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Liquid-Vapor Equilibria for the $N_2 + CH_4 + C_2H_6$ System from 260 to 280 K

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Recent industrial interest in the low-temperature high-pressure processing of hydrocarbons has increased the need for reliable data on the components found in natural gas. The objective of the work reported here is to provide accurate experimental measurements on a system of industrial interest and to assess the feasibility of modeling the phase equilibria with simple cubic equations of state. Liquid-vapor equilibria were measured for the binary systems $N_2 + C_2H_6$ and $CH_4 + C_2H_6$ and the ternary system $N_2 + CH_4 + C_2H_6$ at 260.00, 270.00, and 280.00 K over the pressure regions of industrial interest. The data at 270.00 K were modeled with three cubic equations of state: the Peng-Robinson equation, the Soave modification of the Redlich-Kwong equation, and a modified Clausius equation. All of the equations gave satisfactory results at lower pressures, but all failed to model the data satisfactorily near the critical points of the binary and ternary systems.

Introduction

The $N_2 + CH_4 + C_2H_6$ phase equilibrium is quite important, since these components will generally account for 95% of the total material in a typical natural gas. However, only limited experimental data are available for this ternary system; there are five published articles, but only two have data above the methane critical (190.56 K) and they contain only eight widely scattered data points. The available literature is summarized in Table I.

The literature references for the binary systems $N_2 + CH_4$, $N_2 + C_2H_6$, and $CH_4 + C_2H_6$ are available in several recent bibliographies (*6-8*). A complete evaluation of the methane + ethane system has also been undertaken (*9*).

The experimental work reported here involves the binary systems $N_2 + C_2H_6$ and $CH_4 + C_2H_6$ and the ternary system $N_2 + CH_4 + C_2H_6$ at pressures of 35, 50, 65, 75, and 85 atm.

For practical calculations, it is desirable to have a simple equation of state that is capable of modeling the experimental data over all the temperature and pressure regions of interest. The Soave modification (*10*) of the Redlich-Kwong equation (*11*) and the Peng-Robinson equation (*12*) are presently widely used industrially for this purpose. These two equations along with a modified Clausius equation were used to model the experimental binary and ternary data.

Experimental Equipment and Procedure

The experimental apparatus and procedures have been described previously (*13*), and thus only a brief discussion will be presented here.

The system was of the vapor recirculation type utilizing a high-pressure diaphragm pump operating at ambient conditions to force the vapor through the liquid. A stirred liquid bath using excess refrigeration balanced with proportional controlled electric heating was used as the cryostat. The temperatures were measured to ±0.02 K with a calibrated (IPTS-68) platinum resistance thermometer, and the pressures were measured to ±0.5 psi in the region 0-500 psia and ±1.5 pisa in the region above 500 psia with one of two Heise gauges. A gas chromatograph equipped with a thermal conductivity detector was used in the analysis. The chromatograph conditions were adjusted to obtain very sharp, symmetric peaks, and the peak areas were obtained with an electronic integrator.

Table I. Previous Studies of the $N_2 + CH_4 + C_2H_6$ System

ref	temp range, K	pressure range, atm	remarks
1	144, 200	34, 68	3 data points at 200 K, 3 data points at 144 K
2	122, 171	2-28	liquid-liquid-vapor at 122 K. 59 data points
3	112	14	1 data point of 3 liquid phases and 1 vapor phase
4	114-129	15-35	liquid-liquid-vapor, 32 data points
5	153-203	11-50	a total of 15 data points at 6 temperatures

The calibration curves were established by using a series of mixtures containing nitrogen, methane, and ethane prepared gravimetrically in this laboratory. For all conditions encountered in this work, the calibration curves were linear. All of the experimental compositions obtained in this work have been normalized. The analysis system is believed to be accurate to ±0.002 in the mole fraction, but the mole fractions presented in the tables are reported to four significant figures, since the precision of the chromatographic measurements is considerably greater than the accuracy. Random errors due primarily to gas or liquid sampling, especially near the critical region, will cause some data points to exhibit more scatter than is attributable to the pressure, temperature, or composition calibrations.

The suppliers specified purity for the methane and ethane was 99.0 mol % minimum while the nitrogen was 99.7 mol % minimum. All gases were found to be chromatographically pure, producing no extraneous peaks in the gas chromatograph recordings.

The vapor pressure of ethane was measured frequently during the course of the experimental program. The average measured value of 21.68 atm at 270.00 K compares favorably with the value of 21.81 atm reported by Goodwin et al. (*14*). The slight difference between the two vapor pressues may be due in part to the small amount of impurities in the ethane.

As a further check on the accuracy of the pressure and temperature measurements, the vapor pressure of carbon dioxide (99.99% minimum purity) was measured on several occasions. The average value of 31.59 atm at 270.00 K is in excellent agreement with that of Meyers and Van Dusen (*15*), 31.61 atm, adjusted to the IPTS-68 temperature scale.

Results

The results of all the experimental measurements are presented in Tables II-VI, and representative data are shown in Figures 1-6.

$N_2 + C_2H_6$ System. There have been seven previous studies of this system covering the temperature range 93-302 K. Figure 1 shows the excellent agreement between this work and the measurements of Grausø et al. (*16*). In Figure 2, the critical pressures estimated from Stryjek et al. (*17*), Grausø et al. (*16*),

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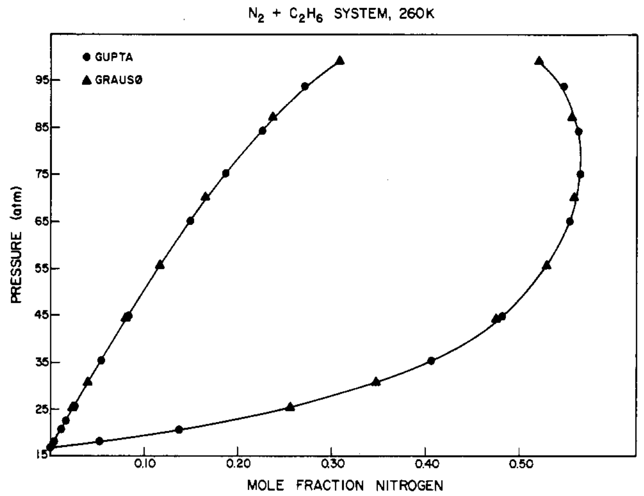

Figure 1. $N_2 + C_2H_6$ system at 260.00 K.

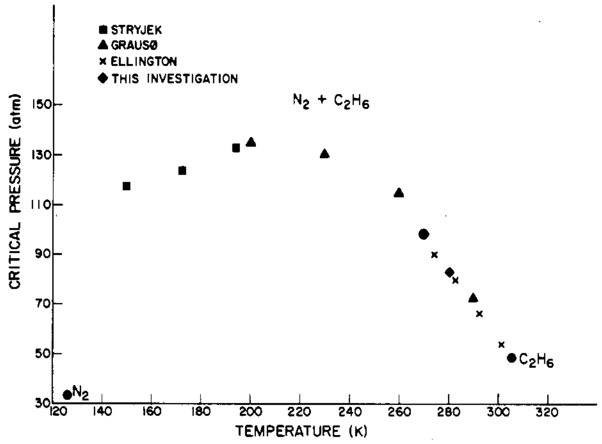

Figure 2. Critical pressures in the $N_2 + C_2H_6$ system.

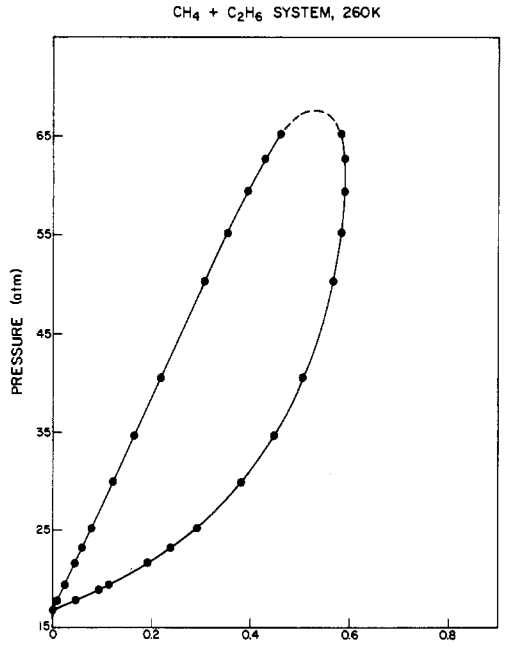

Figure 3. $CH_4 + C_2H_6$ system at 260.00 K.

and Ellington et al. (*18*) are compared with critical pressures estimated from the isotherms at 270 and 280 K. The 260 K isotherm was not extended to high enough pressure to allow the evaluation of the critical point. With the possible exception of the 150 K value, the data are in good agreement.

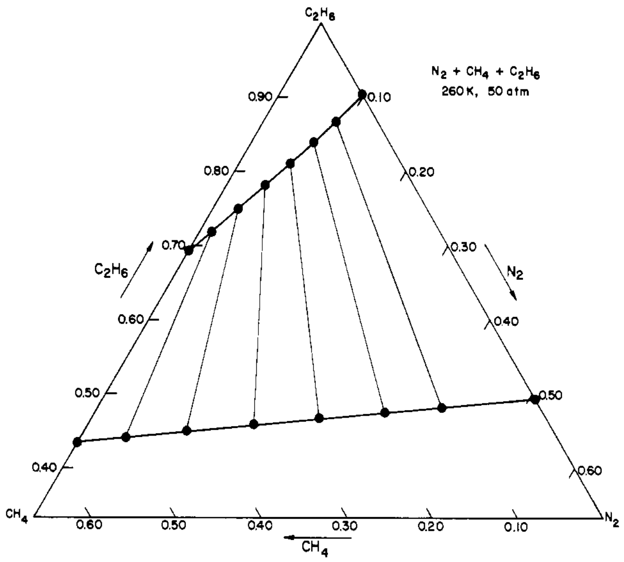

Figure 4. $N_2 + CH_4 + C_2H_6$, 260.00 K and 50 atm.

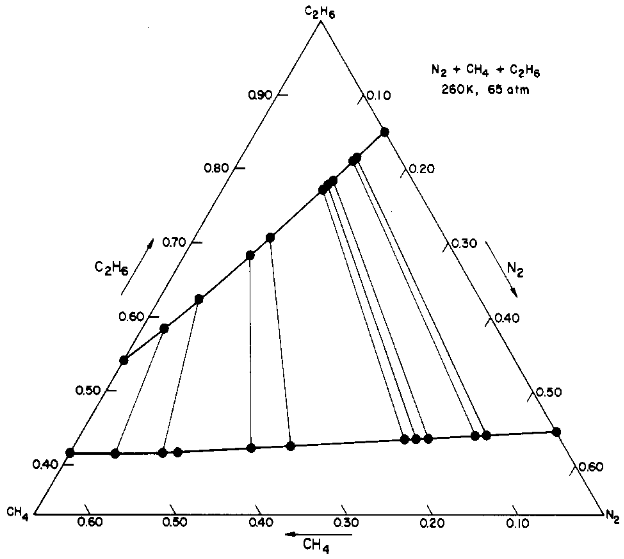

Figure 5. $N_2 + CH_4 + C_2H_6$, 260.00 K and 65 atm.

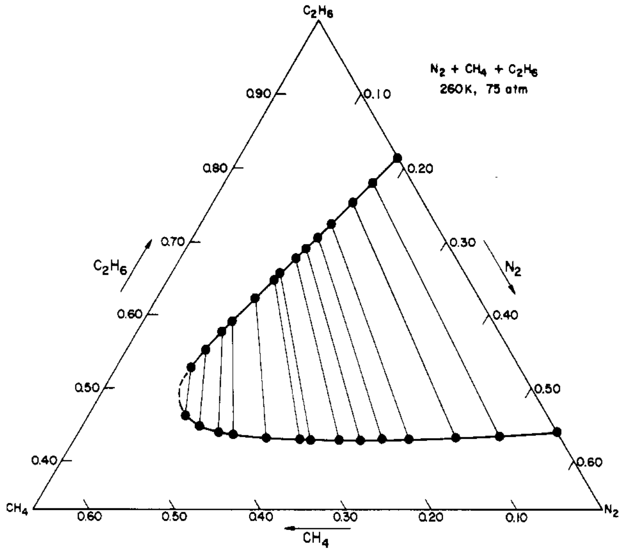

Figure 6. $N_2 + CH_4 + C_2H_6$, 260.00 K and 75 atm.

Table II. $N_2 + C_2H_6$ Vapor-Liquid Equilibria

260.00 K			270.00 K			280.00 K		
P, atm	y_{N_2}	x_{N_2}	P, atm	y_{N_2}	x_{N_2}	P, atm	y_{N_2}	x_{N_2}
16.80	0.0000	0.0000	21.68	0.0000	0.0000	27.60	0.0000	0.0000
18.10	0.0523	0.0036	23.50	0.0523	0.0051	29.50	0.0437	0.0061
20.59	0.1375	0.0106	24.35	0.0770	0.0077	30.72	0.0684	0.0097
22.55		0.0161	25.13	0.0942	0.0098	31.80	0.0866	0.0128
25.63		0.0254	27.65	0.1489	0.0157	36.23	0.1558	0.0265
35.36	0.4065	0.0541	28.63	0.1698	0.0193	40.32	0.2047	0.0394
44.88	0.4823	0.0828	30.00	0.1889	0.0233	45.35	0.2511	0.0556
65.05	0.5541	0.1494	30.40		0.0251	51.69	0.2943	0.0767
75.20	0.5653	0.1873	32.52	0.2378	0.0302	55.89	0.3167	0.0921
84.27	0.5632	0.2258	32.62	0.2262	0.0302	60.20	0.3331	0.1078
93.80	0.5473	0.2714	34.52	0.2636	0.0359	65.30	0.3471	0.1284
			34.70	0.2646	0.0382	71.68	0.3542	0.1570
			35.26	0.2668	0.0390	76.90	0.3484	0.1852
			37.31	0.2938	0.0435	80.25	0.3360	0.2088
			40.39	0.3216	0.0543	80.90	0.3339	0.2162
			40.53	0.3321	0.0563	82.25	0.3177	0.2311
			41.19	0.3339	0.0554	83.55	(single phase)[a]	
			45.50	0.3618	0.0696			
			47.42	0.3811	0.0687			
			50.31	0.3921	0.0848			
			53.47	0.4156	0.0951			
			55.20	0.4127	0.0989			
			57.70	0.4290	0.1076			
			60.18	0.4291	0.1165			
			65.62	0.4506				
			70.43	0.4545	0.1555			
			80.50	0.4631	0.2030			
			80.59	0.4631				
			81.42	0.4611	0.2079			
			84.12		0.2263			
			85.45		0.2306			
			89.81	0.4652	0.2572			
			90.71		0.2636			
			93.25		0.2849			
			93.50	0.4594				
			93.70		0.2931			
			96.42	0.4446				
			96.45	0.4475				
			96.67		0.3361			
			97.72		0.3742			

[a] Single phase indicates that identical compositions were obtained for the liquid and vapor samples.

Table III. $CH_4 + C_2H_6$ Vapor-Liquid Equilibria

260.00 K			270.00 K			280.00 K		
P, atm	y_{CH_4}	x_{CH_4}	P, atm	y_{CH_4}	x_{CH_4}	P, atm	y_{CH_4}	x_{CH_4}
16.80	0.0000	0.0000	21.68	0.0000	0.0000	27.60	0.0000	0.0000
17.80	0.0467	0.0088	22.53	0.0298	0.0070	28.50	0.0279	0.0081
18.88	0.0942		23.89	0.0762	0.0188	30.35	0.0744	0.0231
19.42	0.1150	0.0239	26.10	0.1332	0.0357	31.62	0.1036	0.0335
21.60	0.1922	0.0445	30.69	0.2361	0.0739	36.08	0.1864	0.0693
23.22	0.2387	0.0592	35.07	0.3140	0.1127	39.85	0.2404	0.0996
25.26	0.2924	0.0788	40.00	0.3768	0.1550	43.58	0.2818	0.1292
29.98	0.3810	0.1220	45.30	0.4237	0.1984	46.50	0.3091	0.1528
34.69	0.4483	0.1652	45.50	0.4251		49.75	0.3336	0.1798
40.59	0.5052	0.2189	49.06	0.4484	0.2315	52.60	0.3512	0.2044
50.30	0.5664	0.3087	50.26	0.4558	0.2419	55.72	0.3654	0.2333
55.18	0.5823	0.3545	55.02		0.2819	59.06	0.3719	0.2668
59.40	0.5896	0.3952	60.22	0.4889	0.3321	60.07	0.3711	0.2774
62.65	0.5897	0.4297	62.96	0.4896		60.51	0.3699	
65.18	0.5823	0.4615	64.53		0.3862	61.10	0.3675	0.2913
69.90	(single phase)[a]		65.14		0.3980	61.84	0.3609	0.3046
			65.44	0.4856		62.10	0.3557	0.3109
			66.50	(single phase)[a]		62.40	(single phase)[a]	

[a] Single phase indicates that identical compositions were obtained for the liquid and vapor samples.

Since the experimental data of this investigation were gathered by several individuals over a period of 18 months, the $N_2 + C_2H_6$ system at 270 K was used as a standard; that is, periodically new measurements would be made on this system to ensure that chromatographic calibrations, sampling techniques, and pressure and temperature measurements were all satisfactory. This is the reason for the large number of data points in Table II.

$CH_4 + C_2H_6$ System. The previous experimental studies for this system have been summarized and evaluated by Hiza et al. (*9*). Henry's law constants and critical pressures evaluated from Table III are in good agreement with the earlier work (*9*).

Table IV

$N_2 + CH_4 + C_2H_6$ System at 260.00 K and 50 Atm

P, atm	Y_{N_2}	Y_{CH_4}	$Y_{C_2H_6}$	X_{N_2}	X_{CH_4}	$X_{C_2H_6}$
50.05	0.0533	0.5049	0.4418	0.0139	0.2665	0.7196
50.01	0.1200	0.4293	0.4507	0.0296	0.2205	0.7499
49.90	0.1940	0.3464	0.4596	0.0452	0.1734	0.7814
50.02	0.2667	0.2652	0.4681	0.0592	0.1300	0.8107
49.92	0.3396	0.1852	0.4752	0.0723	0.0890	0.8387
50.07	0.4147	0.1032	0.4821	0.0847	0.0486	0.8667

$N_2 + CH_4 + C_2H_6$ System at 260.00 K and 65 Atm

P, atm	Y_{N_2}	Y_{CH_4}	$Y_{C_2H_6}$	X_{N_2}	X_{CH_4}	$X_{C_2H_6}$
65.13	0.3811	0.1839	0.4350	0.1172	0.1114	0.7714
65.00	0.3945	0.1692	0.4362	0.1198	0.1021	0.7781
65.09	0.4091	0.1546	0.4363	0.1230	0.0929	0.7841
64.96	0.2091	0.3681	0.4227	0.0767	0.2400	0.6832
65.08	0.2541	0.3203	0.4256	0.0886	0.2047	0.7068
65.16	0.0537	0.5316	0.4147	0.0260	0.3897	0.5843
65.02	0.1262	0.4574	0.4164			
65.00	0.4624	0.0969	0.4407	0.1327	0.0570	0.8103
65.00	0.4744	0.0848	0.4408	0.1351	0.0499	0.8150
64.98	0.1081	0.4749	0.4170	0.0463	0.3297	0.6240
65.00[a]	0.5541		0.4459	0.1494		0.8506
65.00[a]		0.5833	0.4167		0.4585	0.5415

$N_2 + CH_4 + C_2H_6$ System at 260.00 K and 75 Atm

P, atm	Y_{N_2}	Y_{CH_4}	$Y_{C_2H_6}$	X_{N_2}	X_{CH_4}	$X_{C_2H_6}$
74.80	0.4963	0.0703	0.4336	0.1734	0.0464	0.7802
75.18	0.4984	0.0684	0.4332	0.1750	0.0453	0.7797
75.08	0.4463	0.1221	0.4315	0.1645	0.0821	0.7533
75.13	0.4507	0.1176	0.4317	0.1663	0.0795	0.7542
75.06	0.3925	0.1773	0.4302	0.1532	0.1219	0.7249
75.13	0.4031	0.1666	0.4303	0.1565	0.1146	0.7290
75.13	0.3350	0.2357	0.4293	0.1415	0.1676	0.6910
75.00	0.3611	0.2094	0.4295	0.1472	0.1469	0.7058
74.90	0.3103	0.2606	0.4290	0.1349	0.1874	0.6776
75.02	0.2765	0.2940	0.4295	0.1274	0.2162	0.6564
75.08	0.2245	0.3442	0.4313	0.1141	0.2629	0.6229
75.09	0.2636	0.3051	0.4312	0.1245	0.2270	0.6484
75.20	0.1824	0.3811	0.4365	0.1040	0.3046	0.5914
75.10	0.2237	0.3453	0.4309	0.1145	0.2643	0.6213
75.17	0.1366	0.4143	0.4490	0.0926	0.3548	0.5526
75.07	0.1641	0.3966	0.4392	0.0987	0.3239	0.5775
74.90	0.1121	0.4245	0.4635	0.0878	0.3848	0.5274
75.07	0.1340	0.4159	0.4501	0.0919	0.3579	0.5502

[a] Binary points.

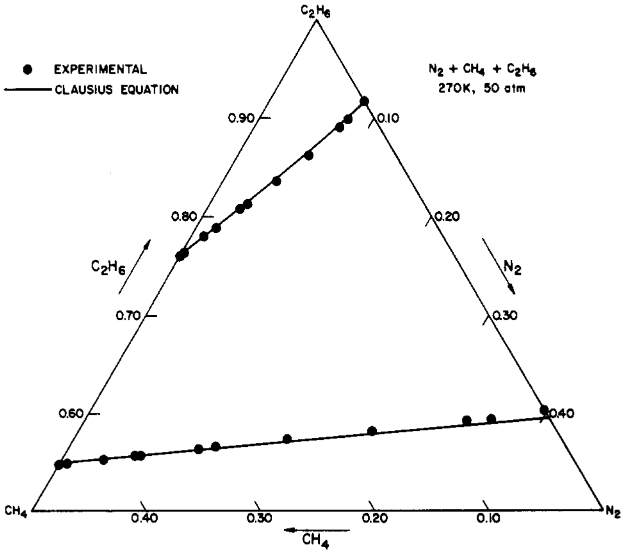

Figure 7. Predicted vapor + liquid equilibria with the Clausius equation.

Table V. $N_2 + CH_4 + C_2H_6$ System

P, atm	Y_{N_2}	Y_{CH_4}	$Y_{C_2H_6}$	X_{N_2}	X_{CH_4}	$X_{C_2H_6}$
$N_2 + CH_4 + C_2H_6$ System at 270.00 K and 35 atm						
35.00	0.2297	0.0470	0.7232	0.0341	0.0160	0.9500
35.01	0.1892	0.0936	0.7172	0.0285	0.0322	0.9393
35.01	0.1446	0.1450	0.7104	0.0223	0.0505	0.9272
35.01	0.1270	0.1652	0.7078	0.0196	0.0576	0.9228
35.00	0.0736	0.2284	0.6979	0.0116	0.0814	0.9069
35.00	0.0482	0.2572	0.6946	0.0077	0.0921	0.9002
35.00	0.0797	0.2201	0.7001			
$N_2 + CH_4 + C_2H_6$ System at 270.00 K and 50 Atm						
50.00	0.3546	0.0503	0.5951	0.0783	0.0231	0.8986
50.00	0.3335	0.0740	0.5925	0.0749	0.0347	0.8904
50.00	0.2564	0.1602	0.5834	0.0602	0.0766	0.8631
50.00	0.1862	0.2392	0.5746	0.0463	0.1173	0.8364
50.00	0.1283	0.3060	0.5657	0.0331	0.1535	0.8133
50.01	0.1139	0.3222	0.5638	0.0297	0.1619	0.8084
50.00	0.0066	0.4466	0.5468	0.0019	0.2361	0.7619
50.00	0.0362	0.4114	0.5524	0.0096	0.2089	0.7815
50.01	0.0664	0.3775	0.5561	0.0177	0.1948	0.7875
50.00	0.0627	0.3807	0.5565			
49.99	0.3955		0.6045	0.0827		0.9173
$N_2 + CH_4 + C_2H_6$ System at 270.00 K and 65 Atm						
64.95	0.3712	0.0906	0.5382	0.1213	0.0539	0.8247
64.85	0.3701	0.0923	0.5376	0.1205	0.0548	0.8247
65.15	0.2526	0.2192	0.5281	0.0937	0.1381	0.7682
64.92	0.2546	0.2167	0.5287	0.0935	0.1361	0.7704
65.00	0.2589	0.2124	0.5286	0.0948	0.1333	0.7719
64.98	0.1449	0.3348	0.5203	0.0622	0.2245	0.7133
64.95	0.1412	0.3375	0.5212	0.0610	0.2285	0.7106
65.05	0.1510	0.3284	0.5207	0.0646	0.2212	0.7142
65.10	0.0667	0.4152	0.5181	0.0343	0.3047	0.6610
64.92	0.0610	0.4213	0.5178	0.0313	0.3104	0.6583
65.06	0.0582	0.4238	0.5180			
65.00	0.2026	0.2723	0.5250	0.0760	0.1714	0.7526
65.00	0.2194	0.2543	0.5263	0.0846	0.1633	0.7521
65.00	0.2921	0.1755	0.5324	0.1008	0.1061	0.7931
$N_2 + CH_4 + C_2H_6$ System at 270.00 K and 75 Atm						
75.00	0.3559	0.1135	0.5306	0.1525	0.0716	0.7759
74.97	0.4200	0.0476	0.5323	0.1673	0.0317	0.8010
74.94	0.4540	0.0124	0.5335	0.1747	0.0080	0.8173
74.90	0.1444	0.2917	0.5639	0.1117	0.2604	0.6279
75.00	0.1545	0.2891	0.5564	0.1130	0.2519	0.6351
75.10	0.1586	0.2861	0.5553	0.1130	0.2467	0.6403
74.92	0.2065	0.2556	0.5378	0.1213	0.2023	0.6764
75.08	0.2030	0.2581	0.5389	0.1205	0.2050	0.6745
74.95	0.2590	0.2089	0.5321	0.1331	0.1559	0.7110
75.00	0.3282	0.1410	0.5308	0.1483	0.0993	0.7524
75.10	0.2987	0.1705	0.5307			
$N_2 + CH_4 + C_2H_6$ System at 270.00 K and 85 Atm						
84.90	0.4034	0.0506	0.5460	0.2202	0.0396	0.7403
85.10	0.4232	0.0320	0.5449			
84.97	0.4242	0.0316	0.5443	0.2229	0.0242	0.7530
84.90	0.3534	0.0922	0.5543			
84.97	0.3288	0.1093	0.5619	0.2152	0.0918	0.6930
85.10	0.3024	0.1241	0.5734	0.2177	0.1083	0.6739
85.02	0.2991	0.1260	0.5749	0.2178	0.1106	0.6716
85.17	0.2602	0.1382	0.6016	0.2394	0.1287	0.6319
84.90	0.3628	0.0848	0.5524			
84.90	0.3643	0.0837	0.5520	0.2153	0.0675	0.7172

$N_2 + CH_4 + C_2H_6$ System. The pressures selected for measurement were 50, 65, and 75 atm at 260 and 280 K, and 35, 50, 65, 75, and 85 atm at 270 K. As mentioned previously, there are no other data at temperatures above 203 K, and thus it is not possible to directly compare the results of this work with earlier investigations.

Discussion

Recently there has been considerable interest in the use of simple cubic equations of state to model phase equilibria, especially for hydrocarbon systems in the refining and natural gas industries. The work of Soave (*10*), Peng and Robinson (*12*), and Graboski and Daubert (*19*) are excellent examples of this trend. The $N_2 + CH_4 + C_2H_6$ system of this work provides a severe test of these simple equations, since two of the com-

Table VI. $N_2 + CH_4 + C_2H_6$ System

P, atm	Y_{N_2}	Y_{CH_4}	$Y_{C_2H_6}$	X_{N_2}	X_{CH_4}	$X_{C_2H_6}$
$N_2 + CH_4 + C_2H_6$ System at 280.00 K and 50 Atm						
50.00[a]	0.2835		0.7165	0.0709		0.9291
50.00[a]		0.3352	0.6648		0.1820	0.8180
50.10	0.2336	0.0600	0.7064	0.0609	0.0290	0.9101
50.15	0.1706	0.1340	0.6954	0.0467	0.0666	0.8866
49.90	0.1030	0.2113	0.6857	0.0296	0.1077	0.8627
50.12	0.0455	0.2814	0.6730	0.0139	0.1489	0.8372
$N_2 + CH_4 + C_2H_6$ System at 280.00 K and 65 Atm						
65.08	0.2021	0.1575	0.6404	0.0900	0.1051	0.8048
65.10	0.2511	0.1041	0.6448	0.1037	0.0668	0.8295
65.05	0.3046	0.0460	0.6494	0.1173	0.0286	0.8541
65.00	0.1451	0.2183	0.6366	0.0723	0.1540	0.7737
64.90	0.1018	0.2620	0.6362	0.0565	0.1944	0.7491
65.00	0.0787	0.2830	0.6383	0.0483	0.2211	0.7306
65.00	0.0909	0.2725	0.6366	0.0530	0.2078	0.7392
65.05	0.0667	0.2925	0.6408	0.0438	0.2369	0.7193
65.10	0.0746	0.2861	0.6392	0.0471	0.2271	0.7258
65.10	0.0717	0.2892	0.6392	0.0454	0.2290	0.7256
65.15	0.0633	0.2947	0.6420	0.0425	0.2407	0.7168
65.15	0.0623	0.2957	0.6420	0.0423	0.2437	0.7139
65.10	0.0574	0.2985	0.6441	0.0400	0.2488	0.7112
64.88	0.0480	0.3021	0.6499	0.0360	0.2616	0.7024
64.92	0.0575	0.2989	0.6436	0.0394	0.2477	0.7129
64.90	0.0430	0.2996	0.6574	0.0349	0.2699	0.6951
65.00[a]	0.3463		0.6537	0.1277		0.8723
$N_2 + CH_4 + C_2H_6$ System at 280.00 K and 75 Atm						
75.03	0.3115	0.0400	0.6485	0.1663	0.0297	0.8040
74.98	0.2579	0.0873	0.6548	0.1573	0.0691	0.7736
75.00	0.2091	0.1222	0.6687	0.1534	0.1054	0.7412
75.05	0.1980	0.1260	0.6760	0.1566	0.1126	0.7307
74.89	0.1849	0.1273	0.6878	0.1596	0.1182	0.7222
74.95	0.1941	0.1255	0.6803	0.1580	0.1139	0.7281
75.00[a]	0.3521		0.6479	0.1743		0.8257

[a] Binary point.

ponents are supercritical and thus both of the binary systems and the ternary system at higher pressures exhibit critical points.

In addition to the Peng–Robinson and Soave–Redlich–Kwong relations, a modified Clausius equation was applied to the data. The equations are

Peng–Robinson

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \tag{1}$$

Soave–Redlich–Kwong

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \tag{2}$$

Clausius

$$P = \frac{RT}{V - b} - \frac{a}{(V + c)^2} \tag{3}$$

In all of the equations, the *a* term is temperature dependent; in (1) and (2) the *b* term is independent of temperature, while in (3) both the *b* and *c* terms are functions of temperature. All of the equations use a single binary interaction coefficient to modify the *a* term. The original references (*10*, *12*) should be consulted for details concerning the evaluation of the constants and the application to phase equilibria calculations for eq 1 and 2.

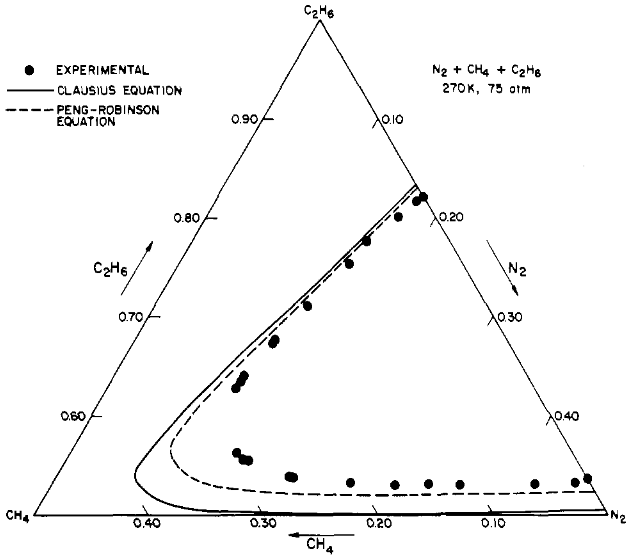

Figure 8. Predicted vapor + liquid equilibria with the Clausius and Peng–Robinson equations.

In eq 3 the *a* term was evaluated from vapor pressure data in a manner similar to that of Soave (*10*), while the *b* and *c* terms were obtained from saturated liquid densities. At temperatures above the critical, *b* and *c* were obtained by extrapolation. The mixing rules used were those of Peng and Robinson (eq 20–22 of ref 12). Lu and co-workers (*20*, *21*) have also used the Clausius equation for thermodynamic calculations but in a somewhat different fashion than in the present investigation.

In all equations the binary interaction coefficients for $N_2 + C_2H_6$ and $CH_4 + C_2H_6$ were obtained by fitting the equations to the data of Tables II and III. For $N_2 + CH_4$ the data of Stryjek et al. (*22*) and Kidnay et al. (*23*) were used to obtain an interaction coefficient, which was assumed independent of temperature. Table VII summarizes the interaction coefficients and the constants.

The calculations on the ternary system were made by using only the constants evaluated from the pure fluid and binary system data. Some typical results are shown in Figures 7 and 8. The results of all the calculations can be briefly summarized as follows: for both the binary and ternary systems, all of the equations give satisfactory results except in the critical regions, where all of the equations fail badly. It is of course possible to force a better fit in the critical regions by adjusting the binary interaction coefficients, but only at the expense of a poorer fit in the lower pressure regions. The conclusion reached is that the cubic equations of state are inadequate for modeling ternary phase equilibria data in the critical region using only a single-temperature independent-interaction coefficient for each set of binary data. This same conclusion was reached by Somait and

Table VII. Equation of State Constants and Binary Interaction Coefficients

					binary interaction coefficients		
equation	compd	a, (cm^3/g-mol)^2 bar	b, cm^3/g-mol	c, cm^3/g-mol	$N_2 + CH_4$	$N_2 + C_2H_6$	$CH_4 + C_2H_6$
Peng–Robinson	N_2	9.4374×10^5	24.0136		0.038	0.080	0.021
	CH_4	2.1416×10^6	26.8028				
	C_2H_6	6.4325×10^6	40.5437				
Soave–Redlich–Kwong	N_2	7.7237×10^5	26.7422		0.039	0.082	0.020
	CH_4	1.9123×10^6	29.8483				
	C_2H_6	6.0918×10^6	45.1504				
Clausius	N_2	6.8316×10^5	12.041	26.541	0.031	0.048	0.00
	CH_4	1.7969×10^6	13.873	29.191			
	C_2H_6	6.0533×10^6	35.655	29.486			

Kidnay (*13*) for the $N_2 + CH_4 + CO_2$ system.

Glossary

a	equation of state parameter
b	equation of state parameter
c	equation of state parameter
P	total pressure
R	gas constant
T	temperature
V	molar volume
X	liquid-phase mole fraction
Y	vapor-phase mole fraction

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Densities and Refractive Indexes of Binary Mixtures in the System Methyl Isobutyl Ketone–2-Butanol. Mathematical Relations Obtained

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Densities and refractive indexes were determined for binary mixtures of methyl isobutyl ketone–2-butanol at temperatures of 20, 25, 30, and 35 °C and at atmospheric pressure. An empirical relation between density, composition, and temperature and, on the other hand, an empirical relation between refractive index, composition, and temperature of the mixture were obtained. The properties of the mixtures predicted through empirical relations were found to be in fairly good agreement with the experimental data and to have validity over the temperature range 20–35 °C.

One need of much importance is the measurement of properties of binary mixtures at different temperatures. To facilitate the interpolation of the data, we derived equations in which the effects of temperature and composition were incorporated.

Materials. Methyl isobutyl ketone (analytical reagent, Merck, Darmstadt) was distilled, refluxed, and fractionated. The fraction boiling between 115 and 116 °C was collected and used in the experimental measurements (*2*). 2-Butanol (analytical reagent, Merck, Darmstadt) was used without further purification and drying (*2*). The physical properties of the substances used were compared with corresponding data reported in the literature (Table I).

Table I. Properties of Methyl Isobutyl Ketone and 2-Butanol

		density, g cm^{-3}		refractive index	
material	temp, °C	present work (exptl)	lit	present work (exptl)	lit
methyl isobutyl ketone	20	0.8010	0.8008 (*1, 2*)	1.395 76	1.3962 (*4*)
	25	0.7963	0.7961 (*2*)	1.393 61	1.3933 (*2*)
	30	0.7920		1.391 45	
	35	0.7868		1.389 29	
2-butanol	20	0.8066	0.8063 (*4*)	1.397 06	1.3974 (*4*)
	25	0.8025	0.8026 (*2*)	1.395 30	1.3950 (*2*)
	30	0.7987		1.393 42	
	35	0.7938		1.391 55	

Experimental Section

Solutions of different composition of the binary system methyl isobutyl ketone–2-butanol were prepared by weight in ground-glass-joint conical flasks by using a Mettler balance H-311 with an accuracy of ±0.0005 g. The densities were obtained with a Robertson specific gravity bottle (*3*) with an accuracy of ±0.0001 g cm^{-3}. In making determinations, we maintained the pycnometer in a bath until two consecutive measurements of the liquid height in the capillary indicated that the sample had reached the temperature of the bath.

Refractive indexes for the sodium D line of the pure components and mixtures were measured with a Jena dipping refractometer with an accuracy of ±0.00002. In both cases, a thermostatically controlled bath, constant to 0.01 °C, was used.

Results and Discussion

The density data at 20, 25, 30, and 35 °C for the system methyl isobutyl ketone–2-butanol are given in Table II. The

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