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PρT and VLE for Ethane + Hydrogen Sulfide from (254.05 to 363.21) K at Pressures up to 20 MPa

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Pressure, density, and temperature (PρT) data are presented for ethane (1) + hydrogen sulfide (2) at z_2 = (0.0380, 0.0563, 0.0977, and 0.1430) and various temperatures in the (254.05 to 363.21) K range. A vibrating tube densimeter, with the forced path mechanical calibration model, was used to determine both PρT data and vapor−liquid equilibrium (VLE) even when the mixture is close to its critical temperature. PρT and VLE results were correlated with the Benedict−Webb−Rubin−Starling's equation of state (BWRS EoS), the re-evaluated pure component parameters, and the mixing parameters derived using Starling's generalized mixing rules. Finally, we have compared, in VLE conditions, the BWRS EoS to a Peng−Robinson EoS using quadratic mixing rules.

Introduction

Hydrocarbon processes continue to need data for simulating the behavior of complex fluid mixtures that include components such as hydrogen sulfide. vapor−liquid equilibrium (VLE) data exist for systems containing light hydrocarbon and hydrogen sulfide.[1−3] However, there are few density data of systems containing hydrogen sulfide in the single-phase regions.

Moreover, most equations of state (EoS) used to represent VLE data do not give good density values. The simplest cubic equations of state, with three parameters, are not efficient to simultaneously represent PVT and VLE data. Among various multiparameter equations, we have focused our attention on equations involving virial expansions well-known for their high efficiency representing volumetric properties. In 1940, Benedict, Webb, and Rubin (BWR)[4] proposed an EoS based on the virial expansion to correlate light hydrocarbon densities. In 1971, Starling included new parameters to improve this viral type EoS (BWRS)[5,6] and proposed generalized mixing rules with one binary interaction parameter.

In this work, pressure, temperature, and density (PρT) data sets are presented for the C_2H_6 (1) + H_2S (2) system. Four compositions are studied with z_2 ranging from 0.0380 up to 0.1430 at temperatures between (250 and 360) K.

The forced path mechanical calibration model[7] was used to convert acquired vibrating periods into density data. The chosen experimental procedure allows recording large amount of data points over 1 MPa. Bubble and dew points are precisely estimated from these numerous accurate densities data.

Experimental Section

Materials. Ethane was purchased from Messer France with a volume fraction certified purity higher than 99.95. Hydrogen sulfide was purchased from Alpha Gaz with a volume fraction certified purity higher than 99.5.

Table 1. Critical Properties of Pure Compounds[14]

	M	P_c	T_c	v_c	ρ_c[a]
compound	kg/mol	MPa	K	$10^{-5}\cdot$(m^3/mol)	kg/m^3
ethane	0.030096	4.872	305.32	14.6	206.9
hydrogen sulfide	0.034082	8.963	373.53	9.85	346.0

[a] Critical density was calculated as $\rho_c = M/v_c$.

Apparatus. The apparatus, shown in Figure 1, is based on an Anton Paar DMA 512P cell. The vibrating tube technique able to work at pressures up to 40 MPa has been described.[8] The new cell, with its vibrating tube made of Hastelloy, can work up to 70 MPa. The fluid (pure compound or mixture) was introduced into the loading and pressurizing cell (1) and was maintained above its bubble pressure at ambient temperature. The period of the vibrating tube was measured by a HP 53131A data acquisition unit (12). The uncertainty on vibrating period data is ± 1 × 10^{-8} s. The temperature of the vibrating tube was controlled by a regulated bath (LAUDA RE206) through inlet/outlet ports (6) with a stability of ± 0.01 K. Another bath (15) (HUBER Variostat P1-C50P) regulates the temperature of the remaining parts of the circuit. Positive or negative differences of about 0.3 K were set between the vibrating tube temperature and the remaining circuit temperature to allow formation of the first bubble or first liquid droplet strictly inside the vibrating tube when the pressure reached the vapor pressure of the mixture. Temperatures were measured by two Pt100 probes (11 and 14) connected to the HP 34970A data acquisition unit (13). These Pt100 probes are periodically calibrated against a 25 Ω reference thermometer (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol. Resulting uncertainties in temperatures are less than ± 0.01 K. Vacuum was achieved with a vacuum pump (AEG type LN38066008), working for several hours to obtain a reference vibrating period at very low pressures (< 5 × 10^{-4} MPa). Pressure was measured using three sensors (8) (from Druck, all being of PTX611 type, but with different operating ranges: (0 to 0.2) MPa, (0 to 5) MPa, and (0 to 40) MPa). These sensors were calibrated against

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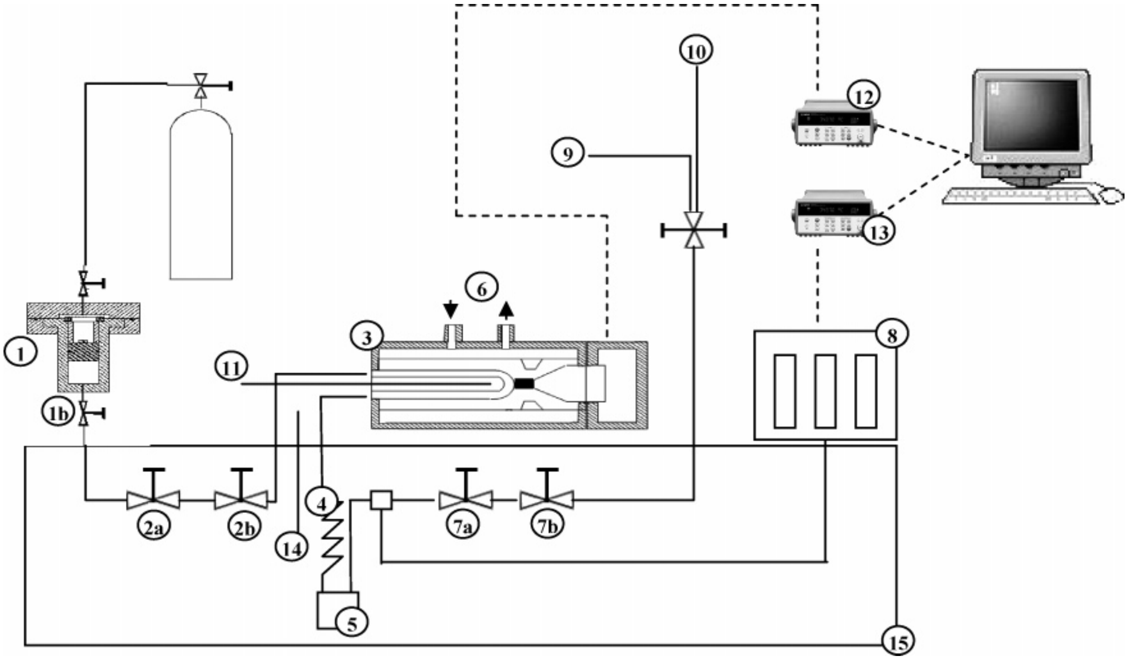

Figure 1. Flow diagram of the equipment: 1, loading cell; 2a and 2b, regulating and shut-off valves; 3, DMA 512 P densimeter (Anton Paar); 4, heat exchanger; 5, bursting disk; 6, inlet and outlet of the temperature regulating fluid; 7a and 7b, regulating and shut-off valves; 8, pressure sensors maintained at constant temperature (373 K); 9, to vacuum pump; 10, vent; 11, vibrating cell temperature sensor; 12, HP 53131A unit; 13, HP 34970A unit; 14, bath temperature sensor; 15, liquid bath.

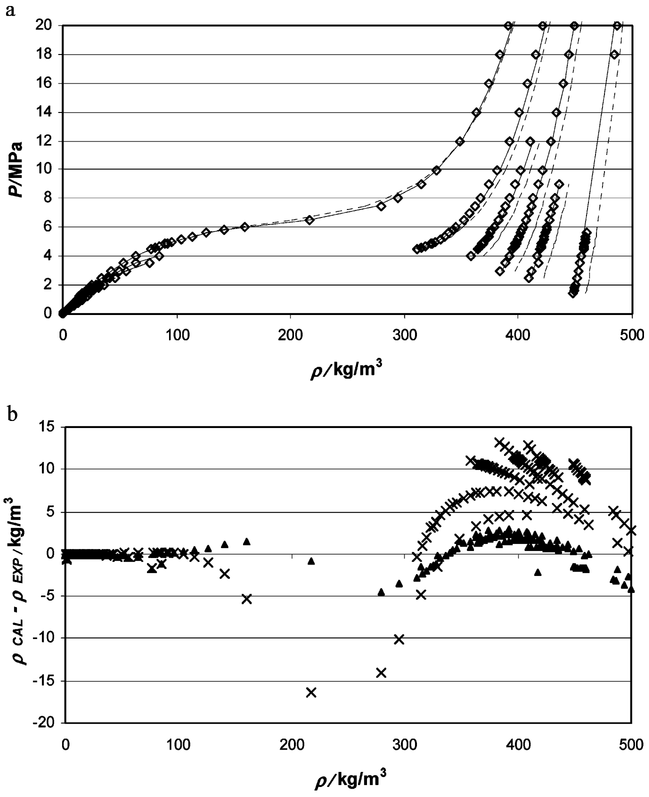

Figure 2. (a) (PρT) data of ethane: ◇, Younglove and Ely[11] (250, 270, 280, 290, 300, and 320) K; - - -, calculated with BWRS EoS and Starling correlation;[6] —, calculated with BWRS EoS and parameters used in this work. (b) Deviation plots: ×, deviations observed using BWRS EoS and Starling correlation;[6] ▲, deviations observed using BWRS EoS and parameters adjusted in this work.

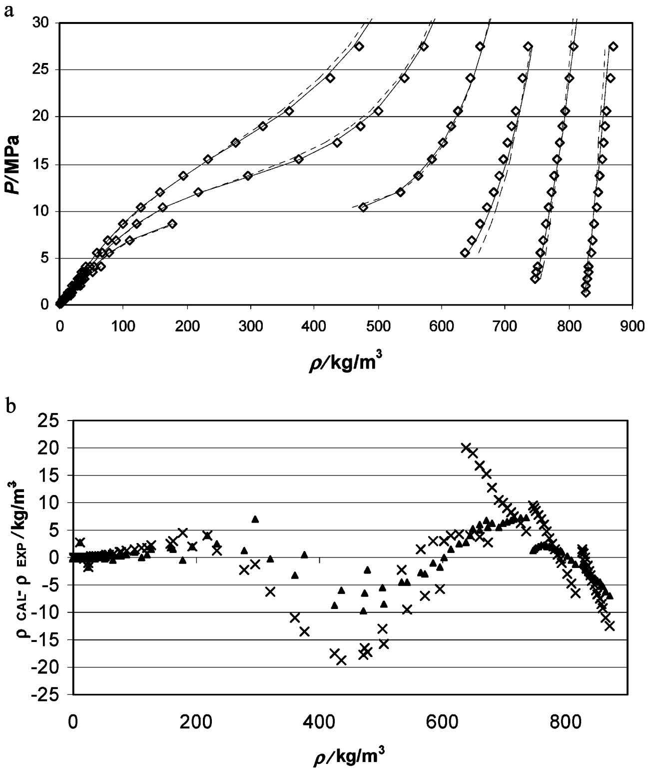

Figure 3. (a) (PρT) data of hydrogen sulfide: ◇, Reamer et al.[12] (278, 311, 344, 378, 411, and 444) K; - - -, calculated with BWRS EoS and Starling correlation;[6] —, calculated with BWRS EoS and parameters used in this work. (b) Deviation plots: ×, deviations observed using BWRS EoS and Starling correlation;[6] ▲, deviations observed using BWRS EoS and parameters adjusted in this work.

a dead weight pressure balance (5202S model from Desgranges & Huot) for the range (0.3 to 40) MPa and against an electronic balance (fundamental digital pressure standard, model 24610 from Desgranges & Huot) for pressures below 0.3 MPa. The pressure transducers were connected to the HP 34970A data acquisition unit. The global uncertainties on pressures after calibration were (± 0.00015, ± 0.001, and ± 0.002) MPa, respectively, to sensor ranges: (0.2, 5 and 40) MPa. Real time data are recorded simulta-

Table 2. BWRS Parameters

	ethane			hydrogen sulfide		
	correlation [5−6]	adjusted (this work)	DU/%[a]	correlation [5−6]	adjusted (this work)	DU/%[a]
A_0	0.44054	0.43968	−0.2	0.36636	0.36729	0.3
B_0	$6.6228 \cdot 10^{-5}$	$6.9120 \cdot 10^{-5}$	4.4	$4.4774 \cdot 10^{-5}$	$4.4258 \cdot 10^{-5}$	−1.2
C_0	$1.8121 \cdot 10^{4}$	$1.8532 \cdot 10^{4}$	2.3	$2.2074 \cdot 10^{4}$	$1.9924 \cdot 10^{4}$	−9.7
D_0	$5.1087 \cdot 10^{5}$	$5.1087 \cdot 10^{5}$	0.0	$7.5952 \cdot 10^{5}$	$7.5952 \cdot 10^{5}$	0.0
E_0	$1.5857 \cdot 10^{7}$	$1.5857 \cdot 10^{-7}$	0.0	$2.9727 \cdot 10^{7}$	$2.9727 \cdot 10^{7}$	0.0
A	$3.0042 \cdot 10^{-5}$	$3.1702 \cdot 10^{-5}$	5.5	$1.6723 \cdot 10^{-5}$	$1.6082 \cdot 10^{-5}$	−3.8
B	$1.1927 \cdot 10^{-8}$	$1.1525 \cdot 10^{-8}$	−3.4	$5.4480 \cdot 10^{-9}$	$5.3120 \cdot 10^{-9}$	−2.5
C	3.1844	3.3101	3.9	2.6427	2.3443	−11.3
D	$1.9590 \cdot 10^{-3}$	$1.9590 \cdot 10^{-3}$	0.0	$1.3160 \cdot 10^{-3}$	$1.3160 \cdot 10^{-3}$	0.0
α	$2.0361 \cdot 10^{-13}$	$2.0565 \cdot 10^{-13}$	1.0	$6.3397 \cdot 10^{-14}$	$5.5638 \cdot 10^{-14}$	−12.2
γ	$1.0967 \cdot 10^{-8}$	$1.0291 \cdot 10^{-8}$	−6.2	$5.0400 \cdot 10^{-9}$	$4.2823 \cdot 10^{-9}$	−15.0

[a] Deviation on variable U is calculated by $\mathrm{DU} = (U_{\mathrm{adjusted}} - U_{\mathrm{correlation}})/U_{\mathrm{correlation}}$.

Table 3. PρT Data for Ethane (1) + Hydrogen Sulfide (2) System; $z_2 = 0.0380$[a]

T = 263.43 K			T = 293.24 K			T = 333.23 K		
P	ρ_{exp}	ρ_{cal}	P	ρ_{exp}	ρ_{cal}	P	ρ_{exp}	ρ_{cal}
MPa	kg/m^3	kg/m^3	MPa	kg/m^3	kg/m^3	MPa	kg/m^3	kg/m^3
0.037	0.5	0.5	0.042	0.5	0.5	0.039	0.5	0.4
0.499	7.4	7.3	0.505	6.6	6.5	0.523	6.0	5.9
1.013	16.1	15.9	1.009	13.7	13.7	1.025	11.9	11.8
1.515	26.2	26.0	1.528	21.9	21.8	1.541	18.5	18.4
1.873	35.1	34.7	2.029	30.9	30.7	2.023	25.0	24.9
******	*****	*****	2.507	40.9	40.7	2.526	32.4	32.2
1.989	430.6	429.8	3.019	54.1	53.6	3.001	39.8	39.6
2.503	432.8	432.1	3.505	71.0	70.2	3.521	48.8	48.6
3.007	435.0	434.3	3.798	86.6	84.7	4.004	57.9	57.8
3.507	437.0	436.4	******	*****	*****	4.502	68.4	68.4
4.010	439.0	438.3	4.013	350.5	347.5	5.002	80.5	80.6
4.505	440.8	440.2	4.507	359.1	357.3	5.502	94.1	94.9
5.023	442.6	442.0	5.001	365.5	364.9	6.007	110.8	112.3
5.511	444.3	443.7	5.501	371.2	371.2	6.506	130.9	133.4
6.016	445.9	445.3	6.017	376.3	376.7	7.009	155.6	159.3
6.500	447.5	446.9	6.516	380.7	381.4	7.516	184.0	188.0
7.009	449.1	448.4	7.025	384.7	385.7	8.006	211.3	213.9
7.488	450.5	449.8	7.532	388.3	389.6	8.512	235.7	236.5
8.012	452.0	451.4	8.009	391.5	392.9	9.012	255.1	254.7
8.487	453.4	452.7	8.535	394.7	396.3	9.503	270.4	269.4
9.000	454.8	454.1	9.023	397.5	399.2	10.032	283.7	282.6
9.484	456.1	455.3	9.501	400.1	401.9	10.508	293.6	292.7
10.009	457.5	456.7	10.000	402.6	404.6	11.006	302.5	301.9
10.481	458.7	457.8	10.528	405.2	407.2	11.511	310.4	310.0
11.024	460.0	459.2	11.010	407.5	409.5	12.065	318.0	317.9
11.515	461.2	460.3	11.511	409.8	411.8	12.530	323.8	323.8
12.032	462.5	461.5	12.026	412.0	414.0	13.022	329.3	329.5
12.500	463.5	462.6	12.516	414.0	416.0	13.545	334.9	335.0
13.005	464.7	463.7	13.050	416.0	418.1	14.078	339.8	340.2
13.543	465.9	464.8	13.529	417.9	420.0	14.500		344.0
14.011	467.0	465.8	14.043	419.8	421.8	15.000		348.2
14.498	468.0	466.8	14.532	421.5	423.6	15.500		352.1
14.864	468.9	467.6	15.006	423.1	425.2	16.000		355.8
15.000		467.9	15.500		426.8	16.500		359.2
15.500		468.8	16.000		428.4	17.000		362.5
16.000		469.8	16.500		430.0	17.500		365.6
16.500		470.8	17.000		431.5	18.000		368.6
17.000		471.7	17.500		433.0	18.500		371.4
17.500		472.6	18.000		434.4	19.000		374.0
18.000		473.6	18.500		435.8	19.500		376.6
18.500		474.4	19.000		437.1	20.000		379.1
19.000		475.3	19.500		438.5			
19.500		476.2	20.000		439.8			
20.000		477.0						

[a] The asterisks separate liquid data from vapor data.

neously by a computer linked to both HP units. Mixtures were prepared carefully,[9] weighing being achieved using a CC3000 analytical balance, from Sartorius AG Göttingen. The uncertainties on mass determinations are ± 10^{-3} g.

Experimental Procedure. First of all, both baths were programmed at constant temperatures with temperature difference corresponding to the requested measurements: bubble or dew pressures. The whole circuit was evacuated using the vacuum pump (with 9, 7a, and 7b valves open and valves 10 and 2b closed). During this time, the mixture was loaded into the loading cell (1) according to the method presented by Galicia-Luna et al.[9] A few period values were recorded to have a reference vibrating period at the lowest pressure (< 5 × 10^{-4} MPa). After connecting the loading cell to the circuit through valve (1b), vacuum was made until (1b) by opening valves (2a and 2b). The loading cell

Table 4. PρT Data for Ethane (1) + Hydrogen Sulfide (2) System; z_2 = 0.0563[a]

T = 273.41 K			T = 313.14 K			T = 353.15 K		
P	ρ_{exp}	ρ_{cal}	P	ρ_{exp}	ρ_{cal}	P	ρ_{exp}	ρ_{cal}
MPa	kg/m^3	kg/m^3	MPa	kg/m^3	kg/m^3	MPa	kg/m^3	kg/m^3
0.026	0.3	0.4	0.047	0.6	0.6	0.104	1.1	1.0
0.520	7.5	7.3	0.511	6.2	6.1	0.559	6.1	5.9
1.508	24.3	24.2	1.538	20.2	20.0	1.556	17.5	17.3
2.022	35.7	35.4	2.016	27.4	27.4	2.026	23.2	23.1
2.402	46.5	45.9	2.502	35.7	35.4	2.549	29.9	29.8
******	*****	*****	3.024	45.6	45.3	3.050	36.8	36.7
2.518	411.5	411.2	3.511	56.2	56.0	3.516	43.6	43.5
3.015	414.6	414.5	4.004	69.1	68.8	4.014	51.3	51.2
3.539	417.6	417.8	4.505	85.7	85.3	4.543	60.3	60.0
4.013	420.2	420.5	5.001	108.6	108.9	5.016	68.7	68.8
4.504	422.6	423.1	5.502	149.0	156.7	5.504	77.9	78.2
5.023	425.1	425.7	6.009	244.1	249.0	6.017	88.8	89.4
5.528	427.4	428.1	6.547	287.4	286.9	6.503	100.1	100.7
6.035	429.6	430.3	7.010	305.9	305.1	7.021	113.4	114.2
6.526	431.6	432.4	7.595	321.3	320.9	7.506	126.9	128.1
7.027	433.6	434.4	8.067	330.6	330.9	8.023	142.6	143.7
7.500	435.4	436.2	8.569	338.7	339.4	8.512	158.5	159.5
8.008	437.2	438.1	9.087	345.8	346.8	9.014	175.3	175.8
8.504	438.9	439.9	9.611	352.0	353.2	9.519	192.2	192.0
9.040	440.8	441.7	10.001	356.1	357.6	10.001	207.8	206.5
9.541	442.4	443.3	10.527	361.2	362.9	10.508	223.0	220.7
10.025	443.9	444.9	11.077	365.9	367.8	11.024	236.8	233.7
10.511	445.4	446.4	11.554	369.7	371.7	11.504	248.6	244.9
11.020	447.0	447.9	12.109	373.8	375.9	12.040	259.9	256.2
11.521	448.4	449.3	12.503	376.6	378.7	12.516	268.8	265.4
12.056	449.9	450.8	13.060	380.4	382.4	13.052	278.6	274.6
12.528	451.3	452.1	13.548	383.3	385.5	13.588	286.4	283.1
13.016	452.6	453.4	14.000		388.1	14.050	292.6	289.7
13.521	453.9	454.7	14.500		390.9	14.564	298.9	296.6
14.053	455.3	456.1	15.000		393.6	15.065	304.9	302.7
14.544	456.5	457.3	15.500		396.1	15.533	309.9	308.1
15.000		458.4	16.000		398.5	16.020	314.8	313.4
15.500		459.5	16.500		400.8	16.557	319.9	318.8
16.000		460.7	17.000		403.0	17.112	324.8	323.9
16.500		461.8	17.500		405.2	17.529	328.2	327.6
17.000		462.9	18.000		407.2	18.000		331.5
17.500		464.0	18.500		409.2	18.500		335.5
18.000		465.0	19.000		411.1	19.000		339.3
18.500		466.1	19.500		412.9	19.500		342.8
19.000		467.1	20.000		414.7	20.000		346.2
19.500		468.1						
20.000		469.1						

[a] The asterisks separate liquid data from vapor data.

is also connected to a pressurizing cylinder to pressurize the mixture to be studied at a pressure much higher than its bubble pressure to maintain it in homogeneous liquid state even when loading the vibrating tube. Then, valves (7a and 2b) were closed and valve (1b) was opened. Small amounts of fluid (small flow rates controlled by regulating valve (2b)) can be continuously introduced into the vibrating tube. Then pressure increases continuously up to the dew point at controlled rate of a maximum 0.005 MPa/s. During this process the fluid was assumed to be in equilibrium and pressure, period, and temperature (PτT) were recorded every 0.3 s. After recording dew point, (determined through the drastic change in the Pτ (or Pρ) behavior going from single phase to diphasic properties as described by Bouchot and Richon[8]), the fluid was fully condensed in the whole circuit by increasing pressure up to the chosen maximum pressure of the study (about 20 MPa in this work). Valves (9) and (10) were closed and valve (7a) was opened. The condensation over a pressure range leads to composition gradient inside the vibrating tube and circuit. It is necessary to introduce fresh mixture from the loading cell to purge the circuit. By opening valve (10) the fluid was allowed to circulate. (It is assumed that the liquid inside the vibrating tube is representative of the fluid from loading cell when measured period remains constant and is not dependent on further purging.) Then, liquid phase was studied from the chosen upper pressure limit down to bubble point determined through the drastic change in the Pτ (or Pρ) behaviors going from single phase to diphasic properties as described by Bouchot and Richon.[8] The pressure decreases continuously at controlled rate of a maximum 0.005 MPa/s using regulating valve (7a). During this process the fluid was assumed to be in equilibrium and pressure, period (s), and temperature (PτT) were recorded every 0.3 s. Periods are converted into densities using the forced path mechanical calibration model (FPMC),[7] whose parameters are calculated from (PρT) data of a reference fluid (R134a)[10].

Estimation of Uncertainties. The global uncertainty on density data in the liquid or vapor phase is estimated to be within ± 0.05 % with a minimum value of ± 0.2 kg/m^3, due to the uncertainties of the mechanical parameters used in the FPMC model. Global temperature uncertainties are estimated to be about ± 0.02 K, which includes temperature uncertainty of the bath regulation. The uncertainty on pressure measurements is about ± 0.002 MPa.

This intersection between the two branches of Pτ (or Pρ) curves one pertaining to single-phase region and the second to diphasic region being more or less well-defined depending on operating conditions that can be close or far from

Table 5. PρT Data for Ethane (1) + Hydrogen Sulfide (2) System; z_2 = 0.0977[a]

T = 254.05 K			T = 303.14 K			T = 363.21 K		
P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3	P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3	P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3
0.016	0.3	0.3	0.111	1.4	1.3	0.045	0.5	0.4
0.506	8.0	7.9	0.542	6.9	6.8	0.536	5.6	5.6
1.004	17.0	16.7	1.037	13.6	13.6	1.025	10.9	10.7
******	*****	*****	1.552	21.3	21.2	1.513	16.4	16.2
1.593	462.8	460.6	2.031	29.3	29.1	2.042	22.6	22.4
2.020	464.2	462.1	2.540	38.8	38.6	2.511	28.4	28.2
2.513	465.8	463.8	3.032	49.4	49.2	3.022	35.0	34.8
3.032	467.5	465.5	3.508	61.8	61.7	3.522	41.9	41.6
3.527	468.9	467.1	4.005	78.6	78.6	4.030	49.2	49.0
4.027	470.4	468.6	******	*****	*****	4.526	56.8	56.7
4.526	471.8	470.1	5.002	322.8	304.5	5.036	64.8	65.0
5.004	473.1	471.4	5.501	339.8	329.0	5.513	72.9	73.2
5.501	474.5	472.8	6.016	350.8	343.7	6.000	81.9	82.3
6.013	475.8	474.1	6.512	358.9	353.8	6.503	91.8	92.3
6.529	477.1	475.5	7.005	365.5	362.0	7.010	102.5	103.2
7.007	478.4	476.7	7.505	371.2	368.6	7.504	113.7	114.5
7.506	479.6	477.9	8.005	376.2	374.5	8.019	126.2	127.2
8.074	480.8	479.3	8.528	380.9	380.0	8.520	139.1	140.1
8.538	482.0	480.4	9.039	385.1	384.7	9.002	152.0	153.0
9.038	483.1	481.5	9.533	388.8	388.8	9.515	166.3	167.1
9.505	484.2	482.6	10.019	392.2	392.6	10.026	180.6	180.9
10.025	485.3	483.7	10.550	395.7	396.3	10.507	193.9	193.5
10.547	486.4	484.8	11.030	398.7	399.5	11.005	207.3	205.9
11.048	487.5	485.8	11.526	401.5	402.6	11.521	220.4	218.3
11.515	488.5	486.8	12.049	404.4	405.6	12.017	232.1	229.4
12.026	489.5	487.8	12.537	406.9	408.3	12.517	243.0	239.7
12.502	490.5	488.8	13.057	409.5	411.0	13.011	252.9	249.1
13.029	491.5	489.8	13.553	411.8	413.4	13.528	262.4	258.4
13.515	492.4	490.7	14.063	414.2	415.8	14.033	270.9	266.7
14.025	493.4	491.7	14.529	416.2	417.9	14.520	278.3	274.2
14.544	494.4	492.6	15.040	418.3	420.1	15.007	285.3	281.2
15.049	495.3	493.5	15.545	420.4	422.3	15.520	292.0	288.1
15.530	496.2	494.4	16.002	422.2	424.1	16.005	297.9	294.2
16.018	497.0	495.2	16.554	424.3	426.2	16.547	304.1	300.5
16.561	498.0	496.1	17.059	426.1	428.1	17.035	309.2	305.8
17.029	498.8	496.9	17.529	427.8	429.8	17.512	313.9	310.8
17.503	499.7	497.7	18.066	429.6	431.6	18.010	318.5	315.7
18.027	500.6	498.6	18.581	431.4	433.4	18.518	322.9	320.4
18.519	501.4	499.3	19.021	432.8	434.8	19.041	327.2	324.9
19.017	502.2	500.1	19.584	434.6	436.6	19.500		328.8
19.513	503.0	500.9	20.082	436.1	438.1	20.000		332.7
20.002	503.8	501.7	20.583	437.6	439.6			
20.521	504.5	502.5	21.039	439.1	441.0			
21.008	505.3	503.2						
21.521	506.1	503.9						

[a] The asterisks separate liquid data from vapor data.

critical point. As a consequence uncertainties on saturating properties are higher than those corresponding to condensed phases. The temperature, pressure, and density uncertainties are estimated correspondingly to each bubble and dew points (see Table 8) from visual treatment of Pτ (or Pρ) curves. Uncertainties of mixture compositions are within $\pm\ 2 \times 10^{-4}$ in mole fractions.

Pure Compound Density Correlations

PρT data were fitted using the of Benedict−Webb−Rubin−Starling[5] (BWRS) EoS, which corresponds to a modification of the Benedict−Webb−Rubin[4] (BWR) EoS, i.e.:

$$P = \rho RT + \left(B_0RT - A_0\frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha.\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^3}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

This EoS needs 11 parameters (A_0, B_0, C_0, D_0, E_0, a, b, c, d, α, and γ) for each compound. Starling proposed a correlation[6] to estimate values of these parameters using critical properties (T_c and ρ_c, see Table 1). Literature density data[11,12] were used to test validity of the BWRS EoS and Starling correlation parameters. Deviations between calculated and experimental data were studied using two indicators:

$$\text{average deviation:}\quad \Delta\bar{\rho} = \frac{1}{N}(\rho_{cal} - \rho_{exp})$$

$$\text{standard deviation:}\quad \sigma_{\Delta\rho} = \frac{1}{N}\sqrt{\sum_N(\rho_{cal} - \rho_{exp})^2}$$

In the following comparisons, results are given with the form $\Delta\bar{\rho} \pm \sigma_{\Delta\rho}$. Figure 2a shows P$\rho$T data and BWRS representation while Figure 2b shows deviations between experimental and predicted values of 217 ethane density data[11] from (250 to 320) K, up to 20 MPa. Observed deviations are within (4.4 ± 5.3) kg/m^3. Figure 3 shows the same comparison for hydrogen sulfide using 166 data[12] from (278 to 444) K up to 31 MPa. The deviations are

Table 6. PρT Data for Ethane (1) + Hydrogen Sulfide (2) System; z_2 = 0.1430[a]

T = 268.15 K			T = 283.30 K			T = 322.21 K		
P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3	P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3	P / MPa	ρ_{exp} / kg/m^3	ρ_{cal} / kg/m^3
0.112	1.6	1.5	0.025	0.3	0.3	0.066	0.8	0.8
0.531	7.8	7.7	0.510	7.0	6.9	0.538	6.4	6.4
1.029	16.0	16.0	1.001	14.4	14.3	1.031	12.6	12.5
1.511	25.3	25.2	1.526	23.4	23.3	1.549	19.5	19.6
2.007	37.0	37.0	2.015	33.0	32.7	2.001	26.1	26.1
******	*****	*****	2.500	44.5	44.3	2.529	34.3	34.4
2.514	445.3	443.5	3.014	60.8	60.0	3.032	43.1	43.1
3.011	447.8	446.2	3.511	407.8	404.8	3.522	52.5	52.7
3.510	450.1	448.8	4.003	412.1	409.8	4.000	62.8	63.2
4.024	452.3	451.2	4.509	415.9	414.4	4.512	75.6	76.3
4.524	454.4	453.4	5.032	419.5	418.6	5.022	91.1	92.4
5.004	456.3	455.5	5.512	422.6	422.1	5.501	108.7	111.9
5.503	458.2	457.5	6.017	425.7	425.6	6.008	134.7	141.4
6.002	460.1	459.5	6.532	428.5	428.7	6.510	173.9	186.0
6.521	461.8	461.4	7.013	431.1	431.5	7.013	226.0	233.4
7.025	463.6	463.2	7.509	433.6	434.2	7.521	267.2	266.9
7.512	465.2	464.9	8.035	436.1	436.9	8.028	292.3	289.9
8.011	466.8	466.6	8.513	438.3	439.2	8.532	309.1	306.6
8.503	468.3	468.2	9.029	440.5	441.6	9.019	321.4	319.5
9.020	469.9	469.8	9.513	442.5	443.7	9.526	331.6	330.4
9.528	471.4	471.3	10.033	444.6	445.9	10.007	339.7	339.1
10.040	472.8	472.8	10.546	446.6	448.0	10.531	347.3	347.2
10.516	474.2	474.2	11.020	448.3	449.8	11.064	354.0	354.4
11.023	475.6	475.5	11.539	450.2	451.7	11.514	358.8	359.9
11.531	476.9	476.9	12.016	451.9	453.4	12.004	363.7	365.3
12.028	478.2	478.2	12.516	453.5	455.1	12.563	368.8	370.9
12.514	479.4	479.4	13.046	455.3	456.9	13.066	373.0	375.5
13.007	480.7	480.7	13.521	456.8	458.4	13.509	376.5	379.2
13.514	481.9	481.9	14.029	458.3	460.0	14.045	380.5	383.4
14.025	483.2	483.1	14.527	459.8	461.5	14.514	383.7	386.8
14.504	484.2	484.2	15.050	461.4	463.1	15.012	387.0	390.3
15.003	485.4	485.3	15.502	462.7	464.4	15.525	390.2	393.6
15.538	486.6	486.5	16.044	464.2	465.9	16.068	393.3	397.0
16.001	487.6	487.5	16.513	465.5	467.1	16.524	395.9	399.6
16.547	488.8	488.7	17.058	467.0	468.6	17.097	399.0	402.8
17.012	489.8	489.7	17.510	468.1	469.8	17.555	401.3	405.2
17.551	490.9	490.8	18.015	469.4	471.1	18.041	403.7	407.7
18.078	492.0	491.9	18.542	470.8	472.4	18.541	406.0	410.1
18.516	492.9	492.7	19.002	471.9	473.5	19.084	408.5	412.7
19.014	493.9	493.7	19.545	473.2	474.8	19.607	410.8	415.0
19.551	494.9	494.7	20.029	474.4	475.9	20.046	412.6	416.9
20.022	495.9	495.6	20.565	475.6	477.1	20.528	414.6	418.9
20.523	496.8	496.5	21.034	476.6	478.1			
21.032	497.8	497.4	21.519	477.8	479.2			
21.503	498.6	498.3						

[a] The asterisks separate liquid data from vapor data.

within (−0.11 ± 5.9) kg/m^3. These results are closed to the average deviations presented by Starling[6] (3 kg/m^3 for ethane and 7 kg/m^3 for hydrogen sulfide). For ethane, the pressure range of data used by Starling was limited to 6.9 MPa versus 20 MPa in this paper.

As the deviations on pure compounds noted above effect the prediction of the mixture properties, the BWRS parameters were adjusted in order to better represent density literature data. BWR described a procedure to determine these parameters[4] using data in compressed phases and along the VLE line. In this work, four classes were defined in which each parameter has about the same influence on EoS behavior: (A_0), (b, α, γ), (B_0, C_0, a, c), and (D_0, E_0, d). Thus, the adjustment of parameters was made classes by classes beginning with the parameter class having the highest weight (in the order just cited). The Starling correlation was used to initialize the values of the parameters.

The new parameter values are presented in Table 2. Deviations between literature and calculated (using the new parameters from Table 2) pure compound densities are presented in Figures 2 and 3. Average and standard deviations were thus reduced to (0.2 ± 1.4) kg/m^3 for ethane and to (0.0 ± 3.0) kg/m^3 for hydrogen sulfide.

Isothermal PρT Data of Mixture

Tables 3 to 6 and Figure 4 present the experimental isothermal PρT data sets at four compositions of the ethane (1) + hydrogen sulfide (2) binary system. The representation of mixture properties needs mixing rules to define the pseudo-parameters of the BWRS EoS from the values corresponding to pure compounds. The mixing rules chosen in this work were developed by Starling[6] and are presented in Table 7. A binary interaction parameter (k_{ij}) specific to the ij mixture, is introduced. We have adjusted this parameter on 178 experimental mixture density data selected over the whole range of PρT data. Adjustment has been done using the simplex algorithm with the following "objective" function:

$$F = \frac{100}{N}\sqrt{\sum_{N}^{i}\left(\frac{(\rho_{cal} - \rho_{exp})}{\rho_{exp}}\right)^2}$$

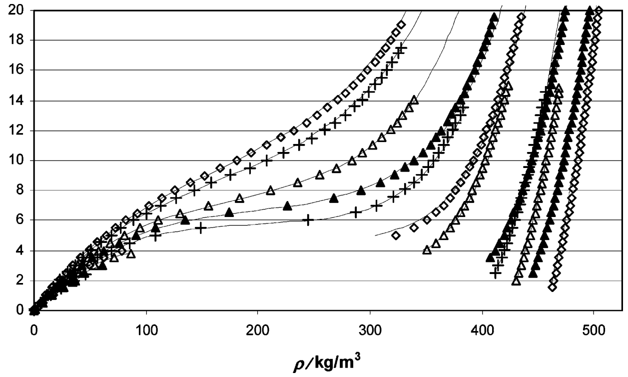

Figure 4. Experimental and calculated (PρT) data for the ethane (1) + hydrogen sulfide (2) system: △, $z_2 = 0.0380$ (263.43, 293.24, and 333.23 K); +, $z_2 = 0.0563$ (273.41, 313.14, and 353.15 K); ◇, $z_2 = 0.0977$ (254.05, 303.14, and 363.21 K); ▲, $z_2 = 0.1430$ (268.15, 283.30, and 322.21 K); —, BWRS representation using parameters adjusted in this work.

Table 7. BWRS Generalized Mixing Rules[6] [a]

$A_0 = \sum_i^n \sum_j^n z_i z_j \sqrt{A_{0i}A_{0j}}(1 - k_{ij})$

$B_0 = \sum_i^n z_i B_{0i}$

$C_{0m} = \sum_i^n \sum_j^n z_i z_j \sqrt{C_{0i}C_{0j}}(1 - k_{ij})^3$

$D_0 = \sum_i^n \sum_j^n z_i z_j \sqrt{D_{0i}D_{0j}}(1 - k_{ij})^4$

$E_0 = \sum_i^n \sum_j^n z_i z_j \sqrt{E_{0i}E_{0j}}(1 - k_{ij})^5$

$a = (\sum_i^n z_i a_i^{1/3})^3$

$b = (\sum_i^n z_i b_i^{1/3})^3$

$c = (\sum_i^n z_i c_i^{1/3})^3$

$d = (\sum_i^n z_i d_i^{1/3})^3$

$\gamma = (\sum_i^n z_i \sqrt{\gamma_i})^2$

$\alpha = (\sum_i^n z_i \alpha_i^{1/3})^3$

[a] k_{ij} is a binary interaction parameter.

Table 8. VLE Data for Ethane (1) + Hydrogen Sulfide (2) System

Bubble Points

x_2	T/K	P/MPa	ρ/kg/m^3
0.0380	263.43 ± 0.02	1.913 ± 0.002	430.1 ± 0.2
0.0380	293.25 ± 0.02	3.816 ± 0.020	346.4 ± 0.2
0.0563	273.40 ± 0.02	2.424 ± 0.002	410.8 ± 0.2
0.0977	254.10 ± 0.08	1.511 ± 0.012	462.5 ± 0.2
0.0977	303.15 ± 0.02	4.727 ± 0.020	304.4 ± 0.9
0.1430	268.17 ± 0.02	2.144 ± 0.020	443.6 ± 0.2
0.1430	283.31 ± 0.02	3.089 ± 0.008	403.8 ± 0.2

Dew Points

y_2	T/K	P/MPa	ρ/kg/m^3
0.0380	263.43 ± 0.02	1.881 ± 0.002	35.3 ± 0.2
0.0380	293.25 ± 0.02	3.806 ± 0.002	87.3 ± 0.2
0.0563	273.40 ± 0.02	2.420 ± 0.010	47.2 ± 0.2
0.0977	254.10 ± 0.08	1.474 ± 0.020	27.3 ± 0.3
0.0977	303.15 ± 0.02	4.725 ± 0.050	131.9 ± 0.5
0.1430	268.17 ± 0.02	2.141 ± 0.020	40.9 ± 0.3
0.1430	283.31 ± 0.02	3.078 ± 0.005	63.6 ± 0.2

The k_{ij} parameter was initialized with the value suggested by Starling[6] from VLE data representation ($k_{ij} = 0.045$). The adjusted value using density data is $k_{ij} = 0.0542$. Calculated data are also presented in Tables 3 to 6 and plotted in Figure 4. Average and standard deviations on 445 density data are (0.0 ± 2.1) kg/m^3. This deviation is of the same order as for the pure compounds. Thus, the mixture density data are as accurate as the densities of pure ethane and pure hydrogen sulfide.

However, we can note in Figure 4 that the isothermal PρT data set at 0.0977 H_2S mole fraction and 303.14 K is poorly represented with the BWRS EoS in the pressure range close to the vapor pressure region. This result is certainly due to temperature value that is close to both critical temperatures of ethane and of the mixture. Indeed, 303.14 K corresponds to 0.994 for ethane-reduced temperature (see Table 1).

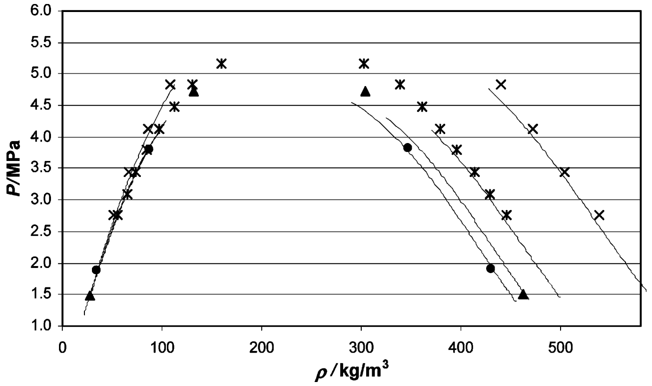

Figure 5. VLE Boundaries for ethane (1) + hydrogen sulfide (2) system: This work (●, $z_2 = 0.0380$; ▲, $z_2 = 0.0977$); Kay and Brice[3] (∗, $z_2 = 0.221$; ×, $z_2 = 0.5001$); —, BWRS representation using parameters adjusted in this work.

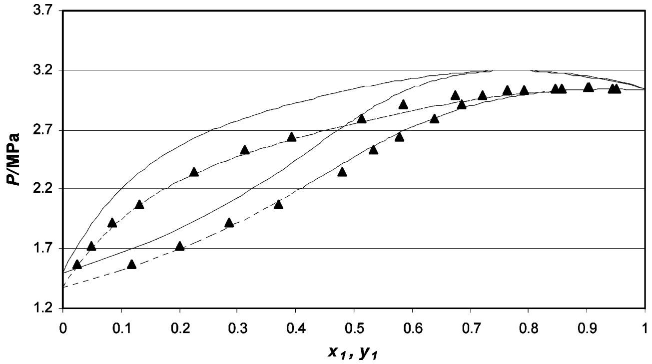

Figure 6. VLE of the ethane (1) + hydrogen sulfide (2) system at 283.16 K: ▲, Kalra et al.[2]; —, calculated with BWRS EoS using parameters adjusted in this work; - - -, calculated with model used by Kalra et al.[2]

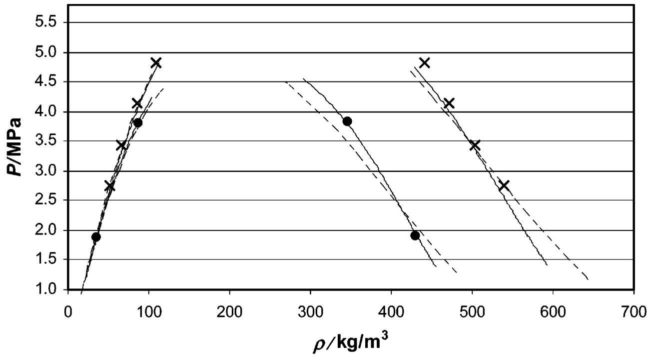

Figure 7. VLE Boundaries for ethane (1) + hydrogen sulfide (2) system: ●, this work ($z_2 = 0.0380$); ×, Kay and Brice[3] ($z_2 = 0.5001$); —, calculated with BWRS EoS using parameters adjusted in this work; - - -, calculated with Peng–Robinson model used by Kalra et al.[2]

Vapor–Liquid Equilibrium (VLE). As shown by Bouchot and Richon,[8] the vibrating tube densimeter allows estimating dew and bubble points. These points are obtained from intersection of density plots (single phase and diphasic regions) as a function of pressure. Results and corresponding estimated uncertainties are presented in Table 8.

Our saturated Pρ data are compared with those of Kay and Brice[3] in Figure 5. For these purposes, BWRS parameters adjusted in our compressed phase data are used to predict isothermal VLE boundaries. Presented data are in good agreement in both liquid and vapor phases. The four boundary lines (solid lines) are in good agreement with experimental data except for a small systematic deviation between calculated data and Kay and Brice data. It is important to note that calculations corresponding to Kay and Brice data come from extrapolation with respect to our composition range.

The BWRS EoS used here (parameters adjusted only on density data) is unable to represent VLE data whatever near or far the critical region. To illustrate this remark, VLE data was calculated with BWRS EoS and compared to experimental values presented by Kalra et al.[2] at 283.16 K. These experimental data are well-represented using the Peng−Robinson equation of state (PR EoS)[15] and corresponding adjusted parameter (deviations on pressures are within 0.5 MPa, see Figure 6):

$$P = \frac{RT}{v - b^*} - \frac{a^*(T)}{v(v + b^*) + b^*(v - b^*)}$$

where

$$a^*(T) = a^*_{\mathrm{c}}\alpha(\mathrm{T}) \begin{cases} a^*_{\mathrm{c}} = 0.45724\dfrac{R^2 T_{\mathrm{c}}^{\ 2}}{P_{\mathrm{c}}} \\ \alpha(T) = [1 + (0.37464 + 1.54226\omega - \\ \qquad 0.26992\omega^2)\left(1 - \sqrt{\dfrac{T}{T_{\mathrm{c}}}}\right)\Bigg]^2 \end{cases}$$

For mixture EoS parameters, the quadratic mixing rules were used with $k_{ij} = 0.08$:[2]

$$\begin{cases} a^* = \sum_i \sum_j z_i z_j (1 - k_{ij})\sqrt{a^*_i a^*_j} \\ a^* = \sum_i z_i b^*_i \end{cases}$$

Bubble and dew points were calculated at two compositions with the PR EoS. The resulting densities are compared to values obtained with the BWRS EoS in Figure 7. The PR EoS is not suitable to represent liquid densities, and deviations are very high at low pressures and near the critical region. Such a comparison illustrates the importance of choosing an EoS suitable for a particular property.

Conclusion

About 450 PρT data of ethane + hydrogen sulfide system are presented at various temperatures and at fout compositions. The consistency of mixture data was checked using the BWRS EoS. New sets of parameters tuned on literature data are presented for the pure compounds. The model shows limitations near the critical region of ethane and of the mixtures. Saturating densities are presented and compared with the Kay and Brice[3] data. BWRS EoS with parameters adjusted on compressed phase densities represent well the bubble and dew densities. However, this model is not suitable to represent VLE data (pressure, temperature, and compositions of each phase).

The model based on PR EoS (following Kalra et al.[2]) is not suitable for saturating liquid densities. The use of the presented two models illustrates the difficulties of obtaining reliable simultaneous representation of volumetric properties and vapor liquid equilibrium data.

Literature Cited

(1) Valderrama, J. O.; Arce, P. F.; Ibrahim, A. A. Vapor−liquid equilibrium of H_2S−hydrocarbon mixtures using a generalized cubic equation of state. *Can. J. Chem. Eng.* **1999**, *77*, 1239−1243.

(2) Kalra, H.; Robinson, D. B.; Krishnan, T. R. The equilibrium phase properties of the ethane−hydrogen sulfide system at subambient temperatures. *J. Chem. Eng. Data* **1977**, *22*, 85−88.

(3) Kay, W. B.; Brice, D. B. Liquid−vapor equilibrium relations in ethane−hydrogen sulfide system. *Ind. Eng. Chem.* **1953**, *45*, 615−618.

(4) Benedict, M.; Webb, G. B.; Rubin, L. C. An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. *J. Chem. Phys.* **1940**, *8*, 334−345.

(5) Starling, K. E. Thermo data refined for LPG. *Hydrocarbon Process.* **1971**, *3*, 101−104.

(6) Starling, K. E. *Fluid Thermodynamic Properties for Light Petroleum Systems*; Gulf Publishing Co.: Houston, 1973.

(7) Bouchot, C.; Richon, D. An enhanced method to calibrate vibrating tube densimeters. *Fluid Phase Equilib.* **2001**, *191*, 189−208.

(8) Bouchot, C.; Richon, D. Direct pressure−volume−temperature and vapor−liquid equilibrium measurements with a single equipment using a vibrating tube densimeter up to 393 K and 40 MPa: description of the original apparatus and new data. *Ind. Eng. Chem. Res.* **1998**, *37*, 3295−3304.

(9) Galicia-Luna, L. A.; Richon, D.; Renon, H. New loading technique for a vibrating tube densimeter and measurements of liquid densities up to 39.5 MPa for binary and ternary mixtures of the carbon dioxide-methanol-propane system. *J. Chem. Eng. Data* **1994**, *39*, 424−431.

(10) Tillner-Roth, R.; Baehr, H. D. An international standard formulation for the properties of 1,1,1,2-tetrafluoroethane (HFC-R134a) for temperatures from 170 K to 455 K and pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1994**, *23*, 657−729.

(11) Younglove, B. A.; Ely, J. F. Thermophysical properties of fluids. II. Methane, ethane, propane, isobutane, and normal butane. *J. Phys. Chem. Ref. Data* **1987**, *16*, 577−798.

(12) Reamer, H. H.; Sage, B. H.; Lacey, W. N. Volumetric behavior of hydrogen sulfide. *Ind. Eng. Chem.* **1950**, *42*, 140−143.

(13) Laugier, S.; Richon, D. Use of artificial neural networks for calculating derived thermodynamic quantities from volumetric property data. *Fluid Phase Equilib.* **2003**, *210*, 247−255.

(14) Reid, R. C., Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill Book Company: New York, 1987.

(15) Peng, D.; Robinson, D. B. A new two parameters equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

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