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PVT Properties and Bubble Point Pressures for Compositionally Characterized Commercial Grade Butane, 2-Methylpropane, and Natural Gasoline

Chih-An Hwang, James C. Holste, and Kenneth R. Hall*

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

Bruce E. Gammon and Kenneth N. Marsh

Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843

William R. Parrish

Phillips Petroleum Company, Bartlesville, Oklahoma 74004

The *PVT* properties and bubble point pressures for compositionally characterized commercial grade samples of butane, 2-methylpropane, and natural gasoline have been measured using a continuously weighed pycnometer and a vibrating tube densimeter. The results cover the range of pressures from the bubble point to 9.7 MPa in the temperatures range from 255 K to 322 K. Experimental uncertainties are reported for the temperature, pressure, and density measurements. Measurements conducted at Texas A&M University and at Phillips Petroleum Co. agree within the estimated uncertainities of the two experimental methods.

Introduction

Experimental densities and bubble point pressures for compositionally characterized commercial grade samples of butane, 2-methylpropane, and a natural gasoline have been measured at pressures ranging from the bubble point to 9.7 MPa and at temperatures ranging between 255 K and 322 K. The measurements have been made independently, using two different experimental methods, at Texas A&M University and at Phillips Petroleum Co. as part of an effort to test American Petroleum Institute (API) procedures as discussed by Patterson (1991) for calculating compressibilities, coefficients of thermal expansion, and volume correction factors. These measured results are necessary for the metering and custody transfer of natural gas liquids. The measurements provide a direct comparison between the different experimental methods as well as an independent set of data to check values calculated using the COSTALD (corresponding states liquid density) correlation proposed by Hankinson and Thomson (1979) and Thomson *et al.* (1982).

Experimental Section

Materials. The Mid-America Pipeline Co. (MAPCO) supplied specification grade samples of butane, 2-methylpropane, and natural gasoline (shipped and stored in commercial piston samplers). The nitrogen backing pressures for these samples were butane, 3.2 MPa; 2-methylpropane, 2.9 MPa; and natural gasoline, 1.5 MPa. The samples were analyzed using gas chromatography following GPA standard 2177-84. The results of analyses determined at Texas A&M University, at Phillips Petroleum Co., and at MAPCO before and after the experimental measurements appear in Table 1.

Table 1. MAPCO Specification Grade Sample Composition in Mole Percent[a]

butane	N_2	C_3	iC_4	nC_4	iC_5	nC_5	
cylinder no. 2761							
MAPCO before	0.00	0.00	1.30	97.63	1.07	0.00	
A&M	0.00	0.00	1.33	97.62	1.05	0.00	
MAPCO after	0.00	0.00	1.31	97.65	1.04	0.00	
cylinder no. 2762							
MAPCO before	0.00	0.00	1.31	97.64	1.05	0.00	
Phillips before	0.00	0.00	1.33	97.27	1.33	0.07	
Phillips after	0.00	0.00	1.32	97.62	1.01	0.05	
MAPCO after	0.00	0.00	1.32	97.63	1.05	0.00	
2-methylpropane	N_2	C_3	iC_4	nC_4	iC_5	nC_5	
cylinder no. 2760							
MAPCO before	0.00	1.42	96.36	2.22	0.00	0.00	
A&M	0.00	1.46	96.25	2.29	0.00	0.00	
MAPCO after	0.00	1.44	96.35	2.21	0.00	0.00	
cylinder no. 2759							
MAPCO before	0.00	1.43	96.37	2.20	0.00	0.00	
Phillips before	0.00	1.13	96.66	2.21	0.00	0.00	
Phillips after	0.01	1.50	96.32	2.17	0.00	0.00	
MAPCO after	0.00	1.44	96.35	2.21	0.00	0.00	
gasoline	N_2	iC_4	nC_4	iC_5	nC_5	C_6	C_{7+}
cylinder no. 2762-S1							
MAPCO before	0.00	0.07	3.44	25.43	30.79	21.20	19.07
A&M	0.07	0.04	3.44	27.41	28.06	21.01	19.97
MAPCO after	0.00	0.05	3.44	25.29	30.66	21.37	19.19
cylinder no. 2762-S2							
MAPCO	0.03	0.05	3.48	25.24	30.61	21.37	19.22
cylinder no. 2759							
MAPCO before	0.09	0.07	3.44	25.41	30.76	21.18	19.05
Phillips	0.02	0.07	3.02	25.29	30.74	20.96	19.90
MAPCO after	0.09	0.08	3.43	25.32	30.65	21.29	19.14

[a] iC_4 = 2-methylpropane; nC_4 = butane; iC_5 = 2-methylbutane; C_6 = various C_6 isomers; C_{7+} = C_7 + higher isomers.

Apparatus. The Texas A&M density measurements were made using a pycnometer in which a cell of known volume is suspended from an electronic balance. Lau (1986) and Hwang *et al.* (1988) describe this continuously weighed pycnometer although some modifications have been made in configuration and method of operation for this work. Figure 1 is a cross-sectional diagram of the balance chamber and the isothermal bath. The pycnometer

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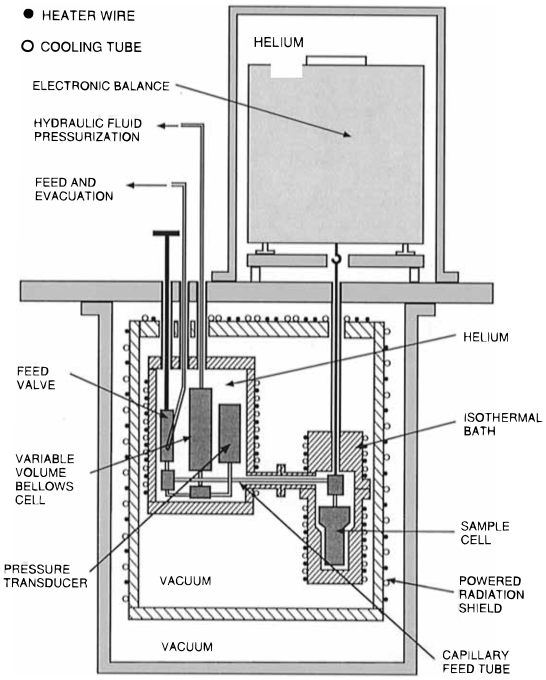

Figure 1. Schematic diagram of apparatus.

cell is filled and evacuated through a straight, stainless-steel capillary, which is attached to the cell along an axis at a right angle to the axis of the suspension wire leading to the balance. The entire balance and the pycnometer cell are totally immersed in helium at a controlled pressure to eliminate changes in buoyancy. Helium is used because of its high thermal conductivity and low density. The sample densities result from the measured masses and the known volume of the pycnometer cell. Carbon dioxide and ethane calibrations established the pycnometer cell volume as a function of temperature and pressure before performing these measurements. After the measurements reported here were completed, carbon dioxide and water were used to redetermine the cell volume.

The apparatus utilized a 500 g capacity, electronic balance capable of a precision of 0.1 mg, which maintained vertical position to within 1 μm during the weighing operations. Pressures were measured with a Rosemount (model 1333G10) strain-gauge pressure transducer above 1.4 MPa and with a Ruska (type XR-38) pressure counter (for butane and 2-methylpropane density measurements) or a T-Hydronics (model TH-1) pressure transducer (for natural gasoline density measurements) below 1.4 MPa. All the pressure measuring devices were calibrated against a DH Instruments (type 26000) automatic pressure standard (dead-weight gauge). A Paroscientific (model 700) Digiquartz pressure transducer, located inside the isothermal bath, provided vapor pressure measurements that were below the room temperature vapor pressure of the samples; this transducer was calibrated *in situ* on each isotherm with the Ruska pressure counter or the T-Hydronics pressure transducer. Temperatures were measured with a four-lead platinum resistance thermometer (PRT) (MINCO model S1059PA5X10) placed adjacent to the pycnometer cell on the inside surface of a copper compartment used for controlling the temperature of the pycnometer cell. Previous measurements showed that the temperature gradients across the pycnometer cell were less than 5 mK and that the difference between the pycnometer cell temperature and the PRT was less than 5 mK. The characteristic constants of the PRT were determined by the manufacturer with an NBS-traceable calibration, and the ice point resistance was determined locally with the same circuit used for the temperature measurements.

The density data from Phillips Petroleum Co. were measured with a Mettler-Paar DMA 512 vibrating tube densimeter. Parrish (1986) provides complete system details and only a brief description is presented here. The measurement system consists of the densimeter, a 100 cm^3 positive displacement pump, and a magnetically-driven mixing pump immersed in a constant temperature bath held constant to ±0.01 K. A calibrated quartz thermometer measures the bath temperature. Estimated uncertainty in the reported temperatures is ±0.1 K.

The system pressure is taken as the pressure required to null a differential pressure gauge having a resolution of 35 Pa. The nulling pressure is measured using a 0−13 MPa quartz bourdon gauge calibrated against an oil dead weight gauge. Estimated total uncertainty in the pressure is ±13 kPa.

The vibrating tube densimeter required two calibration fluids. For this work Pure Grade argon (99.998% minumum) and Phillips Research Grade butane with a stated minimum purity of 99.9 mol % were used. The argon did not require additional purification, but the butane was subjected to two low-pressure flashes to remove any dissolved air. Calibrations were made at each temperature and pressure measured.

Procedures. At Texas A&M, the sample handling procedure for density measurements was as follows. After establishing the selected temperature of the isothermal bath containing the evacuated cell, the pycnometer cell and sample charging lines were flushed with butane vapor to ensure that the last traces of light gases were purged from the system (the lines were not flushed with the natural gasoline vapor because heavy hydrocarbons might have condensed in the charging lines). The pycnometer cell was then filled with liquid from the piston sampler in which the sample was shipped. Several cycles of compression of the sample to 9.7 MPa and the decompression to the pressure of filling were made with a screw pump to ensure that any heavy components condensed in the sample charging lines were forced into the pycnometer cell. The density measurements were made in a series of decreasing pressures; usually, decompression of the samples was effected with a screw pump. For pressures below the room temperature vapor pressure of the sample, the sample was isolated with a feed valve and decompressed with a variable volume bellows cell, and the pressures were measured with the Paroscientific pressure transducer. The bellows cell, feed valve, and the Paroscientific pressure transducer were housed in another copper compartment controlled at the same temperature as the pycnometer cell.

The values of the vapor pressures were determined after the density measurements were completed for each isotherm. The bellows cell was expanded to permit a vapor bubble of about 1 cm^3 to form in the presence of 12 cm^3 of liquid within the pycnometer and bellows cell. The vapor pressures were less precise than pressures for the rest of the measurements because the two-phase fluid present in the Paroscientific pressure transducer diminished its performance. For every isotherm, the liquid was expanded metastably to pressures below the vapor pressure, and the vapor bubble was formed by cycling the pressure in this metastable region or by slightly opening and closing the feed valve to initiate nucleation. This expansion indicated no insoluble gas in the samples because the presence of an insoluble gas would have provided a nucleation site for the vapor to form and have prevented metastable expansion of the liquid.

Table 2. Pycnometer Densities at Experimental Pressures for Commercial Grade Butane[a]

273.15 K		288.71 K		305.37 K		322.04 K	
P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}
0.1048[b]	0.601 83[c]	0.1806[b]	0.584 30[c]	0.6020[b]	0.564 83[c]	0.4813[b]	0.543 43[c]
0.1418	0.601 95	0.2435	0.584 39	0.3468	0.564 90	0.5515	0.543 76
0.2087	0.602 04	0.2780	0.584 44	0.4158	0.565 02	0.5860	0.543 93
0.2760	0.602 07	0.3469	0.584 53	0.4847	0.564 14	0.6205	0.544 05
0.3449	0.602 13	0.4159	0.584 69	0.5537	0.565 30	0.6894	0.544 32
0.6897	0.602 57	0.6917	0.585 10	0.6916	0.565 54	1.3789	0.546 13
1.3798	0.603 41	1.3818	0.586 17	1.3811	0.566 82	2.7579	0.549 25
2.7588	0.605 11	2.7601	0.588 19	2.7600	0.569 24	4.1375	0.552 22
4.1370	0.606 78	4.1391	0.590 16	4.1390	0.571 67	5.5165	0.554 97
5.5460	0.608 39	5.5187	0.592 05	5.5173	0.573 96	6.8948	0.557 63
6.8957	0.609 96	6.8977	0.593 92	6.8969	0.576 16	8.2730	0.560 15
8.2732	0.611 52	8.2752	0.595 69	8.2759	0.578 28	9.6520	0.562 55
9.6536	0.612 98	9.6549	0.597 43	9.6548	0.580 34		

[a] Measurement precision (68% confidence limits): $\sigma_i(T) = 0.002$ K, $\sigma_i(P) = 0.0001P + 0.069$ kPa, $\sigma_i(\rho) = 0.05$ g·cm^{-3}. Estimated accuracies in measurements (68% confidence limits): $\sigma_a(T) = 0.01$ K, $\sigma_a(P) = 0.0003P + 0.069$ kPa, $\sigma_a(\rho) = 0.0004\rho + 0.05$ g·cm^{-3}. [b] Saturated vapor pressure; precision 0.7 kPa. [c] Extrapolated saturated density.

Table 3. Pycnometer Densities at Experimental Pressures for Commercial Grade 2-Methylpropane[a]

273.15 K		288.71 K		305.37 K		322.04 K	
P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}
0.1655[b]	0.580 26[c]	0.2792[b]	0.562 51[c]	0.4426[b]	0.541 31[c]	0.6771[b]	0.518 82[c]
0.2086	0.580 41	0.3448	0.562 63	0.5171	0.541 52	0.7583	0.519 08
0.2783	0.580 67	0.4137	0.562 76	0.5515	0.541 63	0.8272	0.519 31
0.3448	0.580 99	0.4827	0.562 90	0.6205	0.541 78	0.8962	0.519 53
0.5517	0.581 28	0.6206	0.563 11	0.6894	0.541 91	1.0341	0.519 99
0.6896	0.581 47	0.6895	0.563 24	1.3789	0.543 51	1.3788	0.521 09
1.3797	0.582 53	1.3797	0.564 52	2.7579	0.546 52	2.7585	0.525 01
2.7587	0.584 51	2.7586	0.566 90	4.1368	0.549 40	4.1374	0.528 64
4.1370	0.586 46	4.1376	0.569 24	5.5158	0.552 21	5.5164	0.532 06
5.5159	0.588 41	5.5152	0.571 48	6.8954	0.554 82	6.8961	0.535 29
6.8949	0.590 18	6.8948	0.573 64	8.2737	0.557 30	8.2730	0.538 37
8.2738	0.591 96	8.2745	0.575 68	9.6534	0.559 69	9.6526	0.541 24
9.6528	0.593 65	9.6527	0.577 68				

[a] Measurement precision (68% confidence limits): $\sigma_i(T) = 0.002$ K, $\sigma_i(P) = 0.0001P + 0.069$ kPa, $\sigma_i(\rho) = 0.05$ g·cm^{-3}. Estimated accuracies in measurements (68% confidence limits): $\sigma_a(T) = 0.01$ K, $\sigma_a(P) = 0.0003P + 0.069$ kPa, $\sigma_a(\rho) = 0.0004\rho + 0.05$ g·cm^{-3}. [b] Saturated vapor pressure; precision 0.7 kPa. [c] Extrapolated saturated density.

Table 4. Pycnometer Densities at Experimental Pressures for MAPCO M-Grade Natural Gasoline[a]

255.37 K		273.15 K		288.71 K		299.82 K		310.93 K		322.04 K	
P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}	P/MPa	ρ/g·cm^{-3}
0.0116[b]	0.689 60[c]	0.0250[b]	0.673 63[c]	0.0469[b]	0.659 42[c]	0.0674[b]	0.649 10[c]	0.0958[b]	0.638 67[c]	0.1259[b]	0.628 06[c]
0.0364	0.689 63	0.371	0.673 64	0.0725	0.659 46	0.1058	0.649 15	0.1403	0.638 73	0.1747	0.628 13
0.0708	0.689 66	0.0716	0.673 70	0.1403	0.659 52	0.1403	0.649 21	0.2092	0.638 81	0.2092	0.628 20
0.1405	0.689 71	0.1404	0.673 76	0.2093	0.659 59	0.2093	0.649 33	0.2782	0.638 88	0.2781	0.628 31
0.3473	0.689 88	0.3472	0.673 97	0.3472	0.659 75	0.3472	0.649 51	0.3471	0.638 98	0.3471	0.628 42
0.6920	0.690 15	0.6920	0.674 29	0.6919	0.660 10	0.6919	0.649 94	0.6919	0.639 47	0.6918	0.628 94
1.3795	0.690 70	1.3808	0.674 92	1.3800	0.690 84	1.3800	0.650 74	1.3806	0.640 36	1.3806	0.629 94
2.7598	0.691 83	2.7590	0.676 16	2.7583	0.662 31	2.7583	0.652 40	2.7596	0.642 20	2.7589	0.631 94
4.1387	0.692 89	4.1380	0.677 46	4.1386	0.663 77	4.1386	0.653 93	4.1372	0.643 97	4.1378	0.633 87
5.5177	0.693 97	5.5176	0.678 70	5.5162	0.665 10	5.5162	0.655 46	5.5175	0.645 64	5.5175	0.635 71
6.8973	0.695 02	6.8952	0.679 91	6.8959	0.666 47	6.8965	0.656 93	6.8951	0.647 28	6.8957	0.637 52
8.2756	0.696 04	8.2742	0.681 06	8.2748	0.667 81	8.2748	0.658 37	8.2747	0.648 88	8.2747	0.639 31
9.6546	0.697 04	9.6531	0.682 17	9.6531	0.669 09	9.6530	0.659 84	9.6537	0.650 42	9.6537	0.641 00

[a] Measurement precision (68% confidence limits): $\sigma_i(T) = 0.002$ K, $\sigma_i(P) = 0.0001P + 0.069$ kPa, $\sigma_i(\rho) = 0.05$ g·cm^{-3}. Estimated accuracies in measurements (68% confidence limits): $\sigma_a(T) = 0.01$ K, $\sigma_a(P) = 0.0003P + 0.069$ kPa, $\sigma_a(\rho) = 0.0004\rho + 0.05$ g·cm^{-3}. [b] Saturated vapor pressure; precision 0.34 kPa. [c] Extrapolated saturated density.

For the natural gasoline sample, the density at 0.17 MPa was determined at 335 K in measurements associated with removing the sample before starting a new isotherm. The gasoline was pumped out; the pycnometer cell and charging lines were then flushed two or three times with petroleum ether. The mass of the cell filled with fluid at a pressure of about 0.17 MPa and the mass of the evacuated cell were recorded for monitoring the condition of the sample. The condition of 335 K and 0.17 MPa was common to all sample fillings; and the mass difference between the filled and evacuated cell provided a consistency test for the samples charged.

For the Phillips Petroleum measurements the samples were introduced into the previously evacuated densimeter system. The positive displacement pump compressed the sample well above its bubble point. The mixing pump then homogenized the sample. Complete sample mixing required 60 to 90 min, as indicated by the density becoming constant. At this time, the mixing pump was turned off and the desired pressure was set by adjusting the positive

Table 5. Comparison of Densities of Commercial Grade Butane

		ρ/g·cm^{-3}			
T/K	P/MPa	COSTALD (CO)	vib tube (VT)	pycn (PY)	$100(\rho_{PY} - \rho_{VT})/\rho_{CO}$
273.15	0.1379	0.6015	0.6011	0.6020	0.14
	0.2068	0.6016	0.6012	0.6020	0.13
	0.2758	0.6017	0.6013	0.3021	0.13
	0.3447	0.6018	0.6014	0.6021	0.12
	0.6895	0.6023	0.6019	0.6026	0.12
	1.3788	0.6033	0.6028	0.6034	0.10
	2.7579	0.6054	0.6045	0.6051	0.10
	4.1369	0.6073	0.6062	0.6068	0.10
	5.5158	0.6093	0.6079	0.6084	0.08
	6.8948	0.6111	0.6095	0.6100	0.08
	8.2737	0.6129	0.6111	0.6115	0.07
	9.6527	0.6147	0.6126	0.6130	0.07
288.71	0.2413	0.5842	0.5841	0.5844	0.05
	0.2758	0.5842	0.5842	0.5844	0.03
	0.3447	0.5844	0.5843	0.5845	0.03
	0.4137	0.5845	0.5844	0.5847	0.05
	0.6895	0.5850	0.5848	0.5851	0.05
	1.3788	0.5862	0.5859	0.5862	0.05
	2.7579	0.5885	0.5880	0.5882	0.03
	4.1369	0.5908	0.5900	0.5902	0.03
	5.5158	0.5929	0.5919	0.5921	0.03
	6.8948	0.5950	0.5938	0.5939	0.02
	8.2737	0.5971	0.5956	0.5957	0.02
	9.6527	0.5991	0.5974	0.5974	0.00
305.37	0.3447	0.5646	0.5649	0.5649	0.00
	0.4137	0.5648	0.5651	0.5650	−0.02
	0.4826	0.5649	0.5652	0.5651	−0.02
	0.5516	0.5651	0.5654	0.5653	−0.02
	0.6895	0.5654	0.5656	0.5655	−0.02
	1.3788	0.5668	0.5669	0.5668	−0.02
	2.7579	0.5695	0.5694	0.5692	−0.03
	4.1369	0.5722	0.5718	0.5717	−0.02
	5.5158	0.5747	0.5741	0.5740	−0.02
	6.8948	0.5772	0.5763	0.5762	−0.02
	8.2737	0.5795	0.5784	0.5783	−0.02
	9.6527	0.5818	0.5805	0.5803	−0.03
322.04	0.5516	0.5439	0.5445	0.5438	−0.13
	0.5861	0.5440	0.5445	0.5439	−0.11
	0.6205	0.5441	0.5446	0.5441	−0.09
	0.6895	0.5443	0.5448	0.5443	−0.09
	1.3788	0.5460	0.5464	0.5461	−0.05
	2.7579	0.5494	0.5495	0.5493	−0.04
	4.1369	0.5525	0.5525	0.5522	−0.05
	5.5158	0.5556	0.5553	0.5550	−0.05
	6.8948	0.5584	0.5580	0.5576	−0.07
	8.2737	0.5612	0.5605	0.5602	−0.05
	9.6527	0.5639	0.5630	0.5626	−0.07

displacement pump. Normally, density stability required about 10 min after changes in pressure. Unlike the Texas A&M work, no attempt was made to determine the bubble point.

Experience showed that the densimeter calibration was constant over several days. Therefore, the densimeter was calibrated only before and after all samples were run at each given temperature. Parrish (1986) provides the equations for calculating the densities of the calibration fluids. Before injecting each sample, the system was cleaned by back-filling and evacuating with argon. This procedure was repeated until the density remained constant at the given pressure.

Results and Discussion

At Texas A&M a pycnometer cell volume recalibration after the density measurements were complete determined that a nonvolatile oil had accumulated in the cell. Measurement on a second gasoline sample (taken from the original composite) at 322.04 K indicated the total density offset to be about 2.6 kg·cm^{-3}. The oil apparently leaked from the housing of the Paroscientific pressure transducer.

Table 6. Comparison of Densities of Commercial Grade 2-Methylpropane

		ρ/g·cm^{-3}			
T/K	P/MPa	COSTALD (CO)	vib tube (VT)	pycn (PY)	$100(\rho_{PY} - \rho_{VT})/\rho_{CO}$
273.15	0.2758	0.5808	0.5806	0.5807	0.02
	0.3447	0.5809	0.5807	0.5810	0.05
	0.5516	0.5813	0.5810	0.5813	0.05
	0.6895	0.5815	0.5812	0.5815	0.05
	1.3788	0.5827	0.5822	0.5825	0.05
	2.7579	0.5851	0.5843	0.5845	0.03
	4.1369	0.5874	0.5863	0.5865	0.03
	5.5158	0.5897	0.5882	0.5884	0.03
	6.8948	0.5918	0.5901	0.5902	0.02
	8.2737	0.5939	0.5919	0.5920	0.02
	9.6527	0.5959	0.5937	0.5937	0.00
288.71	0.3447	0.5623	0.5622	0.5626	0.07
	0.4137	0.5624	0.5623	0.5628	0.09
	0.4826	0.5626	0.5624	0.5629	0.09
	0.6205	0.5629	0.5627	0.5631	0.07
	0.6895	0.5631	0.5628	0.5632	0.07
	1.3788	0.5645	0.5641	0.5645	0.07
	2.7579	0.5673	0.5666	0.5669	0.05
	4.1369	0.5700	0.5689	0.5692	0.05
	5.5158	0.5725	0.5712	0.5715	0.05
	6.8948	0.5750	0.5734	0.5736	0.03
	8.2737	0.5774	0.5756	0.5757	0.02
	9.6527	0.5797	0.5776	0.5777	0.02
305.37	0.5171	0.5414	0.5414	0.5415	0.02
	0.5516	0.5415	0.5414	0.5416	0.04
	0.6205	0.5417	0.5416	0.5418	0.04
	0.6895	0.5418	0.5417	0.5419	0.04
	1.3788	0.5436	0.5433	0.5435	0.04
	2.7579	0.5470	0.5464	0.5465	0.02
	4.1369	0.5502	0.5493	0.5494	0.02
	5.5158	0.5533	0.5521	0.5522	0.02
	6.8948	0.5662	0.5547	0.5548	0.02
	8.2737	0.5590	0.5573	0.5573	0.00
	9.6527	0.5617	0.5597	0.5597	0.00
322.04	0.7854	0.5189	0.5188	0.5191	0.06
	0.8274	0.5191	0.5191	0.5193	0.04
	0.8963	0.5193	0.5193	0.5195	0.04
	1.0342	0.5198	0.5197	0.5200	0.06
	1.3788	0.5209	0.5208	0.5211	0.06
	2.7579	0.5251	0.5247	0.5250	0.06
	4.1369	0.5291	0.5285	0.5286	0.02
	5.5158	0.5329	0.5319	0.5321	0.04
	6.8948	0.5364	0.5352	0.5353	0.02
	8.2737	0.5397	0.5383	0.5384	0.02
	9.6527	0.5429	0.5412	0.5412	0.00

The experimental results had three jump-shifts in the density. When the shifts occurred, the pressure readings from the Paroscientific pressure transducer during the cell evacuation were unstable. The first offset occurred at 273.15 K for the butane sample which caused a 1.43 kg·cm^{-3} difference in the density measurement. This difference propagated to the 2-methylpropane density measurements at 305.37 K and 322.04 K which were obtained after the butane measurements. The second offset occurred at 288.71 K for the 2-methylpropane sample which contributed another 0.86 kg·cm^{-3} difference or a total of 2.29 kg·cm^{-3} difference in the density measurements for 2-methylpropane at 273.15 K and 288.71 K. This difference, 2.29 kg·cm^{-3}, was included for all the subsequent measurements of natural gasoline densities. The third offset, 0.31 kg·cm^{-3}, occurred after the natural gasoline density measurements were completed but before recalibrations. Corrections for the difference amounts of oil residing in the pycnometer cell during the periods of measurements were made accordingly.

Minor adjustments have been made to experimental values of the densities which were measured near the nominal temperatures and pressures, and the adjusted results along with the observed bubble point pressures and

Table 7. Comparison of Natural Gasoline Densities

		ρ/g·cm^{-3}			
T/K	P/MPa	COSTALD (CO)	vib tube (VT)	pycn (PY)	$100(\rho_{PY} - \rho_{VT})/\rho_{CO}$
273.15	0.3447	0.6712	0.6755	0.6740	−0.22
	0.6895	0.6716	0.6759	0.6743	−0.24
	1.3788	0.6725	0.6765	0.6749	−0.24
	2.7579	0.6741	0.6778	0.6762	−0.24
	4.1369	0.6757	0.6791	0.6775	−0.24
	5.5158	0.6772	0.6804	0.6787	−0.25
	6.8948	0.6788	0.6817	0.6799	−0.26
	8.2737	0.6803	0.6830	0.6811	−0.28
	9.6527	0.6818	0.6841	0.6822	−0.28
288.71	0.1379	0.6565	0.6610	0.6595	−0.23
	0.2068	0.6566	0.6610	0.6596	−0.21
	0.3447	0.6568	0.6611	0.6598	−0.20
	0.6895	0.6572	0.6616	0.6601	−0.23
	1.3788	0.6581	0.6623	0.6608	−0.23
	2.7579	0.6599	0.6638	0.6623	−0.23
	4.1369	0.6616	0.6653	0.6638	−0.23
	5.5158	0.6633	0.6667	0.6651	−0.24
	6.8948	0.6650	0.6681	0.6665	−0.24
	8.2737	0.6666	0.6695	0.6678	−0.25
	9.6527	0.6682	0.6709	0.6691	−0.27
299.82	0.3447	0.6462	0.6504	0.6495	−0.14
	0.6895	0.6467	0.6509	0.6499	−0.15
	1.3788	0.6476	0.6517	0.6507	−0.15
	2.7579	0.6496	0.6534	0.6524	−0.15
	4.1369	0.6514	0.6550	0.6539	−0.17
	5.5158	0.6532	0.6566	0.6555	−0.17
	6.8948	0.6550	0.6581	0.6569	−0.18
	8.2737	0.6567	0.6596	0.6584	−0.18
	9.6527	0.6584	0.6611	0.6598	−0.20
310.93	0.6895	0.6359	0.6401	0.6395	−0.09
	1.3788	0.6370	0.6410	0.6404	−0.09
	2.7579	0.6390	0.6429	0.6422	−0.10
	4.1369	0.6410	0.6446	0.6440	−0.09
	5.5158	0.6429	0.6464	0.6456	−0.12
	6.8948	0.6448	0.6481	0.6473	−0.12
	8.2737	0.6467	0.6497	0.6489	−0.12
	9.6527	0.6485	0.6513	0.6504	−0.14
322.04	0.3447	0.6243	0.6285	0.6284	−0.02
	0.6895	0.6249	0.6289	0.6289	0.00
	1.3788	0.6260	0.6300	0.6299	−0.02
	2.7579	0.6282	0.6321	0.6319	−0.03
	4.1369	0.6304	0.6340	0.6339	−0.02
	5.5158	0.6324	0.6359	0.6357	−0.03
	6.8948	0.6345	0.6378	0.6375	−0.05
	8.2737	0.6364	0.6396	0.6393	−0.05
	9.6527	0.6384	0.6413	0.6410	−0.05

liquid densities appear in Tables 2−4. The bubble point densities result from extrapolation of higher pressure data. Imprecision in the density measurements results mainly from the balance readings. Inaccuracies in the density measurements are dominated by errors in the pycnometer cell volume calibration and instability of the balance zero as discussed by Hwang (1988). Imprecision and estimated accuracies (68% confidence limits) in the temperature, pressure, and density measurements are in Tables 2−4.

For the Phillips Petroleum density measurements, the estimated total uncertainty (combined bias and precision) is ±0.2%. This is comparable to the estimated uncertainty of densities calculated for the calibration fluids.

The experimental results of butane and 2-methylpropane from both participating laboratories, Texas A&M and Phillips Petroleum Co., along with values calculated using the COSTALD correlation are compared in Tables 5 and 6, respectively. Table 7 gives comparisons of densities of the natural gasoline sample in the region of overlap for both laboratories. The agreement among results from the two laboratories is within 0.1% in most cases; the maximum percentage deviation for butane is 0.14% and that of natural gasoline samples is 0.28%. Impurities in the samples were sufficiently high to render comparisons to density results for pure butane and 2-methylpropane meaningless.

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Literature Cited

Hankinson, R. W.; Thomson, G. L. A new correlation for saturation densities of liquids and their mixtures. *AIChE J.* **1979**, *25*, 653.

Hwang, C.-A. Ph.D. Dissertation, *PVT measurements of carbon dioxide + methane mixtures and an equation of state development*. Texas A&M University, **1988**.

Hwang, C.-A.; Brugge, H. B.; Lau, W. R.; Iglesias-Silva, G. A.; Gammon, B. E.; Rogers, W. J.; Marsh, K. N.; Hall, K. R.; Holste, J. C. Presented at the 10th Symposium on Thermophysical Properties, Gaithersburg, Md, 1988.

Lau, W. R. Ph.D. Dissertation, Texas A&M University, **1986**.

Parrish, W. R. Compressed liquid densities of propane - normal butane mixtures between 10 and 60 °C at pressures up to 9.6 MPa. *Fluid Phase Equilib.* **1986**, *25*, 65.

Patterson, H. E. Personal communications, 1991.

Thomson, G. H.; Brobst, K. R.; Hankinson, R. W. *AIChE J.* **1982**, *28*, 671.

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