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Volumetric (PVT) and Calorimetric ($C_V VT$) Measurements for Pure Methanol in the Liquid Phase

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Volumetric (PVT) and calorimetric ($C_V VT$) properties of pure methanol were measured in the liquid phase with a twin-cell adiabatic calorimeter. Temperatures were measured in a range from 314 to 411 K, densities between 699.3 and 775.6 $\mathrm{kg \cdot m^{-3}}$, and pressures to 20 MPa. The calorimetric cell (70 $\mathrm{cm^3}$ capacity) was surrounded by adiabatic thermal shielding (high vacuum). The sample pressures were measured by means of a quartz crystal transducer to within an uncertainty of about ±7 kPa. The relative uncertainty of C_V was estimated to be 2%, with a coverage factor $k = 2$, by combining the various sources of experimental uncertainty using a root-sum-of-squares formula. The results for pure methanol were compared with other recent measurements performed with a second high-temperature, high-pressure adiabatic calorimeter. Deviations of less than 3% were found between the earlier C_V data and the present results for pure methanol. The uncertainty of the density measurements was estimated to be 0.2% ($k = 2$). The measured densities and isochoric heat capacities were compared with values calculated with an IUPAC equation of state. Agreement of density was within 0.088% and that for isochoric heat capacity was within 0.95%. Values of vapor pressure were determined by extrapolating experimental P–T data to the saturated temperature along a fixed isochore. In the temperature range of this study, decomposition of methanol was not observed.

KEY WORDS: coexistence curve; density; isochoric heat capacity; methanol; saturated density; vapor pressure.

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1. INTRODUCTION

Experiments that measure thermodynamic properties of a thermally labile species over a wide temperature range are often hindered by chemical reactions, including decomposition. A number of previous studies have explored the effects of reactions on the properties of methanol [1–7]. It has been reported that a serious complication exists at $T > 405$ K, since methanol begins to decompose at this temperature [1, 2]. It has been reported that if methanol is confined in a *PVT* piezometer at $T > 405$ K for more than a few hours, decomposition of the methanol molecules will have a significant effect on measured values of pressure or other thermodynamic properties. The decomposition products have been shown to depend on the metals and metallic oxides in contact with the vapor [3, 6, 8]. Measurements at high temperatures for methanol by Straty et al. [2] and by Ta'ani [3] reported a measurable effect of decomposition on *PVT* measurements. Subsequent chemical analysis of the methanol sample after experiments showed the presence of hydrogen, carbon monoxide, carbon dioxide, formaldehyde, methyl formate, and dimethyl ether [1, 6, 7]. The observed range of products is an indication of a somewhat complex reaction scheme. In two recent calorimetric studies [4, 5], after experiments were completed, dissolved gases were detected in liquid methanol, as evidenced by a residual gas pressure in the calorimeter volume after the liquid sample was withdrawn. Bruno and Hume [9] described several experimental approaches for dealing with chemical reactions or decomposition which can occur when making thermodynamic property measurements at high temperatures and pressures.

Methanol is a small and highly polar molecule, and may be expected to interact strongly with other fluids molecules in a hydrogen-bonded network [10]. Raman spectroscopic studies on hydrogen-bonding in methanol under high temperature and pressure, by Ebukuro et al. [11], reported that weak hydrogen bonds remain even at elevated temperatures, up to the critical temperature. There are several theoretical studies of the structure of liquid methanol [12] and methanol clusters [13]. Methanol is known to be a structured, associating liquid. Instead of forming tetrahedral networks, alcohols appear to prefer to form winding chains whose structures are also characteristic of their solid state [14].

Our knowledge of molecular theory and working models of liquids and liquid mixtures is still imperfect, particularly for strongly interacting, highly polar or associating substances such as methanol. Particularly, development of the equation of state for chemically reacting (or thermally unstable fluids) fluids is still a problem. Thermodynamic properties of associating fluids such as methanol provide insight to our understanding of the effect of hydrogen-bonding on their behavior.

In addition to the theoretical problems connected with the behavior of hydrogen-bonds in liquid methanol and the structure of associating fluids, methanol has significant technological interest. Methanol is an often used additive in natural gas processing and pipeline transport because of its value as a hydrate inhibitor [15]. Methanol is an important liquid fuel and feedstock with connections to coal gasification, transport and storage of hydrogen, natural refrigeration, and working fluids in new power cycles. Methanol is used also as a polar modifier to increase solvating power (yield) of supercritical carbon dioxide in supercritical fluid extraction processes [16–18] and supercritical fluid chromatography [19–22] to improve selectivity.

2. LITERATURE REVIEW

Thermodynamic properties of pure methanol were reviewed and compiled extensively under the auspices of IUPAC and reported in the International Thermodynamic Tables of the Fluid State-12 [23], along with a fundamental equation of state for Helmholtz energy $A(V, T)$. de Reuck and Craven [23] reported a comprehensive review of all methanol measurements that were made between 1887 and 1992. Eubank [24] reported also, in 1970, a review of earlier work on the volumetric, thermodynamic, and other physical properties of methanol. Therefore, some of the data reported after 1992 will be briefly reviewed here.

Table I shows selected *PVT* and C_VVT data sets for CH_3OH published after 1992. In this table the first author and the year published are given together with the method employed, the uncertainty indicated by the authors, and the temperature, pressure, and density ranges. It is apparent that experimental isochoric heat capacity data for CH_3OH are scarce. No isochoric heat capacity data were published before 1992. Therefore, the IUPAC formulated equation of state [23] was developed without C_V data. Thus, the primary objective of this work was to expand the existing thermodynamic database. A brief analysis of some of the selected data sets is given below.

A knowledge of thermodynamic properties for pure methanol in the liquid phase is restricted because existing data are few and scattered. *PVT* measurements on methanol by Straty et al. [2] very clearly demonstrated the effect of thermal decomposition (chemical reaction) on thermodynamic property measurements. They found a rate of change of pressure due to degradation of the methanol sample that was proportional to the density and temperature. Straty et al. [2] corrected their pressure data and compared them with values reported by Zubarev and Bagdonas [29] and Machado and Streett [30] in the region of overlap. Excellent agreement

Table I. Summary of Thermodynamic Property Measurements for Pure Methanol[a]

First author	Year	Method	Property	Uncertainty	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
Xiao [25]	1997	VTD	PVT	$0.4\ kg \cdot m^{-3}$	323–573	up to 13.5	165–763
Osada [26]	1999	MBVV	PVT, P_S, ρ'_S	$0.001\rho, 0.001P$	320–420	up to 200	651–884
Yokoyama [27]	2003	MBVV	PVT, P_S, ρ'_S	$0.002\rho, 0.001P$	320–4209	up to 200	652–885
Bazaev [7]	2003	CVP	PVT	0.15%	423–653	up to 40	113–370
Abdulagatov [4]	2000	HTHPAC	$C_V VT, \rho'_S, \rho''_S$	3.0% (vap.) 1.5% (liq.) 4.5% (crt.)	443–521	up to 30	266–449
Kuroki [28]	2001	TCTC	$C_V VT, PVT$	1.0% (C_V) 0.2% (ρ)	300–400	up to 20	705–798
Polikhronidi [5]	2003	HTHPAC	$C_V VT, \rho'_S, \rho''_S$	2 to 3%	300–556	up to 35	136–690

[a] CVP, Constant volume piezometer; TCTC, Twin-cell type calorimeter; HTHPAC, High-temperature and high-pressure adiabatic calorimeter; MBVV, Metal-bellows variable volumometer; VTD, Vibrating-tube densimeter.

was found at low temperatures and high densities with data by Machado and Streett [30]. Agreement between Straty et al. [2] and Zubarev and Bagdonas [29] was about 0.2%, except at low densities and for data in the critical region. Differences between these data and the data reported by Finkelstein and Stiel [31] were significant (about 2.5%). The values of compressibility factor Z derived from PVT data reported by Zubarev and Bagdonas [29] agree with data reported in 1887 by Ramsay and Young [32] at $T = 503$ K within $\pm 3\%$. Their sample had an organic impurity of 0.05%, and after measurements were completed, the water content of the sample was 0.16 to 0.2%. Decomposition of the methanol in the supercritical region up to 513 K was not observed.

Three liquid density measurements by Xiao et al. [25], Osada et al. [26], and Yokoyama and Uematsu [27] were reported for pure methanol after the IUPAC equation of state [23] was developed. The data reported by Xiao et al. [25] agree with values calculated from Goodwin's [33] equation of state within 0.066% or $0.33\ kg \cdot m^{-3}$. Deviations between these data and the data reported by Straty et al. [2] are within 0.75%. Density measurements by Osada et al. [26] agree with the data reported by Straty et al. [2] with a deviation of 0.0002ρ. The Machado and Streett [30] data deviate from the results of Osada et al. [26] by 0.0008ρ to 0.0014ρ. Most deviations between measurements by Osada et al. [26] and values calculated with the IUPAC formulation [23] are within 0.001ρ. The differences between Xiao et al. [25] and Osada et al. [26] measurements is smaller than 0.0015ρ. The liquid-density and vapor-pressure data reported by Osada et al. [26] also agree with reported data sets and values calculated from the IUPAC equation of state [23], deviations are within 0.002ρ (or 0.1%) and $0.002P_S$. Recently Yokoyama and Uematsu [27] reported new measurements for pure methanol. The vapor pressures reported in this work agree with the IUPAC formulation within 0.2 kPa at low temperatures (360 K) and 0.3 kPa at high temperatures (420 K). The measured liquid saturated densities are larger than those of previous measurements by Osada et al. [26] by 0.0006ρ to 0.0016ρ in the temperature range from 320 to 400 K. The liquid densities for both data sets show agreement within ±0.2%. The deviations of these density data from the IUPAC calculations [23] are within 0.0011ρ to 0.0013ρ. Excellent agreement (±0.1%) is observed between the data reported by Yokoyama and Uematsu [27] and the data by Xiao et al. [25].

Recently Bazaev et al. [7] measured *PVT* relationships for pure methanol along seven isochores, namely, 113.5, 138.6, 177.6, 252.4, 305.2, 360.5, and 368.2 $\mathrm{kg \cdot m^{-3}}$. Measurements for three isochores, 113.5, 252.4, and 368.2 $\mathrm{kg \cdot m^{-3}}$, were performed in heating and cooling runs to study the effect of thermal decomposition of methanol molecules on the measured values of pressure. Bazaev et al. [7] found that the difference in pressure between both heating and cooling runs reached up to 50% at high temperatures (653 K). Decomposition of the methanol at a temperature of 573 K was found. Analysis of the liquid phase after measurements showed the presence of formaldehyde (HCOH)-5.16 mass%, dimethyl ether (CH_3OCH_3)-1.19 mass%, and some gases which were not identified. The agreement between Bazaev et al. [7] and data reported by other authors is within 0.5% in the range far from the critical point and is about 2% in the critical region. Differences between data reported by Bazaev et al. [7] and the values calculated with the IUPAC equation of state are within 0.4%

Three isochoric heat capacity data sets (Abdulagatov et al. [4], Polikhronidi et al. [5], and Kuroki et al. [28]) are available for pure methanol. In a work currently in progress, Polikhronidi et al. [5] has measured the isochoric heat capacity for pure methanol in the critical and supercritical regions. They also reported saturated properties (ρ_S, T_S, C_{VS}) and new critical parameters ($T_C = 512.785$ K, $\rho_C = 278.4\ \mathrm{kg \cdot m^{-3}}$) for pure methanol. The agreement between C_V data by Polikhronidi et al. [5] and IUPAC [23] is good (AAD = 1 to 2%) in the range of regular behavior of C_V.

Abdulagatov et al. [4] reported the results of isochoric heat capacity measurements for pure methanol at six densities, 266.20, 270.86, 271.26, 303.79, 404.66, and 448.59 $\mathrm{kg \cdot m^{-3}}$. Measurements were performed with a high-temperature, high-pressure integrated adiabatic calorimeter described in Refs. 5 and 34. The measurements include both the one- and two-phase regions and the coexistence curve. The results of the measurements were compared with values calculated with the IUPAC fundamental equation of state [23]. Random deviations of 2.5 to 3% in the C_V values at saturation were seen; however, the one-phase data showed systematic deviations up to 25%. The most likely causes were the presence of 0.5 mass% water in their methanol sample and sample decomposition that was evidenced by the release of a significant volume of gas from the calorimetric cell after the experiments were completed.

Kuroki et al. [28] reported PVT and C_V measurements for liquid methanol. The measurements were made with a twin-cell type adiabatic calorimeter [35, 36]. The results were compared with the same IUPAC [23] fundamental equation. The measured values of C_V for methanol deviated by $+1.8\%$ to $+4.5\%$ from the equation of state. This amount is considerably more than the uncertainty of the measurements.

Table II summarizes available equations of state and selected correlation equations for the saturated properties for pure methanol. No scaling type equation of state was developed for pure methanol. All of these equations of state were developed without using any experimental isochoric heat capacity data for pure methanol. Therefore, more experimental isochoric heat capacity data are needed to check the reliability of the proposed equations of state for pure methanol.

The present paper reports the results of accurate volumetric (PVT) and calorimetric (C_VVT) measurements for pure liquid methanol. The pressure and heat capacity versus temperature data were measured at nearly constant density (quasi-isochores). Four quasi-isochores ranging in density from 699.3 to 775.6 $\mathrm{kg \cdot m^{-3}}$ were measured. The data cover the temperature range from 314 to 411 K. The results will extend the range and quality of previous investigations.

3. EXPERIMENTAL SECTION

3.1. Construction of the Calorimeter

A high-temperature adiabatic calorimeter for constant volume heat capacity measurements of liquid and compressed gases, developed by Magee et al. [35, 36], was employed to measure PVT and C_V properties of pure liquid methanol. The twin-bomb calorimeter [35, 36] consists of sample and reference sides which are nearly identical in construction. Each side of the apparatus consists of a spherical cell (volume of 70 $\mathrm{cm^3}$) and was made from Inconel 718 surrounded by adiabatic thermal shielding, a reference platinum resistance thermometer, and a steel-sheathed electric heater wound tightly on its surface.

Table II. Summary of Equations of State and Correlations for Pure Methanol[a]

First author	Year	Temp. range (K)	Pressure range (MPa)	Structure of the equation	Number of adjustable parameters	Uncertainty
				Equations of state		
Zubarev [37]	1973	178–573	up to 50	Virial type (vap.) and polynomial (liq.) $P(\rho, T)$ EOS	16 16	0.30% (Z) 0.35% (V)
Machado [30]	1983	298–489	up to 104	Polynomial $P(\rho, T)$ EOS	16	0.03% (ρ) 20% (C_P)
Goodwin [33]	1987	176–673	up to 70	Nonanalytical $P(V, T)$ EOS	8	0.5–0.9% (ρ)
Polt [38]	1992	298–703	up to 63	Bender's type EOS	20	0.35% (ρ) 0.89% (P)
de Reuck [23]	1993	176–620	up to 800	Helmholtz energy, $A(T, V)$	44	0.1% (ρ) 2% (W)
Kozlov [39]	2002	176–600	up to 300	Helmholtz energy, $A(T, V)$	45	0.50% (ρ) 0.46% (P) 2.8% (C_V) 3.7% (C_P) 0.6% (W)
				Vapor pressure and saturated liquid correlations		
Ambrose [40, 41]	1989	up to T_C	–	Vapor pressure $P_S(T)$	4	n.a.
Zubarev [37]	1973	373–512.65	–	Vapor pressure and saturated liquid	7 5	0.20% (P_S) 0.03% (ρ'_S)
Hales [42]	1976	293–440	–	Saturated liquid $\rho'_S(T)$	5	0.25%
Goodwin [33]	1987	175.59–512.6	–	Vapor pressure and saturated liquid and vapor	6 4	0.34% (P_S) 0.17% (ρ'_S) 0.21% (ρ''_S)
IUPAC [23]	1992	175.61–513.38	–	Vapor pressure and saturated liquid and vapor	4 5, 13	0.05% (P_S) 0.05% (ρ'_S)
Cibulka [43]	1993	175–508.5	–	Saturated liquid $\rho'_S(T)$	6	0.18%
Kozlov [39]	2002	175.6–512.6	–	Vapor pressure and saturated liquid and vapor	7 5	0.18% (P_S) 0.06% (ρ'_S)

[a] $Z = PV/(RT)$, compressibility factor; V, specific volume; ρ, density; ρ'_S, saturated liquid density; ρ''_S saturated vapor density; P, pressure; P_S, vapor pressure; C_P, isobaric heat capacity; C_V, isochoric heat capacity; W, speed of sound.

The entire calorimeter assembly was placed inside a high-temperature forced-air convection furnace. A differential thermocouple provides a continuous reading of the temperature difference between the sample and the reference bombs. A three-junction differential thermopile provides readings of the temperature difference between each bomb and its associated adiabatic shield. An oscillating quartz-crystal pressure transducer attached to the charging manifold provides measurements of pressure.

3.2. Principle of Operation

For a single calorimetric bomb, we would measure the temperature rise ΔT occurring when a measured quantity of heat energy Q is supplied to the bomb which contains a mass m of substance. Subtracting the heat energy needed to heat the empty bomb Q_0, also widely known as the heat equivalent, we obtain the sample heat capacity,

$$C_V = \frac{(Q - Q_0)}{m\,\Delta T}. \tag{1}$$

For a twin calorimeter, we would simply replace values of Q with the differential quantity, ΔQ. It is defined as the heat energy supplied to the sample bomb minus that supplied to the evacuated reference cell. The value of ΔQ accounts for the heat absorbed by the sample fluid. When we subtract the energy difference between the empty sample cell and the reference, ΔQ_0, we calculate the specific heat capacity at constant volume,

$$C_V = \frac{(\Delta Q - \Delta Q_0 - \Delta W_{PV})}{m\,\Delta T}, \tag{2}$$

where ΔW_{PV} is the change-of-volume work due to the slight dilation of the cell and m is the mass of sample in the cell. The values of ΔW_{PV} were calculated as

$$\Delta W_{PV} = \Delta V \left[T_2 \left(\frac{\partial P}{\partial T} \right)_{V_2} - \frac{1}{2} \Delta P \right], \tag{3}$$

where $\Delta P = P_2 - P_1$, $\Delta V = V_2 - V_1$, and $V_1(P_1, T_1)$ and $V_2(P_2, T_2)$ can be calculated from the calibrated cell volume $V_b(P, T)$ equation,

$$V_b(P, T) = [69.464 + 3.2 \times 10^{-3}(T - 273.15)][1 + 1.36 \times 10^{-4} P], \tag{4}$$

with $V_b(P, T)$ in cm^3, P in MPa, at conditions of (P_1, T_1) and (P_2, T_2). The value of $V_b(P, T)$ was previously calibrated from well-established density values of pure water (IAPWS standard [44]). The uncertainty in density of the IAPWS equation of state [44] is 0.001% in the liquid phase. The values of the derivatives $(\frac{\partial P}{\partial T})_{V_2}$ were calculated from the IUPAC [23] equation of state.

Equation (2) is the apparatus working equation. Experience with a single-bomb calorimeter has shown that the quantity Q_0 in Eq. (1) is as much as 95% of the measured heat energy Q. As a result, the relative expanded uncertainty propagated to C_V from the total uncertainty in evaluating Q_0 (0.02%) may be up to 0.4% for the single-bomb calorimeter. This shortcoming of the single-bomb calorimeter may be avoided with a twin-bomb design. The quantity ΔQ_0 in Eq. (2) is small by design and, in practice, is nearly zero. The result of this technique is to make the uncertainty propagated from the heat equivalent measurements a negligible effect. The net result is an improved accuracy of the measurements, allowing us to achieve our goal of a relative uncertainty of 0.4% for the measured specific heat capacities at constant volume for the twin-cell calorimeter.

3.3. Assessment of Uncertainties

The accuracy of this method is limited by the uncertainty of the temperature rise measurement and the change-of-volume-work adjustment. In the following discussion, we use a definition for the expanded uncertainty which is twice the standard uncertainty. In other words, the expanded uncertainty has a coverage factor $k = 2$ and, thus, is a two-standard-deviation estimate.

Different sources, including calibration of the platinum resistance thermometer, radiation to or from the thermometer head, and drift of the ice-point resistance, contribute to an expanded uncertainty of 3×10^{-2} K for the absolute temperature measurement. Uncertainty of the temperature rise, however, also depends on the reproducibility of temperature measurements. The temperatures assigned to the beginning T_1 and to the end T_2 of a heating interval are determined from a linear fit of temperature with elapsed time, near integer degrees. The experimental ramp rate is approximately $+4 \times 10^{-2}$ K$\cdot$min^{-1}. This procedure leads to an uncertainty of 5×10^{-4} K for the interpolated temperatures T_1 and T_2, leading to values of 7×10^{-4} K for the uncertainty of the temperature rise, $\Delta T = T_2 - T_1$. For a typical experimental value of $\Delta T = 1$ K, this corresponds to a relative uncertainty in C_V of 0.07%.

The uncertainty of the change-of-volume work influences primarily the single-phase values since two-phase experiments are performed over a small pressure interval. For H_2O, the ratio of the change-of-volume work to the total applied heat is as large as 0.04 in the worst case. Estimated relative uncertainties of 2% in the change-of-volume work are due to both the deviations of the calculated pressure derivatives and the uncertainty of the volume change. This leads to a relative uncertainty in C_V of 0.08%.

The energy applied to the calorimeter is the integral of the product of voltage and current from the initial to the final heating time. The voltage and current are measured 80 times during a heating interval of 1 K. The measurements of the electrical quantities have a relative uncertainty of 0.02%. However, we must account for the effect of radiation heat losses or gains which occur when a spurious lag of the controller leads to a small temperature difference of about 10^{-2} K between the bomb and radiation shield. Since heat transfer by radiation is proportional to $T_1^4 - T_2^4 \approx 4T^3\,\Delta T$, we would expect radiation losses to substantially increase with the bomb temperature. Therefore, the uncertainty in the applied heat is estimated to be 0.5 $\mathrm{J \cdot K^{-1}}$ in the temperature range of this study.

The energy difference ΔQ_0 applied to the empty calorimeter has been measured in repeated experiments and fitted by a function of temperature. Its uncertainty is less than 0.5 $\mathrm{J \cdot K^{-1}}$. Its influence on the uncertainty of the heat capacity is relatively small. The mass of each sample was determined within 0.01% by differential weighings before and after trapping the sample. The density calculated from this mass and the bomb volume has a relative uncertainty of 0.2%. For pressure, the uncertainty of the gauge of 7 kPa is added to the cross term for the pressure derivative in the change-of-volume-work adjustment. However, neither the uncertainty of P nor ρ contributes appreciably to the combined uncertainty for the measured heat capacity. The uncertainty of the cell volume (Eq. (4)) is estimated to be 0.007 $\mathrm{cm^3}$. The amount of sample mass in the noxious volume was calculated from densities calculated with the IUPAC [23] equation of state. The relative uncertainty of C_V is determined to be 2%, by combining the various sources of experimental uncertainty using a root-sum-of-squares formula.

3.4. Performance Tests

The empty calorimeter function was determined from heating the completely evacuated bombs. Heating runs in the temperature range 300 to 425 K were repeated until we were confident in the precision of the results. The energy data are shown in Fig. 1. The data were fit by the function,

$$\Delta Q_0 = 16.3382 - 0.074738T, \tag{5}$$

where ΔQ_0 is in joules and T is in kelvin. Over 300 individual measurements agreed with Eq. (5) within a maximum deviation of ± 0.5 J. This equation is linear in temperature, and ΔQ_0 ranges from -6 to -15 J at temperatures from 300 to 425 K. This calorimeter has been previously used for measurements of isochoric heat capacities of pure water [36], and pure methanol and water + methanol mixtures [28] in the liquid phase.

4. RESULTS AND DISCUSSION

4.1. *PVT* Measurements

Each density was calculated from the measured sample mass and the calibrated cell volume (Eq. (4)) at the measured temperature T and pressure P. Measurements of the PVT properties of methanol were performed

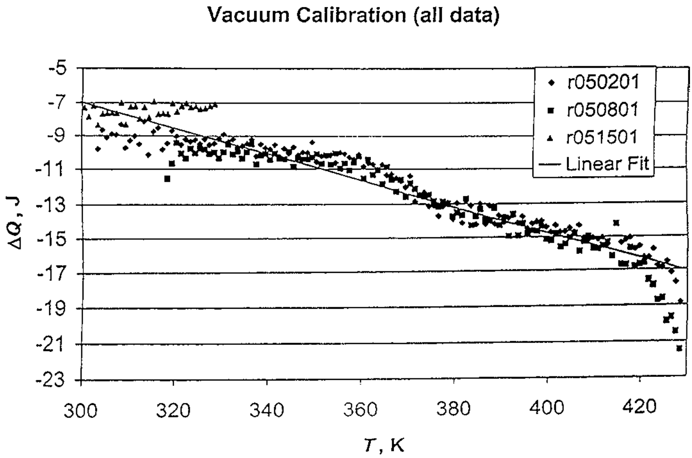

Fig. 1. Measured ΔQ_0 as a function of temperature for different runs. Measured prior to this study [54].

along four liquid quasi-isochores: 699.3, 726.2, 745.7, and 775.6 $\mathrm{kg \cdot m^{-3}}$. The temperature ranged from 314 to 411 K, and the pressure ranged from 2 to 20 MPa. The results are given in Table III. Figure 2 shows the temperature dependence of measured pressures along each quasi-isochore together with values calculated with IUPAC model [23] and a 16-constant equation of state developed by Machado and Streett [30]. Slight deviations between measured and calculated values of pressures at high temperatures are due to the increase in bomb volume with increasing pressure and temperature during the measurements. Figure 2 also shows data reported by other authors [42, 45]. As one can see from this figure, there is good consistency between present and previously reported data sets and calculated values. A deviation plot for the present *PVT* measurements is shown in Fig. 3. One can see from Fig. 3 that the measured values of density show systematic positive deviations within their experimental uncertainty. Deviation statistics for the measured values of density are as follow ($N = 218$): AAD = 0.088%, bias = 0.09%, SD = 0.015%, SE = 0.001%, and maximum deviation = 0.15% (two data points).

The pressure of the methanol was measured as a function of temperature at nearly constant density. The experimental cell was filled at room temperature, sealed off, and heated along a quasi-isochore. After reaching the desired temperature, the sample was maintained in the cell for 2 to 3 hours. After the temperature was stabilized, the pressure did not change with time (3 to 4 hours). This means that in the temperature range of this study (up to 411 K), no decomposition of the methanol was observed.

By linear extrapolation of P–T curves to the saturated temperature (calculated with the IUPAC [23] equation) for each fixed isochore, we derived values of the vapor pressure P_S. The results are presented in Table IV and in Fig. 4 together with values of vapor pressures for pure methanol reported by other authors in the literature. Because the experimental P–T isochores are almost linear, the extrapolation is reliable. The uncertainty in derived values of P_S is 0.2 to 0.3%. As one can see from

Table III. Experimental *PVT* and Heat Capacities (C_V) for Pure Methanol

T_1 (K)	T_2 (K)	P_1 (MPa)	P_2 (MPa)	ΔP (MPa)	ΔQ (J)	$-\Delta Q_0$ (J)	ΔW_{PV} (J)	C_V ($\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)	ρ_1 ($\text{kg}\cdot\text{m}^{-3}$)	ρ_2 ($\text{kg}\cdot\text{m}^{-3}$)
Run 1 (m=54.0754 g, ρ=775.6 $\text{kg}\cdot\text{m}^{-3}$)										
314.0	315.0	3.967	4.775	0.808	109.8808	8.14927	3.0684	2.1260	776.5854	776.4644
315.0	316.0	4.775	5.584	0.809	114.1034	8.22701	3.0838	2.2052	776.4644	776.3433
316.0	317.0	5.584	6.390	0.806	114.2656	8.30475	3.0885	2.2095	776.3433	776.2226
317.0	318.0	6.390	7.200	0.810	115.5031	8.38248	3.1120	2.2334	776.2226	776.1015
318.0	319.0	7.200	8.008	0.808	114.0099	8.46022	3.1193	2.2071	776.1015	775.9806
319.0	320.0	8.008	8.817	0.809	117.1810	8.53796	3.1352	2.2669	775.9806	775.8597
320.0	321.0	8.817	9.625	0.808	115.0716	8.61570	3.1453	2.2291	775.8597	775.7389
321.0	322.0	9.625	10.431	0.806	115.5135	8.69344	3.1526	2.2386	775.7389	775.6183
322.0	323.0	10.431	11.238	0.807	116.3260	8.77117	3.1683	2.2548	775.6183	775.4977
323.0	324.0	11.238	12.043	0.805	115.1778	8.84891	3.1754	2.2349	775.4977	775.3773
324.0	325.0	12.043	12.852	0.809	116.6343	8.92665	3.1994	2.2628	775.3773	775.2565
325.0	326.0	12.852	13.659	0.807	114.9967	9.00439	3.2071	2.2338	775.2565	775.1359
326.0	327.0	13.659	14.469	0.810	117.5016	9.08213	3.2284	2.2812	775.1359	775.0151
327.0	328.0	14.469	15.273	0.804	113.1942	9.15986	3.2244	2.2030	775.0151	774.8949
328.0	329.0	15.273	16.084	0.811	115.8309	9.23760	3.2575	2.2526	774.8949	774.7741
Run 2 (m=54.0754 g, ρ=775.6 $\text{kg}\cdot\text{m}^{-3}$)										
314.0	315.0	3.974	4.783	0.809	107.9455	8.14927	3.0715	2.0901	776.5846	776.4635
315.0	316.0	4.783	5.590	0.807	113.6083	8.22701	3.0788	2.1961	776.4635	776.3427
316.0	317.0	5.590	6.403	0.813	114.3435	8.30475	3.1077	2.2106	776.3427	776.2212
317.0	318.0	6.403	7.216	0.813	114.2717	8.38248	3.1205	2.2105	776.2212	776.0998
318.0	319.0	7.216	8.024	0.808	112.6475	8.46022	3.1197	2.1819	776.0998	775.9790
319.0	320.0	8.024	8.833	0.809	115.5074	8.53796	3.1352	2.2360	775.9790	775.8580
320.0	321.0	8.833	9.640	0.807	114.1866	8.61570	3.1429	2.2128	775.8580	775.7373
321.0	322.0	9.640	10.450	0.810	115.2458	8.69344	3.1639	2.2335	775.7373	775.6163
322.0	323.0	10.450	11.259	0.809	115.6109	8.77117	3.1740	2.2415	775.6163	775.4955
323.0	324.0	11.259	12.067	0.808	113.7331	8.84891	3.1841	2.2080	775.4955	775.3748
324.0	325.0	12.067	12.876	0.809	115.4530	8.92665	3.2001	2.2409	775.3748	775.2540
325.0	326.0	12.876	13.689	0.813	116.2055	9.00439	3.2242	2.2558	775.2540	775.1328
326.0	327.0	13.689	14.498	0.809	114.5083	9.08213	3.2263	2.2259	775.1328	775.0121
327.0	328.0	14.498	15.306	0.808	115.2557	9.15986	3.2364	2.2409	775.0121	774.8915
328.0	329.0	15.306	16.113	0.807	114.4878	9.23760	3.2469	2.2280	774.8915	774.7710
329.0	330.0	16.113	16.922	0.809	117.1556	9.31534	3.2655	2.2784	774.7710	774.6504
330.0	331.0	16.922	17.734	0.812	115.2584	9.39308	3.2874	2.2443	774.6504	774.5294
331.0	332.0	17.734	18.539	0.805	115.6748	9.47082	3.2808	2.2536	774.5294	774.4093
332.0	333.0	18.539	19.349	0.810	116.3809	9.54855	3.3082	2.2676	774.4093	774.2886

Table III. *(Continued)*

T_1 (K)	T_2 (K)	P_1 (MPa)	P_2 (MPa)	ΔP (MPa)	ΔQ (J)	$-\Delta Q_0$ (J)	ΔW_{PV} (J)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	ρ_1 ($\mathrm{kg \cdot m^{-3}}$)	ρ_2 ($\mathrm{kg \cdot m^{-3}}$)
Run 1 ($m = 52.0666$ g, $\rho = 745.7\ \mathrm{kg \cdot m^{-3}}$)										
343.0	344.0	2.551	3.269	0.718	116.4847	10.40367	2.73086	2.3846	746.8847	746.7775
344.0	345.0	3.269	3.990	0.721	117.7864	10.48141	2.75263	2.4107	746.7775	746.6700
345.0	346.0	3.990	4.709	0.719	116.8468	10.55915	2.76113	2.3939	746.6700	746.5628
346.0	347.0	4.709	5.444	0.735	120.6564	10.63689	2.81714	2.4675	746.5628	746.4540
347.0	348.0	5.444	6.165	0.721	117.1691	10.71462	2.79459	2.4025	746.4540	746.3466
348.0	349.0	6.165	6.890	0.725	118.0996	10.79236	2.81900	2.4214	746.3466	746.2388
349.0	350.0	6.890	7.616	0.726	117.3761	10.87010	2.83592	2.4087	746.2388	746.1309
350.0	351.0	7.616	8.349	0.733	120.0816	10.94784	2.86859	2.4615	746.1309	746.0224
351.0	352.0	8.349	9.076	0.727	117.6736	11.02558	2.86691	2.4168	746.0224	745.9145
352.0	353.0	9.076	9.805	0.729	118.9109	11.10331	2.88634	2.4416	745.9145	745.8064
353.0	354.0	9.805	10.530	0.725	119.1606	11.18105	2.88959	2.4479	745.8064	745.6987
354.0	355.0	10.530	11.268	0.738	122.0988	11.25879	2.93912	2.5048	745.6987	745.5898
355.0	356.0	11.268	12.001	0.733	120.2229	11.33653	2.93970	2.4703	745.5898	745.4814
356.0	357.0	12.001	12.733	0.732	119.5422	11.41427	2.95120	2.4585	745.4814	745.3731
357.0	358.0	12.733	13.462	0.729	119.5404	11.49200	2.95718	2.4598	745.3731	745.2651
358.0	359.0	13.462	14.201	0.739	122.4006	11.56974	2.99925	2.5155	745.2651	745.1561
359.0	360.0	14.201	14.937	0.736	120.9211	11.64748	3.00531	2.4884	745.1561	745.0475
360.0	361.0	14.937	15.669	0.732	120.0866	11.72522	3.00815	2.4738	745.0475	744.9393
361.0	362.0	15.669	16.403	0.734	119.6098	11.80296	3.02820	2.4658	744.9393	744.8310
362.0	363.0	16.403	17.146	0.743	122.7385	11.88069	3.06817	2.5266	744.8310	744.7217
363.0	364.0	17.146	17.886	0.740	121.7156	11.95843	3.07426	2.5083	744.7217	744.6128
364.0	365.0	17.886	18.624	0.738	118.8324	12.03617	3.08279	2.4543	744.6128	744.5041
365.0	366.0	18.624	19.364	0.740	122.2708	12.11391	3.10317	2.5214	744.5041	744.3952
Run 2 ($m = 52.0666$ g, $\rho = 745.7\ \mathrm{kg \cdot m^{-3}}$)										
344.0	345.0	3.269	3.990	0.721	116.5936	10.48141	2.75263	2.3878	746.7775	746.6700
345.0	346.0	3.990	4.714	0.724	116.7768	10.55915	2.77417	2.3924	746.6700	746.5623
346.0	347.0	4.714	5.446	0.732	119.7584	10.63689	2.80963	2.4504	746.5623	746.4537
347.0	348.0	5.446	6.170	0.724	118.4204	10.71462	2.80249	2.4264	746.4537	746.3460
348.0	349.0	6.170	6.892	0.722	118.3486	10.79236	2.81105	2.4263	746.3460	746.2386
349.0	350.0	6.892	7.617	0.725	119.6298	10.87010	2.83326	2.4520	746.2386	746.1308
350.0	351.0	7.617	8.350	0.733	121.4919	10.94784	2.86859	2.4886	746.1308	746.0223
351.0	352.0	8.350	9.078	0.728	120.3716	11.02558	2.86959	2.4685	746.0223	745.9143
352.0	353.0	9.078	9.804	0.726	121.1241	11.10331	2.87824	2.4843	745.9143	745.8065
353.0	354.0	9.804	10.531	0.727	120.3028	11.18105	2.89502	2.4697	745.8065	745.6986
354.0	355.0	10.531	11.266	0.735	124.0246	11.25879	2.93094	2.5420	745.6986	745.5900
355.0	356.0	11.266	11.999	0.733	122.0529	11.33653	2.93970	2.5054	745.5900	745.4816
356.0	357.0	11.999	12.729	0.730	121.0661	11.41427	2.94570	2.4879	745.4816	745.3735
357.0	358.0	12.729	13.460	0.731	120.8354	11.49200	2.96271	2.4846	745.3735	745.2653
358.0	359.0	13.460	14.199	0.739	124.5110	11.56974	2.99925	2.5560	745.2653	745.1563
359.0	360.0	14.199	14.935	0.736	122.6924	11.64748	3.00531	2.5224	745.1563	745.0477
360.0	361.0	14.935	15.670	0.735	122.4482	11.72522	3.01657	2.5190	745.0477	744.9392
361.0	362.0	15.670	16.407	0.737	122.7716	11.80296	3.03666	2.5263	744.9392	744.8306
362.0	363.0	16.407	17.146	0.739	124.5620	11.88069	3.05684	2.5618	744.8306	744.7217
363.0	364.0	17.146	17.888	0.742	122.7725	11.95843	3.07995	2.5285	744.7217	744.6126
364.0	365.0	17.888	18.626	0.738	123.4584	12.03617	3.08279	2.5431	744.6126	744.5039
365.0	366.0	18.626	19.361	0.735	121.8953	12.11391	3.08843	2.5145	744.5039	744.3955

Table III. *(Continued)*

T_1 (K)	T_2 (K)	P_1 (MPa)	P_2 (MPa)	ΔP (MPa)	ΔQ (J)	$-\Delta Q_0$ (J)	ΔW_{PV} (J)	C_V ($kJ \cdot kg^{-1} \cdot K^{-1}$)	ρ_1 ($kg \cdot m^{-3}$)	ρ_2 ($kg \cdot m^{-3}$)
Run 3 ($m=52.0666$ g, $\rho=745.7$ $kg \cdot m^{-3}$)										
343.0	344.0	2.551	3.272	0.721	114.7865	10.40367	2.73860	2.3518	746.8847	746.7772
344.0	345.0	3.272	3.992	0.720	115.3393	10.48141	2.75004	2.3637	746.7772	746.6698
345.0	346.0	3.992	4.715	0.723	117.4303	10.55915	2.77191	2.4049	746.6698	746.5622
346.0	347.0	4.715	5.448	0.733	118.3712	10.63689	2.81225	2.4237	746.5622	746.4535
347.0	348.0	5.448	6.171	0.723	117.5597	10.71462	2.79985	2.4099	746.4535	746.3459
348.0	349.0	6.171	6.892	0.721	118.8133	10.79236	2.80841	2.4353	746.3459	746.2386
349.0	350.0	6.892	7.617	0.725	118.4460	10.87010	2.83326	2.4293	746.2386	746.1308
350.0	351.0	7.617	8.349	0.732	121.4543	10.94784	2.86591	2.4879	746.1308	746.0224
351.0	352.0	8.349	9.077	0.728	119.3782	11.02558	2.86959	2.4494	746.0224	745.9144
352.0	353.0	9.077	9.802	0.725	120.4805	11.10331	2.87554	2.4720	745.9144	745.8067
353.0	354.0	9.802	10.530	0.728	120.8274	11.18105	2.89773	2.4797	745.8067	745.6987
354.0	355.0	10.530	11.266	0.736	121.9868	11.25879	2.93366	2.5028	745.6987	745.5900
355.0	356.0	11.266	11.999	0.733	121.1534	11.33653	2.93970	2.4882	745.5900	745.4816
356.0	357.0	11.999	12.729	0.730	120.5305	11.41427	2.94570	2.4776	745.4816	745.3735
357.0	358.0	12.729	13.461	0.732	119.7200	11.49200	2.96548	2.4631	745.3735	745.2652
358.0	359.0	13.461	14.201	0.740	123.2590	11.56974	3.00203	2.5319	745.2652	745.1561
359.0	360.0	14.201	14.935	0.734	120.8852	11.64748	2.99972	2.4878	745.1561	745.0477
360.0	361.0	14.935	15.670	0.735	121.3820	11.72522	3.01657	2.4985	745.0477	744.9392
361.0	362.0	15.670	16.406	0.736	121.0216	11.80296	3.03384	2.4928	744.9392	744.8307
362.0	363.0	16.406	17.146	0.740	123.5149	11.88069	3.05967	2.5417	744.8307	744.7217
363.0	364.0	17.146	17.886	0.740	122.1809	11.95843	3.07426	2.5173	744.7217	744.6128
364.0	365.0	17.886	18.623	0.737	121.7215	12.03617	3.07993	2.5098	744.6128	744.5042
365.0	366.0	18.623	19.361	0.738	122.7987	12.11391	3.09705	2.5317	744.5042	744.3955
Run 1 ($m=50.7523$ g, $\rho=726.2$ $kg \cdot m^{-3}$)										
362.0	363.0	2.649	3.332	0.683	120.5737	11.88069	2.61211	2.5584	727.3870	727.2861
363.0	364.0	3.332	4.012	0.680	119.3162	11.95843	2.61881	2.5350	727.2861	727.1855
364.0	365.0	4.012	4.692	0.680	121.2656	12.03617	2.63287	2.5746	727.1855	727.0850
365.0	366.0	4.692	5.373	0.681	121.3597	12.11391	2.64992	2.5777	727.0850	726.9843
366.0	367.0	5.373	6.062	0.689	122.6639	12.19165	2.68532	2.6042	726.9843	726.8829
367.0	368.0	6.062	6.746	0.684	122.2513	12.26938	2.68649	2.5976	726.8829	726.7820
368.0	369.0	6.746	7.429	0.683	123.3957	12.34712	2.69812	2.6215	726.7820	726.6813
369.0	370.0	7.429	8.116	0.687	119.3723	12.42486	2.72339	2.5432	726.6813	726.5801
370.0	371.0	8.116	8.808	0.692	124.8795	12.50260	2.75112	2.6527	726.5801	726.4785
371.0	372.0	8.808	9.501	0.693	120.4194	12.58034	2.76830	2.5660	726.4785	726.3768
372.0	373.0	9.501	10.192	0.691	121.7089	12.65807	2.77746	2.5928	726.3768	726.2753
373.0	374.0	10.192	10.883	0.691	121.4537	12.73581	2.79166	2.5890	726.2753	726.1739
374.0	375.0	10.883	11.577	0.694	122.1159	12.81355	2.81443	2.6031	726.1739	726.0722
375.0	376.0	11.577	12.276	0.699	124.4518	12.89129	2.84243	2.6501	726.0722	725.9700
376.0	377.0	12.276	12.969	0.693	123.1307	12.96903	2.84035	2.6257	725.9700	725.8684
377.0	378.0	12.969	13.664	0.695	122.6477	13.04676	2.86063	2.6173	725.8684	725.7666
378.0	379.0	13.664	14.363	0.699	117.0291	13.12450	2.88619	2.5076	725.7666	725.6645
379.0	380.0	14.363	15.072	0.709	121.0893	13.20224	2.92865	2.5883	725.6645	725.5614
380.0	381.0	15.072	15.770	0.698	118.3358	13.27998	2.91249	2.5359	725.5614	725.4594
381.0	382.0	15.770	16.471	0.701	119.5457	13.35772	2.93555	2.5608	725.4594	725.3572
382.0	383.0	16.471	17.263	0.792	136.1073	13.43545	3.20983	2.8833	725.3572	725.2460

Table III. *(Continued)*

T_1 (K)	T_2 (K)	P_1 (MPa)	P_2 (MPa)	ΔP (MPa)	ΔQ (J)	$-\Delta Q_0$ (J)	ΔW_{PV} (J)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	ρ_1 ($\mathrm{kg \cdot m^{-3}}$)	ρ_2 ($\mathrm{kg \cdot m^{-3}}$)
Run 2 ($m=50.7523$ g, $\rho=726.2\ \mathrm{kg \cdot m^{-3}}$)										
364.0	365.0	4.009	4.683	0.674	107.6726	12.03617	2.61738	2.3071	727.1858	727.0859
365.0	366.0	4.683	5.380	0.697	121.1513	12.11391	2.69183	2.5728	727.0859	726.9836
366.0	367.0	5.380	6.063	0.683	114.5624	12.19165	2.66965	2.4449	726.9836	726.8828
367.0	368.0	6.063	6.743	0.680	117.8504	12.26938	2.67599	2.5111	726.8828	726.7823
368.0	369.0	6.743	7.427	0.684	116.3176	12.34712	2.70076	2.4819	726.7823	726.6815
369.0	370.0	7.427	8.118	0.691	121.4906	12.42486	2.73400	2.5847	726.6815	726.5799
370.0	371.0	8.118	8.805	0.687	117.8357	12.50260	2.73778	2.5142	726.5799	726.4788
371.0	372.0	8.805	9.498	0.693	122.1704	12.58034	2.76830	2.6005	726.4788	726.3771
372.0	373.0	9.498	10.186	0.688	118.5377	12.65807	2.76901	2.5305	726.3771	726.2759
373.0	374.0	10.186	10.888	0.702	125.7072	12.73581	2.82146	2.6722	726.2759	726.1734
374.0	375.0	10.888	11.574	0.686	117.9825	12.81355	2.79265	2.5221	726.1734	726.0724
375.0	376.0	11.574	12.271	0.697	120.2828	12.89129	2.83696	2.5681	726.0724	725.9705
376.0	377.0	12.271	12.965	0.694	117.2448	12.96903	2.84310	2.5097	725.9705	725.8688
377.0	378.0	12.965	13.666	0.701	123.3779	13.04676	2.87722	2.6314	725.8688	725.7664
378.0	379.0	13.666	14.372	0.706	120.2807	13.12450	2.90564	2.5713	725.7664	725.6636
379.0	380.0	14.372	15.067	0.695	119.8862	13.20224	2.88955	2.5654	725.6636	725.5619
380.0	381.0	15.067	15.766	0.699	119.2988	13.27998	2.91530	2.5548	725.5619	725.4598
381.0	382.0	15.766	16.477	0.711	120.1471	13.35772	2.96376	2.5721	725.4598	725.3566
382.0	383.0	16.477	17.179	0.702	119.8952	13.43545	2.95306	2.5689	725.3566	725.2542
383.0	384.0	17.179	17.886	0.707	121.6120	13.51319	2.98165	2.6037	725.2542	725.1514
384.0	385.0	17.886	18.593	0.707	117.7138	13.59093	2.99649	2.5281	725.1514	725.0487
385.0	386.0	18.593	19.306	0.713	126.1075	13.66867	3.02862	2.6944	725.0487	724.9453
Run 3 ($m=50.7523$ g, $\rho=726.2\ \mathrm{kg \cdot m^{-3}}$)										
361.0	362.0	1.980	2.656	0.676	110.9697	11.80296	2.57995	2.3682	727.4866	727.3863
362.0	363.0	2.656	3.333	0.677	114.5193	11.88069	2.59678	2.4394	727.3863	727.2860
363.0	364.0	3.333	4.010	0.677	115.5174	11.95843	2.61111	2.4603	727.2860	727.1857
364.0	365.0	4.010	4.694	0.684	112.5892	12.03617	2.64356	2.4035	727.1857	727.0848
365.0	366.0	4.694	5.374	0.680	119.2176	12.11391	2.64732	2.5355	727.0848	726.9842
366.0	367.0	5.374	6.062	0.688	116.1649	12.19165	2.68270	2.4762	726.9842	726.8829
367.0	368.0	6.062	6.741	0.679	114.9096	12.26938	2.67337	2.4532	726.8829	726.7825
368.0	369.0	6.741	7.432	0.691	114.8616	12.34712	2.71960	2.4529	726.7825	726.6810
369.0	370.0	7.432	8.119	0.687	116.5601	12.42486	2.72339	2.4878	726.6810	726.5798
370.0	371.0	8.119	8.808	0.689	116.2372	12.50260	2.74312	2.4826	726.5798	726.4785
371.0	372.0	8.808	9.499	0.691	117.7949	12.58034	2.76294	2.5144	726.4785	726.3770
372.0	373.0	9.499	10.194	0.695	111.1852	12.65807	2.78824	2.3852	726.3770	726.2751
373.0	374.0	10.194	10.886	0.692	109.4970	12.73581	2.79437	2.3534	726.2751	726.1736
374.0	375.0	10.886	11.583	0.697	114.8971	12.81355	2.82260	2.4607	726.1736	726.0716
375.0	376.0	11.583	12.275	0.692	116.0754	12.89129	2.82328	2.4855	726.0716	725.9701
376.0	377.0	12.275	12.979	0.704	118.6636	12.96903	2.87098	2.5371	725.9701	725.8674
377.0	378.0	12.979	13.671	0.692	117.2053	13.04676	2.85233	2.5102	725.8674	725.7659
378.0	379.0	13.671	14.373	0.702	119.6359	13.12450	2.89452	2.5588	725.7659	725.6635
379.0	380.0	14.373	15.068	0.695	120.0798	13.20224	2.88955	2.5692	725.6635	725.5618
380.0	381.0	15.068	15.775	0.707	120.3763	13.27998	2.93775	2.5756	725.5618	725.4589
381.0	382.0	15.775	16.474	0.699	117.2449	13.35772	2.92991	2.5156	725.4589	725.3569
382.0	383.0	16.474	17.180	0.706	119.4539	13.43545	2.96440	2.5600	725.3569	725.2541
383.0	384.0	17.180	17.889	0.709	119.8012	13.51319	2.98773	2.5679	725.2541	725.1511
384.0	385.0	17.889	18.592	0.703	119.0822	13.59093	2.98503	2.5553	725.1511	725.0488
385.0	386.0	18.592	19.306	0.714	121.8821	13.66867	3.03150	2.6111	725.0488	724.9453

Table III. *(Continued)*

T_1 (K)	T_2 (K)	P_1 (MPa)	P_2 (MPa)	ΔP (MPa)	ΔQ (J)	$-\Delta Q_0$ (J)	ΔW_{PV} (J)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	ρ_1 ($\mathrm{kg \cdot m^{-3}}$)	ρ_2 ($\mathrm{kg \cdot m^{-3}}$)
Run 4 ($m = 50.7523$ g, $\rho = 726.2\ \mathrm{kg \cdot m^{-3}}$)										
363.0	364.0	3.333	4.007	0.674	117.4896	11.95843	2.60305	2.4993	727.2860	727.1860
364.0	365.0	4.007	4.691	0.684	118.1225	12.03617	2.64320	2.5125	727.1860	727.0851
365.0	366.0	4.691	5.374	0.683	118.3863	12.11391	2.65511	2.5190	727.0851	726.9842
366.0	367.0	5.374	6.059	0.685	117.6502	12.19165	2.67487	2.5056	726.9842	726.8832
367.0	368.0	6.059	6.741	0.682	116.6257	12.26938	2.68124	2.4869	726.8832	726.7825
368.0	369.0	6.741	7.431	0.690	117.5746	12.34712	2.71696	2.5064	726.7825	726.6811
369.0	370.0	7.431	8.120	0.689	116.3931	12.42486	2.72870	2.4844	726.6811	726.5797
370.0	371.0	8.120	8.807	0.687	118.0179	12.50260	2.73778	2.5178	726.5797	726.4786
371.0	372.0	8.807	9.498	0.691	114.4144	12.58034	2.76294	2.4478	726.4786	726.3771
372.0	373.0	9.498	10.193	0.695	119.2566	12.65807	2.78824	2.5442	726.3771	726.2752
373.0	374.0	10.193	10.888	0.695	116.8928	12.73581	2.80250	2.4989	726.2752	726.1734
374.0	375.0	10.888	11.583	0.695	117.4323	12.81355	2.81716	2.5108	726.1734	726.0716
375.0	376.0	11.583	12.274	0.691	117.5453	12.89129	2.82054	2.5145	726.0716	725.9702
376.0	377.0	12.274	12.972	0.698	120.2384	12.96903	2.85448	2.5684	725.9702	725.8681
377.0	378.0	12.972	13.670	0.698	115.3765	13.04676	2.86892	2.4739	725.8681	725.7660
378.0	379.0	13.670	14.370	0.700	122.1051	13.12450	2.88897	2.6076	725.7660	725.6638
379.0	380.0	14.370	15.066	0.696	119.9320	13.20224	2.89234	2.5662	725.6638	725.5620
380.0	381.0	15.066	15.771	0.705	119.7333	13.27998	2.93214	2.5631	725.5620	725.4593
381.0	382.0	15.771	16.477	0.706	119.9277	13.35772	2.94965	2.5681	725.4593	725.3566
382.0	383.0	16.477	17.181	0.704	119.7050	13.43545	2.95873	2.5650	725.3566	725.2540
383.0	384.0	17.181	17.890	0.709	120.7928	13.51319	2.98773	2.5874	725.2540	725.1510
384.0	385.0	17.890	18.597	0.707	118.9245	13.59093	2.99649	2.5520	725.1510	725.0483
385.0	386.0	18.597	19.303	0.706	123.1504	13.66867	3.00848	2.6365	725.0483	724.9456
Run 1 ($m = 48.9213$ g, $\rho = 699.3\ \mathrm{kg \cdot m^{-3}}$)										
385.0	386.0	2.018	2.603	0.585	124.4332	13.66867	2.30421	2.7758	700.4659	700.378
386.0	387.0	2.603	3.232	0.629	122.2708	13.74641	2.42817	2.7307	700.3781	700.286
387.0	388.0	3.232	3.860	0.628	121.1422	13.82414	2.43991	2.7090	700.2862	700.194
388.0	389.0	3.860	4.493	0.633	118.2573	13.90188	2.46688	2.6510	700.1943	700.102
389.0	390.0	4.493	5.131	0.638	117.7729	13.97962	2.49405	2.6422	700.1020	700.009
390.0	391.0	5.131	5.771	0.640	119.7544	14.05736	2.51371	2.6839	700.0092	699.916
391.0	392.0	5.771	6.407	0.636	115.7476	14.13510	2.51761	2.6035	699.9162	699.824
392.0	393.0	6.407	7.050	0.643	120.7460	14.21283	2.55000	2.7066	699.8237	699.731
393.0	394.0	7.050	7.699	0.649	116.4578	14.29057	2.58039	2.6199	699.7305	699.637
394.0	395.0	7.699	8.344	0.645	118.0766	14.36831	2.58400	2.6545	699.6367	699.543
395.0	396.0	8.344	8.990	0.646	117.5468	14.44605	2.60110	2.6449	699.5434	699.450
396.0	397.0	8.990	9.636	0.646	121.4028	14.52379	2.61525	2.7250	699.4500	699.357
397.0	398.0	9.636	10.281	0.645	118.6270	14.60152	2.62677	2.6696	699.3566	699.263
398.0	399.0	10.281	10.938	0.657	120.2725	14.67926	2.67357	2.7039	699.2633	699.169
399.0	400.0	10.938	11.586	0.648	119.6359	14.75700	2.66334	2.6927	699.1689	699.075
400.0	401.0	11.586	12.245	0.659	117.6426	14.83474	2.70752	2.6526	699.0753	698.981
401.0	402.0	12.245	12.900	0.655	119.9417	14.91248	2.71114	2.7011	698.9808	698.887
402.0	403.0	12.900	13.556	0.656	116.7662	14.99021	2.72802	2.6375	698.8866	698.792
403.0	404.0	13.556	14.214	0.658	117.8075	15.06795	2.74772	2.6599	698.7923	698.698
404.0	405.0	14.214	14.878	0.664	124.0483	15.14569	2.77898	2.7885	698.6979	698.603
405.0	406.0	14.878	15.544	0.666	117.0144	15.22343	2.79893	2.6459	698.6030	698.508
406.0	407.0	15.544	16.206	0.662	117.5267	15.30117	2.80218	2.6579	698.5079	698.413
407.0	408.0	16.206	16.867	0.661	122.5268	15.37890	2.81341	2.7614	698.4131	698.319
408.0	409.0	16.867	17.542	0.675	125.9443	15.45664	2.86745	2.8318	698.3185	698.223
409.0	410.0	17.542	18.212	0.670	126.0572	15.53438	2.86793	2.8356	698.2226	698.127
410.0	411.0	18.212	18.879	0.667	119.7940	15.61212	2.87362	2.7091	698.1272	698.032
411.0	412.0	18.879	19.548	0.669	123.7389	15.68986	2.89323	2.7909	698.0320	697.937

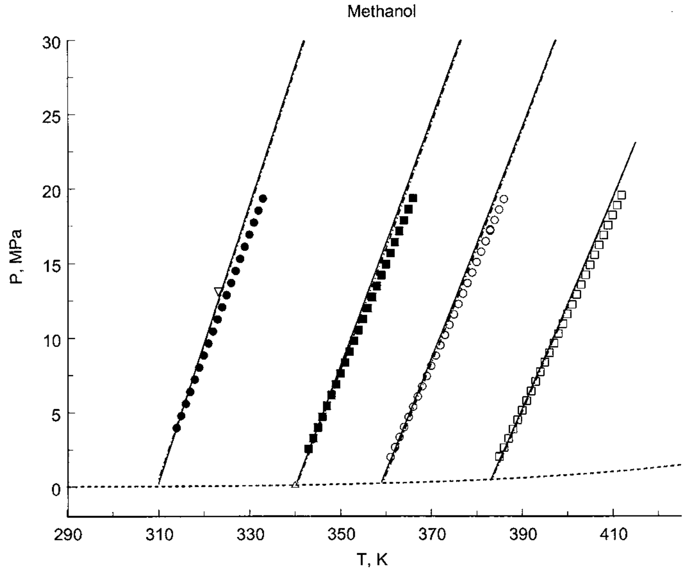

Fig. 2. Measured and calculated values of pressure of liquid methanol as a function of temperature along quasi-isochores. ●, 775.6 kg·m^{-3} (this work); ■, 745.7 kg·m^{-3} (this work); ○, 726.2 kg·m^{-3} (this work); □, 669.3 kg·m^{-3} (this work); ▽, Kubota et al. [45]; △, Hales and Ellender [42]; ——, Machado and Streett [30]; –·–·–, IUPAC [23]; - - - - -, vapor-pressure curve (IUPAC [23]).

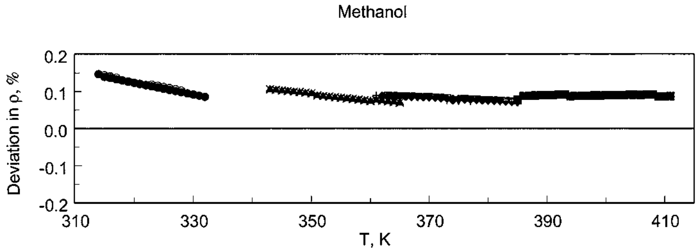

Fig. 3. Percentage density deviations, $\delta\rho = 100((\rho_{\text{exp}} - \rho_{\text{cal}})/\rho_{\text{exp}})$, of the experimental densities for pure methanol from values calculated with IUPAC [23] equation of state. **Run-1**: ●, 775.6 kg·m^{-3}; ▲, 745.7 kg·m^{-3}; ◆, 726.2 kg·m^{-3}; ■, 699.3 kg·m^{-3}; **Run-2**: ○, 775.6 kg·m^{-3}; △, 745.7 kg·m^{-3}; ◇, 726.2 kg·m^{-3}; **Run-3**: ×, 745.7 kg·m^{-3}; +, 726.2 kg·m^{-3}; **Run-4**: ▽, 726.2 kg·m^{-3}.

Table IV. Comparisons of Derived Values of the Vapor Pressure (in MPa) for Methanol with Selected Literature Values

First author	309.15 K	339.65 K	358.44 K	382.34 K	AAD (%)
This work	0.0291	0.1093	0.2178	0.4708	–
Ambrose [40]	0.0293	0.1094	0.2175	0.4680	0.37
Eubank [24]	0.0287	0.1086	0.2165	0.4608	1.18
IUPAC [23]	0.0294	0.1096	0.2179	0.4688	0.44
Kozlov [39]	0.0294	0.1096	0.2178	0.4685	0.45
Osada [26]	–	0.1096	0.2186	0.4719	0.29
Hirata [46]	–	–	0.2174	0.4742	0.44
Machado [30]	0.0300	0.1104	0.2195	0.4687	1.30
Holldorff [47]	0.0294	0.1100	0.2184	–	0.64
Goodwin [33]	0.0292	0.1095	0.2182	0.4695	0.25
Ramsay [32]	–	–	0.2179	0.4650	0.65
Stull [48]	–	–	0.2144	0.4600	1.95
Yokoyama [27]	–	0.1100	0.2206	0.4765	1.04

Table IV, the agreement between derived values of the vapor pressure and reported data are good (deviations within 0.45 to 1.0%), except for the data reported by Stull [48] and Eubank [24].

The values of densities corresponding to the saturated temperatures (saturated liquid densities) are given in Table V together with values

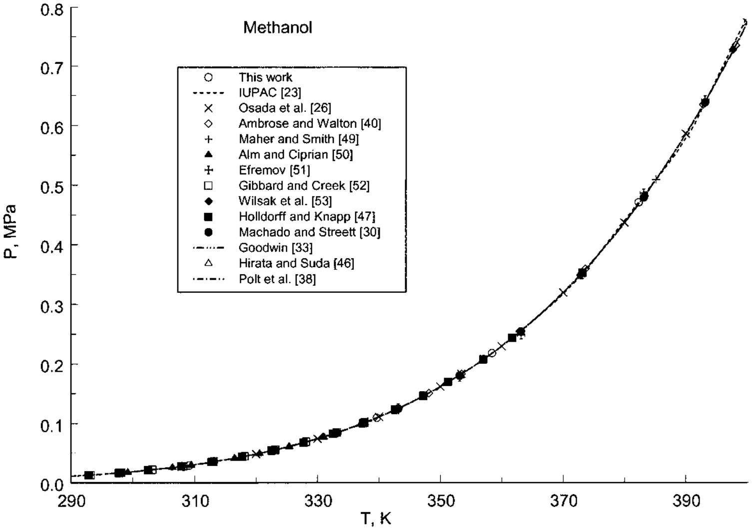

Fig. 4. Comparisons of derived values of the vapor pressure for pure methanol with data reported in the literature by various authors.

Table V. Comparisons of Derived Values of the Saturated Liquid Density (in $\mathrm{kg \cdot m^{-3}}$) for Methanol with Selected Literature Values

T_S (K)	This work	Cibulka [43]	Eubank [24]	IUPAC [23]	Kozlov [39]	Osada [26]	Polt [38]	Machado [30]	Hales [42]	Goodwin [33]
309.15	775.60	776.03	776.32	775.89	776.34	–	776.14	776.15	775.93	776.19
339.65	745.68	746.73	746.23	746.85	746.44	745.51	747.02	746.16	746.22	746.23
358.44	726.23	726.81	727.15	727.02	726.73	726.20	726.97	726.62	726.82	726.62
382.34	699.26	700.23	700.44	700.37	699.67	699.45	700.13	700.11	700.18	699.74
AAD (%)	–	0.105	0.116	0.115	0.081	0.119	0.019	0.078	0.082	0.068

reported by other authors in the literature and calculated with correlation equations. As this table shows, the agreement between the present derived values of the saturated densities and the values reported in the literature is good. The average absolute deviation is within 0.068 to 0.119%. This is confirms the reliability and accuracy of the present data and demonstrates the consistency between derived vapor-pressure and saturated-liquid-density data.

4.2. C_V Measurements

The isochoric heat capacity values C_V of each run are shown in Table III. The measured values of isochoric heat capacity for pure methanol were compared with values calculated from the IUPAC [23] and Polt et al. [38] equations of state. Figure 5 shows temperature dependencies of measured values of the heat capacity C_V along two quasi-isochores at 726.23 and 775.60 $\mathrm{kg \cdot m^{-3}}$ together with values calculated with IUPAC [23] and Polt et al. [38] equations of state. Comparisons of the measured values of the isochoric heat capacity C_V for pure methanol along two quasi-isochores 699.3 and 745.7 $\mathrm{kg \cdot m^{-3}}$ with values reported by Polikhronidi et al. [5] are shown in Fig. 6. This figure also contains the values of C_V calculated from IUPAC [23], Machado and Streett [30], and Polt et al. [38] equations of state. As one can see from Figs. 5 and 6, the present C_V data show satisfactory agreement with data reported by Polikhronidi et al. [5] and those calculated with the IUPAC [23] equation of state. The data reported by Polikhronidi et al. [5] for the isochore of 745.7 $\mathrm{kg \cdot m^{-3}}$ are systematically larger by 4% than the present results while the values of C_V calculated with the IUPAC [23] equation of state show deviations of less than 2%. The systematic character of the deviations between the present and Polikhronidi et al. [5] data can be explained by the uncertainty of the empty calorimeter heat capacity C_0 in the experiment reported by

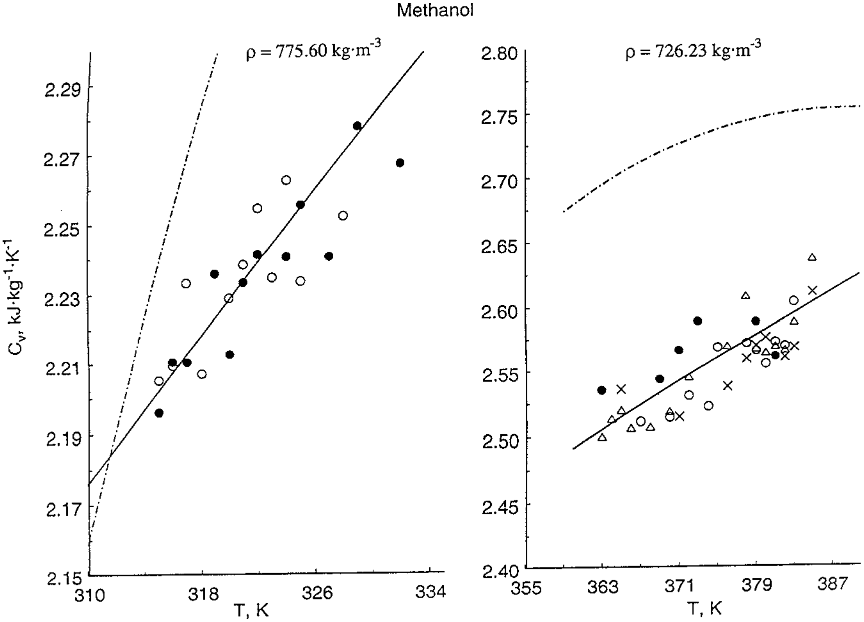

Fig. 5. Measured heat capacities C_V of liquid methanol as a function of temperatures along two quasi-isochores together with values calculated with IUPAC [23] equation of state. **775.6 kg·m^{-3}**: ●, Run-1; ○, Run-2; ——, IUPAC [23]; **726.2 kg·m^{-3}**: ●, Run-1; ○, Run-2; △, Run-3; ×, Run-4; –·–·–, Polt et al. [38].

Polikhronidi et al. [5]. Acceptable agreement (within 3%) between the present results and the data reported by Polikhronidi et al. [5] is found for the isochore of 699.3 kg·m^{-3} while the values of C_V calculated with the IUPAC [23] equation of state show nonsystematic deviations within 1% (maximum deviation is 2%). A deviation plot for the present C_V measurements is shown in Fig. 7. One can see from Fig. 7 that the measured values of heat capacity show nonsystematic deviations within their experimental uncertainty. Deviation statistics for the measured values of heat capacity are as follows ($N = 180$): AAD = 0.95%, bias = 0.02%, SD = 1.12%, SE = 0.09%, and maximum deviation = 2.5%.

5. CONCLUSIONS

By means of a twin-bomb calorimeter, isochoric heat capacities and densities of liquid methanol were measured in the range of temperature from 314 to 411 K, densities between 699.3 and 775.6 kg·m^{-3}, and pressures up to 20 MPa with an estimated uncertainty of 2% for heat capacity

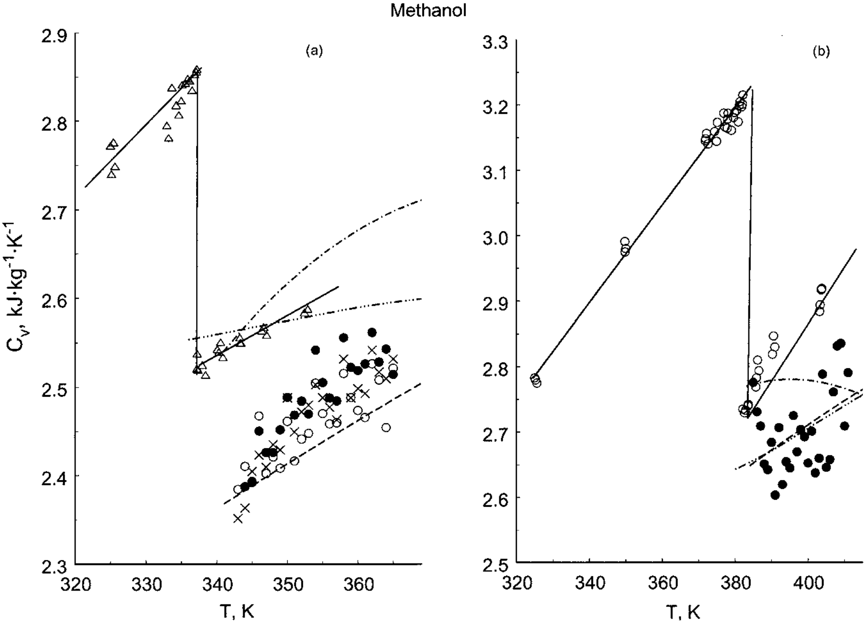

Fig. 6. Comparison of measured heat capacity C_V data for methanol with values calculated from the IUPAC [23] equation of state and values reported by Polikhronidi et al. [5] - - - - -, IUPAC [23]; —···—···—, Machado and Streett [30]; —·—·—, Polt et al. [38]; (a) **745.7 kg·m^{-3}**: ●, Run-1 (this work); ○, Run-2 (this work); ×, Run-3 (this work); △, **750.1 kg·m^{-3}** (Polikhronidi et al. [5]); (b) ●, **699.3 kg·m^{-3}** (this work); ○, (Polikhronidi et al. [5]). Solid lines are guides for the eye.

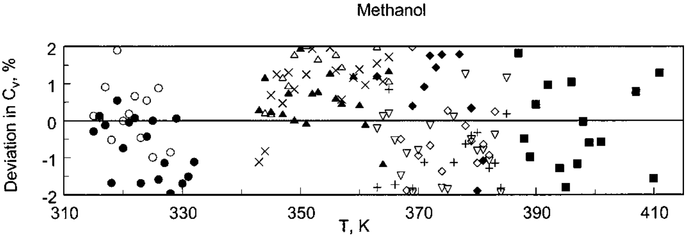

Fig. 7. Percentage heat capacity deviations, $\delta C_V = 100((C_{V_{\mathrm{exp}}} - C_{V_{\mathrm{cal}}})/C_{V_{\mathrm{exp}}})$, of the experimental heat capacity for pure methanol from values calculated with IUPAC [23] equation of state. **Run-1**: ●, 775.6 kg·m^{-3}; ▲, 745.7 kg·m^{-3}; ◆, 726.2 kg·m^{-3}; ■, 699.3 kg·m^{-3}; **Run-2**: ○, 775.6 kg·m^{-3}; △, 745.7 kg·m^{-3}; ◇, 726.2 kg·m^{-3}; **Run-3**: ×, 745.7 kg·m^{-3}; +, 726.2 kg·m^{-3}; **Run-4**: ▽, 726.2 kg·m^{-3}.

and 0.2% for density. All of the measured values of density and isochoric heat capacity show good agreement within 0.088% for density and 0.950% for heat capacity with calculations by the IUPAC [23] equation of state. Values of vapor pressure and saturated liquid densities were determined by extrapolating experimental *P–T* data to the saturated temperature along an isochore. Effects of decomposition of methanol on density and heat capacity measurements in the measured temperature (up to 411 K) and pressure (20 MPa) ranges were not observed.

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