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Vapor−Liquid Equilibria Measurements of Methane + 2-Methylpropane (Isobutane) at Temperatures from (150 to 250) K and Pressures to 9 MPa

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A 60 cm^3 temperature-controlled pressure cell was constructed for vapor−liquid equilibria (VLE) measurements in methane-dominant mixtures at conditions representative of those found in cryogenic gas processing plants. The experimental system included a pressure transducer located in the cell's lid, temperature-controlled sampling capillaries, automated microliter sampling valves, and a gas chromatograph (GC) with two columns and multiple detectors for the simultaneous measurements of phase compositions. A gravimetrically prepared mixture of methane + 2-methylpropane (isobutane) $\{CH_4(1) + i\text{-}C_4H_{10}(2)\}$ with the overall mole fraction $z_2 = (0.0724 \pm 0.0001)$ was loaded into the cell, and P,T,x,y data for this mixture were obtained along two isochoric pathways over the temperature range from (150 to 250) K at pressures to 9 MPa. The measured VLE data extend into a temperature range not previously studied for this system and are compared with previous literature data and with the predictions of the Groupe European de Recherche Gaziere (GERG-2004) multiparameter equation of state (EOS). Where they overlap, the new data are consistent with the existing VLE data for this binary mixture, within the estimated uncertainties of the new data. At temperatures above 190 K, the relative average absolute deviation (AAD) from the GERG-2004 EOS is about 6 % for both x_2 and y_2. Including the data measured below 190 K, the relative AAD for x_2 increases to 9 %. Analysis of the new data also indicates a possible inconsistency in overall density predictions for the two-phase region made using the GERG-2004 EOS.

Introduction

The construction and operation of a cryogenic gas processing facility requires significant expenditure of capital. Process simulations of such facilities have the potential to reduce the total cost of ownership if they are sufficiently optimized.[1] Process simulators are used to estimate the operating parameters of the liquefaction plant and to size the equipment. Central to the simulation is the calculation of the thermodynamic properties of hydrocarbon fluid mixtures at each process condition, which are usually calculated with an equation of state (EOS). The thermodynamic properties of natural gas have been studied extensively and are relatively well-known at most noncryogenic conditions. However, the availability of reliable thermodynamic data for multicomponent mixtures at the high-pressure, cryogenic conditions relevant to liquefied natural gas (LNG) production is limited.[2] Additional accurate vapor−liquid equilibria (VLE), volumetric, and calorimetric data for multicomponent mixtures at LNG process conditions would improve the reliability of liquefaction facility simulations. This increased reliability would then improve the prospects of optimizing of the facility's design and operating parameters.

Several authors have examined the impact of uncertainties in the thermodynamic properties on the reliability of process simulations.[3−5] Kister[6] reviewed several examples of problems associated with the simulation of distillation columns and identified the inability to predict the equilibrium phase compositions, y_i (vapor) and x_i (liquid), as the leading cause of problematic simulations. The most widely used thermodynamic models for such predictions in high-pressure phase equilibria applications are EOS's. For hydrocarbon processes such as LNG production, the cubic EOS's of Soave, Redlich, and Kwong (SRK)[7] and Peng and Robinson (PR)[8] are used most frequently. These equations are both more than 30 years old; their deficiencies are well-known, and an array of correction techniques (e.g., volume translation[9]) and sophisticated mixing rules (e.g., excess Gibbs energy[10]) are available to extend the applicability of these equations. Furthermore, many other cubic EOS's have been developed (for a review see, for example, Valderrama[11]) and are available for selection in modern process simulators such as Aspen HYSYS[12] available from AspenTech and PRO/II[13] available from Invensys Sytems, Inc. Nevertheless, for predicting the VLE behavior of multicomponent mixtures of light hydrocarbons, the (almost) unmodified SRK and PR EOS are still recommended for use in most process simulators.

For an increasing number of important fluids, multiparameter EOS's are able to represent the available thermodynamic data significantly more accurately than cubic EOS's, although their computational complexity generally limits their use in process simulators. Kunz et al.[2] on behalf of the Groupe European de Recherche Gaziere (GERG), have recently developed a multiparameter EOS for natural gas mixtures (up to 18 components) valid at temperatures between (90 and 450) K and pressures to

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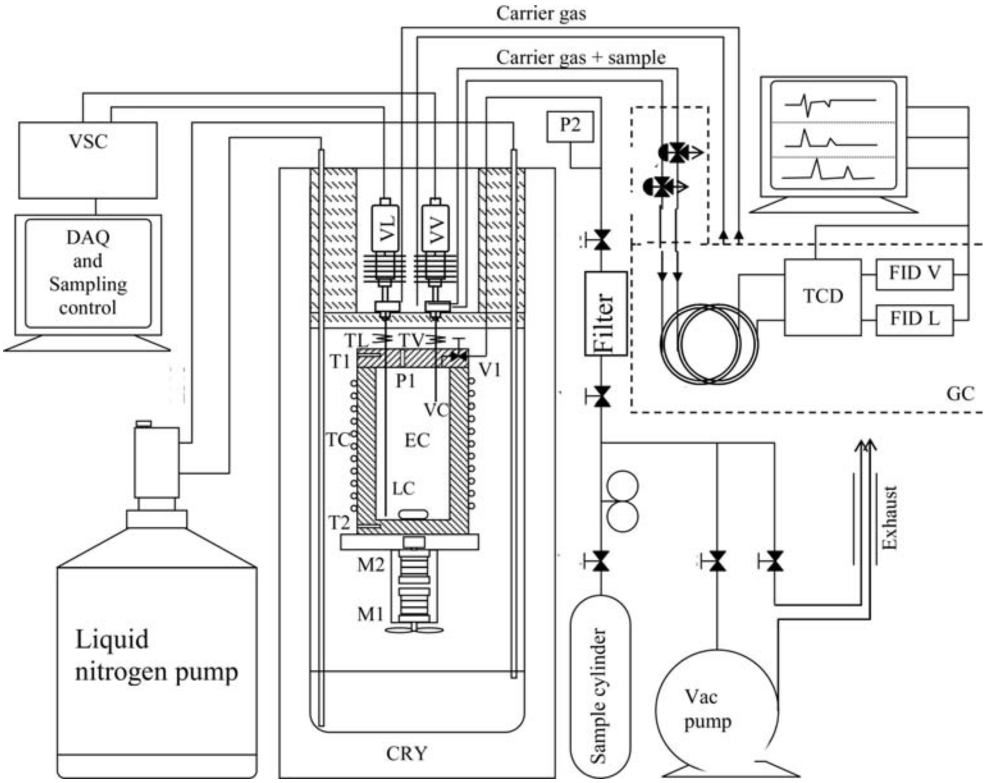

Figure 1. Schematic diagram of the VLE apparatus. The explanations of the labels are given in the text.

35 MPa. The uncertainties of the GERG-2004 EOS are claimed to be equal to that of available experimental data for binary and multicomponent mixtures of natural gas components: typically relative deviations of 0.1 % for gas densities, (0.1 to 0.5) % for liquid densities, (0.5 to 2) % for enthalpy differences, and (1 to 5) % for VLE properties. These claims are based on the fact that the GERG-2004 EOS was regressed to a very large set of binary mixture data and compared to several data sets for multicomponent mixtures. Kunz et al.[2] stated that the VLE data situation for mixtures of natural gas components is still poor, particularly for multicomponent mixtures at cryogenic conditions. More high-quality VLE data for such systems will improve the predictions of both complex multicomponent EOS's, such as GERG-2004, as well as the cubic EOS used in process simulators.

This paper describes the experimental system we have developed to measure VLE in binary and multicomponent mixtures of natural gas components at pressures and temperatures representative of cryogenic process plants. The experimental method and the subsequent data analysis are described, and finally VLE data are presented for the methane + 2-methylpropane (isobutane) system over the temperature range from (150 to 255) K and at pressures to 9 MPa. Our P,T,x,y data for the methane + isobutane system extend 45 K below those of Barsuk et al.[14] which, together with the measurements of Olds et al.,[15] were the only P,T,x,y data for methane + isobutane used in the development of the GERG-2004 EOS. The comparisons of our data with this EOS presented in the Results and Discussion Section also indicate a deficiency in the model's prediction of densities within the two-phase region.

Apparatus and Materials

A schematic of the cryogenic VLE apparatus is shown in Figure 1 and is similar in concept to the system described by Baba-Ahmed et al.[16] An equilibrium cell (EC) machined from a single billet of stainless steel grade 316 served as the pressure vessel with a maximum operating pressure of up to 30 MPa. The cell had an internal diameter of 3 cm and a volume of approximately 60 cm^3. The outer surface of the cell was plated with 1 mm of thick copper to improve heat transfer and temperature uniformity. A foil-type heating element was wrapped and glued to the outer surface of the cell using high thermal conductivity epoxy suitable for cryogenic operation. A 100 Ω platinum resistance thermometer (PRT) was glued to the cell's external surface, directly underneath the heating foil, and used as the sensor for temperature control (TC). Wells were bored in the top (lid) and the bottom of the equilibrium cell to house two 100 Ω PRTs (T1) and (T2). These two PRTs were calibrated to ITS-90 by their supplier (LakeShore Cryotronics) over the temperature range from (60 to 330) K with a claimed uncertainty of ± 0.02 K.

The cell was placed inside a cryogenic Dewar (CRY) equipped with an automatic liquid nitrogen pump (LNP) that filled and controlled the liquid nitrogen level inside the Dewar. An attachment to the bottom of the cell was used to mount two cryogenically compatible, variable speed motors. The lower motor (M1) was used to drive a fan that stirred the nitrogen boil-off vapor inside the Dewar to improve cooling rates and/or prevent stratification of the boil-off vapor. The second motor (M2) was used to generate a rotating magnetic field, which in turn drove a Teflon-coated magnetic bar sitting inside the cell on the bottom surface. In this way M2 was used to mix the sample fluid. To prevent any wear from the spinning magnetic bar a Mylar film was placed between the Teflon-coated magnetic bar and the cell bottom. (Teflon and Mylar are registered trademarks of E.I. du Pont de Nemours & Co.)

The lid of the cell was machined carefully to fit a custom, cryogenically compatible fill valve (V1), with a nonrotating stem that was flush with the inner surface of the cell lid when closed. This minimized any dead volume associated with the fill valve.

Also housed in the lid to minimize dead volume was a pressure transducer (P1) (Kulite model CT-190). This transducer utilized a strain-gauge on a silicon diaphragm and was suitable for operation at temperatures from (77 to 393) K. It was calibrated in situ by comparison with a reference quartz-crystal pressure transducer (Paroscientific Digiquartz series 1000) with a full scale of 14 MPa and a relative uncertainty of 0.008 % of full scale as stated by the manufacturer. The relative standard deviation of the Kulite transducer's calibration was ± 0.5 % for the pressure range from (1 to 14) MPa.

Two capillary tubes made from Monel 400 and with internal diameters of less than 0.015 cm were also mounted in the cell lid. One of the capillaries (VV) was used to sample the vapor phase in the cell; it extended 1.5 cm below the bottom of the cell lid and had a total length of 13 cm. The other capillary (VL) was used to sample the liquid phase; it extended nearly to the bottom of the cell and had a total length of 20 cm. A thin Teflon spacer placed on the cell bottom was used to constrain the end of the longer capillary and to prevent the rotating magnetic bar from hitting it. The top of this spacer was 0.3 cm above the bottom of the cell. The other end of each capillary sampling tube was located inside a specialized ROLSI electromagnetic solenoid valve supplied by Transvalor.[17] The two ROLSI sampling valves were mounted on the top side of a steel plate approximately 5 cm above the top of the VLE cell lid and were not in direct contact with the nitrogen boil-off vapor. A temperature control system for the ROLSI sampling valves was used to maintain them at a temperature above 273 K. The temperatures of the two capillary sampling tubes (which were in contact with the nitrogen boil-off vapor) were controlled independently; this was found to be essential for obtaining representative samples of the equilibrium phases in the VLE cell. A resistive heating wire and a 100 Ω PRT were attached to the external surface of each capillary (TL, TV) and integrated into a proportional−integral (PI) control loop.

A helium carrier gas line was also connected to each of the ROLSI sampling valves, and helium flowed continuously through each of the valves and into their respective gas chromatograph (GC) columns. When the valves were actuated, the carrier gas would ensure that the samples from the vapor and liquid phases in the cell were swept along heated transfer lines into the GC columns. The ROLSI sampling valves were actuated using a control box (VSC), which allowed specification of the valve opening time with a resolution of 0.01 s. Thus, for a given pressure in the VLE cell, the amount of sample withdrawn by opening the valves could be adjusted by varying the specified opening time. The temperatures of the sampling valves and of the transfer lines were set using the ROLSI control box.

The GC used was a Varian model 3800 equipped with two capillary columns and two flame ionization detectors: one (FID V) for samples from the vapor phase inside the cell EC and the other (FID L) for samples from the liquid phase inside the cell EC. The two capillary columns connected to the FIDs were both 25 m long. The column used for the vapor phase was connected to the sample side of a thermal conductivity detector (TCD) placed in line before the two FIDs, whereas the column used for the liquid-phase sample was connected to the reference side of the TCD. It was possible to program the GC method (flow rates, oven temperatures, etc.) so that a component separated from the mixture on the vapor column would pass through the sample side of the TCD before the same component from the mixture on the liquid column would pass through the reference side. This allowed the TCD to resolve each of the components in each of the phases. However, since all of the components studied in this work were combustible, the response of the TCD was not used to determine the phase compositions. Future work will include mixtures containing noncombustible fluids.

Table 1. Details of the GC Method Used for Detector Calibration and Sample Analysis

instrument	Varian CP-3800
column length	25 m
column diameter	0.53 mm
column packing	PoroPlot Q
inlet temperature	423 K
injector split ratio	20:1
column head pressure (constant)	69 kPa
oven temperature (isothermal)	393 K
FID temperature	423 K

The gas mixture was prepared gravimetrically using a high-pressure, 300 cm^3 sample cylinder and an 1100 g electronic balance with a 0.001 g resolution. Mixing was accomplished by shaking, a metal ball having been placed inside the cylinder. The mole fractions of the component gases were specified by the supplier to be 0.99995 for methane and 0.9995 for isobutane. The principal mole fraction impurities in the methane were reported by the supplier as $25 \cdot 10^{-6}$ air, $15 \cdot 10^{-6}$ C_2H_6, $5 \cdot 10^{-6}$ H_2O, $5 \cdot 10^{-6}$ other hydrocarbons, and $1 \cdot 10^{-6}$ CO_2. For isobutane, the principal impurity was measured in our laboratory to be 2-methylbutane (isopentane) at the level of 0.0008 mol fraction. The mole fraction of the gravimetrically prepared mixture of methane (1) + isobutane (2) was $z_2 = (0.0724 \pm 0.0001)$, where the uncertainty bound includes the effect of impurities.

Methods and Analysis

The details of the GC methods used for both detector calibration and sample analysis are listed in Table 1, with the only difference being the injection method. The FIDs used to analyze the equilibrium phase compositions were calibrated in a two-stage process. First, the linearity of their response to the number of moles of an injected sample was established by manually injecting 0.0025 mL of several solutions containing hexane in methanol. The solutions were prepared by serial dilution and ranged in mass fraction from ($7 \cdot 10^{-5}$ to 1) hexane. The relation between the integrated area of each FID's response to the hexane, A_{C6}, and the number of moles of hexane injected per sample, n_{C6}, (accounting for the injector flow split ratio) was linear for $A_{C6} \le 10^8$ counts. Over this range, the values of $k_{C6} \equiv A_{C6}/n_{C6}$ were $4.4 \cdot 10^{13}$ counts per mole for FID V and $3.8 \cdot 10^{13}$ counts per mole for FID L.

The second stage of the calibration involved injecting into the GC a gravimetrically prepared gas mixture containing an approximately equal number of moles of methane, isobutane, and hexane in helium. The response coefficient k_1 of each FID to methane was determined using the relation

$$k_1 = k_{C6}\left(\frac{A_1}{A_{C6}}\right)\left(\frac{x_1}{x_{C6}}\right) \qquad (1)$$

Here, x_1 and x_{C6} are the mole fractions of methane and hexane, respectively, in the calibration gas mixture, A_1 and A_{C6} are the integrated area responses of the FID to the methane and hexane, respectively, in the injected sample, and k_{C6} is the detector's response coefficient to hexane determined in the first stage of the calibration. The response coefficient k_2 of each FID for isobutane was determined in the same way.

Prior to commencing an experiment with the VLE apparatus, the 300 cm^3 cylinder containing the gravimetrically prepared

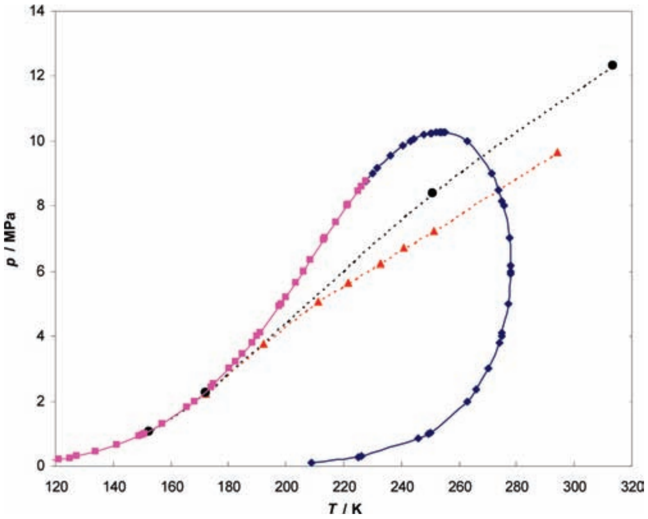

Figure 2. Pressures and temperatures of the VLE measurements relative to the phase envelope of the methane (1) + isobutane (2) mixture with $z_2 = 0.0724$ calculated using the GERG-2004 EOS. ♦, EOS dew curve; ■, EOS bubble curve; ▲, isochor 1; ●, isochor 2.

mixture was connected to the apparatus so that the equilibrium cell and the connecting lines could be evacuated and flushed several times with the mixture. After a sample of the gas mixture was transferred to the apparatus, the system was allowed to equilibrate at a temperature well above the mixture's cricondentherm. The measured pressure and temperature were then used with the GERG-2004 EOS to estimate the overall molar density of the single-phase mixture inside the equilibrium cell. As a further consistency check, samples of the single-phase mixture were taken from the "liquid" and "vapor" sampling lines and analyzed using the GC. The mixture composition measured was $z_2 = (0.0724 \pm 0.0001)$ where the uncertainty bound indicates the consistency of the samples from the cell top and bottom. This analysis was based on eq 2 and, as for all of our composition measurements with the GC, ignored the contribution of any impurities. However, no measurable levels of impurities were observed during any of the mixture measurements.

The overall molar density determined with the GERG-2004 EOS from the measured (single-phase) pressure and temperature was used for the purposes of planning subsequent VLE measurements. The set of (p, T) conditions measured is shown in Figure 2 relative to the phase envelope for the mixture with overall mole fraction $z_2 = 0.0724$ calculated using the GERG-2004 EOS. Also indicated are the approximate isochors measured: (5153 and 5940) $\text{mol} \cdot \text{m}^{-3}$. Reliable measurements of the liquid-phase composition required that a minimum volume of liquid be present in the cell such that the liquid level in the cell was well above 3 mm from the cell bottom, corresponding to the height of the Teflon spacer. There was, however, no mechanism in the cell for measuring the liquid level. The liquid volume in the cell at each two-phase point was thus estimated using the GERG-2004 EOS with the overall sample density and composition as constant inputs and the measured cell temperature. To account for the uncertainty in the EOS, the minimum liquid volume required for any VLE measurement was chosen to be 3 mL of liquid, corresponding to a minimum liquid height of 5 mm.

The first two-phase point measured on the first isochor was at 171 K. The cell temperature was raised in steps of between (10 and 20) K up to 251 K, the temperature corresponding to the calculated minimum measurable liquid volume condition. Upon reaching each temperature, the magnetic stirrer was activated for 15 min while the temperatures of the liquid and vapor sampling capillaries were set using their respective control systems. Relative to the cell temperature, the vapor capillary temperature was set to at least +4 K, and the liquid capillary was set to at least −4 K. After the mixing finished, the system was left to equilibrate for about 15 min, and then the sampling process was initiated. Often, the cell was left at a single condition for up to several hours, but no systematic drift in the measured composition was observed over this time.

The opening time of the ROLSI valves was adjusted at each condition to ensure that the amount of sample acquired upon each opening was larger than the amount of material occupying the internal volume of the capillaries. The amount of sample that reached the GC column after opening the valve was estimated from the observed peak areas and the detector response coefficients, that is, $n_{\text{col}} = k_1A_1 + k_2A_2$. The total amount of sample taken from the cell was determined from n_{col} by multiplying it by the injector split-ratio specified in the GC method. The number of moles in each capillary was estimated from the internal volume of the capillary ($\approx 0.001\ \text{cm}^3$) and the molar phase density at the cell temperature and pressure calculated using the GERG-2004 EOS. The required opening times of the ROLSI valves ranged between (0.1 and 1) s, depending on the cell pressure.

For each measurement, five to eight samples of both phases were acquired simultaneously by setting the ROLSI valves to open every (4 to 10) s on a cycle time that lasted in total between (30 and 80) s. The purpose of these multiple samplings was to minimize the residence time of material in the capillary tubes and also to obtain a measure of the reproducibility of the compositions measured at each (p,T) point. However, to obtain a reliable measurement it was important to avoid the coelution at the detectors of the component species from any of the samples. This was achieved by varying some of the details of the GC method (e.g., carrier flow rate, oven temperature), the number of samples, and the times between samples.

The first and second samples were discarded as being unrepresentative of the VLE in the cell. For each of the remaining samples, a phase mole fraction for the isobutane in the binary mixture was calculated from the detector response. For example, the mole fraction of isobutane in the liquid phase of the methane (1) + isobutane (2) mixtures was calculated from the integrated area responses of the liquid-phase species measured with the GC using

$$x_2 = \frac{k_2A_2}{k_1A_1 + k_2A_2} = \frac{A_2/A_1}{(k_1/k_2) + (A_2/A_1)} \tag{2}$$

The average and standard deviation of isobutane phase mole fractions were calculated for the remaining samples. For temperatures of 193 K and above, the measurement was considered successful if (1) the standard deviation in y_2 was less than (either 0.0015 *or* $0.01\langle y_2\rangle$) *and* (2) the standard deviation in x_2 was less than $0.01\langle x_2\rangle$. Here, $\langle y_2\rangle$ and $\langle x_2\rangle$ denote the averages of y_2 and x_2, respectively, for the set of samples acquired.

At lower temperatures, we were able to obtain measurements of the liquid-phase composition that were repeatable at approximately $0.02\langle x_2\rangle$, but we were unable to obtain any repeatable measurements of the vapor composition. For example, at (1.06 MPa, 151.4 K), 25 measurements were made of the saturated liquid's composition, each of which was comprised of multiple samples as described above. The relative standard deviations of x_2 for each set of samples were about 8 %; however, the relative standard deviation of x_2 for all 25

Table 2. VLE Data for the Methane (1) + 2-Methylpropane (2) (Isobutane) Binary System Measured in This Work[a]

p	$u(p)$	T	$u(T)$						
MPa	MPa	K	K	x_2	$u(x_2)$	$u_{\mathrm{tot}}(x_2)$	y_2	$u(y_2)$	$u_{\mathrm{tot}}(y_2)$
1.065	0.012	151.4	0.6	0.0777	0.0018	0.0312			
2.214	0.011	171.2	0.3	0.1134	0.0024	0.0118			
2.251	0.015	170.8	0.7	0.0935	0.0017	0.0250			
3.767	0.020	191.5	0.1	0.1972	0.0016	0.0063	0.0023	0.0001	0.0001
5.071	0.030	210.6	0.7	0.3279	0.0024	0.0111	0.0063	0.0014	0.0014
5.637	0.028	220.9	0.3	0.3776	0.0024	0.0052	0.0118	0.0002	0.0002
6.226	0.034	232.1	0.9	0.4116	0.0030	0.0082	0.0196	0.0003	0.0006
6.703	0.034	240.5	0.8	0.4327	0.0032	0.0066	0.0261	0.0003	0.0006
7.231	0.038	251.4	0.5	0.4506	0.0027	0.0046	0.0394	0.0008	0.0009
8.378	0.042	250.7	0.3	0.3658	0.0023	0.0043	0.0472	0.0006	0.0007

[a] Here $u(X)$ represents the uncertainty in the quantity X, as discussed in the text, while the columns $u_{\mathrm{tot}}(x_2)$ and $u_{\mathrm{tot}}(y_2)$ show the effect of the propagated temperature and pressure uncertainties on the measured compositions combined with the uncertainties of the composition measurements. No reproducible vapor-phase compositions were measurable at temperatures below 190 K.

measurements was only 2 %. Similar results were obtained for the measurements at (2.25 MPa, 170.8 K) and (2.21 MPa, 171.2 K). The values of x_2 reported here at these three conditions correspond to the weighted averages of all of the measurements made at each of these conditions. It seems that, at these low temperatures, the increased scatter observed in measurements of the saturated liquid-phase composition could be mitigated by averaging over a large number of samples. Unfortunately, the same was not found to be true of the vapor-phase composition measurements at (151.4, 170.8, and 171.2) K. At (1.06 MPa, 151.4 K), the relative standard deviations of y_2 for each set of samples had an average value of about 40 %, but the relative standard deviation of y_2 for all 25 measurements was 150 %. We are not able to completely explain the problem observed with sampling the vapor phase at these low temperatures; it may be caused by the proximity of the measurement pressure and temperature to the bubble-point curve of the overall mixture. Accordingly, in Table 2 no vapor compositions are given for the three lowest temperatures.

Following the first composition measurement at a given (p,T) point, the following procedure was carried out at least once: mix for 5 min, wait for 5 min, and then perform the sampling and analysis procedure. The results of these repeat measurements were consistent within the standard deviations of the phase mole fraction measurements described above. The time taken to complete all of the measurements at a given (p,T) point was at least 30 min. Over this time, the cell temperatures had a standard deviation of less than 0.53 K, and the pressure's standard deviation was less than 0.015 MPa. The standard deviations of x_2 and y_2 for all of the multiple measurements at each (p,T) condition had maxima of 0.0021 and 0.0014, respectively, and average values of 0.0013 and 0.0004, respectively.

Following the measurement at (7.23 MPa, 251.4 K), an additional amount of the mixture was transferred from the 300 cm^3 sample cylinder to the VLE cell. This raised the pressure and molar density in the VLE cell, and after several hours of mixing, a new VLE measurement was made at (8.38 MPa, 250.7 K). Two additional two-phase measurements were made along this second isochor, at (151.4 and 170.8) K. Finally, the temperature of the VLE cell was raised, returning the mixture to the single-phase region at (12.33 MPa, 313.2 K), and after mixing, samples from the top and bottom of the cell were acquired and analyzed. The overall composition of the new mixture within the cell was measured with the GC to be $z_2 = (0.0686 \pm 0.0002)$, where the uncertainty bound indicates the consistency between the samples from the cell top and bottom.

Results and Discussion

The measured VLE data for the methane (1) + isobutane (2) mixture are listed in Table 2, together with the estimated uncertainty for each of the p, T, x_2, and y_2 values. The pressure uncertainty was calculated from the quadrature combination of the standard error of the transducer's calibration with the standard deviation of the pressure over the measurement and had an average value of 0.03 MPa. The temperature uncertainty was calculated from the quadrature combination of the temperature difference between the thermometers in the cell bottom and cell lid, the standard deviation of the temperature over the course of the measurement, and the (negligible) uncertainty of the PRT calibrations. The average value of the temperature uncertainty was 0.5 K. At low temperatures and pressures, the temperature and pressure uncertainties are not insignificant in terms of their propagated impact on the composition uncertainties, particularly for x_2. Two estimated uncertainty columns are shown for each of x_2 and y_2. The first (labeled $u(x_2)$ and $u(y_2)$ for the liquid and vapor phases, respectively) shows the uncertainty due to the sampling process and composition measurements, which are independent of the temperature and pressure uncertainties. The second (labeled $u_{\mathrm{tot}}(x_2)$ and $u_{\mathrm{tot}}(y_2)$ for the liquid and vapor phases, respectively) combines in quadrature the first column with the propagated effects of the temperature and pressure uncertainties. The propagation of $u(T)$ and $u(p)$ into $u_{\mathrm{tot}}(x_2)$ and $u_{\mathrm{tot}}(y_2)$ was estimated using the GERG-2004 EOS.[2]

Three contributions to the uncertainties $u(x_2)$ and $u(y_2)$ were considered: the repeatability of sampling, the repeatability of the ratios A_2/A_1 measured with the GC, and the uncertainty of the ratio of the FID response coefficients k_1/k_2. The combined effect of the first two contributions is manifest in the observed standard deviations for x_2 and y_2 described in the previous section. To assess the contribution of k_1/k_2, we investigated its variability with several different gravimetrically prepared mixtures over a range of A_2/A_1 and as a function of A_1 at a fixed value of A_2/A_1. On the basis of these supplementary experiments it was determined that the relative standard uncertainty of k_1/k_2 in eq 2 was 1 %. The magnitude of this contribution to the uncertainty of x_2 and y_2 is comparable to the observed standard deviations for repeated measurements, and consequently, the average values of $u(x_2)$ and $u(y_2)$ are 0.0024 and 0.0005, respectively.

In Figure 3 the deviations $\{x_2 - x_2^{\mathrm{calc}}(p, T, z_2^*)\}$ and $\{y_2 - y_2^{\mathrm{calc}}(p, T, z_2^*)\}$ are plotted as a function of temperature, where no superscript denotes a measurement of the methane (1) + isobutane (2) binary system and the superscript "calc" corresponds to a calculation using the GERG-2004 EOS. The error bars shown on the data from this work correspond to the values of $u_{\mathrm{tot}}(x_2)$ and $u_{\mathrm{tot}}(y_2)$ in Table 2. For the deviations shown in Figure 3 the arguments for the calculation were the measured (p, T) and an arbitrary overall composition z_2^*. The values of x_2^{calc} and y_2^{calc} predicted by the EOS are insensitive to the value of z_2^* chosen because this is a VLE calculation, unless, however, the measured (p,T) point lies outside the phase envelope predicted by the EOS for that value of z_2^*.

Three sets of literature data for the methane (1) + isobutane (2) system are compared with the GERG-2004 EOS in addition to those measured in this work. These include the (p, T, x, y) measurements of Barsuk et al.,[14] which cover the temperature range from (198 to 377) K at pressures up to 11.8 MPa, the (p, T, x, y) measurements of Olds et al.,[15] which cover the temperature range from (310 to 377) K at pressures up to 11.5 MPa, and the saturated liquid $(p, T, x, \rho_{\mathrm{liq}}^{\mathrm{sat}})$ measurements of

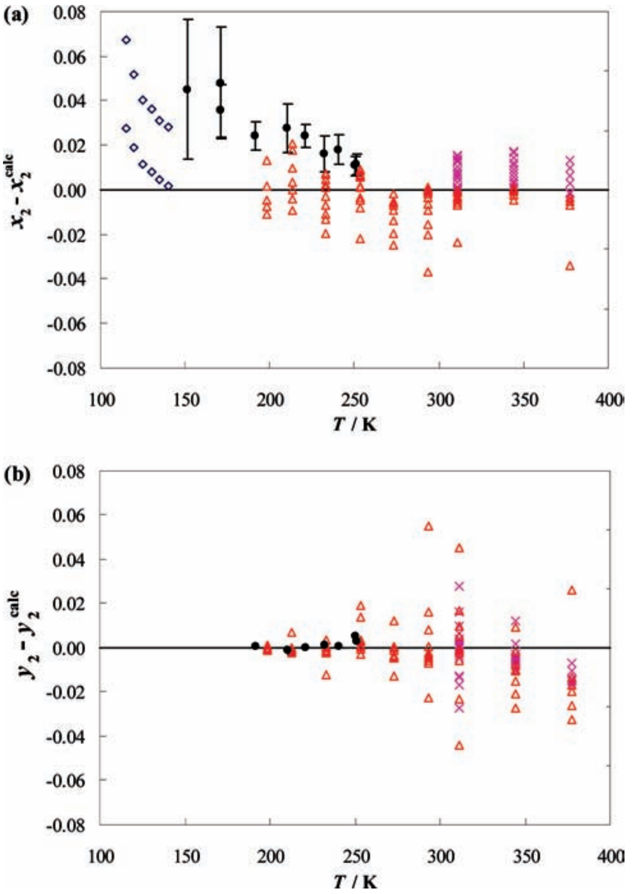

Figure 3. Deviations of measured isobutane phase mole fractions from those calculated with the GERG-2004 EOS[2] using the measured pressure and temperature, for the methane (1) + isobutane (2) binary system. (a) Liquid-phase mole fractions and (b) vapor-phase mole fractions. ●, this work with estimated uncertainties; ×, Olds et al.;[15] △, Barsuk et al.;[14] ◇, Haynes[18] (from measured saturated liquid densities).

Haynes,[18] which cover the range from (110 to 140) K at pressures up to 0.6 MPa. All three data sets were included in the development of the GERG-2004 EOS, although only 110 of the 171 points in the first two data sets were actually used by the GERG-2004 EOS developers.[2] The data sets of Barsuk et al.[14] and Olds et al.[15] have an approximately uniform distribution about the zero lines in Figure 3. However, it is apparent that the deviations of $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$ for the two low temperature data sets increase systematically with decreasing temperature and increasing pressure. (In Figure 3, if two or more values of $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$ or $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ are plotted at the same temperature, then the measurements were made at different pressures.)

As shown in Figure 3a, the saturated liquid-phase composition data measured in this work extend into the temperature range from (150 to 200) K, which has not been previously studied for this system. At higher temperatures the new data are consistent with the measurements of Barsuk et al.[14] made at similar pressures. The average value of $(x_2 - x_2^{calc}(p, T, z_2^*))$ for the data measured in this work was 0.026; at temperatures of 191 K and above, the average relative deviation was equivalent to about $0.06\langle x_2\rangle$. Although the deviations of the data from Barsuk et al.[14] are distributed about zero, the scatter of $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$ for that data set is comparable in magnitude. At each temperature a systematic pressure dependence exists for $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$ for the data of both Barsuk et al.[14] and Olds et al.,[15] with the deviations becoming more positive at higher pressures. At the lower temperatures, the new data are also consistent with those of Haynes[18] within the uncertainty $u_{tot}(x_2)$ of this work; the higher pressure data set of Haynes[18] had an overall isobutane fraction very similar to those of the mixtures studied in this work. In future work, we will aim to reduce $u_{tot}(x_2)$, particularly at low temperatures, by reducing $u(T)$ through better thermal control of the VLE cell.

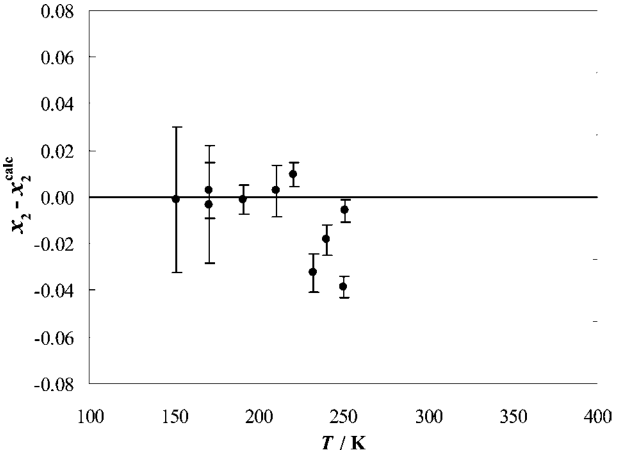

Figure 4. Deviations of measured isobutane liquid-phase mole fractions from those calculated with the GERG-2004 EOS[2] using the measured pressure and the overall molar density corresponding to the measurement isochor. The overall molar density was estimated from the single-phase (p, T) measurement for that isochor. ●, this work with estimated uncertainties.

In Figure 3b the deviations $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ are shown for this work and for the data of Barsuk et al.[14] and Olds et al.[15] The average absolute deviation (AAD) of the $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ for the data measured in this work was 0.0013, which is equivalent to about $0.06\langle y_2\rangle$. For the data measured between (191.5 and 240.5) K at pressures ranging from (3.7 to 6.7) MPa, the AAD was 0.0009, whereas the $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ values at 250 K were 0.0023 at 7.2 MPa and 0.0041 at 8.4 MPa. At higher temperatures the deviations $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ calculated from the data of Barsuk et al.[14] and Olds et al.[15] exhibit increasing scatter with different pressures.

The purpose of Figure 4 is to show that some of the average offset apparent in the deviations $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$ shown in Figure 3a for our data could be attributable to internal inconsistencies with the GERG-2004 EOS. Figure 4 shows the deviations $\{x_2 - x_2^{calc}(p,\rho^*,z_2^*)\}$, where ρ^* was the overall molar density for the isochor, determined using the GERG-2004 EOS and the measured (p, T) for the single-phase condition measured on that isochor. While the deviations $\{y_2 - y_2^{calc}(p, T, z_2^*)\}$ and $\{y_2 - y_2^{calc}(p, \rho^*, z_2^*)\}$ are about the same, the average of the absolute values of $\{x_2 - x_2^{calc}(p, \rho^*, z_2^*)\}$ is about $0.03x_2$ for all of the temperatures measured in this work, which is a significant reduction in comparison with $\{x_2 - x_2^{calc}(p, T, z_2^*)\}$. This suggests that the deficiencies of the GERG-2004 EOS in predicting the VLE properties of the methane + isobutane system may be, in part, due to the deficiences of the EOS in predicting two-phase densities. Of course, the assumption of constant overall density in the cell is violated by the sampling process; however, the amount of mixture in the cell was about 0.3 mol, while the amount sampled per measurement was about 10^{-5} mol. At a fixed pressure and temperature, the effect of sampling on the measured pressure was below the transducer's resolution, which is a further indication that the perturbation to the overall density caused by sampling was negligible.

The experimental uncertainties in temperature and pressure also contribute to the apparent inconsistency of the EOS, but they are unable to completely account for it. For example, on the first isochor, with $z_2 = 0.0724$, the first point measured was a single-phase condition at (9.660 ± 0.048) MPa and (294.0 ± 0.2) K, which corresponds to a GERG-2004 EOS molar density in the range of (5112 to 5194) $\mathrm{mol \cdot m^{-3}}$. The next point measured on the isochor was at (2.214 ± 0.011 MPa) and (171.2 ± 0.3) K; because this was the next point and the first two-phase point of the isochor, the perturbations due to sampling should be at a minimum. At this two-phase condition, to achieve an overall density using the GERG-2004 EOS that falls within the range of (5112 to 5194) $\mathrm{mol \cdot m^{-3}}$, the experimental temperature would need to be increased by 0.9 K, or the experimental pressure would need to be decreased by 0.06 MPa. These required shifts are about three and six times the estimated experimental uncertainty in the temperature and pressure, respectively.

An apparatus is being constructed that will be capable of simultaneously measuring VLE and phase densities at conditions representative of cryogenic gas processing plants. The data generated with this new apparatus will be critical to the development of new, more accurate EOS's both of the reference variety and the more computationally efficient equations required by process simulators.

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