

Densities and Mixture Virial Coefficients for Wet Natural Gas Mixtures

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Experimental densities plus second and third mixture virial coefficients are reported for two well-defined natural gases, one sweet and one sour, with varying amounts of water vapor to 10% (mole basis). The Burnett–isochoric densities, which range from 50 to 210 °C and 0.1–18.9 MPa, are precise to ±0.01% and are considered accurate to ±0.04%.

Introduction

Few experimental measurements exist for the density of wet (water containing) natural gas mixtures in the temperature range from 50 to 210 °C at pressures to the dew point. Comprehensive and accurate densities over a range of temperature, density, and water level are necessary to test equation of state (EOS) predictions used by the natural gas industry. Our present sweet and sour dry gases were selected to represent those natural gases found in practice.

Composition of Dry Natural Gases

Tables I and II contain the composition of the dry, sweet gas and the dry, sour gas, respectively. Both gases were obtained from the Phillips Petroleum Co. The sour gas decomposition disclaimer published by Phillips at the bottom of Table II was not a serious consideration. Periodic chromatographic analyses indicated no significant decomposition of the sour gas in the original cylinder, even after 2 years.

Because water is simply added to the dry gas (sweet or sour) to make up the wet gas mixtures, the composition of our 5 mol % water/sweet gas, for example, is 5 mol % water plus 95 mol % dry, sweet gas or 0.95 is multiplied by the mole percentages of Table I to obtain the mole percent of each dry gas component in the wet gas mixture.

Experimental Apparatus

The Burnett–isochoric (B–I) density apparatus was described previously by Mansoorian et al. (1) and Eubank et al. (2). A complete description of the apparatus and experimental techniques may be found in the dissertation of Scheloske (3). Water was weighed before mixing with the natural gas in a variation of the Burnett mixing method of ref 2.

Because the water content did not exceed 10% (mole basis), the usual adsorption diagnostics (4) were negative even for the sour gas mixtures. That is, the limiting pressure ratio (or apparatus constant) on a Burnett isotherm was the same as for helium at the same temperature.

Results

The experimental dew point pressures and enthalpy residuals for these same systems have been published previously (5). A

Table I. Composition of Sweet Natural Gas (G-8)^a

components	chromatog comp, mol %	wt %
hydrogen	0.01	0.001
helium	0.14	0.03
oxygen	<0.01	
nitrogen	1.67	2.54
methane	90.31	78.48
ethane	2.99	4.87
carbon dioxide	0.30	0.72
propane	2.00	4.78
propylene	0.01	0.2
isobutane	0.97	3.05
<i>n</i> -butane	0.97	3.05
isopentane	0.31	1.21
<i>n</i> -pentane	0.32	1.25
total	100.00	100.00

^a Molecular weight = 18.460.

Table II. Composition of Sour Natural Gas^a

component	gravimetr comp, ^b mol %	wt %
methane	89.26	77.73
nitrogen	0.04	0.05
octenes		0.02
water	0.01	0.01
propylene	0.01	0.03
carbonyl sulfide	0.01	0.04
carbon dioxide	4.29	10.29
hydrogen sulfide	3.05	5.65
isobutane	0.01	0.02
ethane	2.26	3.68
propane	1.06	2.53
total	100.00	100.00

^a Molecular weight = 18.424. ^b Composition as weighed into cylinder. Composition will change with time because of hydrogen sulfide activity.

detailed account of all the experimental results is also contained in a research report to the principal sponsor (6). Because dew points and densities are measured for the same systems in the same apparatus, the combined data are particularly useful for testing dew-point prediction methods (vapor/liquid equilibria) from EOS (7).

Tables III–V contain the pressures and temperatures of 1.85%, 5.0%, and 10.0% water, respectively, in with the dry, sweet natural gas of Table I. The measurements were made along pseudoisochores (or isomasses) because the 304 stainless steel cell distorts in volume with temperature T and, very slightly, with pressure P . The distortion of the primary cell is described by

$$V(P, T) = V_0(1 + \gamma P)[(1 + \bar{\alpha}(T - T_0))^3] \quad (1)$$

where V_0 is the volume at zero pressure and the reference temperature T_0 (K), $\gamma = [28.72 + (4.50 \times 10^{-3})T]10^{-6}/\text{MPa}$, P is in megapascals, $\bar{\alpha} = [14.77 + (2.915 \times 10^{-3})(T + T_0)] \times 10^{-9}/\text{K}$, and T is in degrees kelvin. To obtain the true density at the experimental P and T (K = 273.15 + °C) for Tables

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Table III. *P-V-T* Surface of 1.85% Water-98.15% Sweet Natural Gas

isochore no.	pressure, MPa							density at 210 °C × 10 ³ , mol/cm ³
	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	210 °C	
1				14.24265	15.34466	16.43983	16.87308	4.18175
2				9.65416	10.34249	11.02714	11.29922	2.82893
3			6.13119	6.57410	7.01434	7.45293	7.62721	1.91364
4			4.18890	4.47692	4.76369	5.04926	5.16307	1.29443
5		2.66471	2.85548	3.04497	3.23386	3.42215	3.49723	0.87556
6		1.81586	1.94254	2.06832	2.19367	2.31884	2.36871	0.59223
7	1.15006	1.23486	1.31926	1.40335	1.48704	1.57072	1.60408	0.40057
8	0.78151	0.83834	0.89494	0.95130	1.00753	1.06362	1.08604	0.27094
9	0.53028	0.56850	0.60655	0.64447	0.68227	0.72025	0.73509	0.18326
10	0.35944	0.38516	0.41094	0.43635	0.46185	0.48728	0.49746	0.12395
11	0.24347	0.26082	0.27811	0.29534	0.31253	0.32971	0.33659	0.08384
12	0.16482	0.17656	0.18825	0.19988	0.21147	0.22306	0.22772	0.05670
13	0.11152	0.11944	0.12732	0.13520	0.14300	0.15085	0.15404	0.03835

Table IV. *P-V-T* Surface at 5.0% Water-95.0% Sweet Natural Gas

isochore no.	pressure, MPa							density at 210 °C × 10 ³ , mol/cm ³
	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	210 °C	
1					13.26185	14.18376	14.55059	3.63777
2					8.98298	9.56525	9.79799	2.46011
3				5.72282	6.10077	6.47628	6.62547	1.66361
4				3.89718	4.14426	4.39004	4.48781	1.12495
5			2.48556	2.64987	2.81239	2.97475	3.03953	0.76069
6			1.68983	1.79867	1.43150	2.01540	2.05854	0.51436
7			1.14693	1.21963	1.29238	1.36466	1.39349	0.34780
8		0.72835	0.77753	0.82621	0.87499	0.92361	0.94290	0.23517
9		0.49360	0.52676	0.55939	0.59218	0.62481	0.63781	0.15902
10		0.33408	0.35628	0.37832	0.40040	0.42240	0.43119	0.10752
11	0.21086	0.22600	0.24099	0.25576	0.27061	0.28539	0.29135	0.07270
12	0.14265	0.15275	0.16284	0.17281	0.18284	0.19279	0.19680	0.04916
13	0.09640	0.10320	0.10996	0.11662	0.12342	0.13010	0.13282	0.03324
14	0.06521	0.06978	0.07432	0.07879	0.08337	0.08785	0.08970	0.02248

Table V. *P-V-T* Surface of 10.0% Water-90.0% Sweet Natural Gas

isochore no.	pressure, MPa						density at 210 °C × 10 ³ , mol/cm ³
	100 °C	125 °C	150 °C	175 °C	200 °C	210 °C	
1					15.76675	16.19173	4.07955
2					10.64732	10.91251	2.75918
3				6.80910	7.22296	7.39307	1.86605
4				4.62567	4.90390	5.01465	1.26198
5			2.95949	3.14412	3.32765	3.40080	0.85343
6			2.01192	2.13449	2.25641	2.30502	0.57713
7			1.36554	1.44745	1.52891	1.56138	0.39028
8		0.87077	0.92585	0.98075	1.03545	1.05720	0.26392
9		0.59013	0.62715	0.66403	0.70084	0.71557	0.17847
10	0.37468	0.39971	0.42464	0.44951	0.47442	0.48421	0.12069
11	0.25359	0.27049	0.28735	0.30413	0.32092	0.32756	0.08161
12	0.17153	0.18293	0.19438	0.20570	0.21706	0.22155	0.05519
13	0.11714	0.12485	0.13270	0.14042	0.14812	0.15088	0.03732
14	0.07925	0.08456	0.08988	0.09501	0.10034	0.10227	0.02524
15	0.05359	0.05718	0.06072	0.06423	0.06786	0.06922	0.01706
16	0.03618	0.03864	0.04103	0.04334	0.04582	0.04678	0.01154

Table VI. *P-V-T* Surface of 100% Sour Natural Gas

isochore no.	pressure, MPa							density at 200 °C × 10 ³ , mol/cm ³
	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	
1	9.95024	11.09384	12.22265	13.34307	14.45443	15.55621	16.65025	4.23181
2	6.98346	7.69709	8.40319	9.10375	9.79957	10.49053	11.17707	2.86377
3	4.86909	5.32509	5.77648	6.22562	6.67160	7.11492	7.55583	1.93786
4	3.36947	3.66565	3.95931	4.25147	4.54217	4.83124	5.11920	1.31127
5	2.31664	2.51159	2.70483	2.89735	3.08908	3.27989	3.46985	0.88725
6	1.58536	1.71454	1.84281	1.97074	2.09813	2.22501	2.35141	0.60034
7	1.08099	1.16733	1.25302	1.33845	1.42356	1.50840	1.59294	0.40620
8	0.73542	0.79319	0.85063	0.90796	0.96511	1.02206	1.07876	0.27484
9	0.49934	0.53829	0.57691	0.61549	0.65397	0.69223	0.73046	0.18596
10	0.33870	0.36491	0.39092	0.41694	0.44281	0.46868	0.49439	0.12582
11	0.22955	0.24729	0.26485	0.28240	0.29984	0.31726	0.33462	0.08513
12	0.15552	0.16752	0.17933	0.19126	0.20299	0.21478	0.22652	0.05760

Table VII. *P-V-T* Surface of 5.5% Water-94.5% Sour Natural Gas

isochore no.	pressure, MPa						density at 200 °C × 10 ³ , mol/cm ³
	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	
1					15.345 45	16.434 80	4.213 76
2					10.409 64	11.095 53	2.858 49
3				6.648 49	7.092 19	7.534 07	1.939 00
4				4.543 66	4.834 03	5.123 15	1.315 23
5			2.907 50	3.100 31	3.292 25	3.483 62	0.892 11
6			1.983 85	2.112 18	2.240 23	2.367 80	0.605 09
7		1.264 62	1.351 13	1.437 16	1.522 91	1.608 46	0.410 42
8		0.860 82	0.919 06	0.976 92	1.034 63	1.092 20	0.278 37
9		0.585 36	0.624 52	0.663 67	0.702 57	0.741 40	0.188 81
10	0.371 10	0.397 67	0.424 17	0.450 59	0.476 85	0.503 10	0.128 06
11	0.252 12	0.270 09	0.287 99	0.305 82	0.323 59	0.341 34	0.086 86
12	0.171 21	0.183 36	0.195 46	0.207 61	0.219 69	0.231 62	0.058 91
13	0.116 29	0.124 52	0.132 78	0.141 00	0.149 18	0.157 31	0.039 97

Table VIII. *P-V-T* Surface of 10.0% Water-90.0% Sour Natural Gas

isochore no.	pressure, MPa						density at 200 °C × 10 ³ , mol/cm ³
	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	
1						14.034 91	3.635 62
2					8.919 13	9.496 43	2.458 65
3					6.070 47	6.443 50	1.662 62
4				3.882 84	4.128 83	4.372 75	1.124 28
5				2.641 91	2.804 61	2.966 24	0.760 24
6			1.685 76	1.794 49	1.902 82	2.010 43	0.514 06
7			1.144 59	1.217 27	1.289 77	1.361 95	0.347 60
8		0.726 91	0.776 13	0.824 86	0.873 55	0.922 06	0.235 04
9		0.492 76	0.525 70	0.558 53	0.591 32	0.623 99	0.158 92
10	0.311 39	0.333 64	0.356 03	0.378 13	0.400 22	0.422 21	0.107 46
11	0.210 78	0.225 83	0.240 93	0.255 81	0.270 70	0.285 64	0.072 66
12	0.142 52	0.152 75	0.163 02	0.173 04	0.183 10	0.192 58	0.049 13
13	0.096 19	0.103 30	0.110 28	0.117 03	0.123 83	0.130 32	0.033 22

Table IX. Mixture Second and Third Virial Coefficients for Wet Natural Gases
Sweet Natural Gases

temp, °C	water content					
	1.85%		5.0%		10.0%	
	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²
210	8.439 ± 0.054	2277.6 ± 12.5	8.457 ± 0.112	2005.9 ± 27.5	11.134 ± 0.030	2009.7 ± 7.3
200	9.881 ± 0.074	2290.4 ± 16.6	9.925 ± 0.069	2015.0 ± 17.0	12.621 ± 0.063	2006.7 ± 14.9
175	13.825 ± 0.058	2334.3 ± 12.9	13.925 ± 0.078	2040.7 ± 31.6	16.488 ± 0.134	1811.1 ± 67.7
150	18.338 ± 0.040	2399.6 ± 9.0	18.468 ± 0.228	2071.3 ± 207.9	20.564 ± 0.403	1268.4 ± 423.3
125	23.545 ± 0.200	2493.3 ± 96.6	23.671 ± 0.019	2108.1 ± 509.3	24.841 ± 1.399	248.1 ± 436.7
100	29.615 ± 0.469	2625.8 ± 490.1				
75	36.771 ± 1.503	2811.2 ± 1312.8				

Sour Natural Gases

temp, °C	water content					
	0%		5.0%		10.0%	
	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²	$-B_m$, cm ³ /mol	C_m , cm ⁶ /mol ²
200	8.484 ± 0.054	2013.295 ± 11.6	10.045 ± 0.065	1896.3 ± 15.4	12.168 ± 0.065	1935.3 ± 17.6
175	12.215 ± 0.045	2060.099 ± 10.2	13.832 ± 0.069	1941.5 ± 16.2	16.036 ± 0.059	1963.6 ± 22.7
150	16.470 ± 0.051	2118.078 ± 11.2	18.061 ± 0.097	1931.3 ± 47.4	20.216 ± 0.260	1851.7 ± 207.5
125	21.365 ± 0.092	2190.468 ± 21.1	22.813 ± 0.330	1843.0 ± 339.9	24.738 ± 0.268	1544.6 ± 2274.7
100	27.051 ± 0.041	2281.694 ± 9.4	28.193 ± 0.348	1644.4 ± 2552.9	29.631 ± 0.816	964.0 ± 1419.7
75	33.730 ± 0.088	2397.924 ± 18.2	34.333 ± 5.050	1289.1 ± 3886.7	34.922 ± 5.751	-2.5 ± 2090.8
50	41.677 ± 0.033	2547.938 ± 7.4				

III-V, divide the density given at 210 °C by $(1 + \gamma P)[1 + \alpha(T - T_0)]^3$ with $T_0 = 483.15$ K. That is

$$\rho = \rho(210 \text{ °C}) [1 + \gamma P]^{-1} [1 + \alpha(T - T_0)]^{-3} \quad (2)$$

Cell distortions with pressure do not exceed 6/10 000 but the lowest temperatures cause distortions approaching 0.8%.

Tables VI-VIII contain the pressures and temperatures of 0% (dry sour gas), 5.5%, and 10.0% water, respectively, in with the dry, sour natural gas of Table II. The base Burnett isotherm is now 200 °C rather than 210 °C. Thus the densities of Tables VI-VIII should be divided by $(1 + \gamma P)[1 + \alpha(T - T_0)]^3$ as previously except with $T_0 = 473.15$ K.

The densities of Tables III-VIII are precise (reproducible) to ±0.01% or 3 times the standard deviation as provided by the maximum likelihood computer program which accounts for random errors in (1) temperature, (2) pressure, and (3) the density measurement itself. This random error analysis is described in detail in ref 1 which also shows previous density measurements for pure ethane to agree to ±0.01% with two other laboratories. For the present mixtures, systematic errors are difficult to estimate; we have assumed that they are 3 times the precision to provide an accuracy of ±0.04%.

Table IX provides the mixture second and third virial coefficients for 1.85%, 5.0%, and 10.0% water in the sweet

natural gas plus 0%, 5.5%, and 10.0% water in the sour natural gas. The uncertainty bands reflect three standard deviations as provided by the maximum likelihood computer program. They do not contain the unknown systematic errors. While the usual experimental diagnostics for adsorption were absent, the adsorption of one molecule out of 1000 causes about $\pm 0.3 \text{ cm}^3/\text{mol}$ in B_m and $\pm 75 \text{ cm}^6/\text{mol}^2$ in C_m . The usual effect of adsorption is to make the computed B_m too negative with C_m too positive for compensation.

Conclusions

PVT data plus second and third virial coefficients have been reported for six wet natural gas mixtures. The presence of small amounts of water is seen to have a major influence on the densities, B_m and, particularly, C_m .

It has been shown elsewhere (7) that B_m and C_m for the sweet natural gas mixtures to 5.0% water content are predicted within experimental uncertainties by the correlations of Tsionopoulos (8) and Orbey and Vera (9), respectively. The prediction is a priori in that the binary interaction constants k_{ij} contained in both correlations were not adjusted to fit the data but rather the values used were those of Prausnitz (10). The 10.0% water/sweet gas virial coefficients are not so well predicted possibly due to poor values of B_{ii} and C_{iii} for pure water. These correlations generally predict reasonable values

of B_{ij} and C_{ijk} as long as no more than one polar molecule is involved in the interaction. Thus, a priori prediction of B_m and C_m for any of the sour gas systems is poor due to the presence of CO_2 , H_2S , and, in the last two systems, water.

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Solubilities of Polynuclear Aromatic Hydrocarbons in Mixtures of Common Organic Solvents

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The solubilities of naphthalene, acenaphthene, fluorene, and phenanthrene have been determined experimentally in five binary mixtures and one quaternary mixture of four common organic solvents (benzene, cyclohexane, thiophene, and pyridine) from 25 °C to the melting points of the solutes. The results have been correlated by using the classical equation for solid-liquid solubility and the experimental activity coefficients obtained have been compared to the values predicted by regular solution theory, extended regular solution theory, Wilson's equation, and UNIQUAC, after obtaining binary parameters from the solubility of each solute in the pure solvents.

Introduction

With the present trend in the petroleum industry toward heavier feedstocks and coal-derived liquids, there is a strong need for expansion of the small database of thermodynamic data on heavier compounds that presently exists. As these heavier feedstocks, rich in polynuclear aromatic hydrocarbons (PAH's), become more common, there will be a corresponding increase in the need for thermodynamic data for design purposes. Activity coefficient data will be needed as will solubility limit data, which are important to ensure that precipitation of these heavy components, with consequent plugging of lines and vessels, does not occur.

The activity coefficient data, usually obtained from VLE results, will have to be obtained by other methods as VLE data will be difficult or impossible to obtain for binary mixtures of species with such widely disparate vapor pressures. The obvious source of the necessary data is solid-liquid solubility results. Because of the need for this type of data, there has been a renewed interest in investigations such as we report here, which have substantially extended the available database (1-7). A good discussion of this area through 1984 is available (8). In this work, we have extended the studies of McLaughlin and Zainal (1-3) and Choi and McLaughlin (4) to mixtures of solvents. This is a continuation of the work presented in Choi et al. (5).

The calculation of activity coefficients from solid-liquid solubility data is discussed in the next section. The third section presents the activity coefficient models used. The fourth and fifth sections present our experimental results and discuss our conclusions concerning the appropriate choice of activity coefficient models.

Experimental Procedures

The chemicals used in this study were purchased and purified by methods discussed in previous papers (4, 5). These chemicals (the solutes) are recovered by rotary evaporation of the solvents in vacuo and reused. The purities of the recovered materials relative to the original are monitored by melting point determinations to ensure that no contamination or degradation