{exp} for (methane + propane) mixtures from saturation pressures p_{GERG} calculated with the GERG-2008 equation of state of Kunz and Wagner[15]; (a) plotted as a function of temperature; (b) plotted as a function of composition; $\boxtimes$, present results (“sorption analysis”); other symbols show literature data as indicated in the legend.

Figure 7. Deviations of experimental dew-point temperatures, $T_{\text{dew,exp}}$, from T_{dew} calculated as a function of experimental dew-point density, $T_{\text{dew,GERG}}(x, \rho_{\text{dew,exp}})$, with the GERG-2008 equation of Kunz and Wagner [15]; $\triangle$, present data (“sorption analysis”); $\diamond$, Sage *et al.* [32]; $\circ$, Reamer *et al.* [33]; $\times$, May *et al.* [4].

references from Fig 6 (note: these are so that EndNote includes the sources plotted on the figure in the reference list)

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