Isobaric heat capacity (C_p) measurements of supercritical fluids using flow calorimetry: equipment design and experimental validation with carbon dioxide, methanol, and carbon-dioxide-methanol mixtures

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Abstract

Accurate thermodynamic property data of dense fluids and supercritical fluids are important in many scientific investigations and engineering applications. A flow calorimeter has been constructed to measure the isobaric heat capacity of pure fluids and fluid mixtures over a range of temperatures, 25–150 °C, and pressures, 1–300 bar. Base measurement accuracy approaches $\pm 1\%$ and is limited by precise equipment calibration and refinement of the measurement technique. Validation of the calorimeter's operation was achieved with supercritical carbon dioxide, methanol, and carbon-dioxide-methanol mixtures, over a range of conditions from sub-critical to supercritical temperatures and densities, demonstrating the calorimeter's robustness.

1.

Introduction

Accurate prediction of thermodynamic properties is essential to creating innovative products, developing new processes, and optimizing current operations. Equations of state (EOS), frequently used to calculate the thermodynamic properties of fluids, are typically fit by regressing a particular model to experimental data. The accuracy and range of a given EOS, whether it is specific to a single fluid or a particular set of similar fluids, depends on the measured experimental properties on which it was built. In order to reliably predict properties, accurate experimental data are needed over a broad range of temperatures and pressures for pure fluids and fluid mixtures. Predictive accuracy of fluid properties is compromised when

property data are sparse (e.g. for many fluid mixtures) or the thermophysical behavior of the fluid is difficult to measure (e.g. near a fluid's critical point). In addition, experimental data can provide insight into fluids' inter- and intramolecular interactions [1] and the extension of a pseudo-liquid-vapor equilibrium curve into the supercritical region [2,3]. To validate and improve EOSs and other empirically based correlations as well as further scientific understanding of the thermophysical behavior of supercritical fluids and fluid mixtures, accurate experimental measurements of thermodynamic properties are required for dense fluid mixtures over a range of temperatures and pressures.

Continual expansion of the thermodynamic library of data is driven by the persistent progress of science and engineering to ever more challenging process conditions and constraints. Supercritical fluid extractions commonly use co-solvents, such as light hydrocarbons or alcohols, to increase extraction efficiency [4,5]. Deep subsurface conditions, like those encountered in oil and gas reservoirs, involve complex multi-component fluids at high temperatures and pressures. Other subsurface engineering applications such as carbon sequestration and geothermal power production, which includes deep hydrothermal and Enhanced Geothermal Systems (EGS), provide additional motivation for thermophysical property characterization at supercritical conditions. As one last example, refrigeration and power generation cycles that utilize mixtures of hydrocarbons and refrigerants as working fluids to improve energy conversion efficiency require accurate EOS models for process design and simulation.

Among the experimentally accessible thermodynamic properties, the direct measurement of isobaric heat capacity (C_p) is of particular importance because of its characteristic description of many practical engineering heat exchange processes. The three predominate calorimetric methods for measuring a dense fluid's C_p are Calvet calorimetry [6,7], Workman calorimetry [8–10], and flow calorimetry [11–15]. Calvet calorimeters offer the advantage of an accurate differential measurement of heat capacity to a known standard, while their shortcomings include a conversion from volumetric to massic heat capacity and an inevitable loss of fluid from the measurement cell when operated in a constant pressure mode. The

Workman calorimeter measures the ratio of C_p at the condition of interest to C_p^* at a known, typically ideal, condition. By measuring a heat capacity ratio, Workman calorimetry offers an advantage by eliminating the necessity of a mass or volumetric flow rate measurement. However, accurate knowledge of the measured fluid's heat capacity at a reference condition limits this method's effectiveness for fluid mixtures and less common pure fluids.

Flow calorimetry involves pumping fluid at a constant rate through a length of tubing at a specified temperature and pressure, delivering a known amount of thermal energy to that fluid, and measuring the resulting temperature rise. As implemented by Ernst and his co-workers [16,17] and many other researchers [18–24], flow calorimetry is deployed as a robust absolute measurement of heat capacity, as opposed to the aforementioned measurement techniques which reference a standard. The flexibility of the method necessitates additional measurements (particularly mass flow rate) and special attention to heat loss issues. It is worth noting that other types of flow calorimeters which do not employ absolute measurement techniques exist and include devices like the Picker flow calorimeter [25] which uses a differential technique particularly well-suited for electrolyte mixtures.

This study focused on equipment design, construction of the calorimeter, and development of the measurement procedure. The calorimeter's accuracy is demonstrated for fluids and fluid mixtures over a wide range of temperatures (25–150 °C), pressures (1–300 bar), and densities (2–800 kg/m³). The basic accuracy of the calorimeter is estimated to be $\pm 1\%$. A detailed description of the apparatus design and typical operating procedures follows. Measurements validating the operation of the calorimeter were done on pure carbon dioxide, pure methanol, and low mole fraction (1.27% and 1.42%) methanol in carbon dioxide mixtures.

2.

Experimental Method

2.1

Calorimeter operating principles

A flow calorimeter at steady state operating conditions approximates the thermodynamic definition of isobaric heat capacity (C_p) by replacing differential quantities with finite differences, as shown in Equation (1).

$$C_p(T, P, x) \equiv \left(\frac{\partial H}{\partial T} \right)_{P, x} \approx \frac{\dot{q}}{\dot{m} \Delta T} \Big|_{\text{low } \Delta P} \quad (1)$$

While maintaining a small pressure drop across the calorimeter, heat ($\dot{q}$) is continuously added to a fluid at steady mass flow ($\dot{m}$) passing through the calorimeter, and the resulting temperature rise (ΔT) is measured. Equation (1) conveys some of the challenges of flow calorimetry: for an accurate measurement, the heat loss must be nearly eliminated or accurately quantified, the fluid must be well-mixed and its mass flow rate needs to be measured accurately, the pressure drop across the calorimeter must be small in order to approximate the isobaric condition, and the loss in accuracy due to approximating differentials with finite quantities needs to be addressed. The following sections describe the design of the experimental apparatus and the measurement methodology used in this study.

2.2

Description of flow system

As shown in Figure 1, a dual syringe pump (1A) draws a compressible fluid, 99.99% pure CO_2 , from a gas cylinder (1B) and dispenses it through a check valve (1C) at a constant volumetric flow rate into one port of a mixing tee (1F). A second component, 99.9% pure methanol, enters through the other port of the mixing tee pumped by a reciprocating positive displacement pump (1E), also operating at constant volumetric flow rate. The mass flow rate of the incompressible fluid is measured using a scale (1D) and a stop watch. The fluid mixture, exiting the mixing tee, enters a Coriolis mass flow meter (1G) where the mixture flow rate is measured. Next, the fluid passes through three sections of tubing placed inside of a temperature controlled fluidized alumina bath (1J): a preheat section, the calorimeter assembly, and an

exhaust section. Preheat and exhaust tubing (1K and 1L) ensure temperature stability of the fluid at the inlet and outlet of the calorimeter assembly, and the thermal bath maintains a temperature stability of ± 0.1 °C.

The calorimeter assembly, schematically detailed in Figure 2, consists of a U-tube (2B) placed inside a vacuum chamber (2C) held at 0.05 mbar by a vacuum pump (1M). Two thermocouples (2A and 2I), placed at the inlet and outlet of the calorimeter, and a heating element (2F), near the bend of the U-tube, are kept in direct contact with the fluid being measured. A power supply provides electric current through insulated copper wires (2H) to the heating element made of Ni-Cr wire (2F). Pressure taps placed at the inlet and outlet of the calorimeter assembly are used to measure absolute pressure. A back pressure regulator (1O) controls and maintains the pressure in the flow system, and a series of pressure regulators (not shown) are used to let down the pressure before exhaust. Suppliers and model numbers for selected sub-components used in the flow calorimeter are listed in Table A of the appendix.

A number of design measures have been incorporated into the system to increase the calorimeter's accuracy and decrease the measurement time. Heat losses were reduced by simultaneously lowering the driving forces for heat transfer and increasing the thermal resistance [11,13]. Use of thin-walled (1.2 mm thickness) 6.35 mm outer diameter Inconel tubing in the calorimeter reduced both heat conduction along the fluid flow path and the measurement section's thermal inertia. The heating element, its connecting wires, and the thermocouples were placed in direct thermal contact with the fluid, decreasing heat loss and reducing the time needed to reach steady state during experiment typically to 1.5 minutes (a complete measurement takes 10 minutes). Convective heat losses from the calorimeter's U-tube were curtailed by encasing it in a vacuum chamber. To reduce heat losses by radiation, the flow tubing has been thoroughly polished. In addition, any residual heat losses from the calorimeter were compensated by placing it in a thermal bath held at the inlet temperature of the calorimeter, substantially lowering the thermal driving

force for conduction, convection, and radiation to produce nearly adiabatic conditions inside the calorimeter.

The fluid must be well mixed while maintaining a small pressure drop for Equation 1 to be valid. To assure efficient heat transfer between the heating element and the passing fluid, the bare Ni/Cr heater wire, shown inset in Figure 2, was wound in a coil to act as a turbulence promoter. The measurement section of tubing is short (0.4 m), and the consequential pressure drop, approximately 0.05 bar, is negligible.

2.3

Assessment of measurement uncertainty

The uncertainties of the constitutive measurements for calculating C_p are listed in Table 1 along with the uncertainty contributions from assigning a measured C_p value to a particular temperature, pressure, and composition.

To reduce the temperature measurement uncertainty, the thermocouple located at the inlet of the calorimeter was calibrated with a platinum resistance thermometer (PRT) standard. The total uncertainty in this absolute temperature measurement is listed in Table 1 and includes uncertainties in the following: the PRT's ice point calibration, conversion of the PRT's resistance signal to temperature, analog to digital signal conversion of the PRT signal, and the repeatability of the thermocouple measurement in comparison to the PRT standard.

The difference in the fluid's temperature as it passes through the calorimeter, denoted as ΔT in Equation (1), is defined as the temperature of the fluid exiting the calorimeter minus the temperature of the fluid at the entrance to the calorimeter. This quantity is continuously monitored over the course of a heat capacity measurement. Sources of error, such as the Joule-Thomson effect or any measurement offsets between the

thermocouples, are greatly reduced by comparing the temperature difference over two distinct periods of operation, when heat ($\dot{q}$) is being added and when it is not. Measurement of the temperature difference when heat is not being added to the fluid, termed a “blank experiment” by some authors [11], significantly reduces many potential systematic errors. The observed temperature inconsistency, listed in Table 1, refers to a repeated experimental observation; the temperature difference before heat ($\dot{q}$) was applied was regularly unequal to the temperature difference after the heater was again off. The most likely cause of this temperature difference inconsistency is temperature fluctuations within the fluidized alumina bath.

Based on repeated C_p measurements, an optimal induced temperature difference in the calorimeter was established to be 2.0–3.5 °C. This range represents a compromise between measurement uncertainty and resolution. The method of approximating the differential temperature increase with a finite temperature increase, as shown in Equation (1), results in an inherent error at conditions where C_p shows strong dependence on pressure, temperature, and composition. This systematic error is particularly large in the vicinity of a critical point, where physical properties show strong dependence on these variables. Depending on the sensitivity of the heat capacity function, one may incur significant errors by inducing too large a temperature change, as illustrated in Figure 3 for pure carbon dioxide.

A Coriolis mass flow meter was used to measure mass flow rate, eliminating the need for fluid density data. Accuracy specifications from the manufacturer were used and further in-house calibration was done to establish typical measurement drift. Mass flow rate of the fluid mixture’s less volatile component (methanol in this study) is taken by measuring the mass difference of the fluid reservoir with time.

The pressure transducer was installed as supplied from the manufacturer, with no further calibration done. The accuracy of the transducer includes additional uncertainty from analog to digital signal conversion.

The power supply to the heating element was calibrated with a highly accurate voltmeter. Uncertainty in the heater power, listed in Table 1, includes a correction for the additional resistance of the copper wire linking the power supply to the heating element.

As a next step, the overall uncertainty in measured heat capacity due to specifying a particular temperature, pressure, and composition was assessed. If a fluid's heat capacity is very sensitive to incremental changes in its temperature, pressure, and composition, the total C_p uncertainty will be heavily influenced by the uncertainty in these three variables. To quantify this effect, experimental data as well as three different EOS models were used to evaluate the following partial derivatives for carbon dioxide, methanol, and carbon dioxide-methanol mixtures [26–28]:

$$\left(\frac{\partial C_p}{\partial T}\right)_{P, x}, \left(\frac{\partial C_p}{\partial P}\right)_{T, x}, \text{ and } \left(\frac{\partial C_p}{\partial x}\right)_{T, P} \quad (2)$$

Using these partial derivatives, all uncertainties in temperature, pressure, and composition have been converted into uncertainty in the measured heat capacity value. The partial derivatives in (2) were also used to shift the experimentally measured values to round values of temperature, pressure, and composition listed in Tables 2–4. The resulting shifts in the measured heat capacity values were insignificant when compared to the measurement uncertainty. Finally, in an effort to reduce the uncertainty from random noise, repeatability, and hysteresis, each experimental measurement was repeated at least twice and in the majority of cases, including all of the carbon dioxide measurements, three times.

To demonstrate that the calorimeter operated with negligible heat loss, heat capacity measurements of carbon dioxide were taken at a high temperature (150 °C) where the fluid's heat capacity is relatively low (1.64 J/gK) and the partial derivatives of C_p with respect to temperature and pressure are small. Keeping flow rate constant, different amounts of thermal energy were added to the fluid in order to vary the induced temperature rise. An increase in the observed heat capacity would indicate heat loss from the

calorimeter due to the increased temperature difference between the calorimeter and its surroundings. Figure 4 verifies the near adiabaticity of the calorimeter because the heat capacity measurement shows no perceivable dependence on the induced temperature difference.

3.

Results and discussion

The calorimeter's accuracy was verified with experimental measurements of both pure fluids and fluid mixtures. Carbon dioxide experiments were used to establish satisfactory measurement of the base quantities ($\dot{q}$, $\dot{n}$, ΔT , P , and T) because it is an extremely well characterized fluid [29]. Measurements of pure methanol, under fluid conditions very different from supercritical carbon dioxide, helped to demonstrate the calorimeter's versatility over a range of fluid densities. With regard to mixtures, the accuracy of controlling the fluid's composition (x) and its effect on measured heat capacity were determined by comparing our results to the literature C_p values of mixtures of methanol in carbon dioxide at low mole fractions of methanol [10].

3.1

Physical calibration of the calorimeter

Following the practice established by other researchers [30–33], after determining the optimal ranges of mass flow rate, induced temperature rise, and heater power, a physical calibration of calorimeter was performed. Physical calibration accounts for non-idealities and systematic experimental errors present within the calorimeter which have not been mitigated by careful equipment design and operating procedures. Calibration was done by comparing 34 heat capacity measurements of pure CO_2 at 150 °C and pressures between 100 and 300 bar to reference values calculated with the Span and Wagner EOS [26]. Span and Wagner report an accuracy of $\pm 0.6\%$ for C_p in this temperature and pressure region. Minimization of the absolute differences between experimental measurements and the EOS yielded a 1.3% correction factor. All the heat capacity values presented in this paper are 1.3% lower than the raw

experimental measurements. Subsequent sections will demonstrate that this 1.3% physical calibration factor is largely independent of the temperature, pressure, and density for carbon dioxide, methanol, and carbon dioxide-methanol mixtures. This work's calibration correction compares favorably with corrections of 2–15% reported by others [30–33].

3.2

Measurements of pure carbon dioxide and pure methanol

The isobaric heat capacity of pure carbon dioxide was measured along 60, 90, 120, and 150 °C isotherms for pressures ranging from 100 to 300 bar. The results are listed in Table 2 and plotted in Figure 5 using carbon dioxide's critical point (31 °C and 73.8 bar) to calculate reduced temperatures and pressures. The measurements of this study agree well with the high accuracy predictions of the Span & Wagner EOS [26] and experimental data collected by Ernst et al. [11], as indicated by mean percent differences of 0.2% and -0.1%, respectively. The Span and Wagner estimates are often taken as the standard reference values by numerous investigators [29]. In nearly all cases, this study's measurements, the measurements by Ernst et al., and calculations from the Span & Wagner EOS, are within the estimated uncertainty bounds listed in Table 2. Measured heat capacity along the 60 °C isotherm tended to be larger than the associated literature values, while at 120 °C the measurements fell below the literature results. The small positive and negative deviations between our results and the literature standards at these isotherms can likely be ascribed to random errors such as measurement drift or slight inaccuracies in calibration. The 60 °C isotherm corresponds to a reduced temperature of 1.1 for CO₂, proving this apparatus's ability to make accurate measurements proximate to the critical point, where C_p maxima are large.

Heat capacity measurements of pure methanol (T_c = 239.5 °C, P_c = 81 bar) in both liquid and vapor states at 150 °C are listed in Table 3 and plotted in Figure 6. In the liquid state, this work's measurements agree to within 2% of the EOS predictions [27,34]. Previous heat capacity measurements of liquid methanol at high temperature [35] show large discrepancies with the EOS predictions, where the EOS is 8% lower on

average than the measured values. Given the uncertainty allocation for the methanol EOS in this region, this work's measurements fit the EOS predictions well and represent an improvement to previous high temperature, high pressure heat capacity measurements of pure methanol. Methanol's heat capacity in the vapor state is more accurately quantified by the EOS, to within 1%. The C_p measurements in this study are 1% lower than the calculated methanol vapor C_p , which is within the 1.2% experimental uncertainty. The measurements for methanol conducted in this study confirm the accuracy of calorimeter across a broad range of fluid densities (2 - 660 kg/m³).

3.3

Comparative measurements of low mole fraction methanol mixtures in carbon dioxide

Table 4 and Figure 7 compare the results of this work to the measurements made by Boulton and Stein on low mole fraction methanol in carbon dioxide mixtures [10]. Reduced temperatures and pressures were not calculated for these mixtures due to the inconsistency of mixture critical points reported in the literature [36–38]. The uncertainty in composition is estimated to be $\pm 4\%$ of the methanol mole fraction. This somewhat large compositional uncertainty is due to the low methanol flowrate. The GERG-2008 EOS model results are presented as a comparison because of the applicability of this EOS for CO₂ and existing mixing rules. Fitting of the GERG-2008 model to methanol-carbon dioxide data has occurred [28,34,39]. Measured C_p values agree favorably with reported values from Boulton and Stein. The measurement at 1.42% methanol, 50 °C, and 73 bar shows the largest deviation but still falls within the experimental uncertainty. Boulton and Stein's claimed uncertainties are shown in Figure 7. We believe it is exceedingly likely that in this near critical region, where the isobaric heat capacity strongly fluctuates with small changes in temperature, pressure/density, and composition, that their uncertainties should be increased beyond their $\pm 1\%$ estimate. In any case, the results of this study as well as those by Boulton and Stein agree to within their respective uncertainties.

4.

Conclusions

Successful operation of flow calorimeters over a wide range of densities, compressibilities, and viscosities is often a challenge due to variations in flow regimes, potential heat loss issues, and pressure drop difficulties. After careful design, construction, and calibration, the flow calorimeter detailed in this study achieved $\pm 1\%$ accuracy at temperatures from 25 to 150 °C and pressures from 1 to 300 bar in the vapor, dense liquid, and supercritical fluid regions for carbon dioxide, methanol, and carbon dioxide methanol mixtures. The experimental measurements presented here agree with the measurements made by Ernst et al. and Boulton and Stein for pure carbon dioxide and carbon dioxide-methanol mixtures, respectively [10,11]. The extensive range of operating conditions and high accuracy of the calorimeter along with its flexibility for studying both pure fluids and mixtures make it a valuable tool for thermophysical property characterization of fluids at supercritical conditions.

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List of Tables:

Measured			Range
Property	Property Range	Uncertainty contributions	uncertainty
Temperature	25–150 °C	Platinum resistance thermometer (PRT) standard	± 0.05 °C
		Thermocouple stability and repeatability	± 0.05 °C
Differential temperature	2.0–3.5 °C	Observed inconsistency in the average temperature difference	± 0.006 °C
Total mass flow rate	10–19 g/min	Coriolis mass flow meter accuracy	± 0.05 g/min
		Signal drift for a constant flow rate	± 0.05 g/min
Methanol mass flow rate	0.1– 0.15 g/min	Mass change measurement of the fluid reservoir	± 0.04 g
		Stopwatch accuracy	± 0.05 s
Pressure	1–300 bar	Accuracy and repeatability of pressure transducer	± 0.4 bar
Heater power	1.1–2.2 W	Accuracy and stability of applied power	± 0.002 W

Table 1. The experimentally accessible properties required for a flow calorimetric determination of isobaric heat capacity. Contribution of each measured property to the overall measurement uncertainty is provided.

Pure CO ₂				
P [bar]	C _p [J/gK] This Study	Estimated	Comparison	
		Uncertainty δ [%]	100 (C _{p,lit} - C _p)/C _p	
			Ernst et al.	Span and Wagner EOS
T = 60 °C (333.15 K)				
100	3.09	2.4	-0.3	-1.7
110	3.89	2.5	0.8	-0.8
120	4.39	1.8	0.9	0.2
130	4.26	1.5	-0.4	0.0
140	3.84	1.6	-0.5	-0.2
150	3.44	1.4	-0.1	-0.2
175	2.85	1.3	-0.6	-0.8
200	2.53	1.1	-1.5	-1.0
300	2.02	1.2	-1.3	-0.6
T = 90 °C (363.15 K)				
100	1.65	1.4	0.3	-0.1
125	2.06	1.6	0.3	-0.3
150	2.44	1.6	0.4	-0.2
175	2.58	1.4	0.4	0.0
189	2.55	1.4	-	0.1
200	2.52	1.3	-0.4	-0.5
225	2.38	1.3	0.7	-0.2
249	2.25	1.3	0.8	0.0
300	2.05	1.2	0.6	0.3
T = 120 °C (393.15 K)				

100	1.37	1.1	0.0	0.1
150	1.71	1.3	1.2	0.6
200	1.97	1.2	1.4	0.9
250	2.01	1.1	0.9	0.9
300	1.95	1.1	0.8	0.7
T = 150 °C (423.15 K)				
100	1.26	1.0	-	-0.4
150	1.46	1.1	-	-0.2
200	1.64	1.0	-	-0.1
250	1.74	1.1	-	0.7
300	1.77	1.0	-	0.4

Table 2. Measured isobaric heat capacity values (C_p) of pure carbon dioxide from 60–150 °C and 100–300 bar. The overall uncertainty (δ) is presented as a percentage of the measured heat capacity. Presented as percent differences, the measurements made in this work are compared to the experimental measurements made by Ernst et al. and the Span and Wagner EOS ($C_{p,lit}$) [11,26].

Pure Methanol			
P [bar]	This Work	Estimated	Comparison
	C_p [J/gK]	Uncertainty δ [%]	$100 (C_{p, \text{lit}} - C_p)/C_p$ De Reuck & Craven EOS
T = 150 °C (423.15 K)			
2	1.80	1.3	-1.0
40	3.71	1.3	1.9
70	3.69	1.3	1.1

Table 3. Measured isobaric heat capacity (C_p) of pure liquid and vapor methanol at 150 °C. The overall uncertainty (δ) is listed as a percentage of the measured heat capacity. The measurements made in this work are compared to the De Reuck and Craven EOS for methanol ($C_{p, \text{lit}}$) [27].

Low Mole Fraction Methanol-CO ₂ Mixtures				
P [bar]	This Work C _p [J/gK]	Estimated	Comparison	
		Uncertainty δ [%]	100 (C _{p,lit} - C _p)/C _p	
			Boulton & Stein	GERG-2008
T = 50 °C (323.15 K), x = 1.42% Methanol in CO ₂				
66	1.92	2.0	1.0	-1.0
73	2.24	2.5	3.3	2.1
82	3.11	3.6	-1.3	2.4
T = 55 °C (328.15 K), x = 1.27% Methanol in CO ₂				
65	1.71	1.8	-0.9	-1.0
72	1.96	2.2	-0.7	0.3
82	2.51	2.8	-2.2	1.0

Table 4. Measured isobaric heat capacity (C_p) of low mole fraction methanol-carbon dioxide mixtures at two isotherms. The overall uncertainty (δ) is listed as a percentage of the heat capacity. The measurements made in this work are compared to the measurements of Boulton and Stein and the GERG-2008 EOS (C_{p,lit}) [10,28].

Appendix:

Table A. Selected sub-components used in the flow calorimeter

Component name	Supplier and model
Dual syringe pump (CO ₂)	Teledyne ISCO 100DX, controller, and temperature control jackets cooled using refrigeration system
HPLC pump (methanol)	Agilent 218 solvent delivery pump
Coriolis mass flow meter	GE Rheonik RHM 015
Alumina bath	Techne SBL-2D with TC-9D controller
Thermocouples	E-type, 1/16", Omega
Vacuum pump	Oerlikon Leybold
Power supply	Tektronix PWS4305
Scale (methanol)	Mettler Toledo
Back pressure regulator	Equilibar EB1
Heating element	34 AWG bar Ni/Cr wire wound around 0.4 mm hollow alumina tube
Wires powering heating element	18 AWG copper wires, 0.007" insulation
Flow tubing	Inconel, 1/4" tubing with 0.049" wall thickness

Figure 1. Process flow diagram of the calorimeter system. Dual syringe pump and controller (A), gas cylinder (B), check valve (C), mass balance (D), high pressure liquid chromatography (HPLC) pump (E), mixing tee (F), coriolis mass flow meter (G), measurement conversion box (H), analog to digital conversion box (I), fluidized alumina sand bath (J), vacuum pump (M), thermal equilibration tubing (K and L), exhaust heat exchanger (N), and back pressure regulator (O).

Calorimeter detail

Figure 2. Schematic of the calorimeter assembly. Vacuum chamber, 6.35 cm OD (C), flow tubing, 0.64 cm OD (B), thermocouples (A and I), heating element/Ni-Cr resistor (F), ceramic insulation (G), 18 AWG copper wires attached to the heating element (H), inlet and outlet thermal equilibration tubing, 0.32 cm OD (D and J respectively), crosses at the fluid inlet (E) and outlet (K), power supply (L, placed outside the heated bath). **Inset:** The custom-made Ni-Cr heating element (F).

Systematic Cp Errors

Figure 3. Calculated systematic errors in heat capacity, shown as a percent error, due to replacement of a differential temperature rise with a finite temperature rise (Equation 1), here $\Delta T = 4\text{ }^{\circ}\text{C}$. The Span and Wagner EOS [26,34] for carbon dioxide is treated as the true heat capacity function. Integral averages of heat capacity were calculated over the induced temperature rise and compared to the true heat capacity value at the average temperature. A temperature rise of $4\text{ }^{\circ}\text{C}$ was chosen based on existing calorimeters described in literature [11,40,41].

Figure 4. Isobaric heat capacity measurements of pure carbon dioxide taken at 150 °C and 200 bar as a function of the induced temperature difference. The y-axis is the percent deviation of a singular experimental measurement from the average value of all the measurements at this condition. The measurements shown here were taken at the same mass flow rate (10 g/min). With the induced temperature difference nearly doubled (4.4 °C compared to 2.5 °C), no appreciable change in the measured heat capacity was observed.

Reduced Pressure (P_r) [-]

2

3

4

Figure 5. Comparison of the measurements made in this work to reference values reported by Span and Wagner EOS [26]. The data agrees with the Span and Wagner EOS values within the specified measurement uncertainty. Experimental measurements made by Ernst et al. agree with the Span and Wagner EOS calculations in this supercritical region [11].

Reduced Pressure (P_r) [-]

Figure 6. Heat capacity measurements of pure methanol at 150 °C as a liquid, at approximately 40 bar and 70 bar, and as a vapor, at approximately 2 bar. The data agrees with the De Reuck and Craven EOS within the specified measurement uncertainty and the accuracy of the EOS [27].

Figure 7. Comparison of this study's measurements to Boulton and Stein's heat capacity measurements [10] of low mole fraction methanol in carbon dioxide. The GERG-2008 EOS is compared to both sets of measurements [28].

Reduced Pressure (P_r) [-]

2

3

4