Vapor−Liquid Equilibria for the Methane−Propane−Carbon Dioxide Systems at 230 K and 270 K

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Vapor−liquid equilibria were measured for the binary systems methane−carbon dioxide, methane−propane, and carbon dioxide−propane at 230 K and 270 K. The ternary system methane−carbon dioxide−propane was studied at 230 K and pressures of 0.8, 4.0, and 7.0 MPa; and at 270 K for 2.8, 5.5, and 8.0 MPa. The Peng−Robinson equation of state was used to model the system.

Introduction

The widespread implementation of computer simulators for the design, control, and optimization of gas-processing facilities has made the use of equations of state to model vapor−liquid equilibria indispensable. All such equations in use in the industry today require binary vapor−liquid equilibria data to fit at least one adjustable parameter. Since the binary data are used in the fitting procedure, they cannot be used to test the predictive capabilities of the thermodynamic models, and thus the ternary data provide an excellent means of evaluating the models.[1] It has been the goal of this laboratory, since 1972, to establish a base of accurate binary and ternary phase equilibria data to be used to determine interaction parameters and also to evaluate equations of state and mixing rules.

Review of Previous Work

The binary systems $CH_4 + CO_2$, $CH_4 + C_3H_8$, and $CO_2 + C_3H_8$ have been studied previously; Table 1 lists all of the published data. There are no data for the $CH_4 + CO_2 + C_3H_8$ ternary system.

Experimental Section

The apparatus used by Wei et al.[15] was rebuilt with modifications to the refrigeration system and the equilibrium cell. The temperature was measured to ±0.001 K with a platinum resistance thermometer calibrated on the IPTS-68 scale. The temperature in the bath was controlled to ±0.01 K. The pressure was measured with a series of Heise bourdon tube gauges with the following pressure ranges: 0 to 100 psia (0 to 0.69 MPa), 0 to 500 psia (0 to 3.5 MPa), 0 to 100 atm (0 to 10.1 MPa), and 0 to 2500 psia (0 to 17.2 MPa). Each gauge has an accuracy of ±0.1% of the full-scale reading. Liquid and vapor samples were analyzed in a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Valco gas sample valve and a thermal conductivity detector. The sample loop size in the gas-sampling valve was adjusted until the responses of all three-component calibration curves were linear. The calibrations were checked with mixtures prepared by a gravimetric method in the laboratory. The estimated error in the calculated mole fractions using these calibration curves is ±0.002. To achieve a well-mixed liquid sample, helium was used to flush the sample from the 10 cm^3 cylinder to the 300 cm^3 cylinder. The carbon dioxide, methane, and propane were purchased commercially and had minimum purities of 99.995 (Coleman Grade), 99.99 mol %, and 99.5 (Instrument Grade), respectively. The gases were used without further purification.

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Table 1. Experimental Data for Systems of Methane, Carbon Dioxide, and Propane

system	ref	temp/K	system	ref	temp/K
CH_4-CO_2	2	219, 240, 270		24	114, 118, 122
	3	253, 273, 288		25	144−283
	4	230, 250, 270		26	278 to 376
	5	219 to 272		27	278 to 361
	6	153 to 219		28	305 to 356
	7	233, 253, 273		29	316
	8	233, 253, 273, 283		30	293−363
	9	90		31	123 to 153
	10	153 to 219		32	91
	11	208.5, 208.8, 220		33	130−214
	12	270		34	278 to 344
	13	160 to 220		35	278, 311
	14	270		36	111
	15	230, 250, 270		37	210−350
	16	288, 293		38	180−329
$CH_4-C_3H_8$	17	271−274	$CO_2-C_3H_8$	39	233, 253, 273
	18	158−273		40	244, 267
	19	116, 135		41	253, 273
	20	92 to 128		42	300, 311, 333, 355
	21	90 to 110		43	232, 253, 273
	22	298		28	305 to 361
	23	214			

Table 2. Comparison of Experimental and Literature Vapor Pressures

	vapor pressure/MPa			±0.1% of gauge
temp/K	meas	lit.	deviation	reading/MPa
		Carbon Dioxide		
230	0.8942	0.8935[a]	+0.0007	0.0034
232	0.9656	0.9632[a]	+0.0024	0.0034
240	1.2863	1.2830[a]	+0.0033	0.0034
250	1.7890	1.7856[a]	+0.0034	0.0034
260	2.4214	2.4194[a]	+0.0020	0.0034
270	3.2026	3.2034[a]	−0.0008	0.0034
		Propane		
230	0.0973	0.09703[b]	+0.0003	0.0069
270	0.4308	0.43042[b]	+0.0004	0.0069

[a] CO_2 reference: Angus et al.[44] [b] C_3H_8 reference: Goodwin and Haynes [45]

Results and Discussion

The accuracy of the temperature and pressure measurements was established by measuring the vapor pressure

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Table 3. Methane + Carbon Dioxide System

P/MPa	Y_{CH_4}	X_{CH_4}	P /MPa	Y_{CH_4}	X_{CH_4}	P/MPa	Y_{CH_4}	X_{CH_4}	P/MPa	Y_{CH_4}	X_{CH_4}
					230 K						
0.894	0.0000	0.0000	1.651	0.4196	0.0307	2.488	0.5851	0.0714	5.573	0.7432	0.3093
1.187	0.2252	-	1.931	0.4900	0.0441	3.375	0.6670	0.1199	5.836	0.7454	0.3404
1.420	0.3385	0.0213	2.257	0.5512	0.0597	4.497	0.7199	0.1994	6.241	0.7443	0.4010
6.417	0.7442	0.4323	6.654	0.7382	0.4815	6.912	0.7286	0.5302	7.072	0.7156	0.5682
6.512	0.7422	0.4530	6.859	0.7312	0.5201	6.970	0.7245	0.5393	7.108		0.5800
6.649	0.7371	0.4862	6.859	0.7314	0.5208	7.004	0.7222	0.5521	7.112	0.7102	0.5774
7.145	0.7066	0.5888									
					270 K						
3.203	0.0000	0.0000	4.104	0.1680	0.0342	4.987	0.2706	0.0723	6.959	0.3847	0.1739
3.883	0.1352	0.0264	4.413	0.2093	0.0477	5.433	0.3085	0.0919	7.305	0.3945	0.1949
3.913	0.1402	0.0276	4.787	0.2517	0.0640	6.537	0.3702	0.1479	7.946	0.3977	0.2435
8.098		0.2559	8.389	0.3762	0.2901						
8.131	0.3934	0.2602	8.419	0.3704	0.2991						
8.207	0.3894	0.2688									

Table 4. Methane + Propane Binary System

P/MPa	Y_{CH_4}	X_{CH_4}	P/MPa	Y_{CH_4}	X_{CH_4}	P/MPa	Y_{CH_4}	X_{CH_4}	P/MPa	Y_{CH_4}	X_{CH_4}
					230 K						
0.0973	0.0000	0.0000	0.865	0.8782	0.0855	1.234	0.9134	0.1244	1.655	0.9291	
0.697	0.8563	0.0657	0.997	0.8925	0.0994	1.353	0.9180	0.1372	1.895	0.9368	0.1972
0.776	0.8670		1.104	0.9028		1.493	0.9238	0.1524	2.020	0.9390	0.2128
2.174	0.9408	0.2269	2.672	0.9485	0.2758	3.382	0.9538	0.3526	4.174	0.9515	0.4337
2.301	0.9419	0.2436	2.792	0.9499	0.2864	3.537	0.9532	0.3738	4.399	0.9546	0.4614
2.466	0.9466	0.2550	2.969	0.9497	0.3178	3.971	0.9556	0.4126	4.575	0.9531	0.4727
5.057	0.9537	0.5291	6.566	0.9448	0.6849	7.270	0.9334	0.7590	7.720	0.9175	0.8255
5.513	0.9524	0.5738	6.946	0.9407	0.7222	7.422	0.9279	0.7833	7.767	0.9155	0.8398
6.050	0.9495	0.6313	7.125	0.9369	0.7468	7.621	0.9214	0.8067			
					270 K						
0.431	0.0000	0.0000	0.812	0.4536	0.0296	1.073	0.5752	0.0474	1.434	0.6670	0.0748
0.667	0.3384		0.904	0.5003	0.0356	1.189	0.6089	0.0588	1.535	0.6874	0.0779
0.754	0.4184	0.0238	0.931	0.5119	0.0385	1.331	0.6526	0.0667	1.544	0.6881	0.0827
1.694	0.7160	0.0928	1.956	0.7418	0.1146	2.563	0.7859	0.1542	3.031	0.8073	0.1901
1.825	0.7269	0.1015	2.170	0.7608	0.1281	2.663	0.7919	0.1638	3.053	0.8083	0.1903
1.917	0.7416	0.1040	2.344	0.7713	0.1397	2.857	0.7998	0.1789	3.407	0.8211	0.2160
3.873	0.8345	0.2493	5.380	0.8467	0.3612	6.687	0.8546	0.4374	7.549	0.8494	0.5012
4.392		0.2941	5.827	0.8520	0.3825	6.546	0.8553	0.4314	8.413	0.8356	0.5642
4.702	0.8468	0.3064	5.838	0.8518	0.3848	7.034	0.8539	0.4655	8.744		0.5956
9.038		0.6214									
9.222	0.8029	0.6429									
9.292	0.7937	0.6543									

of the pure carbon dioxide over a range of temperatures and comparing the results with the IUPAC recommended values of Angus et al.[44] The comparison is shown in Table 2. The maximum deviation found was less than the error in the Heise gauges, ±0.1% of the full-scale reading. Furthermore, as part of standard experimental procedure the vapor pressure of the initially charged component (carbon dioxide or propane) was measured at the beginning of each isotherm studied. The results of the propane vapor pressures, as compared with the literature values of Goodwin and Haynes,[45] are also shown in Table 2. At both operating temperatures the propane vapor pressure measurements matched the literature values within the accuracy of the gauge. The unsmoothed binary and ternary measurements are given in Tables 3−6. Each data point is the averaged result of two or three gas chromatograph runs.

Methane + Carbon Dioxide Binary System. The results for this system at 270 K are compared with those of Al-Sahhaf et al.[2] and Somait and Kidnay[14] in Figure 1. The difficulties of modeling VLE data in the critical region with a cubic equation of state are well-known, and this system is no exception. To achieve a satisfactory fit in the low-pressure region with the Peng−Robinson equation, a number of data points in the critical region were not used in fitting the data. The k_{ij} values obtained at 270 K and 230 K were 0.1 and 0.09, respectively.

Methane + Propane Binary System. Measurements were made at 270 and 230 K, and k_{ij} values for these temperatures are 0.009 and 0.007, respectively. To compare with other investigations at different temperatures, Henry's law constants calculated from the VLE data were plotted versus temperature in Figure 2. The data of this study compare well with the work of Wichterle and Kobayashi.[33]

Carbon Dioxide + Propane Binary System. Measurements were made at 270 and 230 K. Calculated Henry's law constants from the data of other investigators were plotted versus temperature in Figure 3. The constant for this study at 270 K agrees with the three other published data sets that included data in the Henry's law region. The 230 K Henry's constant agrees with the trend set by the results of Reamer, Sage, and Lacey.[43] At the temperatures investigated the VLE isotherms exhibit the standard behavior for a binary system with two subcritical components, with the isotherm extrapolating smoothly at both ends to the vapor pressure of the pure component. However, the vapor phase exhibits a reverse curvature in the carbon dioxide rich region of the isotherm. This curvature is noted in all of the literature published on this system. Poettmann and Katz [42] attribute this behavior to the same forces that form the minimum-boiling azeotrope in the carbon dioxide−ethane system. As noted by Akers et al.[18] and as seen in this study, the reverse curvature becomes more pronounced as the temperature decreases. The Peng−Robinson equation provides an excellent fit to the data using k_{ij} values of 0.120 and 0.123 at 270 K and 230 K, respectively.

Table 5. Carbon Dioxide + Propane Binary System

P/MPa	Y_{CO_2}	X_{CO_2}	P/MPa	Y_{CO_2}	X_{CO_2}	P/MPa	Y_{CO_2}	X_{CO_2}	P/MPa	Y_{CO_2}	X_{CO_2}
					230 K						
0.0971	0.0000	0.0000	0.146	0.3510		0.203	0.5425		0.229	0.5961	
0.127	0.2533		0.165	0.4335		0.212	0.5603		0.232	0.6032	0.0420
0.135	0.2964		0.194	0.5170	0.0275	0.219	0.5807		0.250	0.6313	0.0528
0.265	0.6549	0.0577	0.333	0.7322	0.0879	0.390	0.7740	0.1208	0.426	0.7946	0.1499
0.287	0.6847	0.0690	0.334	0.7296	0.0935	0.394	0.7762	0.1292	0.503	0.8310	0.2009
0.298	0.6965	0.0720	0.366	0.7554	0.1135	0.396	0.7796	0.1371	0.544	0.8480	0.2447
0.594	0.8646		0.693	0.8922	0.4107	0.774	0.9149	0.5925	0.837	0.9374	0.7426
0.644	0.8795	0.3442	0.719	0.8984	0.4524	0.790	0.9177	0.6303	0.854	0.9453	0.8068
0.667	0.8833	0.3825	0.750	0.9062	0.5415	0.818	0.9290	0.6880	0.868	0.9563	0.8766
0.877	0.9656	0.9234	0.881	0.9694	0.9447						
					270 K						
0.430	0.0000	0.0000	0.679	0.3735	0.0490	0.818	0.4786	0.0757	1.251	0.6651	0.1722
0.604	0.2915	0.0337	0.718	0.4061	0.0569	0.977	0.5638	0.1139	1.387	0.7001	0.2169
0.641	0.3347	0.0409	0.750	0.4380	0.0630	1.096	0.6142	0.1407	1.598	0.7444	0.2820
1.758	0.7721	0.3231	2.230	0.8373	0.5051	2.470	0.8645	0.6110	2.783	0.9054	0.7730
1.918	0.7953	0.3742	2.317	0.8489	0.5408	2.601	0.8804	0.6730	2.879	0.9196	0.8174
2.079	0.8214	0.4443	2.406	0.8585	0.5820	2.676	0.8900	0.7089	2.960	0.9339	0.8620
3.035	0.9493	0.9003	3.103	0.9656	0.9403	3.134	0.9745	0.9565			

Table 6. Methane + Carbon Dioxide + Propane Ternary System

P/MPa	Y_{CH_4}	Y_{CO_2}	$Y_{C_3H_8}$	X_{CH_4}	X_{CO_2}	$X_{C_3H_8}$	P/MPa	Y_{CH_4}	Y_{CO_2}	$Y_{C_3H_8}$	X_{CH_4}	X_{CO_2}	$X_{C_3H_8}$
						230 K and 0.8 MPa							
0.802	0.8717	0.0000	0.1283	0.0759	0.0000	0.9241	0.800	0.2311	0.6640	0.1049	0.0207	0.3195	0.6598
0.799	0.7503	0.1254	0.1243	0.0695	0.0316	0.8989	0.799	0.1767	0.7257	0.0976	0.0155	0.3774	0.6071
0.800	0.5926	0.2873	0.1201	0.0544	0.0971	0.8485	0.800	0.1372	0.7663	0.0965	0.0118	0.4238	0.5644
0.798	0.4476	0.4364	0.1160	0.0405	0.1628	0.7967	0.800	0.0000	0.9224	0.0776	0.0000	0.6534	0.3466
0.800	0.3236	0.5690	0.1074	0.0294	0.2433	0.7273							
						230 K and 4.0 MPa							
4.000	0.9558	0.0000	0.0442	0.4179	0.0000	0.5821	3.995	0.7772	0.1918	0.0310	0.3407	0.3461	0.3132
4.000	0.9260	0.0317	0.0423	0.4135	0.0378	0.5487	4.002	0.7603	0.2116	0.0281	0.3247	0.4137	0.2616
4.002	0.9126	0.0451	0.0423	0.4044	0.0548	0.5408	4.002	0.7482	0.2256	0.0262	0.3040	0.4686	0.2274
4.000	0.8935	0.0651	0.0414	0.3970	0.0823	0.5207	3.997	0.7335	0.2541	0.0214	0.2874	0.5525	0.1601
3.995	0.8221	0.1417	0.0362	0.3685	0.2167	0.4148	4.002	0.7277	0.2519	0.0204	0.2746	0.5825	0.1429
4.000	0.8053	0.1600	0.0347	0.3617	0.2598	0.3785	3.999	0.7186	0.2647	0.0167	0.2439	0.6487	0.1074
4.002				0.3538	0.3057	0.3405	4.002	0.7123	0.2750	0.0127	0.2173	0.7120	0.0707
4.002	0.7852	0.1828	0.0320	0.3466	0.3208	0.3327	4.003	0.7012	0.2988	0.0000	0.1617	0.8383	0.0000
3.997	0.7828	0.1852	0.0320	0.3451	0.3260	0.3289							
						230 K and 7.0 MPa							
7.000	0.9415	0.0000	0.0585	0.7298	0.0000	0.2702	7.000	0.7762	0.1814	0.0424	0.6794	0.2366	0.0840
7.000	0.9384	0.0017	0.0599	0.7273	0.0021	0.2706	7.001	0.7334	0.2433	0.0233	0.6369	0.3221	0.0410
7.000	0.8220	0.1278	0.0502	0.7002	0.1719	0.1279	6.992	0.7220	0.2692	0.0088	0.5894	0.3937	0.0169
7.002	0.7975	0.1550	0.0475	0.6858	0.2050	0.1092	7.000	0.7217	0.2783	0.0000	0.5480	0.4520	0.0000
						270 K and 2.8 MPa							
2.798	0.7969	0.0000	2.0310	0.1718	0.0000	0.8282	2.799	0.3265	0.5082	0.1653	0.0746	0.3196	0.6058
2.800	0.7365	0.0642	0.1993	0.1569	0.0303	0.8128	2.799	0.2860	0.5536	0.1604	0.0668	0.3621	0.5711
2.799	0.7138	0.0878	0.1984	0.1564	0.0424	0.8012	2.800	0.2402	0.6059	0.1539	0.0563	0.4186	0.5251
2.801	0.7004	0.1027	0.1969				2.799	0.2084	0.6429	0.1487	0.0480	0.4495	0.5025
2.801	0.6755	0.1292	0.1953	0.1466	0.0628	0.7906	2.799	0.1755	0.6816	0.1429	0.0395	0.4892	0.4713
2.798	0.6515	0.1539	0.1946	0.1400	0.0760	0.7840	2.799	0.1441	0.7191	0.1368	0.0318	0.5306	0.4376
2.799	0.6029	0.2066	0.1905	0.1322	0.1056	0.7622	2.799	0.1008	0.7723	0.1269	0.0219	0.5989	0.3792
2.800	0.5629	0.2502	0.1869	0.1239	0.1314	0.7447	2.798	0.0689	0.8134	0.1177	0.0146	0.6509	0.3345
2.800	0.5154	0.3006	0.1840	0.1150	0.1629	0.7221	2.799	0.0470	0.8419	0.1111	0.0099	0.6923	0.2978
2.798	0.4356	0.3878	0.1766	0.0979	0.2221	0.6800	2.799	0.0000	0.9066	0.0934	0.0000	0.7716	0.2284
2.801	0.3682	0.4621	0.1697	0.0829	0.2785	0.6386							
						270 K and 5.5 MPa							
5.502	0.8543	0.0000	0.1457	0.3601	0.0000	0.6399	5.499	0.4388	0.4741	0.0871	0.1913	0.5440	0.2647
5.503	0.6494	0.2244	0.1262	0.2877	0.2071	0.5052	5.501	0.4180	0.5000	0.0820	0.1803	0.5843	0.2354
5.501	0.6300	0.2454	0.1256	0.2815	0.2313	0.4872	5.501	0.3689	0.5753	0.0558	0.1463	0.7126	0.1411
5.501	0.5493	0.3378	0.1128	0.2477	0.3445	0.4078	5.499	0.3653	0.5800	0.0547	0.1440	0.7227	0.1333
5.505	0.5074	0.3877	0.1049	0.2296	0.4134	0.3570	5.503	0.3128	0.6872	0.0000	0.0948	0.9052	0.0000
						270 K and 8.0 MPa							
8.000	0.8426	0.0000	0.1574	0.5345	0.0000	0.4655	7.999	0.5701	0.2983	0.1316	0.4245	0.3271	0.2484
7.998	0.8307	0.0120	0.1573	0.5297	0.0115	0.4588	8.010	0.4224	0.5113	0.0663			
7.998	0.7832	0.0643	0.1525				7.996	0.4004	0.5711	0.0285	0.2880	0.6715	0.0405
8.000	0.7561	0.0941	0.1498	0.5013	0.0950	0.4037	7.997	0.4004	0.5932	0.0064	0.2528	0.7377	0.0095
7.997	0.6093	0.2524	0.1383	0.4412	0.2739	0.2849	8.003	0.3974	0.6026	0.0000	0.2490	0.7510	0.0000

Methane + Propane + Carbon Dioxide Ternary System. VLE measurements were at 270 K for 2.8, 5.5, and 8.0 MPa and 230 K for 0.8, 4.0, and 7.0 MPa. The pressures were chosen for the same reason at both operating temperatures; the low-pressure point is the pressure where the carbon dioxide−propane binary intercept has an inverted vapor curve, the 5.5 and 4.0 MPa are intermediate pressures, and the high pressures are near the critical

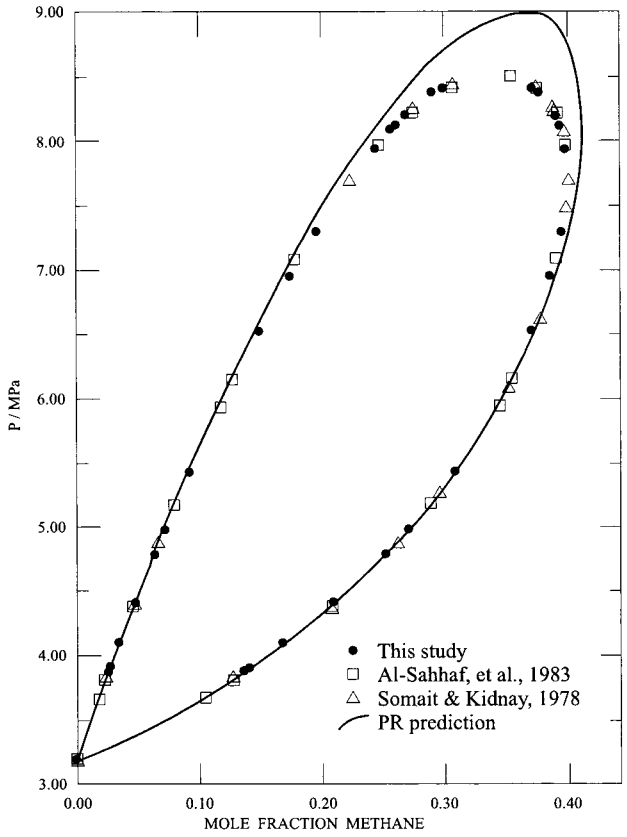

Figure 1. Methane + carbon dioxide at 270 K: ●, this study; □, Al-Sahhaf et al.;[2] △, Somait and Kidnay;[14] curved line, PR prediction.

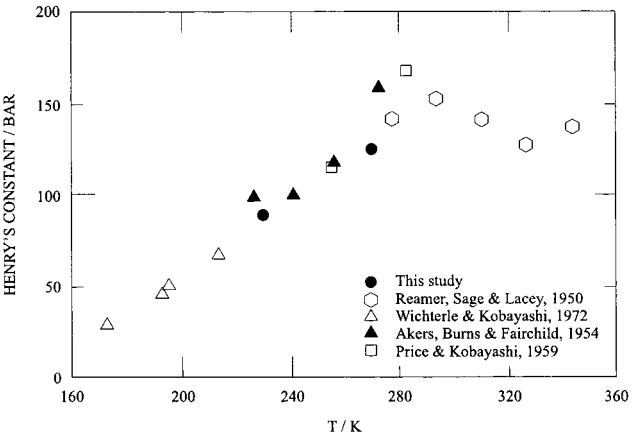

Figure 2. Henry's constants versus temperature for methane + propane: ●, this study; □, Reamer et al.;[27] △, Wichterle and Kobayashi;[33] ○, Akers et al.;[18] □, Price and Kobayashi.[25]

region of both intercepting binaries. The results at 230 K are shown in Figures 4−6. Plotting the binary end point measurements against the previously generated binary data checked the internal consistency of each data set. All 12 binary points fell within 0.002 mole fraction of the previous points.

The standard Peng−Robinson (PR) equation of state[46] was used to model the experimental data. The equation is cubic in volume and is a modified van der Waals equation adapted specifically for the hydrocarbon-processing industry. The equation includes one binary interaction parameter, k_{ij}, which was obtained by data regression of the binary VLE measurements. The Peng−Robinson predictions for the ternary measurements were done using the

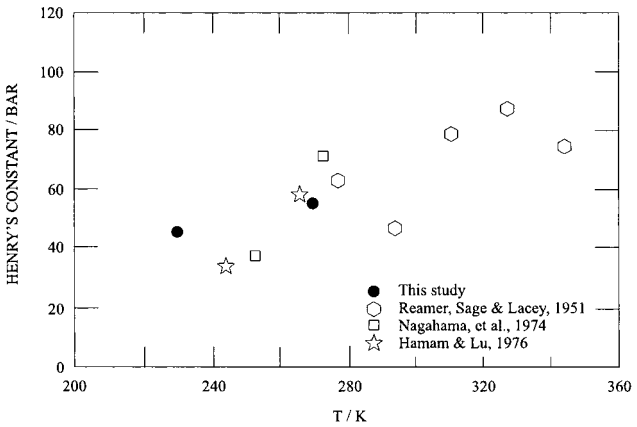

Figure 3. Henry's constants versus temperature for carbon dioxide + propane: ●, this study; □, Reamer et al.;[43] □, Nagahama et al.;[41] s☆, Hamam and Lu.[40]

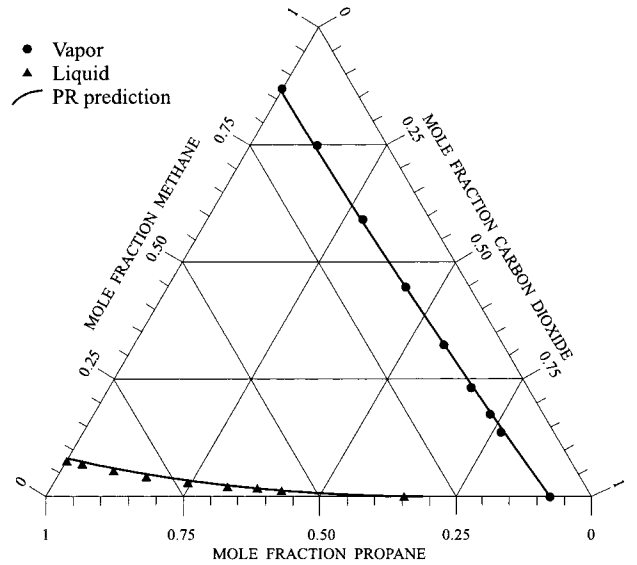

Figure 4. Methane + carbon dioxide + propane at 230 K and 0.8 MPa: ●, vapor; ▲, liquid; curved line, PR prediction.

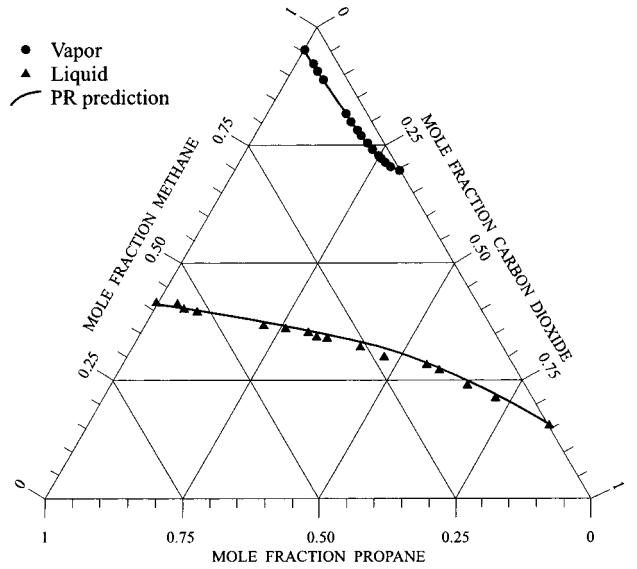

Figure 5. Methane + carbon dioxide + propane at 230 K and 4.0 MPa: ●, vapor; ▲, liquid; curved line, PR prediction.

k_{ij} values obtained from the binary isotherms, as discussed previously. The Peng−Robinson predictions are most ac-

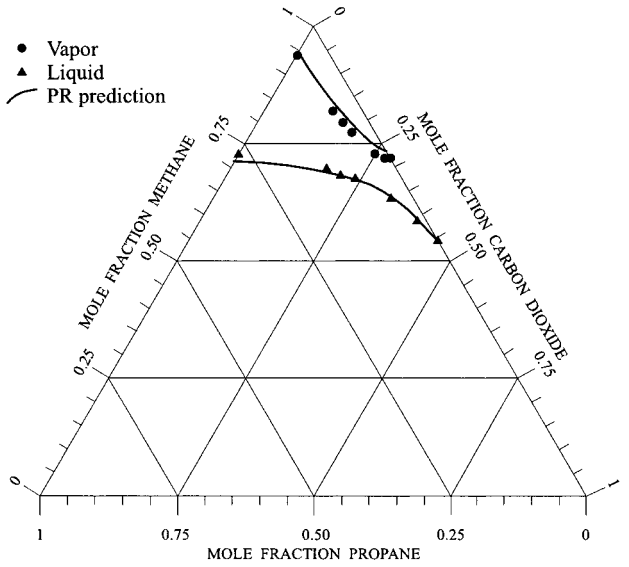

Figure 6. Methane + carbon dioxide + propane at 230 K and 7.0 MPa: ●, vapor; ▲, liquid; curved line, PR prediction.

curate at the low pressures and poorest at the high pressures of 8.0 and 7.0 MPa, which are near the critical points.

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