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Densities of Carbon Dioxide + Hydrogen Sulfide Mixtures from 220 K to 450 K at Pressures up to 25 MPa

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This paper reports ~850 *pVT* measurements at temperatures between 220 K and 450 K at pressures up to 25 MPa for four gravimetrically prepared CO_2 (1) + H_2S (2) mixtures with $x_1 = 0.5011$, 0.7067, 0.9045, and 0.9393. The measurements utilized a Burnett isochoric technique designed to provide both vapor and liquid densities. A detailed error analysis indicates that the densities are accurate to better than 0.08% and 0.3% for the vapor and liquid phases, respectively. Mixture second and third virial coefficients derived from the measurements and correlations to represent them and 52 derived vapor−liquid saturation boundary conditions also are included.

Introduction

Although the volumetric and thermal properties of sour gas mixtures are essential for developing improved methods for producing and processing acid gases and for treating recycled gas in CO_2 flooding operations involving sour crudes, the literature contains very little information about such properties for mixtures containing hydrogen sulfide as a constituent. Measurements on binary mixtures provide insight into the interactions between unlike molecules, and knowledge of the individual pair interactions assists greatly in formulating accurate descriptions of the properties of multicomponent gas mixtures. Vapor−liquid equilibrium measurements have been reported previously by Bierlein and Kay[1] and Sobocinski and Kurata[2] for binary mixtures containing carbon dioxide and hydrogen sulfide, and single-phase *pVT* measurements have been reported for one mixture composition by Liu et al.[3]

This paper reports *pVT* measurements for four binary mixtures of carbon dioxide and hydrogen sulfide at temperatures between 220 K and 450 K and pressures from 0.1 MPa to 23 MPa, as well as densities, second and third virial coefficients, and saturation boundary states derived from the measurements. Enthalpies, entropies, and internal, Helmholtz, and Gibbs energies derived from the *pVT* measurements are reported elsewhere.[4,5]

Experimental Section

Measurement Procedure. Because the two-phase vapor + liquid region extends through the middle of the *p*−*T* region covered in this work and because of the tendency for hydrogen sulfide to decompose at higher temperatures, accurate measurements for these mixtures required substantial modifications to the Burnett isochoric technique first described by Hall and Eubank.[6] Figure 1 illustrates the experimental procedure using the measured values for the approximately equimolar mixture. The sample cell initially is filled to the conditions represented by point 1 in Figure 1. The filling pressure is above the cricondenbar, thus ensuring that all of the fluid, including that in the connecting lines and the supply cylinder, is in a single phase to avoid introducing inhomogeneities in composition during the filling procedure. The first "isochore", which really is a molar isometric (isomole 1), then is measured both in the single-phase region and in the liquid + vapor two-phase region. (The two-phase points are not shown.) At the completion of the first isomole, the liquid is expanded into a second volume, thereby changing the state

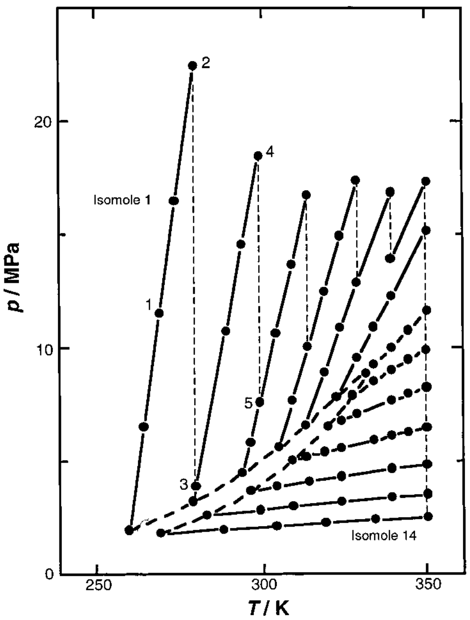

Figure 1. Experimental procedure for isochoric measurements. The solid lines denote molar isometrics, and the dashed lines denote expansions.

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Table 1. Sample Compositions for CO_2 (1) + H_2S (2) Mixtures

		sample 1	sample 2	sample 3	sample 4	sample 5	molar mass/kg·mol^{-1}
m/kg:	CO_2	0.46652	0.392365	0.227848	0.296234	0.442005	0.04401
	H_2S	0.023377	0.019595	0.176357	0.095196	0.036137	0.03408
x:	CO_2	0.9392	0.9394	0.5001	0.7067	0.9045	
	H_2S	0.0608	0.0606	0.4999	0.2933	0.0955	

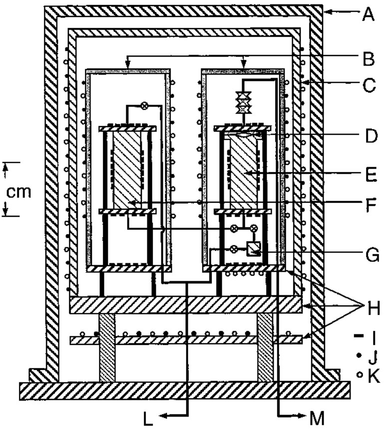

Figure 2. Schematic diagram of Burnett apparatus: A, vacuum vessel; B, radiation shields; C, isothermal shield; D, differential pressure transducer; E, isochoric cell; F, Burnett expansion cell; G, density reduction cell; H, guard plates; I, thin foil heaters; J, Nichrome wire heaters; K, recirculating cooling tube; L, sample inlet and exit; M, differential pressure transducer backpressure supply.

of the liquid from point 2 to point 3. After the completion of the second isomole, the liquid is expanded again (from point 4 to point 5). The experiment continues, mapping the single-phase states (shown in Figure 1) and the two-phase states (not shown), until the $p-T$ surface is covered. In Figure 1, the solid lines denote isomoles 1−14 and the dashed lines indicate expansions. Both the initial and final states are in the single-phase region for all expansions, and all two-phase measurements are made along isomoles. A small expansion ratio (~8% increase) is used between liquid isomoles, and a larger ratio (~50% increase) is used between vapor isomoles. The densities of the isomoles coupled by expansions at 350 K are determined by analysis of a Burnett expansion isotherm, and the densities for isomoles coupled by small ratio expansions are calculated using expansion ratios determined by a separate experiment.

Our previous measurements[3,7] indicated that hydrogen sulfide and its mixtures were stable for a period of days at temperatures of 350 K and below, but at higher temperatures, decomposition adversely affected pVT measurements in tens of hours. Because of our previous experiences, the gas vented during each expansion was analyzed for decomposition products using a gas chromatograph with a sensitivity to impurities of 0.0002 in mole fraction. Significant quantities of water and carbon disulfide were detected in an early experiment when the sample was at 400 K or higher for 18 h before beginning a Burnett isotherm at 450 K. As a result, the Burnett isochoric technique was not used above 350 K. Instead, several repetitions of conventional Burnett expansion series were performed at 400 K and 450 K. To avoid decomposition effects, these expansions were performed as rapidly as possible while the accuracy of the measurement was maintained. No decomposition products were detected in the exhausted gas when using this procedure. Minor amounts of argon were detected in the gases exhausted from the Burnett experiments (see Sample Preparation Procedure) but not in the gases exhausted from the Burnett isochoric experiments.

Apparatus. A schematic diagram of the experimental apparatus used for these investigations appears in Figure 2. The sample chambers were constructed of type 316 stainless steel to resist corrosion by hydrogen sulfide. The main cell (E) in the apparatus serves both as the isochoric chamber and as the initial volume for the expansions. It contains a differential pressure transducer (DPT) built directly into the isochoric cell and a platinum resistance thermometer (PRT) housed in a copper block clamped to the isochoric cell. The Burnett expansion cell (F) effects large changes in the density of the sample in the isochoric cell. These expansions are made in the vapor and supercritical fluid regions. In the liquid region, we use a density reduction cell (G) capable of making small changes in the density of the sample.

Measurements were made at temperatures from 200 K to 450 K and at pressures to 23 MPa. Temperatures were measured with an oil-filled, capsule style PRT that has a long-term stability of ±0.02 K and cycling stability of ±0.01 K. The PRT was calibrated using a Rosemount transfer standard PRT traceable to the National Institute of Standards and Technology. Temperatures are calculated according to ITS-90. Finally, all temperatures within the apparatus were measured relative to the PRT using differential thermopiles. The thermopiles verified that the temperature gradients between the sample chambers were <0.01 K.

A DPT (D) built directly into the isochoric cell measured the difference between the pressure of an intermediate fluid and the sample fluid pressure. The sensing element of the DPT was a thin metal diaphragm, and a linear variable differential transformer (LVDT) with associated electronics measured its null position. The electronic circuitry and the measurement technique were similar to those described by Holste et al.[8] except that the ratio transformer/lock-in amplifier arrangement has been replaced by an integrated circuit described by Stouffer.[9] This arrangement is much less expensive, but provides approximately the same accuracy in differential pressure measurements. At the null position, the pressure of the intermediate fluid was the same as the sample fluid pressure. The pressure of the intermediate fluid was measured using a DH Instruments force balance piston pressure gauge, and the atmospheric pressure was determined using a Paroscientific digital barometer. An Ideal Aerosmith mercury manometer and a DH Instruments automatic dead-weight gauge with an accuracy of ±0.005% were used to confirm the accuracy of the piston pressure gauge and the digital barometer.

Sample Materials. The electronic grade hydrogen sulfide was specified by the supplier (Scott Specialty Gas Co.) to have $x(H_2S) \geq 0.9999$. It was used without further purification. The instrument grade carbon dioxide was specified by the supplier (Scott Specialty Gas Co.) to have $x(CO_2) \geq 0.9999$. It was purified further by repeating several freeze/thaw cycles while the vapor space over the frozen solid was evacuated to <0.01 Pa. The principal impurities in the carbon dioxide as supplied were oxygen (mass fraction $w = 2 \times 10^{-5}$) and nitrogen ($w = 7.5 \times 10^{-5}$).

Table 2. Experimental pVT Results for CO_2 (1) + H_2S (2) at x_1 = 0.9393[a]

T/K	p/MPa	ρ/mol·m^{-3}	Z
Isomole 1 (Sample 2)			
268.025	23.6888	23462	0.4531
260.025	14.9155	23478	0.2939
257.003	11.5848	23483	0.2309
249.972	3.7537	23496	0.07687
245.029	*1.4979*	*23503*	*0.03128*
239.931	*1.2628*	*23509*	*0.02693*
235.038	*1.0654*	*23514*	*0.02318*
230.044	*0.8879*	*23520*	*0.01974*
225.106	*0.7344*	*23526*	*0.01668*
220.540	*0.6115*	*23531*	*0.01417*
Isomole 2 (Sample 2)			
280.071	15.1808	21683	0.3007
270.029	6.6642	21698	0.1368
268.018	4.9672	21701	0.1027
262.088	*2.5243*	*21709*	*0.05336*
259.000	*2.3078*	*21712*	*0.04936*
255.989	*2.1121*	*21716*	*0.04570*
252.995	*1.9288*	*21719*	*0.04222*
249.975	*1.7565*	*21722*	*0.03891*
Isomole 3 (Sample 2)			
300.047	17.9325	20029	0.3589
290.062	11.3376	20042	0.2346
285.050	8.0384	20048	0.1692
280.051	4.7568	20055	0.1019
275.007	*3.5847*	*20060*	*0.07815*
271.921	*3.3048*	*20063*	*0.07286*
268.919	*3.0495*	*20067*	*0.06797*
266.176	*2.8269*	*20069*	*0.06365*
262.969	*2.5857*	*20073*	*0.05892*
Isomole 4 (Sample 2)			
315.007	19.0797	18507	0.3936
310.042	16.4308	18513	0.3443
305.028	13.7516	18519	0.2928
300.032	11.1036	18525	0.2403
292.013	6.9304	18534	0.1540
285.047	*4.6153*	*18541*	*0.1050*
282.030	*4.2848*	*18544*	*0.0985*
278.990	*3.9706*	*18547*	*0.0923*
275.929	*3.6727*	*18550*	*0.0863*
273.133	*3.4152*	*18552*	*0.0811*
Isomole 5 (Sample 2)			
325.004	18.6879	17107	0.4043
320.014	16.4805	17112	0.3620
315.007	14.3016	17118	0.3190
305.009	9.9968	17128	0.2302
300.016	7.8949	17133	0.1847
292.059	*5.4532*	*17141*	*0.1310*
288.995	5.0729	17143	0.1232
285.964	*4.7175*	*17146*	*0.1157*
283.039	*4.3914*	*17149*	*0.1088*
280.834	*4.1583*	*17151*	*0.1038*
Isomole 6 (Sample 1)			
330.002	15.9838	15836	0.3679
325.012	14.3321	15840	0.3348
320.008	12.6860	15845	0.3009
310.010	9.4530	15854	0.2313
305.013	7.8831	15858	0.1960
300.012	*6.5534*	*15863*	*0.1656*
290.071	*5.2036*	*15871*	*0.1360*
290.028	*5.2036*	*15871*	*0.1360*
279.986	*4.0712*	*15879*	*0.1101*
270.062	*3.1441*	*15887*	*0.08814*
260.073	*2.3771*	*15895*	*0.06916*
250.164	*1.7613*	*15903*	*0.05325*
240.270	*1.2722*	*15911*	*0.04002*
230.445	*0.8938*	*15919*	*0.02930*
Isomole 7 (Sample 1)			
330.010	11.6158	10712	0.3952
325.010	10.7508	10715	0.3713
319.873	9.8656	10717	0.3461
Isomole 7 (Sample 1) (Continued)			
310.007	8.1712	10723	0.2956
305.011	7.3268	10726	0.2694
299.992	*6.5429*	*10729*	*0.2445*
295.010	*5.8381*	*10732*	*0.2218*
289.955	*5.1905*	*10734*	*0.2006*
285.184	*4.6279*	*10737*	*0.1818*
285.047	*4.6153*	*18541*	*0.1050*
282.030	*4.2848*	*18544*	*0.09854*
278.990	*3.9706*	*18547*	*0.09229*
275.929	*3.6727*	*18550*	*0.08630*
273.133	*3.4152*	*18552*	*0.08106*
Isomole 8 (Sample 1)			
325.012	9.4285	7247	0.4815
319.916	8.8861	7249	0.4609
315.009	8.3607	7251	0.4403
309.943	7.8057	7253	0.4176
305.042	7.2528	7255	0.3942
299.873	*6.5118*	*7256*	*0.3599*
295.038	*5.8352*	*7258*	*0.3277*
289.979	*5.1838*	*7260*	*0.2961*
284.986	*4.6016*	*7262*	*0.2674*
Isomole 9 (Sample 1)			
325.012	7.9769	4902	0.6022
315.011	7.3255	4904	0.5703
309.950	6.9886	4905	0.5528
304.709	6.6313	4907	0.5334
299.894	6.2966	4908	0.5145
295.512	*5.8753*	*4909*	*0.4871*
287.976	*4.9397*	*4911*	*0.4201*
284.011	*4.4881*	*4912*	*0.3869*
279.492	*4.0125*	*4913*	*0.3514*
Isomole 10 (Sample 1)			
325.009	6.3462	3315	0.7084
315.012	5.9529	3317	0.6852
305.014	5.5503	3319	0.6595
300.013	5.3443	3320	0.6454
295.019	5.1339	3320	0.6303
289.785	4.9103	3321	0.6136
283.125	*4.3662*	*3322*	*0.5583*
279.983	*4.0399*	*3323*	*0.5223*
275.103	*3.5738*	*3324*	*0.4701*
269.780	*3.1106*	*3325*	*0.4171*
259.915	*2.3606*	*3326*	*0.3284*
250.294	*1.7660*	*3328*	*0.2550*
240.278	*1.2702*	*3330*	*0.1910*
230.245	*0.8858*	*3331*	*0.1389*
Isomole 11 (Sample 1)			
325.009	4.8026	2242.5	0.7925
315.212	4.5657	2243.6	0.7765
304.979	4.3142	2244.7	0.7579
295.001	4.0637	2245.8	0.7377
286.304	3.8422	2246.8	0.7184
272.002	*3.2743*	*2248.4*	*0.6439*
269.042	*3.0330*	*2248.7*	*0.6030*
266.000	*2.7950*	*2249.0*	*0.5619*
263.019	*2.5731*	*2249.4*	*0.5231*
260.134	*2.3656*	*2249.7*	*0.4862*
Isomole 12 (Sample 1)			
325.012	3.5043	1516.8	0.8549
315.008	3.3528	1517.5	0.8436
305.015	3.1999	1518.2	0.8311
295.023	3.0446	1519.0	0.8171
286.017	2.9020	1519.7	0.8030
275.172	2.7278	1520.5	0.7841
265.252	2.5631	1521.2	0.7640
257.031	*2.1551*	*1521.8*	*0.6627*
254.025	*1.9700*	*1522.1*	*0.6128*
250.949	*1.7946*	*1522.3*	*0.5650*
248.246	*1.6482*	*1522.5*	*0.5245*
Isomole 13 (Sample 1)			
325.010	2.4945	1025.9	0.8998
310.030	2.3495	1026.6	0.8878
295.087	2.2023	1027.4	0.8737
279.927	2.0517	1028.1	0.8574
264.581	1.8935	1028.9	0.8366
247.970	*1.6079*	*1029.8*	*0.7573*
242.128	*1.3434*	*1030.1*	*0.6478*
239.218	*1.2178*	*1030.2*	*0.5943*
236.250	*1.0964*	*1030.4*	*0.5417*
Isomole 14 (Sample 1)			
325.011	1.2089	469.3	0.9533
310.015	1.1469	469.6	0.9475
295.025	1.0847	470.0	0.9408
279.655	1.0210	470.3	0.9337
265.289	0.9596	470.7	0.9243
Isomole 15 (Sample 1)			
325.006	11.2123	11562	0.3589
349.999	16.2560	11547	0.4838
Isomole 16 (Sample 2)			
325.002	11.0903	11008	0.3728
350.002	15.5482	10995	0.4860
Isomole 17 (Sample 1)			
350.000	10.9656	6094	0.6183
400.000	14.9650	6079	0.7402
Isomole 18 (Sample 2)			
350.012	9.7055	4995	0.6677
400.002	12.7856	4983	0.7716
Isotherm 1 (Sample 1, Isomole Coupling Expansions)			
325.012	14.3315	15840	0.3348
325.006	10.7492	10715	0.3713
325.011	9.4285	7247	0.4815
325.012	7.9766	4902	0.6022
325.009	6.3461	3315	0.7083
325.009	4.8025	2242.5	0.7925
325.012	3.5041	1516.7	0.8550
325.010	2.4944	1025.9	0.8998
325.010	1.7459	693.9	0.9311
325.011	1.2088	469.3	0.9532
325.012	0.8301	317.4	0.9678
325.010	0.5674	214.7	0.9780
325.010	0.3865	145.2	0.9850
325.009	0.2627	98.2	0.9900
325.011	0.1783	66.4	0.9937
325.011	0.1209	44.9	0.9964
Isotherm 2 (Sample 2)			
325.014	4.4908	2056.1	0.8082
325.008	3.2521	1389.2	0.8663
325.008	2.3022	938.5	0.9078
325.009	1.6055	634.1	0.9370
325.017	1.1078	428.4	0.9569
325.013	0.7593	289.4	0.9709
325.012	0.5180	195.5	0.9805
325.010	0.3523	132.1	0.9869
325.010	0.2390	89.2	0.9915
325.010	0.1620	60.2	0.9958
325.012	0.1097	40.7	0.9974
Isotherm 3 (Sample 1)			
350.002	15.5482	10995	0.4860
349.999	12.2845	7429	0.5683
349.998	9.7315	5019	0.6663
350.003	7.4476	3391	0.7547
350.004	5.5013	2291.1	0.8251
350.009	3.9532	1547.9	0.8776
350.006	2.7857	1045.8	0.9153
350.007	1.9367	706.6	0.9418
349.999	1.3342	477.4	0.9604

Table 2. (Continued)

T/K	p/MPa	ρ/mol·m^{-3}	Z
Isotherm 3 (Sample 1) (Continued)			
350.013	0.9133	322.5	0.9731
350.005	0.6225	217.9	0.9817
350.003	0.4230	147.2	0.9875
350.005	0.2871	99.4	0.9925
350.005	0.1945	67.2	0.9946
350.006	0.1316	45.4	0.9961
Isotherm 4 (Sample 2)			
349.999	16.2564	11547	0.4838
350.000	12.6226	7802	0.5560
350.004	10.0332	5271	0.6540
350.007	7.7191	3562	0.7448
350.006	5.7234	2406.3	0.8173
350.005	4.1260	1625.8	0.8721
350.005	2.9134	1098.4	0.9114
350.013	2.0284	742.1	0.9392
350.010	1.3986	501.4	0.9585
350.004	0.9579	338.7	0.9718
350.007	0.6531	228.8	0.9809
350.006	0.4440	154.6	0.9869
350.010	0.3013	104.5	0.9908
350.006	0.2041	70.6	0.9934
350.011	0.1381	47.7	0.9949
Isotherm 5 (Sample 1)			
400.000	14.9649	6079	0.7402
400.002	10.9499	4107	0.8016
399.997	7.8951	2775	0.8554
400.008	5.5980	1875.1	0.8976
400.000	3.9127	1267.0	0.9286
400.013	2.7066	856.0	0.9507
400.005	1.8585	578.4	0.9661
400.004	1.2698	390.8	0.9770
400.010	0.8643	264.0	0.9844
400.006	0.5870	178.4	0.9893
399.999	0.3979	120.5	0.9929
400.009	0.2695	81.4	0.9955
400.004	0.1823	55.0	0.9966
400.007	0.1233	37.2	0.9966
Isotherm 6 (Sample 2)			
400.002	12.7855	4983	0.7716
400.003	9.2938	3367	0.8300
400.007	6.6468	2275	0.8786
400.007	4.6753	1537.0	0.9146
400.006	3.2494	1038.4	0.9409
400.003	2.2379	701.6	0.9591
400.010	1.5326	474.0	0.9722
Isotherm 6 (Continued)			
400.007	1.0450	320.3	0.9810
400.006	0.7103	216.4	0.9869
400.005	0.4820	146.2	0.9913
400.007	0.3266	98.8	0.9939
400.015	0.2215	66.7	0.9985
Isotherm 7 (Sample 2)			
450.044	10.1228	3030	0.8929
450.041	7.0673	2047.2	0.9226
450.044	4.8941	1383.3	0.9455
450.043	3.3648	934.7	0.9621
450.052	2.3015	631.6	0.9738
450.047	1.5682	426.7	0.9822
450.052	1.0656	288.3	0.9878
450.043	0.7228	194.8	0.9916
450.046	0.4898	131.6	0.9947
450.044	0.3316	88.9	0.9968
450.049	0.2243	60.1	0.9974
450.040	0.1517	40.6	0.9986
450.046	0.1025	27.4	0.9997

[a] Values in italics are global values for two-phase vapor + liquid states.

Sample Preparation Procedure. A mixture synthesis manifold described by Hwang[10] and Stouffer[9] was used to introduce the hydrogen sulfide and carbon dioxide into evacuated, floating piston, sampling cylinders equipped with Kalrez O-rings and internal gravity-driven mixers. During the introduction of each substance, the sample container was placed on a Mettler force balance with a load capacity of 24 kg and a sensitivity of 0.1 g. The real-time mass measurements provided by the force balance made it easier to obtain the desired compositions. After each substance was added, the mass of that substance in the mixture was determined more precisely by weighing the container using a Voland double-pan balance having a 25 kg capacity and 2.5 mg sensitivity. Hydrogen sulfide was added first, followed by carbon dioxide. The sample container then was pressurized to 11 MPa by adding argon gas as a back-pressure fluid in the other chamber. Argon was used as the back-pressure fluid because it could be detected more easily as a contaminant following leakage past the piston seals. The sample then was mixed thoroughly by repeated inversions to activate the gravity-driven mixer. The sample for the isochoric experiments was charged into the apparatus as soon as the mixing was completed. The remainder of the sample was kept in the sampling cylinder for the duration of the Burnett isochoric experiments, which generally was 4−6 weeks. During this time, some argon leaked into the sample, so that the sample charges used for the Burnett expansions were contaminated with argon, with mole fractions of argon up to 0.007 for the 450 K isotherm for the equimolar mixture but usually of <0.003.

Table 1 shows the measured masses of each substance in each mixture, and the molar masses used to calculate the mole fractions. Five mixture samples were prepared, two of which had essentially the same composition.

Accuracy and Precision of Measured Values. The measured variables are the masses of each substance, the temperature, and the pressure; therefore, we have taken special care to measure them both precisely and accurately. The reported temperatures are accurate to ±0.01 K and precise to ±1 mK. The reported pressures are accurate to better than ±0.01% for pressures >0.5 MPa and to ±0.1% for pressures <0.5 MPa and are precise to ±0.015% for all pressures. The mass fractions of material added are determined to better than ±0.00001, but impurities in the constituents limit the accuracies of the mole fractions to ±0.0001.

Results and Conclusions

Apparatus Calibration and Performance Tests. Measurements on pure carbon dioxide were used to verify the capabilities of the apparatus. Nine vapor pressures measured between 260 and 300 K showed a bias of +0.03% and a standard deviation about the bias of 0.04% when compared with the correlation of Ely et al.[11] A Burnett isotherm at 350 K yielded values of −84.00 cm^3·mol^{-1} and 3637 cm^6·mol^{-2} for the second and third virial coefficients, respectively. These values differ by 0.09 cm^3·mol^{-1} and −22 cm^6·mol^{-2} from the correlations developed by Holste et al.[12] from their experimental values. Both deviations are well within the combined uncertainty estimates.

The properties of type 316 stainless steel were used to develop a correction for volume distortions with changing temperature and pressure

$$\frac{V(T, P)}{V(T_0,P_0)} = 1 + \gamma(P - P_0) + \beta(T - T_0) \qquad (1)$$

where $\gamma = 2.53 \times 10^{-5}$ MPa^{-1} and $\beta = 4.86 \times 10^{-5}$ K^{-1}. This relationship was verified by measuring two isomoles for CO_2 at nominal densities of 2600 mol·m^{-3} and 6600 mol·m^{-3} and temperatures ranging from 300 K to 450 K. Fourteen measurements had a bias of −0.012% and a standard deviation of 0.037% in density when compared with the correlation of Ely et al.[11]

The expansion ratio for the density reduction cell was measured by expanding helium gas from the isochoric cell to the density reduction cell. Nine determinations at 300 K yielded a value of $N_{DR} = 1.08119$ with a standard deviation of 0.00004. This value was used to calculate density ratios for the liquid expansions during the mixture experiment. Helium gas expansions at 300 K from the isochoric cell to the Burnett expansion cell were used to

Table 3. Experimental pVT Results for CO_2 (1) + H_2S (2) at $x_1 = 0.9045^a$

T/K	p/MPa	ρ/mol·m^{-3}	Z
Isomole 1			
282.974	21.1211	21787	0.4120
275.992	14.9738	21798	0.2994
269.996	9.5981	21808	0.1961
264.019	4.2658	21817	0.08907
251.016	*1.7917*	*21832*	*0.03932*
247.045	*1.5806*	*21836*	*0.03524*
241.997	*1.3400*	*21842*	*0.03049*
236.009	*1.0874*	*21848*	*0.02536*
230.007	*0.8732*	*21855*	*0.02089*
Isomole 2			
297.015	17.8926	20133	0.3599
296.005	17.1850	20134	0.3468
293.397	15.3474	20138	0.3124
284.991	9.6152	20149	0.2014
279.998	6.1266	20155	0.1306
265.022	*2.7046*	*20172*	*0.06085*
260.031	*2.3442*	*20177*	*0.05374*
250.022	*1.7385*	*20187*	*0.04143*
240.005	*1.2532*	*20197*	*0.03109*
230.130	*0.8752*	*20207*	*0.02264*
Isomole 3			
309.997	17.6580	18606	0.3682
304.997	14.8399	18612	0.3144
302.995	13.7504	18614	0.2932
299.996	12.1179	18617	0.2610
290.000	6.6233	18629	0.1475
278.005	*3.8301*	*18641*	*0.08889*
270.005	*3.1028*	*18649*	*0.07411*
260.012	*2.3447*	*18658*	*0.05813*
250.001	*1.7342*	*18668*	*0.04469*
239.976	*1.2470*	*18677*	*0.03346*
Isomole 4			
319.992	17.1517	17198	0.3748
313.000	14.0001	17205	0.3127
307.998	11.7600	17211	0.2668
302.991	9.5129	17216	0.2193
297.993	7.3022	17221	0.1711
285.032	*4.5661*	*17233*	*0.1118*
271.969	*3.2728*	*17245*	*0.08393*
265.047	*2.7061*	*17251*	*0.07118*
Isomole 5			
329.994	17.4930	15898	0.4010
325.000	15.6281	15902	0.3637
315.999	12.2772	15910	0.2937
312.991	11.1792	15913	0.2700
303.995	7.9844	15922	0.1984
288.014	*4.8977*	*15935*	*0.1284*
275.009	*3.5440*	*15946*	*0.09720*
261.999	*2.4864*	*15956*	*0.07153*
250.007	*1.7373*	*15966*	*0.05235*
239.997	*1.2516*	*15974*	*0.03926*
Isomole 6			
337.993	17.6729	14697	0.4279
334.013	16.3709	14700	0.4010
330.001	15.1287	14704	0.3750
324.995	13.5642	14708	0.3413
319.991	12.0070	14712	0.3068
314.997	10.5030	14716	0.2725
309.998	8.9896	14720	0.2369
298.002	*6.1738*	*14730*	*0.1692*
286.021	*4.6603*	*14739*	*0.1330*
272.034	*3.2722*	*14750*	*0.09808*
258.071	*2.2150*	*14760*	*0.06994*
Isomole 7			
344.998	17.7024	13588	0.4542
337.997	15.8276	13593	0.4143
Isomole 8			
349.994	17.3759	12564	0.4752
344.991	16.2109	12568	0.4497
340.010	15.0421	12571	0.4233
334.995	13.8835	12575	0.3964
327.995	12.2758	12579	0.3578
319.992	10.4373	12585	0.3117
317.987	9.9894	12586	0.3002
298.002	*6.1733*	*12600*	*0.1977*
290.015	*5.1362*	*12606*	*0.1690*
270.015	*3.1034*	*12618*	*0.1096*
250.016	*1.7373*	*12631*	*0.06617*
230.069	*0.8735*	*12643*	*0.03611*
241.985	*1.3368*	*17271*	*0.0384*
251.995	*1.8477*	*17262*	*0.0510*
Isomole 9			
349.997	13.1465	8491	0.5320
344.984	12.5080	8493	0.5134
339.996	11.8674	8496	0.4942
334.998	11.2235	8498	0.4742
329.996	10.5707	8500	0.4533
325.000	9.9051	8502	0.4311
321.961	9.4958	8503	0.4172
317.994	8.9759	8505	0.3992
300.000	*6.4393*	*8513*	*0.3032*
290.011	*5.1236*	*8518*	*0.2495*
279.999	*4.0283*	*8522*	*0.2030*
269.521	*3.0723*	*8527*	*0.1608*
240.057	*1.2507*	*8539*	*0.07338*
Isomole 10			
349.999	10.5233	5738	0.6302
344.998	10.1451	5740	0.6162
338.990	9.6748	5742	0.5979
332.003	9.1353	5744	0.5762
325.006	8.5860	5746	0.5530
317.999	8.0166	5748	0.5275
300.009	*6.4098*	*5753*	*0.4467*
290.014	*5.1092*	*5756*	*0.3681*
280.007	*4.0217*	*5759*	*0.3000*
270.006	*3.1022*	*5762*	*0.2398*
260.004	*2.3492*	*5765*	*0.1885*
Isomole 11			
350.001	8.1804	3878	0.7249
339.999	7.7182	3880	0.7037
330.015	7.2418	3882	0.6799
319.998	6.7636	3884	0.6545
310.004	6.2747	3886	0.6265
300.002	5.7629	3888	0.5943
290.020	*5.0706*	*3890*	*0.5406*
279.999	*3.9958*	*3892*	*0.4410*
268.007	*2.9273*	*3894*	*0.3374*
252.002	*1.8466*	*3897*	*0.2261*
240.016	*1.2491*	*3900*	*0.1605*
Isomole 12			
349.999	6.1241	2628.2	0.8007
336.998	5.7460	2629.8	0.7798
325.017	5.4033	2631.4	0.7599
312.005	5.0219	2633.1	0.7352
300.014	4.6561	2634.7	0.7085
293.263	4.4406	2635.5	0.6910
279.010	*3.8420*	*2637.4*	*0.6280*
272.004	*3.2437*	*2638.4*	*0.5436*
266.008	*2.7650*	*2639.2*	*0.4737*
258.003	*2.2049*	*2640.2*	*0.3893*
250.003	*1.7258*	*2641.3*	*0.3143*
Isomole 13			
349.999	4.4435	1776.8	0.8594
340.000	4.2666	1777.6	0.8490
325.002	3.9935	1779.0	0.8307
315.005	3.8104	1779.8	0.8174
295.505	3.4493	1781.5	0.7880
278.581	3.1173	1783.0	0.7548
265.033	*2.6376*	*1784.2*	*0.6708*
260.003	*2.3188*	*1784.7*	*0.6010*
255.001	*2.0069*	*1785.1*	*0.5302*
247.002	*1.5680*	*1785.8*	*0.4275*
240.045	*1.2452*	*1786.5*	*0.3492*
Isomole 14			
350.000	3.1533	1201.0	0.9023
333.999	2.9693	1201.9	0.8896
318.007	2.7878	1202.8	0.8766
301.000	2.5870	1203.8	0.8587
295.908	2.5254	1204.1	0.8524
271.025	2.2240	1205.6	0.8186
250.006	*1.6931*	*1206.9*	*0.6749*
245.005	*1.4574*	*1207.2*	*0.5927*
240.011	*1.2361*	*1207.5*	*0.5130*
235.008	*1.0388*	*1207.8*	*0.4402*
230.046	*0.8669*	*1208.1*	*0.3752*
Isotherm 1 (Coupling Expansions)			
349.997	13.1465	8491	0.5320
349.999	10.5233	5738	0.6302
350.001	8.1804	3878	0.7249
349.999	6.1241	2628.2	0.8007
349.999	4.4435	1776.8	0.8594
350.000	3.1533	1201.0	0.9023
350.002	2.2023	811.4	0.9327
349.995	1.5223	548.4	0.9540
350.000	1.0446	370.6	0.9686
349.999	0.7131	250.4	0.9787
350.000	0.4851	169.1	0.9856
349.999	0.3293	114.3	0.9902
349.999	0.2230	77.2	0.9933
349.994	0.1509	52.1	0.9955
Isotherm 2			
350.000	9.0599	4502	0.6916
349.999	6.8774	3056	0.7734
349.996	5.0465	2067.6	0.8387
349.996	3.6099	1398.0	0.8873
349.998	2.5355	944.8	0.9222
349.998	1.7587	638.4	0.9466
349.999	1.2097	431.4	0.9636
350.000	0.8272	291.5	0.9752
350.000	0.5633	196.9	0.9832
349.997	0.3825	133.0	0.9886
349.999	0.2593	89.8	0.9923
350.002	0.1755	60.6	0.9948
349.999	0.1186	40.9	0.9964
Isotherm 3			
350.007	8.6567	4222	0.7045
350.001	6.5222	2852.0	0.7858
350.000	4.7585	1926.8	0.8487
349.998	3.3886	1301.4	0.8948
350.001	2.3728	879.1	0.9275
350.000	1.6422	593.8	0.9504
350.001	1.1276	401.0	0.9662
350.001	0.7700	270.8	0.9771
349.999	0.5239	182.9	0.9844
350.001	0.3555	123.5	0.9895
349.999	0.2408	83.4	0.9929
349.999	0.1629	56.2	0.9952
350.002	0.1100	37.9	0.9967

Table 3. (Continued)

T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z
	Isotherm 4				Isotherm 5				Isotherm 6		
399.998	11.4463	4385	0.7848	399.997	8.7259	3148	0.8333	450.001	8.8631	2637.3	0.8982
400.002	8.2892	2962.0	0.8415	399.999	6.2231	2123.4	0.8812	449.999	6.1820	1782.0	0.9272
399.999	5.8993	2000.5	0.8867	400.003	4.3709	1434.1	0.9164	450.008	4.2748	1204.1	0.9489
400.001	4.1367	1351.1	0.9206	399.996	3.0343	968.5	0.9420	449.996	2.9362	813.5	0.9646
400.000	2.8684	912.5	0.9452	399.998	2.0887	654.1	0.9601	450.003	2.0067	549.7	0.9757
400.001	1.9725	616.3	0.9624	400.001	1.4293	441.8	0.9729	449.999	1.3666	371.4	0.9835
400.001	1.3491	416.2	0.9747	399.998	0.9737	298.3	0.9814	450.004	0.9282	250.9	0.9886
399.997	0.9190	281.1	0.9831	399.999	0.6616	201.5	0.9873	449.999	0.6295	169.5	0.9923
399.998	0.6243	189.8	0.9889	400.000	0.4485	136.1	0.9911	450.000	0.4264	114.6	0.9950
400.001	0.4232	128.2	0.9926	399.999	0.3037	91.9	0.9939	449.999	0.2886	77.4	0.9966
400.001	0.2865	86.6	0.9949	400.004	0.2054	62.1	0.9949	450.000	0.1951	52.3	0.9974
400.000	0.1936	58.5	0.9958	399.998	0.1387	41.9	0.9952	450.001	0.1319	35.3	0.9981
400.000	0.1307	39.4	0.9975								

[a] Values in italics are global values for two phase vapor + liquid states.

provide a comparison value for the Burnett expansion ratios determined in the analyses of the experimental isotherms.

PVT Results. The experimental temperatures and pressures for the CO_2 (1) + H_2S (2) at $x_1 = 0.9393$ appear in Table 2. There are 18 isomoles coupled by expansions, 2 Burnett isotherms at 350 K, 2 Burnett isotherms at 400 K, and 1 Burnett isotherm at 450 K. The experimental temperatures and pressures for the mixture with $x_1 = 0.9045$ appear in Table 3. There are 14 isomoles coupled by expansions, 2 Burnett isotherms at 350 K, 2 Burnett isotherms at 400 K, and 1 Burnett isotherm at 450 K. The experimental temperatures and pressures for the mixture with $x_1 = 0.7067$ appear in Table 4. There are 14 isomoles coupled by expansions, 1 Burnett isotherm at 350 K, and 1 Burnett isotherm at 400 K. The experimental temperatures and pressures for the mixture with $x_1 = 0.5001$ appear in Table 5. There are 14 isomoles coupled by expansions, 2 Burnett isotherms at 350 K, 2 Burnett isotherms at 400 K, and 1 Burnett isotherm at 450 K.

The densities were determined by first analyzing the Burnett isotherms using a maximum likelihood approach described in detail elsewhere[13,14] to obtain a derived density at the isotherm temperature for each isomole connected by Burnett expansions. For isomoles connected by expansions using the volume reduction cell, the densities at the expansion temperatures were calculated using the expansion ratio determined by the helium experiments and one known isomole density. The starting density for this procedure is that of the highest density isomole connected by Burnett expansions, which is provided by the Burnett analysis. The remaining isomoles then are treated in order of increasing density. For all isomoles, the densities at temperatures other than the expansion temperature were calculated using eq 1 and the density at the expansion temperature.

Phase Boundaries. The vapor−liquid phase boundary conditions were determined by locating the deviations from smooth (p, T) behavior, which occur when the phase boundary is crossed. The boundary states were determined as follows. First, a low-order (quadratic or cubic) polynomial in temperature was fit to the single-phase pressures. Second, another polynomial in temperature was fit to the deviations of the pressures in the two-phase region from the first polynomial. The phase boundary occurs at the state where the deviation calculated with the second polynomial has a zero value. Table 6 gives the phase boundary states determined using this procedure.

Virial Coefficients. The second and third virial coefficients and the apparatus constant, N_{BE}, obtained from analyses of the Burnett isotherms appear in Table 7. Details of the analysis procedure, including the objective function, are provided elsewhere.[13,14] The root-mean-square deviations in pressure for the isotherm fits range from 0.01% to 0.02%. Using the apparatus constant as an adjustable parameter for each fit provides a stringent internal consistency test, because incorrect data cause significant variations in N_{BE}. Table 7 shows that there is no significant temperature dependence of N_{BE}, and the values are consistent with the value of 1.4808 obtained using helium expansions at 300 K. The argon impurities present in the Burnett isotherms alter the mixture second and third virial coefficients by less than 1 cm^3·mol^{-1} and 60 cm^6·mol^{-2}, respectively.

Stouffer[9] concluded that the correlation of Tsonopoulos[15] with the polar correction as it appears in Reid et al.[16] describes the experimental second virial coefficients of pure H_2S within the accuracy of the measurements. This correlation also works well for pure carbon dioxide as shown by comparisons with the results of Holste et al.,[12] which are shown in Table 7. The second virial coefficient for a mixture, B_m, is given by

$$B_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \tag{2}$$

in which the x_i are mole fractions, n is the total number of components, and the B_{ij} are the cross second virial coefficients. We have used the mixing rules suggested for the correlation by Tsonopoulos[15]

$$T_{c,ij} = (T_{c,i} T_{c,j})^{1/2}(1 - k_{ij}) \tag{3}$$

$$P_{c,ij} = \frac{4T_{c,ij}(P_{c,i}V_{c,j}/T_{c,i} + P_{c,i}V_{c,j}/T_{c,i})}{(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3} \tag{4}$$

$$\omega_{ij} = (\omega_i + \omega_j)/2 \tag{5}$$

The optimal value of the interaction parameter, $k_{ij} = 0.08$, was obtained by minimizing the sum of the deviations of the experimental B_m from the correlation. Table 7 shows the deviations for the current measurements as well as those reported by Liu[7] for a mixture with $x_1 = 0.4859$. The standard deviation for all mixture second virial coefficients is 0.74 cm^3·mol^{-1}. Table 8 gives the pure and cross second virial coefficient values used to calculate the deviations in Table 7.

Holste et al.[12] found that the correlation of Orbey and Vera[17] describes the third virial coefficients of carbon

Table 4. Experimental pVT Results for CO_2 (1) + H_2S (2) at $x_1 = 0.7067$[a]

T/K	p/MPa	ρ/mol·m^{-3}	Z
	Isomole 1		
285.010	24.2162	21911	0.4664
274.978	14.9350	21926	0.2979
269.985	10.3379	21934	0.2100
264.985	5.6423	21942	0.1167
262.013	2.8944	21947	0.06054
256.020	*1.9210*	*21954*	*0.04111*
250.044	*1.6017*	*21960*	*0.03508*
244.991	*1.3645*	*21966*	*0.03050*
240.020	*1.1568*	*21971*	*0.02638*
230.113	*0.8114*	*21982*	*0.01929*
	Isomole 2		
299.001	19.2078	20246	0.3816
295.054	16.3447	20252	0.3290
290.013	12.7528	20258	0.2611
285.034	9.1681	20265	0.1909
279.986	5.4376	20272	0.1152
273.015	*3.0704*	*20280*	*0.06669*
266.986	*2.6130*	*20286*	*0.05802*
260.052	*2.1541*	*20293*	*0.04909*
252.983	*1.7478*	*20301*	*0.04093*
245.858	*1.3977*	*20308*	*0.03367*
	Isomole 3		
312.000	17.4304	18711	0.3591
307.000	14.5555	18717	0.3047
303.007	12.2567	18721	0.2599
297.999	9.3903	18727	0.2024
293.011	6.6323	18733	0.1453
282.024	*3.8455*	*18744*	*0.08749*
274.978	*3.2256*	*18751*	*0.07524*
268.008	*2.6892*	*18758*	*0.06434*
260.043	*2.1563*	*18765*	*0.05315*
250.000	*1.5964*	*18775*	*0.04091*
	Isomole 4		
324.002	17.3877	17293	0.3732
316.996	14.1376	17300	0.3101
308.997	10.4376	17309	0.2347
305.006	8.6058	17313	0.1960
300.996	6.7965	17317	0.1568
288.003	*4.4320*	*17329*	*0.1068*
279.029	*3.5684*	*17337*	*0.08872*
270.022	*2.8361*	*17345*	*0.07283*
262.014	*2.2770*	*17352*	*0.06024*
252.991	*1.7513*	*17360*	*0.04796*
	Isomole 5		
332.994	16.9574	15986	0.3831
325.996	14.2562	15993	0.3289
323.995	13.5322	15994	0.3141
322.029	12.7964	15996	0.2988
318.002	11.2999	16000	0.2671
311.996	9.0636	16006	0.2183
300.003	*5.8076*	*16016*	*0.1454*
290.010	*4.6403*	*16025*	*0.1201*
280.017	*3.6567*	*16033*	*0.09796*
269.531	*2.7961*	*16041*	*0.07778*
260.030	*2.1555*	*16049*	*0.06212*
249.969	*1.5942*	*16057*	*0.04777*
	Isomole 6		
341.998	17.3295	14778	0.4124
332.998	14.4096	14786	0.3520
325.012	11.9147	14792	0.2981
319.997	10.3429	14797	0.2627
316.012	9.1444	14800	0.2352
302.004	*6.0597*	*14811*	*0.1629*
294.006	*5.0772*	*14817*	*0.1402*
286.005	*4.2217*	*14823*	*0.1198*
278.003	*3.4815*	*14829*	*0.1016*
269.002	*2.7618*	*14836*	*0.08323*
	Isomole 7		
350.000	17.4702	13662	0.4394
342.001	15.3025	13668	0.3937
	Isomole 8		
350.000	15.8358	12636	0.4306
345.000	14.6819	12640	0.4049
340.000	13.5423	12643	0.3789
334.999	12.4121	12647	0.3524
329.999	11.2799	12650	0.3250
324.999	10.1640	12654	0.2973
320.000	9.0576	12657	0.2690
301.997	*6.0436*	*12669*	*0.1900*
293.004	*4.9492*	*12675*	*0.1603*
284.996	*4.1113*	*12680*	*0.1368*
276.999	*3.3967*	*12685*	*0.1163*
268.982	*2.7601*	*12690*	*0.09725*
	Isomole 9		
349.994	12.3384	8539	0.4966
344.999	11.6905	8541	0.4772
340.000	11.0515	8543	0.4576
335.000	10.3987	8545	0.4369
330.002	9.7404	8547	0.4153
324.998	9.0778	8550	0.3929
310.000	*7.0254*	*8556*	*0.3186*
298.997	*5.6211*	*8561*	*0.2641*
292.995	*4.9338*	*8564*	*0.2365*
277.999	*3.4717*	*8570*	*0.1753*
269.996	*2.8232*	*8574*	*0.1467*
	Isomole 10		
349.996	10.0939	5770	0.6012
342.004	9.4846	5772	0.5779
334.004	8.8516	5774	0.5520
326.007	8.2086	5777	0.5242
317.998	7.5442	5779	0.4938
302.184	*5.8631*	*5784*	*0.4035*
295.000	*5.0418*	*5786*	*0.3553*
289.993	*4.5182*	*5787*	*0.3238*
275.037	*3.1898*	*5792*	*0.2408*
266.913	*2.5914*	*5794*	*0.2015*
260.040	*2.1382*	*5796*	*0.1706*
	Isomole 11		
349.996	7.9670	3899	0.7023
336.999	7.3618	3901	0.6735
329.999	7.0268	3902	0.6563
322.003	6.6368	3904	0.6350
314.999	6.2884	3905	0.6148
297.998	*5.2041*	*3909*	*0.5374*
287.994	*4.2187*	*3911*	*0.4505*
278.050	*3.3650*	*3913*	*0.3720*
261.996	*2.2269*	*3916*	*0.2611*
247.985	*1.4815*	*3919*	*0.1834*
	Isomole 12		
349.990	6.0258	2636.9	0.7853
344.997	5.8823	2637.6	0.7775
334.999	5.5936	2638.9	0.7610
325.005	5.2995	2640.2	0.7428
314.999	5.0011	2641.5	0.7229
305.000	4.6978	2642.8	0.7010
287.290	*3.9693*	*2645.1*	*0.6282*
280.012	*3.4046*	*2646.1*	*0.5526*
264.990	*2.3720*	*2648.1*	*0.4066*
259.032	*2.0198*	*2648.9*	*0.3540*
248.003	*1.4605*	*2650.4*	*0.2672*
	Isomole 13		
349.999	4.4014	1782.0	0.8487
337.993	4.1868	1783.1	0.8355
325.998	3.9682	1784.1	0.8206
314.006	3.7461	1785.2	0.8038
290.002	3.2895	1787.3	0.7633
272.032	*2.6955*	*1788.9*	*0.6662*
264.988	*2.2770*	*1789.5*	*0.5775*
257.996	*1.9100*	*1790.1*	*0.4974*
252.000	*1.6146*	*1790.7*	*0.4304*
244.973	*1.3077*	*1791.3*	*0.3584*
	Isomole 14		
349.992	3.1354	1203.7	0.8951
329.999	2.9065	1204.9	0.8792
315.043	2.7323	1205.8	0.8651
300.002	2.5567	1206.7	0.8494
285.015	2.3743	1207.5	0.8297
244.993	*1.2689*	*1209.9*	*0.5149*
240.002	*1.0832*	*1210.2*	*0.4485*
235.039	*0.9230*	*1210.5*	*0.3901*
229.988	*0.7733*	*1210.8*	*0.3340*
	Isotherm 1 (Coupling Expansions)		
350.001	8.9858	4722	0.6539
349.997	6.9326	3191	0.7466
350.006	5.1441	2156.2	0.8198
350.005	3.7063	1457.0	0.8741
350.001	2.6159	984.6	0.9130
349.990	1.8208	665.3	0.9405
350.000	1.2554	449.5	0.9596
350.005	0.8595	303.8	0.9723
350.000	0.5862	205.3	0.9814
350.001	0.3982	138.7	0.9867
350.000	0.2701	93.7	0.9906
350.000	0.1832	63.3	0.9942
350.001	0.1242	42.8	0.9973
	Isotherm 2		
349.998	9.1961	4878	0.6478
350.002	7.1124	3297	0.7413
350.000	5.2894	2228.4	0.8157
350.000	3.8180	1506.1	0.8712
350.000	2.6985	1017.9	0.9110
350.002	1.8794	687.9	0.9388
350.002	1.2963	464.9	0.9582
350.002	0.8885	314.2	0.9717
350.000	0.6059	212.3	0.9805
350.000	0.4122	143.5	0.9870
350.000	0.2798	97.0	0.9914
350.002	0.1896	65.5	0.9942
350.000	0.1284	44.3	0.9958
	Isotherm 3		
399.996	7.5779	2700.7	0.8437
399.997	5.3893	1824.4	0.8883
400.001	3.7780	1232.3	0.9218
400.000	2.6184	832.4	0.9458
399.999	1.8004	562.3	0.9628
400.001	1.2309	379.8	0.9744
400.000	0.8388	256.5	0.9831
399.999	0.5696	173.3	0.9884
399.999	0.3862	117.1	0.9922
400.000	0.2615	79.1	0.9944
400.000	0.1768	53.4	0.9957

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[a] Values in italics are global values for two phase vapor + liquid states.

Table 5. Experimental pVT Results for CO_2 (1) + H_2S (2) at $x_1 = 0.5001$[a]

T/K	p/MPa	ρ/mol·m^{-3}	Z
Isomole 1			
281.031	22.4272	23455	0.4092
275.039	16.4965	23465	0.3074
270.066	11.5600	23474	0.2193
270.018	11.5117	23474	0.2184
265.022	6.5019	23483	0.1257
255.057	*1.6392*	*23497*	*0.03290*
250.052	*1.4115*	*23503*	*0.02889*
240.030	*1.0239*	*23515*	*0.02182*
230.032	*0.7205*	*23526*	*0.01601*
220.204	*0.4927*	*23538*	*0.01143*
Isomole 2			
300.011	18.4405	21666	0.3412
295.010	14.5908	21673	0.2745
290.030	10.7695	21681	0.2060
290.020	10.7809	21681	0.2062
281.028	3.8799	21694	0.07654
275.031	*2.8190*	*21701*	*0.05681*
270.032	*2.4811*	*21706*	*0.05091*
265.087	*2.1761*	*21712*	*0.04547*
260.033	*1.8929*	*21717*	*0.04031*
250.255	*1.4195*	*21728*	*0.03140*
Isomole 3			
315.008	16.7449	20050	0.3189
310.007	13.6830	20056	0.2647
305.015	10.6577	20062	0.2095
300.016	7.6228	20069	0.1523
300.008	7.6130	20069	0.1521
297.110	5.8576	20073	0.1181
290.074	*4.0235*	*20080*	*0.08308*
286.063	*3.6715*	*20084*	*0.07686*
281.940	*3.3325*	*20089*	*0.07077*
278.043	*3.0393*	*20093*	*0.06543*
274.159	*2.7545*	*20097*	*0.06013*
Isomole 4			
330.016	17.3900	18527	0.3421
325.007	14.9240	18533	0.2980
320.008	12.4788	18538	0.2530
315.014	10.0438	18544	0.2068
315.003	10.0382	18544	0.2067
310.098	7.6698	18550	0.1604
300.007	*4.9833*	*18560*	*0.1076*
294.928	*4.4709*	*18565*	*0.09821*
290.008	*4.0097*	*18569*	*0.08955*
284.927	*3.5693*	*18574*	*0.08112*
280.230	*3.1924*	*18579*	*0.07375*
Isomole 5			
339.996	16.8459	17126	0.3480
330.003	12.8600	17136	0.2735
325.003	10.8788	17141	0.2349
320.005	8.9261	17146	0.1957
310.036	*6.1012*	*17155*	*0.1380*
305.072	*5.5217*	*17160*	*0.1269*
300.138	*4.9858*	*17164*	*0.1164*
295.212	*4.4837*	*17168*	*0.1064*
290.010	*4.0937*	*17173*	*0.09886*
Isomole 6			
349.999	17.2208	15831	0.3738
339.992	13.8878	15840	0.3102
Isomole 7			
350.000	15.0596	14642	0.3534
340.000	12.2688	14650	0.2962
335.003	10.8958	14654	0.2669
330.003	9.5467	14658	0.2374
320.043	*7.3434*	*14666*	*0.1882*
315.003	*6.6704*	*14670*	*0.1736*
310.012	*6.0550*	*14674*	*0.1601*
305.010	*5.4802*	*14678*	*0.1472*
302.012	*5.1542*	*14680*	*0.1398*
Isomole 8			
349.995	11.5407	9906	0.4003
345.000	10.7745	9909	0.3791
340.005	10.0078	9911	0.3572
335.004	9.2451	9914	0.3348
323.010	*7.5305*	*9920*	*0.2827*
320.005	*7.1367*	*9922*	*0.2704*
315.010	*6.5155*	*9924*	*0.2507*
310.029	*5.9327*	*9927*	*0.2319*
300.022	*4.8633*	*9932*	*0.1963*
290.035	*3.9425*	*9937*	*0.1645*
279.986	*3.1325*	*9942*	*0.1354*
270.020	*2.4486*	*9947*	*0.1097*
260.173	*1.8748*	*9952*	*0.08709*
259.993	*1.8723*	*9952*	*0.08703*
250.012	*1.3975*	*9957*	*0.06752*
240.026	*1.0167*	*9962*	*0.05114*
229.987	*0.7124*	*9967*	*0.03738*
220.912	*0.5010*	*9971*	*0.02735*
Isomole 9			
350.005	9.9343	6702	0.5094
345.001	9.4660	6703	0.4923
340.008	8.9925	6705	0.4744
335.006	8.5122	6707	0.4557
325.045	*7.4541*	*6710*	*0.4110*
320.026	*6.8603*	*6712*	*0.3841*
315.013	*6.2814*	*6714*	*0.3572*
310.014	*5.7369*	*6716*	*0.3314*
305.019	*5.2203*	*6717*	*0.3064*
299.998	*4.7353*	*6719*	*0.2826*
Isomole 10			
350.002	8.2556	4534	0.6257
344.995	7.9703	4535	0.6127
340.005	7.6822	4536	0.5991
330.099	7.1014	4538	0.5701
325.008	6.7940	4540	0.5538
318.011	*6.2384*	*4541*	*0.5196*
315.004	*5.9332*	*4542*	*0.4988*
310.009	*5.4470*	*4543*	*0.4652*
307.011	*5.1644*	*4544*	*0.4453*
304.012	*4.8899*	*4544*	*0.4257*
Isomole 11			
350.002	6.4851	3067	0.7265
344.967	6.3103	3068	0.7171
340.005	6.1368	3069	0.7074
335.002	5.9594	3070	0.6970
325.009	5.6000	3071	0.6748
320.003	5.4163	3072	0.6627
314.017	5.1934	3073	0.6473
305.016	*4.6377*	*3074*	*0.5949*
300.015	*4.2476*	*3075*	*0.5538*
290.050	*3.5188*	*3077*	*0.4743*
280.102	*2.8708*	*3078*	*0.4005*
270.054	*2.2823*	*3080*	*0.3301*
260.049	*1.7792*	*3081*	*0.2671*
250.017	*1.3473*	*3083*	*0.2103*
240.046	*0.9912*	*3084*	*0.1610*
229.959	*0.7016*	*3086*	*0.1189*
220.555	*0.4902*	*3087*	*0.08659*
Isomole 12			
350.004	4.8655	2075.1	0.8057
340.008	4.6483	2076.1	0.7920
325.008	4.3140	2077.7	0.7684
315.011	4.0873	2078.7	0.7507
305.016	3.8578	2079.7	0.7314
290.021	*3.2332*	*2081.4*	*0.6442*
280.070	*2.6700*	*2082.3*	*0.5506*
270.083	*2.1608*	*2083.4*	*0.4619*
260.035	*1.7045*	*2084.4*	*0.3782*
Isomole 13			
350.003	3.5342	1403.9	0.8651
340.003	3.3978	1404.6	0.8557
325.004	3.1898	1405.6	0.8398
310.039	2.9783	1406.6	0.8214
300.016	2.8347	1407.3	0.8075
290.031	2.6683	1408.0	0.7859
274.976	*2.1891*	*1409.1*	*0.6795*
272.030	*2.0654*	*1409.3*	*0.6480*
269.990	*1.9778*	*1409.4*	*0.6251*
266.036	*1.8137*	*1409.7*	*0.5817*
262.987	*1.6959*	*1409.9*	*0.5501*
Isomole 14			
350.003	2.5078	949.7	0.9074
335.005	2.3756	950.4	0.8974
320.197	2.2438	951.1	0.8861
305.004	2.1063	951.8	0.8726
289.010	1.9589	952.6	0.8558
265.166	*1.5959*	*953.7*	*0.7590*
259.983	*1.4208*	*953.9*	*0.6891*
256.023	*1.3055*	*954.1*	*0.6428*
252.044	*1.1946*	*954.3*	*0.5973*
248.886	*1.1098*	*954.5*	*0.5619*
244.608	*0.9944*	*954.7*	*0.5121*
Isotherm 1 (Coupling Expansions)			
349.999	15.0580	14642	0.3534
349.998	11.5282	9906	0.3999
350.005	9.9351	6702	0.5094
350.006	8.2557	4534	0.6257
350.006	6.4856	3067	0.7266
350.004	4.8686	2075.1	0.8062
350.011	3.5346	1403.8	0.8652
350.004	2.5077	949.7	0.9074
349.999	1.7511	642.5	0.9366
350.006	1.2103	434.6	0.9570
350.004	0.8306	294.0	0.9708
350.005	0.5674	198.9	0.9803
350.002	0.3863	134.5	0.9870
350.005	0.2625	91.0	0.9912
350.006	0.1782	61.5	0.9957
350.005	0.1207	41.6	0.9970
Isotherm 2			
350.005	10.0874	6799	0.5098
350.005	8.3689	4594	0.6260
349.999	6.5704	3105	0.7373
350.003	4.9258	2097.9	0.8068
350.004	3.5703	1417.7	0.8654
350.004	2.5293	958.0	0.9073
350.006	1.7641	647.3	0.9465
350.005	1.2178	437.4	0.9567
350.005	0.8350	295.5	0.9710
350.005	0.5697	199.7	0.9804
350.006	0.3875	134.9	0.9871
350.003	0.2630	91.2	0.9910
350.005	0.1782	61.6	0.9941
350.006	0.1206	41.6	0.9962
Isotherm 3			
350.005	11.0524	8550	0.4442
350.007	9.4003	5775	0.5504
349.999	7.6162	3901	0.6710
350.002	5.8516	2634.8	0.7632
350.005	4.3161	1779.6	0.8334
350.004	3.0937	1202.0	0.8844
350.004	2.1749	811.9	0.9205
350.007	1.5093	548.4	0.9457
350.005	1.0380	370.4	0.9630
350.007	0.7098	250.1	0.9753
350.004	0.4834	168.9	0.9835
350.006	0.3284	114.1	0.9890
350.005	0.2226	77.0	0.9934
350.005	0.1508	52.0	0.9965

Table 5. (Continued)

T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z
	Isotherm 4				Isotherm 5				Isotherm 6		
399.998	8.3161	3114	0.8031	400.002	10.5288	4234	0.7477	450.050	10.6768	3354	0.8508
400.004	6.0141	2103.1	0.8598	400.003	7.7592	2859.9	0.8158	450.045	7.5660	2265.6	0.8925
400.004	4.2586	1420.5	0.9014	400.004	5.5849	1931.7	0.8693	450.044	5.2940	1530.5	0.9244
400.004	2.9735	959.5	0.9318	400.003	3.9439	1304.8	0.9088	450.044	3.6655	1033.9	0.9475
400.007	2.0544	648.0	0.9533	400.004	2.7466	881.3	0.9371	450.051	2.5191	698.4	0.9639
400.003	1.4092	437.7	0.9681	400.004	1.8946	595.2	0.9571	450.050	1.7219	471.8	0.9753
400.008	0.9619	295.6	0.9784	400.008	1.2979	402.0	0.9708	450.047	1.1725	318.7	0.9832
400.005	0.6543	199.6	0.9856	400.007	0.8853	271.5	0.9804	450.045	0.7992	216.0	0.9888
400.007	0.4442	134.8	0.9908	400.006	0.6019	183.4	0.9868	450.044	0.5419	145.9	0.9926
400.005	0.3009	91.1	0.9931	400.002	0.4084	123.8	0.9919	450.044	0.3669	98.5	0.9955
400.005	0.2037	61.5	0.9959					450.044	0.2483	66.6	0.9964
400.010	0.1378	41.5	0.9984					450.041	0.1680	44.9	0.9999
								450.044	0.1136	30.3	1.0000

[a] Values in italics are global values for two phase vapor + liquid states.

Table 6. Phase Boundary Conditions for CO_2 (1) + H_2S (2) Mixtures

T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z	T/K	p/MPa	ρ/mol·m^{-3}	Z
	$x_1 = 0.9394$				$x_1 = 0.9045$ (Continued)				$x_1 = 0.7067$ (Continued)		
248.09	1.648	23499	0.0340	294.39	5.704	17225	0.1353	309.90	6.856	5781	0.4603
265.43	2.772	21705	0.0579	299.01	6.307	15926	0.1593	301.89	5.620	3908	0.5729
278.83	3.953	20056	0.0850	302.82	6.873	14726	0.1854	290.88	4.262	2645	0.6664
288.26	4.985	18538	0.1122	307.16	7.539	12594	0.2344	277.41	3.044	1788	0.7379
295.13	5.854	17137	0.1392	306.07	7.351	8511	0.3394	263.46	2.111	1209	0.7972
				302.18	6.721	5752	0.4650				
	$x_1 = 0.9392$			292.54	5.371	3889	0.5678		$x_1 = 0.5001$		
301.44	6.762	15861	0.1701	281.04	4.026	2637	0.6533	260.46	1.913	23491	0.0376
303.70	7.103	10727	0.2622	269.54	2.934	1784	0.7339	280.13	3.197	21695	0.0633
304.06	7.143	7256	0.3894	257.21	2.053	1206	0.7957	294.84	4.489	20075	0.0912
297.32	6.116	4909	0.5040					305.84	5.620	18554	0.1191
287.05	4.793	3322	0.6046		$x_1 = 0.7067$			313.99	6.588	17152	0.1471
275.35	3.558	2248	0.6913	261.32	2.242	21948	0.0470	323.62	7.846	14663	0.1989
262.52	2.521	1521	0.7592	277.38	3.436	20276	0.0735	332.45	8.856	9915	0.3231
250.99	1.752	1030	0.8154	289.07	4.548	18738	0.1010	328.63	7.891	6709	0.4305
				298.31	5.598	17320	0.1303	321.00	6.552	4541	0.5406
	$x_1 = 0.9045$			304.72	6.428	16012	0.1585	309.81	5.036	3073	0.6361
261.97	2.466	21820	0.0519	308.94	7.029	14806	0.1848	297.24	3.677	2081	0.7150
276.70	3.709	20160	0.0800	315.86	8.146	12660	0.2450	284.10	2.603	1408	0.7824
286.81	4.771	18633	0.1074	315.51	7.808	8554	0.3480	269.79	1.778	954	0.8312

Table 7. Derived Virial Coefficients for CO_2 (1) + H_2S (2) Mixtures

		B	δB[a]	C	δC[b]	
T/K	x_1	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^6·mol^{-2}	cm^6·mol^{-2}	N_{BE}
325	1.0000	−100.6[c]	−0.5	4163[c]	−173.5	
	0.9393	−102.1	0.1	4277	−134.0	1.4802
	0.4859	−119.8[d]	−0.8	4550[d]	−258.3	
350	1.0000	−84.0	−0.6	3615	−152.7	
	0.9393	−84.7	−0.7	3643	−206.2	1.4802
	0.9045	−86.1	0.1	3899	3.8	1.4797
	0.7067	−92.0	0.4	4017	−126.8	1.4799
	0.5001	−101.2	0.1	4320	−56.8	1.4802
	0.4859	−101.4[d]	−0.5	4063[d]	−328.7	
400	1.0000	−59.8[c]	−0.4	2901[c]	−11.6	
	0.9393	−59.9	−1.0	2831	−156.5	1.4801
	0.9045	−62.3	0.8	3076	45.7	1.4803
	0.7067	−68.2	2.4	3838	566.0	1.4805
	0.5001	−74.4	0.5	3507	−13.3	1.4806
	0.4859	−75.3[d]	0.8	3537[d]	−0.2	
450	1.0000	−43.0[c]	0.0	2429[c]	75.9	
	0.9393	−42.8	−0.9	2482	63.6	1.4800
	0.9045	−45.2	1.0	2177	−278.7	1.4800
	0.5001	−53.6	−1.2	2718	−172.9	1.4804
	0.4859	−55.7[d]	0.3	2562[d]	−344.2	

[a] $\delta B_m = B_m^{exp} - B_m^{corr}$. [b] $\delta C_m = C_m^{exp} - C_m^{corr}$. [c] From Holste et al.[12] [d] From Liu.[7]

dioxide quite well, as shown in Table 7. This correlation also describes the third virial coefficients for these mixtures within the accuracy of the measurements using the mixing rules described below. The expression for the third virial coefficient of a mixture, C_m, is

$$C_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k C_{ijk} \tag{6}$$

where the C_{ijk} are cross third virial coefficients. The mixing rules that describe these mixtures well are

$$T_{c,ijk} = (T_{c,i} T_{c,j} T_{c,k})^{1/3} \tag{7}$$

$$P_{c,ijk} = \frac{9T_{c,ijk}(P_{c,i}V_{c,i}/T_{c,i} + P_{c,j}V_{c,j}/T_{c,j} + P_{c,k}V_{c,k}/T_{c,k})}{(V_{c,i}^{1/3} + V_{c,j}^{1/3} + V_{c,k}^{1/3})^3} \tag{8}$$

$$\omega_{ijk} = (\omega_i + \omega_j + \omega_k)/3 \tag{9}$$

To our knowledge, this work represents the first use of these rules. The differences between the values calculated from the correlation and the experimental values from this work and those reported by Liu[7] are shown in Table 7. The standard deviation of these differences is 186 cm^6·mol^{-2}, which is within the experimental accuracy. Table 8 gives the values of the pure and cross third virials used to calculate the deviations in Table 7. Figure 3 shows the temperature dependence of the Orbey and Vera[17] correlation and selected experimental values.

Accuracy of Derived Values. The error analysis detailed by Hwang et al.[14] indicates that, for these measurements, the densities and compressibility factors derived

Table 8. Values of Pure and Cross Second and Third Virial Coefficients Used To Calculate Deviations Shown in Table 7[a]

	325 K	350 K	400 K	450 K
B_{CO_2}/cm^3·mol^{-1}	−101.2	−84.6	−60.1	−43.0
$B_{CO_2-H_2S}$/cm^3·mol^{-1}	−106.3	−89.9	−65.4	−48.1
B_{H_2S}/cm^3·mol^{-1}	−165.1	−140.1	−104.5	−80.2
C_{CO_2}/cm^6·mol^{-2}	4337	3768	2913	2354
$C_{CO_2-CO_2-H_2S}$/cm^6·mol^{-2}	4757	4220	3234	2710
$C_{CO_2-H_2S-H_2S}$/cm^6·mol^{-2}	4993	4598	3729	3072
C_{H_2S}/cm^6·mol^{-2}	4822	4794	4094	3428

[a] These values were calculated using correlations and mixing rules described in the text and a binary interaction parameter, k_{ij} = 0.08.

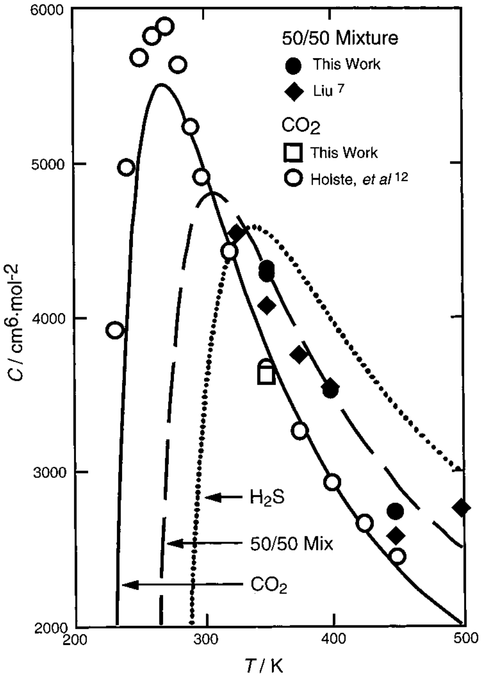

Figure 3. Comparison of the temperature dependence of the Orbey and Vera[17] correlation for third virial coefficients with selected experimental results for CO_2, H_2S, and an equimolar mixture.

from the Burnett analyses are accurate to ±0.08%. The error in the expansion ratio accumulates in the calculation of densities for the isomoles connected by expansions into the density reduction cell; therefore, the errors for those isomoles increase from ±0.08% to ±0.3% as the density increases. The phase boundary temperatures and pressures are accurate to ±0.05 K and ±0.01 MPa, respectively. All values given in this section represent 95% confidence limits.

Summary

Despite the experimental challenges posed by the presence of H_2S, the results presented here have excellent internal consistency. The combination of correlations for second and third virial coefficients provides a reliable representation of the temperature, density, and composition dependence of these measurements; therefore, it provides a reliable method for computing the volumetric behavior of mixtures of carbon dioxide and hydrogen sulfide at densities for which the virial equation truncated after the third term is appropriate.

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