

Isobaric Heat Capacity Measurements of Liquid Methane + Propane, Methane + Butane and a Mixed Refrigerant by Differential Scanning Calorimetry at High Pressures and Low Temperatures

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ABSTRACT: Isobaric heat capacity c_p measurements are reported at temperatures between (108 and 168) K for liquid mixtures of CH₄ (1) + C₃H₈ (3) at $x_1 \approx 0.8$ and $p \approx 5$ MPa; CH₄ (1) + C₄H₁₀ (4) at $x_1 = 0.96, 0.88,$ and 0.60 and $p \approx 5$ MPa; and a five component mixture that is similar in composition to a commercial mixed refrigerant at $p = (1.0$ and $5.0)$ MPa. Measurements were made, with an estimated uncertainty of about $0.02 \cdot c_p$, using a specialized calorimeter further modified to prevent preferential condensation of the less volatile component and minimize possible stratification of the mixture during sample loading. Our results for CH₄ + C₃H₈ agreed within $0.02 \cdot c_p$ of the values predicted using the GERG-2008 equation of state (EOS) whereas literature c_p data over the same temperature range agree within $0.03 \cdot c_p$. In contrast the c_p predicted for this mixture with the Peng Robinson EOS (PR-HYSYS) shows an offset of about $0.02 \cdot c_p$ from the average of the literature data at 165 K, which increases to $0.045 \cdot c_p$ at 120 K. For CH₄ + C₄H₁₀ our data for $x_1 = 0.96$ and 0.88 are within $0.05 \cdot c_p$ of the GERG 2008 predictions; however, at $x_1 = 0.6$, the deviations increase from $0.02 \cdot c_p$ at 168 K to nearly $1.1 \cdot c_p$ at 118 K. The PR-HYSYS predictions for this binary mixture deviate from the measured c_p data by $0.11 \cdot c_p$ at 168 K, which increases to $0.21 \cdot c_p$ at 118 K. For the mixed refrigerant (mole fraction composition 0.247 CH₄ + 0.333 C₂H₆ + 0.258 C₃H₈ + 0.076 C₄H₁₀ + 0.059 N₂) the deviations of the measured c_p from GERG 2008 are less than $0.02 \cdot c_p$ in the range (168 to 148) K increasing to $0.19 \cdot c_p$ at 108 K. The deviations from the predictions of PR-HYSYS range from $0.07 \cdot c_p$ at 168 K to $0.15 \cdot c_p$ at

108 K. Similar trends are observed for the data of Furtado, who measured the c_p of a mixture with a mole fraction composition of 0.359 CH₄ + 0.314 C₂H₆ + 0.327 C₃H₈ at similar temperatures.

■ INTRODUCTION

To design and operate liquefied natural gas (LNG) facilities, calorimetric properties for binary and multicomponent hydrocarbon fluids and refrigerant mixtures over a wide temperature and pressure range are needed for calculating heat balances. The equations of state (EOS) used to calculate the calorimetric properties of these mixtures are usually regressed only to pressure-volume-temperature (PVT) and vapor liquid equilibria (VLE) data, and their ability to provide accurate heat capacity data has been tested rarely. This is in part because there are few accurate measurements of isobaric heat capacity, c_p , for binary and multicomponent hydrocarbon liquid mixtures at conditions relevant to LNG operations. In our previous communication¹ a modification of a commercial differential scanning calorimeter (DSC) Setaram BT2.15 was described that enabled accurate isobaric heat capacity measurements on cryogenic, high pressure pure liquids at temperatures between (108.15 and 258.15) K and pressures between (1.1 and 6.35) MPa. The estimated uncertainty at the 95 % confidence limit ($k \approx 2$) of the heat capacity measurements was about 0.02 c_p . This paper describes a further modification to the apparatus that enables reliable measurements of c_p for liquid hydrocarbon mixtures. The modification pertains to the method of loading the mixture into the DSC cell without any preferential condensation of the heavier component, which could result in separation and/or stratification of the mixture sample. Measurements of isobaric heat capacities for binary and multicomponent liquid mixtures made with the modified calorimeter are then reported with an uncertainty similar

to that for pure fluid measurements over a similar temperature and pressure range.¹ These data are then compared with two EOS of industrial importance: the GERG 2008 EOS² as implemented in the software REFPROP 9.1³ (GERG 2008) and the Peng Robinson EOS.⁴ Two implementations of the Peng Robinson EOS were tested, one being in the process simulation software Aspen HYSYS,⁵ (PR-HYSYS) and the other being in the software REFPROP 9.1³ (PR-REFPROP).

■ METHOD AND MATERIALS

The suppliers and purities of the gases used in this work are listed in Table 1. The compositions chosen reflected the need to prepare a mixture that was a single phase gas at room temperature in an amount sufficient to fill the DSC cell and tubing with a liquid mixture. The methane (1) + propane (3) mixtures were prepared gravimetrically in a 1 L cylinder using a balance with an uncertainty of ± 0.2 g (empty cylinder mass was 3278.9 g, mass after filling with mixture was 3347.8 g). The uncertainty in the mole fraction composition of these mixtures was less than 0.01. The methane (1) + propane (3) mixture was prepared in a larger cylinder so a larger number of experiments could be completed with the same sample. All other mixtures were prepared gravimetrically in 300 mL bottles (empty cylinder mass 1073.089 g) using an electronic balance with uncertainty of 0.001 g, and the calculated uncertainty in the mole fraction compositions of these mixtures was 0.001.

A commercial calorimeter Setaram BT2.15 Tian-Calvet type heat flow DSC with an operational temperature range from (77 to 473) K, modified to allow accurate isobaric heat capacity, c_p , measurements of liquid methane, ethane, and propane between $T = (108.15$ to $258.15)$ K and

pressure up to 6.4 MPa, has been described previously.¹ Figure 1 shows a schematic of the specialized calorimeter, and the modifications made in this work. The details of the calorimeter sensitivity, calibration and measurement method were described by Hughes et al.⁶ In this paper the additional procedures required to make measurements on mixtures are described in detail. The procedure for filling the calorimetric cell completely with a liquid mixture assumes that the mixture exists as a single phase gas at room temperature. If the gas mixture of known composition were condensed directly into the calorimeter cell at low temperature from the sample cylinder at ambient temperature, the mixture in the calorimeter would become richer in the less volatile component and/or the mixture would become stratified. To avoid this and ensure that the transfer of the single phase gas mixture to the low temperature cell did not result an inadvertent change in composition, a procedure of successive batch transfers was adopted.

The calorimeter temperature was set to below the dew temperature of the mixture but above its freezing temperature and allowed to stabilize. Initially the system was evacuated with all valves on the measurement side open except 1M, 3M, and V11. Valve 3M isolated the reference side from the measuring side of the DSC; the reference side was always filled with pure nitrogen at atmospheric pressure. Valves 2M, 4M, 5M, 6M, and 7M were then closed. A portion of the gas mixture was transferred from the sample cylinder in which it was prepared to a volume $V_1 \approx 25 \text{ cm}^3$ shown by a thicker red line in Figure 1 by opening valve V11 and then closing it again once the pressure reading had stabilized. The gas mixture within volume V_1 was condensed into the cell by opening valve V10. The pressure reading would then drop to a value around the saturation pressure corresponding to the temperature of the liquefied sample; often the initial reading was close to the transducer's resolution limit. Valve V10 was then closed and the

procedure was repeated until the DSC cell and half the length of the fill tube was filled with the liquid mixture. The amount transferred and thus the fill level could be estimated by calculating the cumulative number of moles transferred from V_1 to the DSC cell, which had a volume of $(8.506 \pm 0.043) \text{ cm}^3$ at 300 K^1 . In addition, when the system pressure was significantly larger than the mixture's saturation pressure at the calorimeter's temperature, the known temperature profile of the fill stem could be used to confirm the estimated level. The number of transfers required was from 7 to 12 depending on the pressure of the sample cylinder in which the mixture was prepared; mixtures with low sample cylinder pressures required more transfers.

During a measurement the height of liquid in the filling tube was controlled by measuring the temperature with the six resistance thermometers and controlling the three heaters that were installed along the fill tube, as described by Syed et al.¹ For scans at elevated pressure, the gas ballast shown in Figure 1 was first filled with pure methane at slightly above the saturation pressure of the mixture. The pressure of methane in the ballast was then increased gradually so as to not disturb the location of the gas-liquid interface in the fill tube and avoid the mixing of methane with the liquid mixture in the cell. Any mass transfer by diffusion of methane into the liquid mixture contained within the calorimetric cell would be limited by the small surface area of the vapor-liquid interface and the long length of tubing between the interface and the calorimeter cell. There was no evidence that the use of methane in the ballast had any effect on the measured heat capacities or on the final mixture composition, which was determined at the end of the experiment.

To check that neither methane diffusion nor the batch transfer procedure affected the overall composition of the mixture, the composition of the calorimeter cell's contents was measured after the completion of the c_p measurement. The calorimeter cell was heated to close to its normal boiling temperature and then the cell's contents were condensed into an evacuated sample bottle that was immersed in liquid N₂, connected via valve V10 and V11. The sample bottle was of sufficient size to ensure the mixture was single phase. The composition of the cell's contents was then analyzed using a gas chromatograph (GC). The calibrations of the GC and the method of measurements followed those of Kandil et al.^{7,8} and had an estimated mole fraction uncertainty of 0.001. In all cases the measured composition was found to be in agreement within the combined uncertainties with the gravimetrically prepared composition.

Heat capacities were measured using the two step method, as described by Syed et al.¹, with a scan rate of 0.03 K·min⁻¹. Prior to starting a scan, the calorimeter was held at constant temperature for at least 6 h. During the scan, the cell temperature was held constant for 1 h before and 6 h after each step (i.e. 7 h at the temperature between two temperature ramps). These hold times were found to be necessary to allow the net heat flow signal to return to a stable baseline. Baseline scans with nitrogen in both the measurement and reference cell were performed before and after each series of measurements. No shifts in the baseline scans were found.

The volume of the cell at temperatures removed from 300 K was corrected to account for thermal contraction¹. The measured amount of energy required to raise the temperature of this volume of liquid by 10 K allows determination of the volumetric isobaric heat capacity.¹ To convert these

values to massic heat capacities, knowledge of the density of the fluid as a function of temperature and pressure is required. Liquid densities for all the mixtures were calculated using the GERG 2008² equation of state as implemented in the software REFPROP 9.1.³ From our previous work^{1,6} we estimate the combined uncertainty at the 95 % confidence limit ($k \approx 2$) in the heat capacity to be about $0.02 \cdot c_p$. The standard uncertainty in the temperature was estimated to be about 0.25 K above 220 K and 0.5 K below 220 K. The standard uncertainty in the pressure was estimated to be about 35 kPa. Pressure changes due to thermal expansion/contraction over the 10 K steps were within this uncertainty.⁶

■ RESULTS AND DISCUSSION

For the methane (1) + propane (3) system, measurements were made on mixtures with $x_1 \approx 0.8$ because at this compositions the mixtures are single phase at room temperature and have a relative excess heat capacity of 12 %. This is close to the maximum relative excess heat capacity of 16 % for this system, which occurs at $x_1 \approx 0.6$ (calculated using GERG 2008²). The isobaric heat capacity of methane (1) + propane (3), with $x_1 = 0.82$ at $P = 5.2$ MPa, was measured three times between 108.15 K and 128.15 K with 10 K steps, and two times between 143.15 K and 163.15 K with 10 K steps. Additional measurements were made with $x_1 = 0.81$ at $P = 4.7$ MPa and $P = 6.0$ MPa between 108.15 K and 128.15 K with 10 K steps and between 143.15 K and 163.15 K with 10 K steps. The isobaric heat capacities measured for this mixture are listed in Table 2 and shown in Figure 2(a). In Figure 2(b), the isobaric excess heat capacity for this binary mixture $c_p^E = c_p(x_1) - \sum_1^2 x_i c_{p,i}$ at $x_1 = 0.82$, $P = 5.2$ MPa are compared with values calculated from GERG 2008.² Good agreement is observed at higher temperatures but the difference steadily increases at lower temperatures.

Figure 3 shows the relative deviations of our results and literature measurements from GERG 2008.² The error bars on our measurements indicate the repeatability of our measurements. Literature values include the data of Yesavage,⁹ Mather,¹⁰ and Manker¹¹ measured using a freon boil-off total enthalpy flow calorimeter with an estimated relative uncertainty of 3 %, ¹² and the data of Grini et al.,¹³ measured using an electrically heated flow calorimeter with an estimated relative uncertainty of 0.22 % in the measured enthalpy increment. The relative difference between our results and those of Grini et al.¹³ is less than 2 %, while the data of Yesavage,⁹ Mather,¹⁰ and Manker¹¹ are within 3 % of our data, which is within the combined uncertainty of all the measurements. The literature data for methane (1) + propane (3) have a relative scatter of about ± 3 % and are approximately centered on the predictions of GERG 2008.² In contrast the predictions of the Peng Robinson⁴ EOS as implemented in Aspen HYSYS v7.3⁵ (PR-HYSYS) show a relative offset from the average of the literature data with a maximum of 4.5 % at 118 K. The deviations of the Peng Robinson⁴ EOS implemented within REFPROP 9.1³ (PR-REFPROP) follow a similar trend with decreasing temperature but only reach a maximum of about 3.2 % at 108 K.

The isobaric heat capacity of methane (1) + butane (4), with $x_1 = 0.95$ at $P = 5.0$ MPa, was measured between 148.15 K and 178.15 K with 10 K steps. A binary mixture with $x_1 = 0.88$ was measured twice between 118.15 K and 138.15 K and once between 148.15 K and 168.15 K, using 10 K steps. Measurements were also made for a mixture with $x_1 = 0.60$ at $P = 5.15$ MPa: twice between 138.15 K and 168.15 K with 10 K steps and once between 118.15 K and 128.15 K with a 10 K step. The measured isobaric heat capacities for these mixtures are listed in Table 3

and are shown in Figure 4(a) together with the EOS predictions. Figure 4(b) shows the measured excess heat capacities together with the GERG 2008 predictions; the excess mixture heat capacities at temperatures below the freezing point of pure butane (134.9 K)³ are shown as dotted lines because they were calculated by linear extrapolation of the pure butane heat capacities obtained from GERG 2008 over the range (138 to 178) K.

The comparisons in Figure 4 show that the GERG 2008 predictions are in reasonable agreement with the experimental c_p values for mixtures with high methane mole fractions but that as the methane mole fraction or the temperature decreases, the GERG 2008 predictions deviate increasingly from experiment. In contrast, while the PR EOS predictions are less accurate than those of GERG 2008 at high methane mole fractions, they do not deteriorate as drastically as either the methane mole fraction or temperature is decreased. These observations are demonstrated more clearly in Figure 5: for the experiments with $x_1 = 0.88$ and 0.96 , the relative deviations of the measured c_p data from GERG 2008² are shown in Figure 5(a) to be within 3 % between (168 and 118) K, increasing to 5 % at 108 K. Figure 5(b) shows that the divergence of the data from the GERG 2008 predictions at $x_4 = 0.4$ as the temperature decreases is considerable, reaching 21 % at 138 K and nearly 110 % at 118 K. The c_p values for this binary system calculated with PR-HYSYS are more robust over the entire composition range. For $x_1 = 0.88$ and 0.96 (Figure 5(a)), the PR-HYSYS predictions are within 10 % relative to the measured values over the entire temperature range. At higher temperatures the $(\partial c_p / \partial T)_{x,p}$ values from PR-HYSYS are slightly more positive than those of the measurements but at lower temperatures (< 130 K) the differences in slope start to decrease again. For mixtures with higher mole fractions of propane (Figure 5(b)), the PR-HYSYS predictions are also relatively poorer, being

11 % below the measurements at 168 K and 31 % below at 118 K. This deterioration with decreasing temperature is, however, much smaller than that of GERG 2008. Moreover, a different implementation of the Peng-Robinson EOS performs even better for this mixture: Figure 5(b) shows that the relative deviation between the measured c_p and the predictions of PR-REFPROP for the rich mixture is only 4 % at 168 K and 9 % at 118 K. This reflects the fact that different implementations of the Peng-Robinson EOS often use slightly different descriptions of the pure component fluids and/or different binary interaction parameters and that these differences can have an appreciable effect on the model's predictions for mixtures.

The observed deviations of the data from GERG 2008 are not unexpected as the model was developed for methane rich mixtures and data sets used in its development were mainly pure component calorimetric data with very limited binary calorimetric data. Given the complex functional form of GERG 2008, it is not surprising that sufficient extrapolation of the model beyond the range of the data used in its development will result in poor predictions.

Experiments were also made on a mixture representative of a five component mixed refrigerant reported in a patent by Roberts et al.¹⁴ and assigned to Air Products and Chemicals, Inc. for cooling natural gas in the production of LNG. The mixture was prepared gravimetrically and had a mole fraction composition of $0.247 \text{ CH}_4 + 0.333 \text{ C}_2\text{H}_6 + 0.258 \text{ C}_3\text{H}_8 + 0.076 \text{ C}_4\text{H}_{10} + 0.059 \text{ N}_2$. The isobaric heat capacity of this mixed refrigerant at $P = 1 \text{ MPa}$ was measured at 108.15 K and 118.15 K using 10 K steps and at $P = 5 \text{ MPa}$ (by using methane as the ballast gas) between 108.15 K and 168.15 K with 10 K steps. The results reported in Table 4 are shown in Figure 6, with the relative deviations between the measured c_p and the GERG 2008² predictions shown in

Figure 7. For the five component mixed refrigerant system, the GERG 2008 predictions are in excellent agreement at the higher temperature, with relative deviations of less than 2 % in the range (168 to 148) K. At lower temperatures the deviations increase to a maximum of 19 % at 108 K. In contrast, the c_p predictions of the Peng Robinson⁴ EOS deviate from our results by an initially larger but comparatively constant offset: relative to our data, the PR-HYSYS predictions are 7 % lower at 168 K and 15 % lower at 108 K whereas the PR-REFPROP predictions deviate by 5 % and 10 % at these temperatures, respectively. The results of Furtado,¹⁵ who measured a ternary mixture of 0.359 CH₄ + 0.314 C₂H₆ + 0.327 C₃H₈, are shown in Figures 6 and 7 together with the corresponding predictions of the GERG 2008, PR-HYSYS and PR-REFPROP models. The similarity of the deviations between the models and the data of Furtado¹⁵ indicates that the trends observed for our results have a degree of generality.

■ CONCLUSION

This work demonstrates that the modifications made to the specialized, high-pressure DSC calorimeter reported by Syed et al.¹ were successful in enabling it to measure isobaric heat capacities of liquid alkane mixtures at cryogenic temperatures. It also shows that there is still significant room for improving equation of state predictions for the heat capacity of liquid alkane mixtures, including those of significant industrial importance such as the mixed refrigerants used in the LNG industry. New measurements of mixture heat capacities at cryogenic temperatures are therefore needed so that EOS developers can utilize them directly during model regression, instead of only relying principally on measured volumetric properties such as density to produce accurate predictions of caloric ones.

Our results agree well with the prediction of GERG 2008² for methane rich mixtures but as the methane mole fraction and the temperature decrease, the data deviate significantly from the GERG 2008 predictions. The GERG 2008² model is explicit in the Helmholtz free energy and uses a multi fluid approximation to describe the thermodynamic properties of binary mixtures from fundamental equations for the pure components and correlation equations for the mixtures.¹⁶ Experimental data for thermodynamic properties such as density, speed of sound, heat capacities, and phase equilibrium properties from the database detailed in ref 16 were used to determine the coefficients and parameters of the correlation equations. The GERG 2008 model also uses binary specific or generalized departure functions for mixtures depending on the available experimental data, with binary specific departure functions being superior to the generalized departure functions if the specific data needed for their development are available.¹⁶ For methane + propane the model uses a binary specific departure function since the data bank contains sufficient data over a wider range of temperature and composition, and this is reflected in the good agreement observed between the GERG 2008 predictions and our experimental results for that binary system. For methane + butane, GERG 2008 uses a generalised departure function as there was limited mixture data available in the database over a limited composition range, and there was no calorimetric data available at all for this system.^{2,16} Thus it is to be expected that when the model is extrapolated beyond the range of data to which it was regressed that the deviations between measurements and predictions will increase, although the magnitude observed here at temperatures below 135 K for a butane mole fraction of 0.4 is surprising. Accurate isobaric heat capacity data for binary and multi-component mixtures such as those reported here are should be of significant value in future efforts to improve and increase the range of applicability of GERG 2008¹⁶ or similar models.

In contrast with GERG 2008, the data show an appreciable but constant offset from the predictions of the cubic PR EOS⁴, with subtle but noticeable differences apparent between different software implementations of the model. Standard methods for improving mixture predictions with the PR EOS⁴, such as the use of alternative mixing rules or adjusting binary interaction parameters, k_{ij} , are not generally focussed on the accuracy of heat capacity calculations. The k_{ij} parameter is usually determined by regression to experimental vapour-liquid-equilibria (VLE) data. In principle, however, using a temperature dependent k_{ij} may enable both a good representation of VLE data and a better prediction of excess enthalpies and excess heat capacities through the Gibbs Helmholtz relationship. An alternative approach for improving cubic EOS predictions is the volume translation method such as the one described by Peneloux et al.¹⁷ This method was originally developed to improve the prediction of density but it also affects the prediction of the heat capacities. By combining these two modifications it may be possible to tune cubic equations of state to better predict C_p data for binary mixtures.

■ SUPPORTING INFORMATION

The details (e.g. pure component perfect gas heat capacities) of the Peng-Robinson EOS as implemented in the software packages AspenTech HYSYS 7.3 and REFPROP 9.1 are provided as supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest

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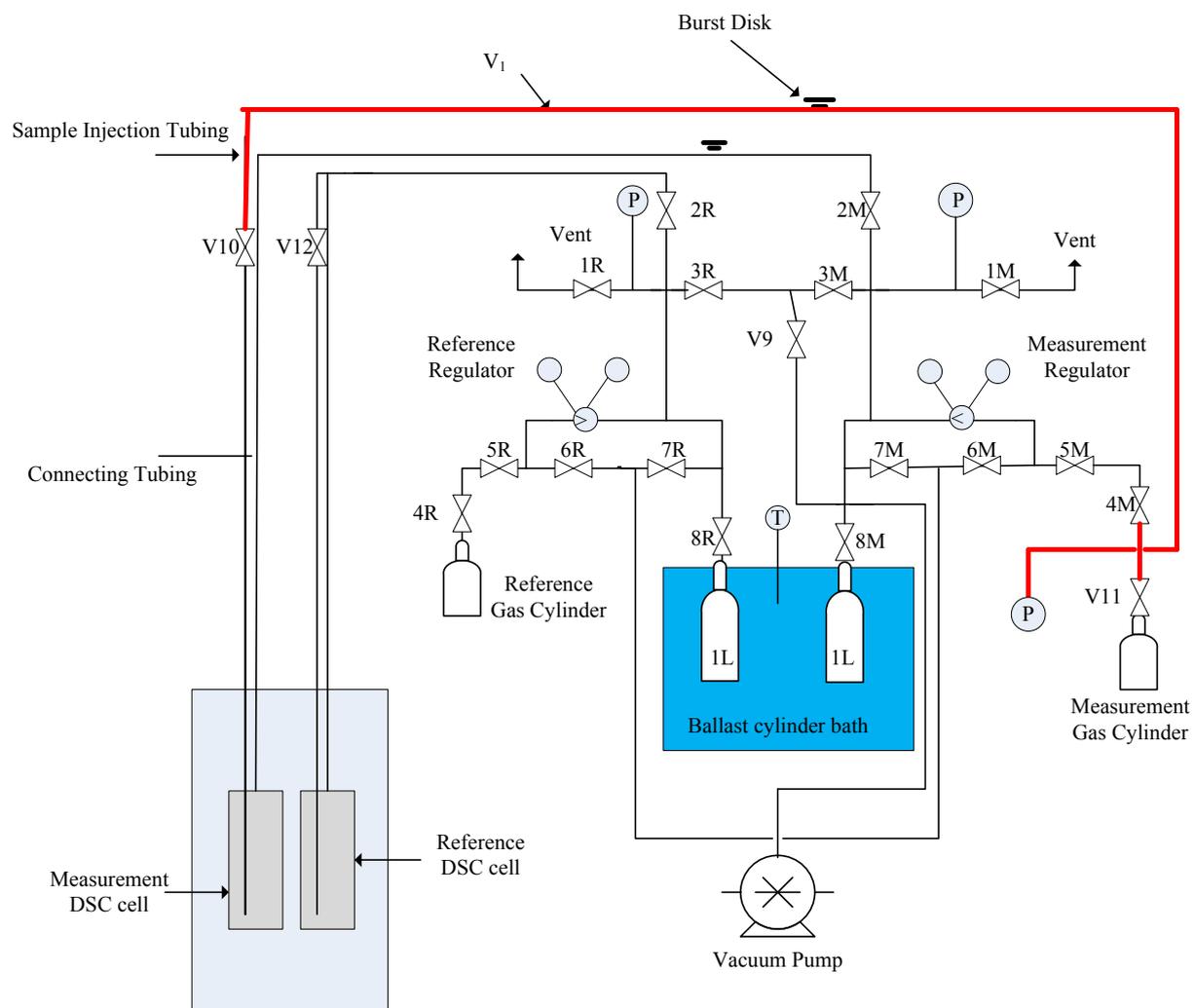


Figure 1. Schematic of the specialized DSC with the new mixture filling system shown in red.

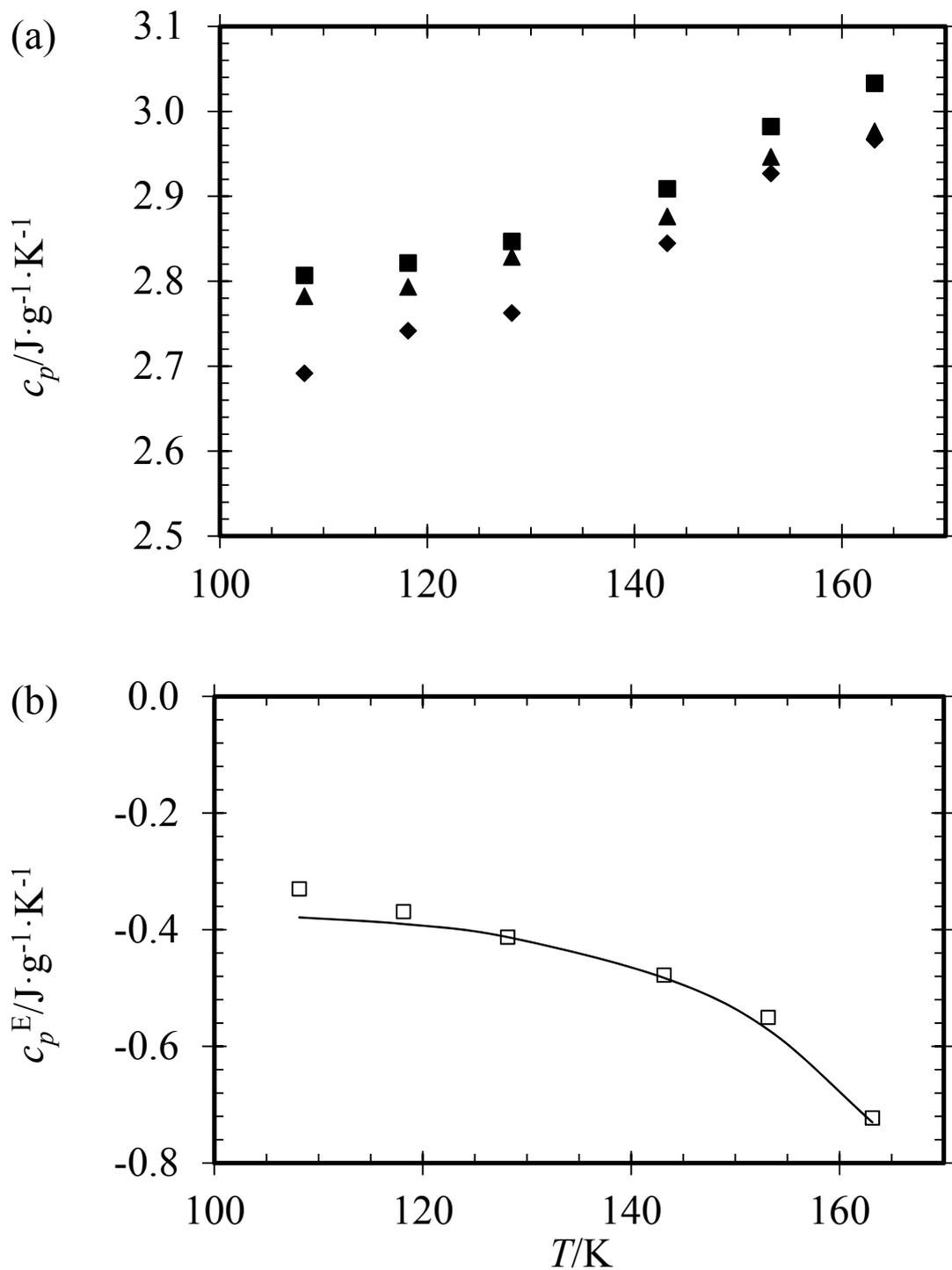


Figure 2. (a) Absolute isobaric heat capacity, c_p , for methane (1) + propane (3). This work: ■, $x_1 = 0.82, p = 5.2 \text{ MPa}$; ◆, $x_1 = 0.81, p = 6.0 \text{ MPa}$; ▲, $x_1 = 0.81, p = 4.7 \text{ MPa}$. (b) Excess heat capacity, c_p^E , at $x_1 = 0.82$ as a function of temperature for methane (1) + propane (3). This work: □, $x_1 = 0.82, p = 5.2 \text{ MPa}$; solid line, calculated from GERG 2008.²

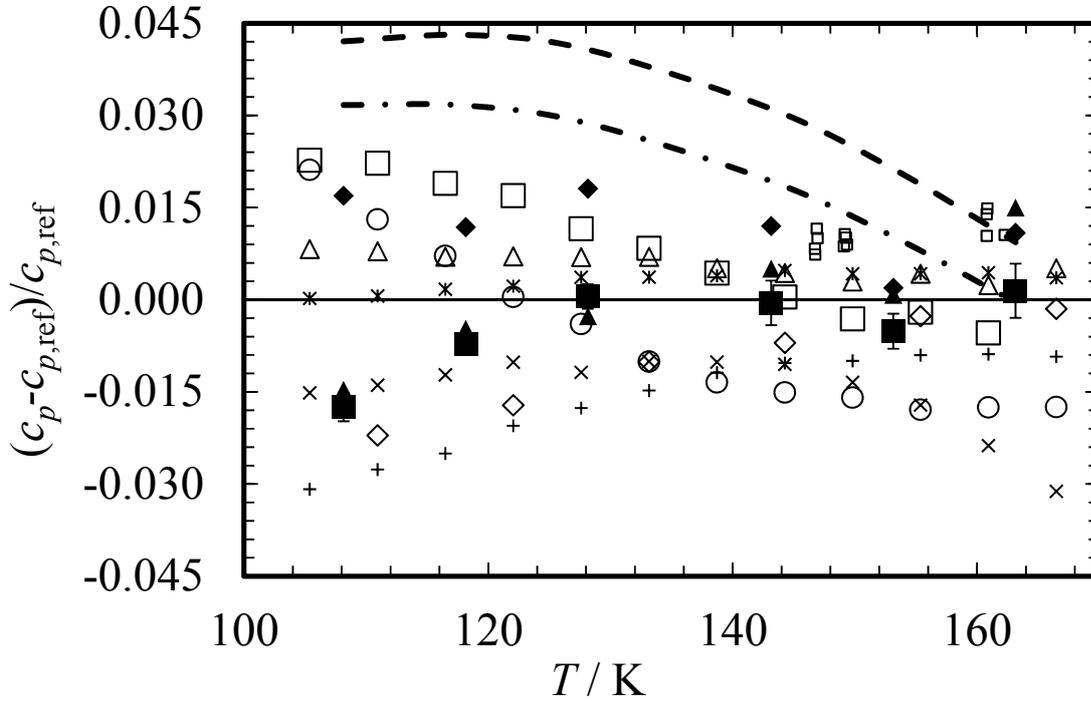


Figure 3. Relative deviations $(c_p - c_{p,\text{ref}})/c_{p,\text{ref}}$ of the measured isobaric heat capacity c_p for methane (1) + propane (3) with $x_1 = 0.82$ from $c_{p,\text{ref}}$ calculated from GERG 2008.² The uncertainty bars on the data from this work indicate the difference between measurements that were repeated. This work: \blacksquare , $x_1 = 0.82$, $p = 5.2$ MPa; \blacklozenge , $x_1 = 0.81$, $p = 6.0$ MPa; \blacktriangle , $x_1 = 0.81$, $p = 4.7$ MPa. Literature: Mather:¹⁰ \times , $x_1 = 0.88$, $p = 6.9$ MPa; \circ , $x_1 = 0.88$, $p = 3.4$ MPa; $+$, $x_1 = 0.72$, $p = 6.9$ MPa; \square , $x_1 = 0.95$, $p = 1.7$ MPa; \triangle , $x_1 = 0.95$, $p = 5.2$ MPa; Manker:¹¹ \ast , $x_1 = 0.95$, $p = 6.9$ MPa; Yesavage:⁹ \diamond , $x_1 = 0.49$, $p = 6.9$ MPa; Grini et al.:¹³ \square , $x_1 = 0.68$, $p = 14$ MPa. Calculated: $---$, PR-HYSYS,⁴ $x_1 = 0.82$, $p = 5.2$ MPa; $- \cdot -$, PR-REFPROP,⁴ $x_1 = 0.82$, $p = 5.2$ MPa.

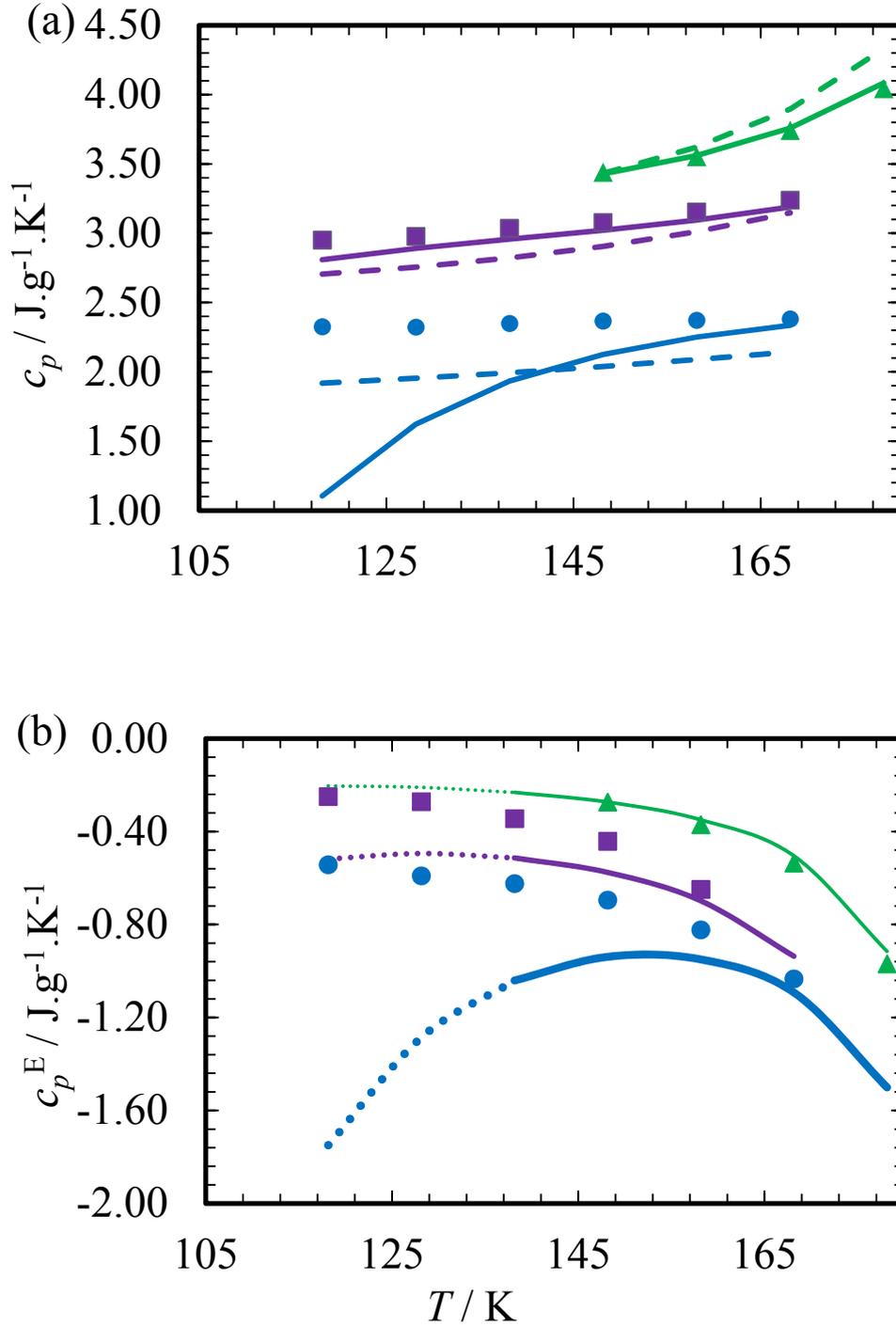


Figure 4. (a) Absolute isobaric heat capacity c_p and (b) excess heat capacity c_p^E for methane (1) + butane (4) as a function of temperature. This work: \blacktriangle , $x_1 = 0.96$, $p = 5.05 \text{ MPa}$; \blacksquare , $x_1 = 0.88$, $p = 5.15 \text{ MPa}$; \bullet , $x_1 = 0.60$, $p = 5.2 \text{ MPa}$. Calculated: dashed curves, PR-HYSYS⁴; solid curves, GERG 2008²; dotted curves, extrapolation using GERG 2008².

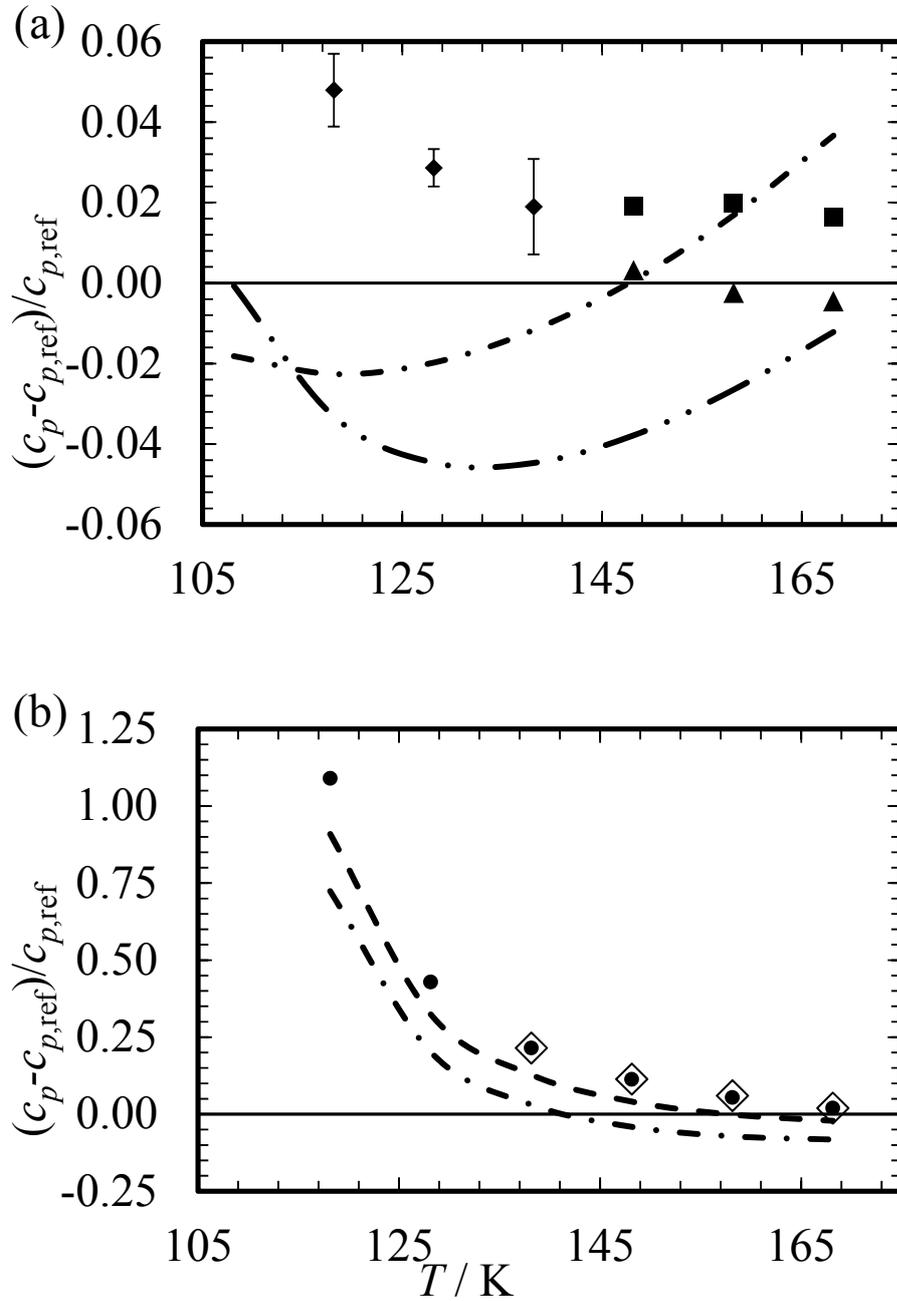


Figure 5. Relative deviations $(c_p - c_{p,\text{ref}})/c_{p,\text{ref}}$ of the measured isobaric heat capacity c_p for methane (1) + butane (4) from $c_{p,\text{ref}}$ calculated using GERG 2008.² The uncertainty bars indicate the difference between measurements that were repeated. (a) This work: \blacksquare , $x_1 = 0.88$, $p = 5.15$ MPa; \blacklozenge , $x_1 = 0.88$, $p = 5.15$ MPa; \blacktriangle , $x_1 = 0.96$, $p = 5.05$ MPa. Calculated: $- \cdot -$, PR-HYSYS,⁴ $x_1 = 0.96$, $p = 5.05$ MPa; $- \cdot \cdot -$, PR-HYSYS,⁴ $x_1 = 0.88$, $p = 5.15$ MPa. (b) This work: \bullet , $x_1 = 0.60$, $p = 5.20$ MPa; \diamond , $x_1 = 0.60$, $p = 5.20$ MPa (repeat). Calculated: $- - -$, PR-REFPROP,⁴ $x_1 = 0.60$, $p = 5.20$ MPa; $- \cdot -$, PR-HYSYS,⁴ $x_1 = 0.60$, $p = 5.20$ MPa.

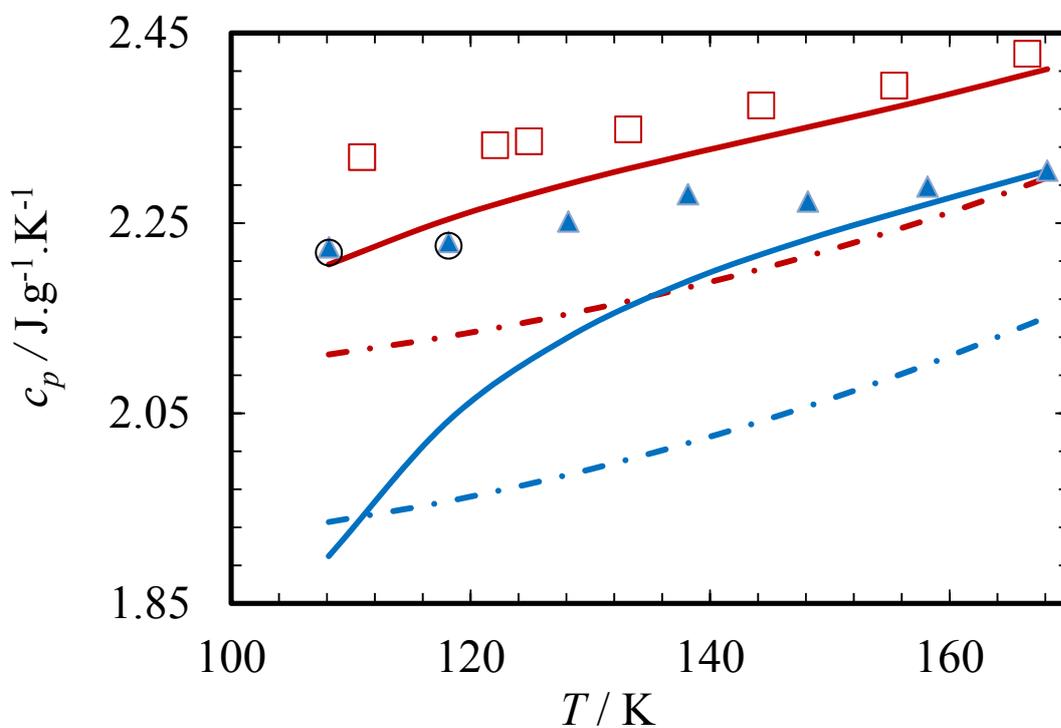


Figure 6. Absolute isobaric heat capacity c_p of the refrigerant mixture with mole fractions 0.247 CH_4 + 0.333 C_2H_6 + 0.258 C_3H_8 + 0.076 C_4H_{10} + 0.059 N_2 . This work: \circ , $p = 1.00$ MPa; \blacktriangle , $p = 5.00$ MPa. Calculated: $-\cdot-$, PR-HYSYS;⁴ $-$, GERG 2008.² Literature: \square , Furtado¹⁵ (with mole fractions 0.359 CH_4 + 0.314 C_2H_6 + 0.327 C_3H_8), $p = 5.0$ MPa. Calculated (for Furtado mixture): $-\cdot-$, PR-HYSYS⁴; $-$, GERG 2008².

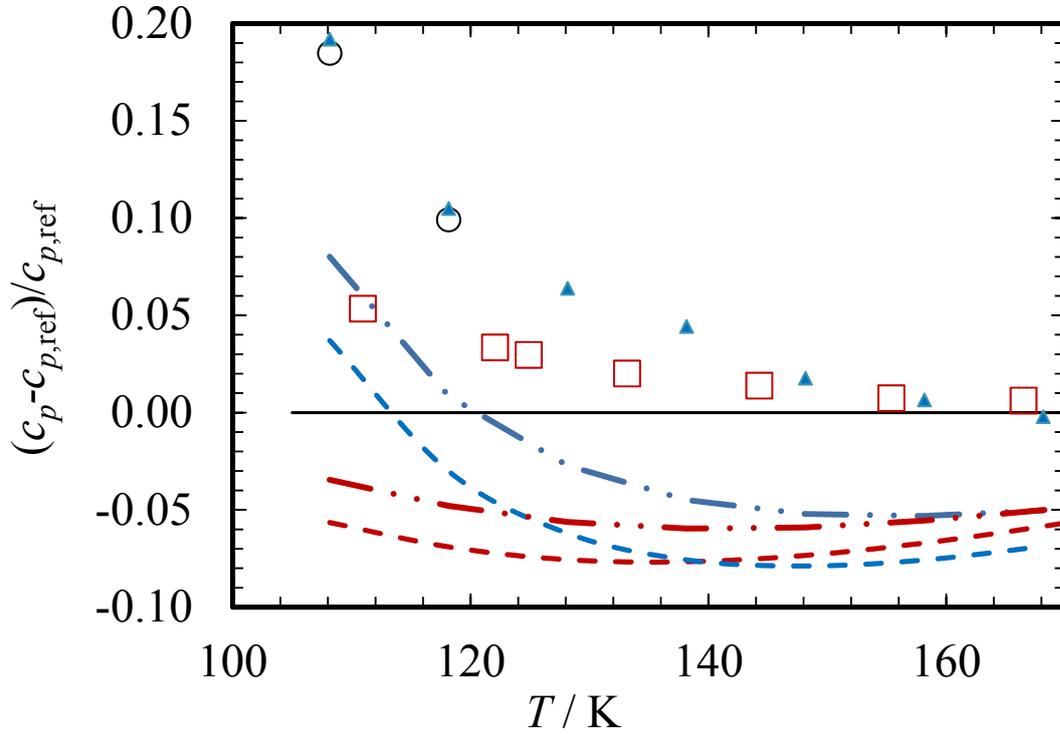


Figure 7. Relative deviations $(c_p - c_{p,\text{ref}})/c_{p,\text{ref}}$ of the measured isobaric heat capacity c_p for the mixed refrigerant with mole fractions $0.247 \text{ CH}_4 + 0.333 \text{ C}_2\text{H}_6 + 0.258 \text{ C}_3\text{H}_8 + 0.076 \text{ C}_4\text{H}_{10} + 0.059 \text{ N}_2$ from $c_{p,\text{ref}}$ calculated from GERG 2008.² This work: \circ , $p = 1.0 \text{ MPa}$; \blacktriangle , $p = 5.00 \text{ MPa}$; \square , Literature: Furtado¹⁵ (with mole fractions $0.359 \text{ CH}_4 + 0.314 \text{ C}_2\text{H}_6 + 0.327 \text{ C}_3\text{H}_8$), $p = 5.00 \text{ MPa}$: Calculated: $---$, PR-HYSYS⁴ (for our work); $- \cdot - \cdot -$, PR-REFPROP⁴ (for our work); $---$, PR-HYSYS (for Furtado mixture); $- \cdot - \cdot -$, PR-REFPROP (for Furtado mixture).

Table 1. Chemical Suppliers and Gas Purities.

Chemical Name	Supplier	Supplier Mole Fraction Purity*
Methane	BOC	0.99995
Ethane	Coregas pty Ltd	0.9999
Propane	Air Liquide	0.9999
Butane	Air Liquide	0.9999
Nitrogen	Coregas pty Ltd	0.9999

*Used without further purification

Table 2. Isobaric Heat Capacities^a for Binary Mixtures of Methane (1) + Propane (3) Measured on a Volumetric Basis and Converted to a Gravimetric Basis Using Densities Calculated from GERG 2008.²

T/K	$c_p/\text{J}\cdot\text{ml}^{-1}\cdot\text{K}^{-1}$	$c_p/\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
$x_1 = 0.82$ at $p = 5.2$ MPa		
108.15	1.434	2.807
118.15	1.406	2.822
128.15	1.383	2.847
143.15	1.355	2.909
153.15	1.347	2.982
163.15	1.325	3.033
$x_1 = 0.81$ at $p = 6.0$ MPa		
108.15	1.387	2.692
118.15	1.379	2.742
128.15	1.355	2.763
143.15	1.339	2.845
153.15	1.338	2.927
163.15	1.313	2.967
$x_1 = 0.81$ at $p = 4.7$ MPa		
108.15	1.431	2.782
118.15	1.402	2.793
128.15	1.384	2.829
143.15	1.350	2.876
153.15	1.342	2.946
163.15	1.311	2.977

^a Standard uncertainties u are $u(x_1) = 0.02$, $u(T) = 0.25$ K, $u(p) = 10$ kPa, and the combined standard uncertainties are $u_c(c_p) = 0.02 \cdot c_p$ with 95 % confidence level ($k \approx 2$) for all points except for the measurements at ($x_1 = 0.82$, $p = 5.2$ MPa and $T = 108.15$ K to 128.15 K) for which $u_c(c_p) = 0.04 \cdot c_p$.

Table 3. Isobaric Heat Capacities^a for Binary Mixtures of Methane (1) + Butane (4) Measured on a Volumetric Basis and Converted to a Gravimetric Basis Using Densities Calculated from GERG 2008.²

T/K	$c_p/\text{J}\cdot\text{ml}^{-1}\cdot\text{K}^{-1}$	$c_p/\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
$x_1 = 0.95$ at $p = 5.05$ MPa		
148.15	1.377	3.441
158.15	1.363	3.554
168.15	1.365	3.742
178.15	1.386	4.044
$x_1 = 0.88$ at $p = 5.15$ MPa		
118.15	1.436	2.932
128.15	1.416	2.968
138.15	1.396	3.010
148.15	1.384	3.078
158.15	1.372	3.155
168.15	1.358	3.239
$x_1 = 0.60$ at $p = 5.15$ MPa		
118.15	1.444	2.326
128.15	1.418	2.323
138.15	1.409	2.350
148.15	1.393	2.368
158.15	1.373	2.379
168.15	1.347	2.383

^a Standard uncertainties u are $u(x_1) = 0.02$, $u(T) = 0.25$ K, $u(p) = 10$ kPa, and combined standard uncertainty $U_c(c_p) = 0.02 \cdot c_p$ with 95 % confidence level ($k \approx 2$).

Table 4. Isobaric Heat Capacities^a for the Mixture with mole fractions 0.247 CH₄ (1) + 0.333 C₂H₆ (2) + 0.258 C₃H₈ (3) + 0.076 C₄H₁₀ (4) + 0.059 N₂ (5) Measured on a Volumetric Basis and Converted to a Gravimetric Basis Using Densities Calculated from GERG 2008.²

<i>T</i> /K	<i>c_p</i> /J·ml ⁻¹ ·K ⁻¹	<i>c_p</i> /J·g ⁻¹ ·K ⁻¹
<i>p</i> = 5.0 MPa		
108.15	1.425	2.225
118.15	1.404	2.230
128.15	1.393	2.252
138.15	1.385	2.281
148.15	1.354	2.273
158.15	1.337	2.289
168.15	1.319	2.305
<i>p</i> = 1.0 MPa		
108.15	1.418	2.219
118.15	1.397	2.226

^a Standard uncertainties *u* are $u(x_1) = 0.02$, $u(T) = 0.25$ K, $u(p) = 10$ kPa, and combined standard uncertainty $U_c(c_p) = 0.02 \cdot c_p$ with 95 % confidence level ($k \approx 2$).

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