these smooth isotherms are appropriate and reflect the precision of surface tension measurements made on the tin, lead, and the four tin–lead alloys.

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Received for review November 21, 1977. Accepted May 30, 1978.

Supplementary Material Available: Tables 3, 4, 5, and 6, surface tension and density data for *xx* Sn/*xx* Pb (3 pages). Ordering information is given on any current masthead page.

Liquid–Vapor Equilibria at 270.00 K for Systems Containing Nitrogen, Methane, and Carbon Dioxide

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Liquid–vapor equilibria for the binary systems nitrogen–carbon dioxide and methane–carbon dioxide and for the ternary system nitrogen–methane–carbon dioxide were measured at 270.00 K and at pressures of 32–122 atm.

Introduction

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 was to provide accurate experimental measurements on a system of industrial interest and to assess the feasibility of modeling the phase equilibria with a simple two-parameter equation of state.

The experimental work involved the binary systems methane + carbon dioxide and nitrogen + carbon dioxide and the ternary system methane + nitrogen + carbon dioxide. There are experimental data available in the literature for the binaries of nitrogen, methane, and carbon dioxide, but there is only one measurement on the ternary system. Previous experimental work prior to 1973 has been reported by Hiza, Kidnay, and Miller (*4*). Table I summarizes all the recent work not covered in ref 1.

The equations of state chosen for study were the equation of Redlich and Kwong in the modified forms proposed by Prausnitz (*12*, *13*), Soave (*17*), and Chaudron et al. (*2*) and a modified van der Waals equation proposed by Peng and Robinson (*10*).

Experimental Equipment and Procedure

A schematic of the experimental apparatus is shown in Figure 1.

Table I. Summary of Data Not Reported by Hiza, Kidnay, and Miller (*4*)

system	temp range, K	pressure range, atm	citation
$CH_4 + CO_2$	253, 273, 288	26–84	1
$CH_4 + CO_2$	230, 250, 270	9–85	3
$CH_4 + CO_2$	153–219	12–64	5
$CH_4 + CO_2$	153, 173, 203, 210, 183, 193, 219	6–64	8
$N_2 + CO_2$	253, 273, 288	20–150	1
$N_2 + CH_4$	112, 120, 130, 140, 150, 160, 170, 180	1–50	6
$N_2 + CH_4 + CO_2$	233, 253, 273	60, 80, 100	15

The cryostat was a stainless-steel dewar having a 27-L capacity. The constant temperature bath fluid was a 50 vol % mixture of carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$). Suspended in the bath was the stainless-steel equilibrium cell, a refrigeration coil where ethylene glycol was circulated as a cooling fluid, two heaters where one had a proportional controller, a two-propeller mixer with variable speed, and a calibrated (IPTS-68) platinum resistance thermometer. Vapor circulation in the loop was obtained with a high-pressure diaphragm pump. The vapor from the pump passed through a heat exchanger in the bath fluid before entering the equilibrium cell. Liquid samples were withdrawn from the equilibrium cell through a capillary line.

The temperature was measured to ±0.02 K using the calibrated (IPTS-68) platinum-resistance thermometer connected to a Mueller bridge and a null detector. The temperature control was maintained by using a 1700-W immersion heater driven by a power proportioning controller with a tested sensitivity of ±0.001 K. To eliminate temperature gradients, a variable-speed, two-propeller stirrer was constantly on.

The pressure measurement was made with one of two Heise gauges, a 0–100 atm or a 0–2000 psia gauge, which were calibrated against dead weight testers. Average deviations of ±0.015 atm and −1.6 psi were measured for the two gauges, respectively, over the pressure regions of interest.

A gas chromatograph equipped with a thermal conductivity detector and a 6 ft, 60/80 mesh silica gel column was used in the analysis. The chromatograph conditions were adjusted to obtain very sharp, symmetric peaks, and these peak heights

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Table II. $CH_4 + CO_2$ System, 270.00 K

P, atm	y_{CH_4}	x_{CH_4}	y_{CO_2}	x_{CO_2}
31.57	0.0000	0.0000	1.000	1.000
37.85	0.1269	0.0237	0.8731	0.9763
43.35	0.2082	0.0455	0.7918	0.9545
48.15	0.2629	0.0666	0.7371	0.9334
52.00	0.2962	0.0838	0.7038	0.9162
60.00	0.3519	0.1226	0.6481	0.8774
65.40	0.3774	0.1533	0.6226	0.8467
73.98	0.3983		0.6017	
76.00	0.4006	0.2224	0.5994	0.7776
79.80	0.3969		0.6031	
81.40	0.3895	0.2740	0.6105	0.7260
81.75	0.3873		0.6127	
83.22	0.3726	0.3060	0.6274	0.6940

Table III. $N_2 + CO_2$ System at 270.00 K

P, atm	y_{N_2}	x_{N_2}	y_{CO_2}	x_{CO_2}
31.57	0.0000	0.0000	1.000	1.000
33.80	0.0472	0.0040	0.9528	0.9960
35.80	0.0851	0.0078	0.9149	0.9922
37.50	0.1140	0.0108	0.8860	0.9892
39.00	0.1331	0.0135	0.8669	0.9865
40.68	0.1598	0.0168	0.8402	0.9832
41.50	0.1683	0.0182	0.8317	0.9818
42.25	0.1783	0.0197	0.8217	0.9803
45.30	0.2156	0.0263	0.7844	0.9737
46.98	0.2323	0.0289	0.7677	0.9711
47.12	0.2325	0.0292	0.7675	0.9708
50.85	0.2674	0.0368	0.7326	0.9632
56.24	0.3069	0.0476	0.6931	0.9524
59.70	0.3280	0.0545	0.6720	0.9455
63.60	0.3473	0.0630	0.6527	0.9370
70.00	0.3770	0.0778	0.6230	0.9222
76.20	0.3961	0.0921	0.6039	0.9079
82.70	0.4126	0.1080	0.5874	0.8920
85.00	0.4139	0.1142	0.5861	0.8858
88.65	0.4190	0.1231	0.5810	0.8769
91.70	0.4173	0.1319	0.5827	0.8681
95.00	0.4210	0.1430	0.5790	0.8570
100.71	0.4188	0.1585	0.5812	0.8415
105.74	0.4134	0.1769	0.5866	0.8231
109.08	0.4094	0.1904	0.5906	0.8096
111.05	0.4061	0.1986	0.5939	0.8014
113.98	0.3986	0.2142	0.6014	0.7858
116.63	0.3857		0.6143	
117.31	0.3800	0.2332	0.6200	0.7668
117.31	0.3808	0.2360	0.6192	0.7640
117.92	0.3762	0.2486	0.6238	0.7514
118.67	0.3720	0.2454	0.6280	0.7546
119.15	0.3664	0.2505	0.6336	0.7495
119.76	0.3640	0.2556	0.6360	0.7444
120.37	0.3524		0.6476	
121.80	0.3530	0.3530	single phase[a]	

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

Table IV. $N_2 + CH_4 + CO_2$ at 270.00 K and 45 atm

y_{N_2}	y_{CH_4}	y_{CO_2}	x_{N_2}	x_{CH_4}	x_{CO_2}
0.0000	0.2300	0.7700	0.0000	0.0538	0.9462
0.0959	0.1251	0.7791	0.0129	0.0271	0.9599
0.1850	0.0269	0.7881	0.0226	0.0060	0.9714
0.2115	0.0000	0.7885	0.0250	0.0000	0.9750

were then related to the composition by the proper use of calibration curves. The calibration curves were established by using a series of mixtures containing nitrogen, methane, and carbon dioxide prepared gravimetrically in the laboratory. For all conditions encountered in this work, the calibration curves were linear. All of the experimental compositions reported in this work have been normalized. The analysis system is believed to be accurate to ±0.002 in the mole fraction. The mole fractions presented in Tables II–VIII are reported to four significant figures, since the precision of the chromatographic measurement is considerably greater than the accuracy.

Random errors due primarily to gas or liquid sampling will cause some data points to exhibit more scatter than is attributable to the pressure, temperature, or composition calibrations.

Table V. $N_2 + CH_4 + CO_2$ at 270.00 K and 60 atm

y_{N_2}	y_{CH_4}	y_{CO_2}	x_{N_2}	x_{CH_4}	x_{CO_2}
0.0000	0.3519	0.6481	0.0000	0.1226	0.8774
0.0336	0.3145	0.6520	0.0071	0.1071	0.8858
0.0441	0.3035	0.6525	0.0093	0.1024	0.8883
0.1173	0.2233	0.6594			
0.1237	0.2178	0.6585	0.0239	0.0690	0.9072
0.1563	0.1822	0.6615	0.0297	0.0564	0.9139
0.2508	0.0815	0.6677	0.0442	0.0240	0.9318
0.2656	0.0655	0.6689	0.0461	0.0192	0.9347
0.3290	0.0000	0.6710	0.0560	0.0000	0.9440

Table VI. $N_2 + CH_4 + CO_2$ at 270.00 K and 85 atm

y_{N_2}	y_{CH_4}	y_{CO_2}	x_{N_2}	x_{CH_4}	x_{CO_2}
0.4139	0.0000	0.5861	0.1142	0.0000	0.8858
0.2689	0.1406	0.5905	0.0887	0.0671	0.8442
0.2656	0.1433	0.5912	0.0885	0.0688	0.8428
0.1747	0.2322	0.5931	0.0667	0.1233	0.8099
0.1670	0.2394	0.5936	0.0652	0.1302	0.8046
0.1473	0.2592	0.5936	0.0600	0.1442	0.7958
0.1172	0.2874	0.5954			
0.0877	0.3105	0.6018	0.0422	0.1929	0.7649
0.0825	0.3161	0.6014	0.0408	0.1959	0.7634
0.0535	0.3374	0.6091	0.0301	0.2322	0.7377
0.0210	0.3474	0.6316	0.0152	0.2863	0.6985
0.0208	0.3479	0.6313	0.0155	0.2864	0.6981
			0.0112	0.3026	0.6862
0.0097	0.3323	0.6579	0.0076	0.3280	0.6645

Table VII. $N_2 + CH_4 + CO_2$ at 270.00 K and 95 atm

y_{N_2}	y_{CH_4}	y_{CO_2}	x_{N_2}	x_{CH_4}	x_{CO_2}
0.4210	0.0000	0.5790	0.1430	0.0000	0.8570
0.3237	0.0897	0.5866			
0.2900	0.1207	0.5893	0.1216	0.0696	0.8088
0.2611	0.1452	0.5937	0.1159	0.0818	0.8023
0.2326	0.1711	0.5963	0.1092	0.0993	0.7915
0.2248	0.1769	0.5983	0.1079	0.1085	0.7836
0.2238	0.1775	0.5986	0.1090	0.1098	0.7812
0.1988	0.1975	0.6037	0.1045	0.1287	0.7668
0.1728	0.2166	0.6107	0.1015	0.1522	0.7463
0.1631	0.2205	0.6164			
0.1597	0.2239	0.6164	0.0971	0.1635	0.7394
0.1482	0.2287	0.6231	0.0941	0.1705	0.7355
0.1475	0.2281	0.6243	0.0961	0.1741	0.7298
0.1445	0.2297	0.6259	0.0946	0.1743	0.7311
0.1398	0.2332	0.6270	0.0947	0.1810	0.7243
0.1384	0.2318	0.6298	0.0947	0.1781	0.7272
			0.0948	0.1868	0.7185
0.1313	0.2329	0.6359	0.0944	0.1882	0.7174
0.1303	0.2335	0.6363	0.0945	0.1905	0.7151
0.1286	0.2333	0.6380	0.0956	0.1941	0.7102
0.1224	0.2336	0.6440	0.0944	0.1982	0.7075
0.1198	0.2313	0.6490	0.0960	0.2008	0.7032
0.1152	0.2306	0.6542	0.0986	0.2098	0.6915
a	a	a	0.1045	0.2260	0.6696

[a] See footnote *a* in Table III.

Table VIII. $N_2 + CH_4 + CO_2$ at 270.00 K and 110 atm

y_{N_2}	y_{CH_4}	y_{CO_2}	x_{N_2}	x_{CH_4}	x_{CO_2}
0.4080	0.0000	0.5920	0.1950	0.0000	0.8050
0.3285	0.0594	0.6121	0.1897	0.0415	0.7688
0.2929	0.0808	0.6263	0.1898	0.0613	0.7489
0.2861	0.0825	0.6314	0.1917	0.0640	0.7443
0.2643	0.0921	0.6436	a	a	a

[a] See footnote *a* in Table III.

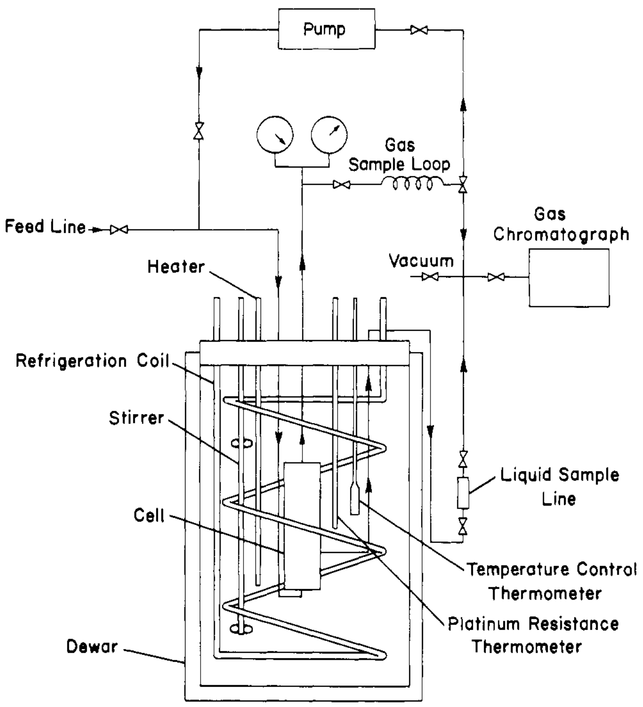

Figure 1. Schematic diagram of experimental equipment.

Results

The systems $N_2 + CO_2$ and $CH_4 + CO_2$ were studied at 270.00 K and over the entire pressure range. The ternary system $N_2 + CH_4 + CO_2$ was studied at 270.00 K and at 45 60, 85, 95, and 110 atm.

Acquisition of accurate vapor-liquid equilibria data is much more difficult than is generally recognized, and thus techniques for checking the accuracy of experimental results (thermodynamic consistency tests) cannot be overlooked. Some of the simpler but widely used tests were made on the data to provide a measure of their internal consistency and, where possible, comparison tests with the data of other investigators were also made to examine external consistency. Letting subscript 1 stand for solute and subscript 2 for solvent, the following tests were made on the binary systems.

(1) A plot of $(P - P_2^\circ)$ against x_1 must extrapolate smoothly to the origin as $x_1 \rightarrow 0$. For very small values of x_1, Henry's law applies, indicating a linear relation according to eq 1.

$$f_1 \simeq \bar{P}_1 = Hx_1 \qquad (1)$$

(2) A plot of K_2P vs. $(P - P_2^\circ)$ must be a smooth curve, extrapolating to P_2° if the liquid and vapor phases are internally consistent in the low-pressure region.

(3) A plot of P vs. $(y_1 - x_1)^2$ must be a smooth curve extrapolating to P_c of the mixture.

(4) A plot of ln H(Henry's constant) vs. $1/T$ must produce a smooth curve or linear behavior over small temperature ranges.

(5) A plot of P_c vs. T must produce a smooth curve.

Tests 4 and 5 are useful for comparing data from different sources over moderate temperature ranges.

$CH_4 + CO_2$ System at 270.00 K. This system was studied earlier at this laboratory by Davalos et al. (*3*). It was initially planned that the earlier data would be used in this investigation, but a spot check turned up a discrepancy in the vapor-phase compositions for the high-pressure region (Figure 2), and thus data for the entire isotherm were taken (Table II). Agreement with Davalos et al. for the liquid phase is excellent, and the vapor-phase agreement is also excellent up to a total pressure of 50 atm. The small discrepancy in some of the high-pressure gas-phase data is believed due to sampling problems in the earlier work.

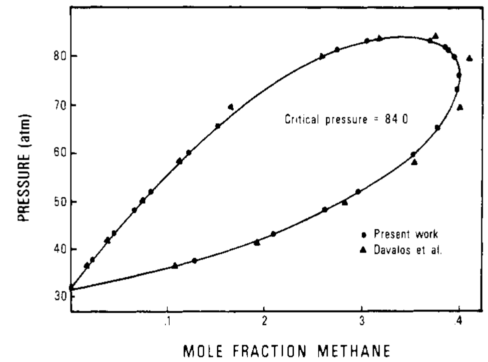

Figure 2. $CH_4 + CO_2$ system, 270.00 K.

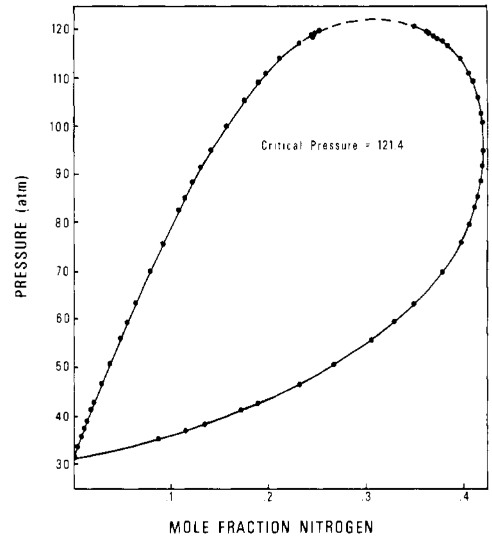

Figure 3. $N_2 + CO_2$ system, 270.00 K.

Tests 1, 2, and 3 discussed above were made on this system, and the results indicate excellent internal consistency. Davalos et al. compared their results with those of other investigators.

The measured value of 31.57 atm for the vapor pressure of CO_2 (Table II) is in excellent agreement with the value of 31.61 atm from Myers and Van Dusen (*7*) adjusted to IPTS-68.

$N_2 + CO_2$ System at 270.00 K. There are no published data for this system at 270.00 K. Table III contains the data, which are also shown graphically in Figure 3.

Tests 1 through 5 discussed previously were carried out on this system. The smoothness of the curves, the lack of scatter, and the linearity when applicable are an excellent indication of the internal consistency. Comparisons with the data of Arai et al. (*1*) and Zenner and Dana (*18*) through cross-plotting of data indicate external consistency.

$N_2 + CH_4 + CO_2$ System at 270.00 K. Examination of the binary data shows that the measurable pressure region for the ternary system is between 31.57 and 121.4 atm. The pressures 45, 60, 85, 95, and 110 atm were selected for data generation. Tables IV through VIII and Figures 4 through 8 contain the data collected for this system. The data show very little scatter, indicating a good degree of internal consistency. The isothermal data at 45 and 60 isobars exhibit a straight line relation. Nonlinear behavior is observed for pressures higher than the critical pressure of $CH_4 + CO_2$ binary, that is, at 85, 95, and 110 atm. The nonlinearity increased with pressure making the completion of the 110-atm isotherm impossible with the existing equipment.

Discussion

There are two basic methods for modeling high-pressure liquid-vapor equilibria. The first uses an equation of state to

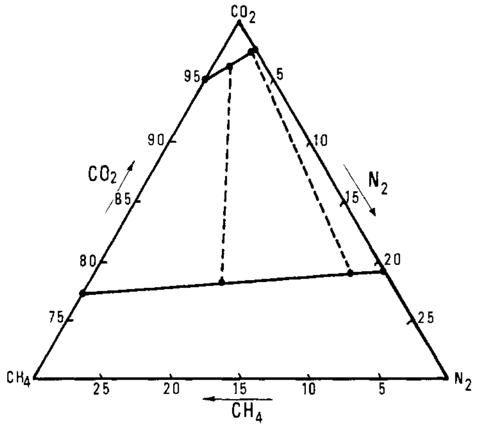

Figure 4. $N_4 + CH_4 + CO_2$ system, 270.00 K and 45 atm.

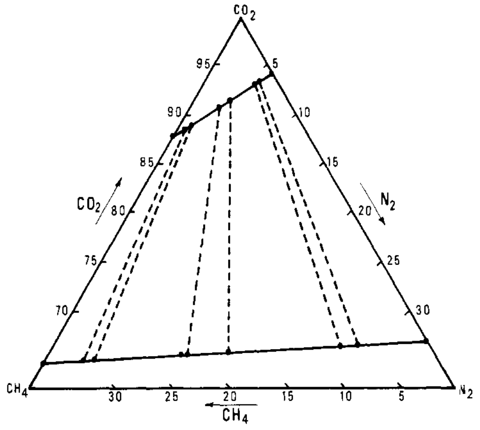

Figure 5. $N_2 + CH_4 + CO_2$ system, 270.00 K and 60 atm.

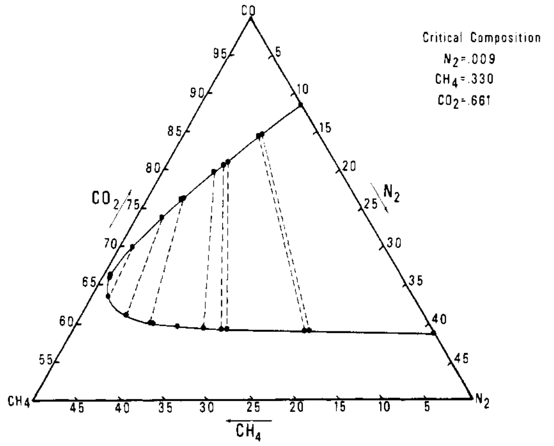

Figure 6. $N_2 + CH_4 + CO_2$ system at 270.00 K and 85 atm.

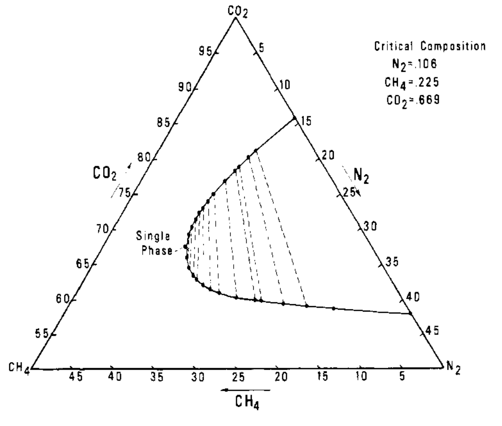

Figure 7. $N_2 + CH_4 + CO_2$, 270.00 K and 95 atm.

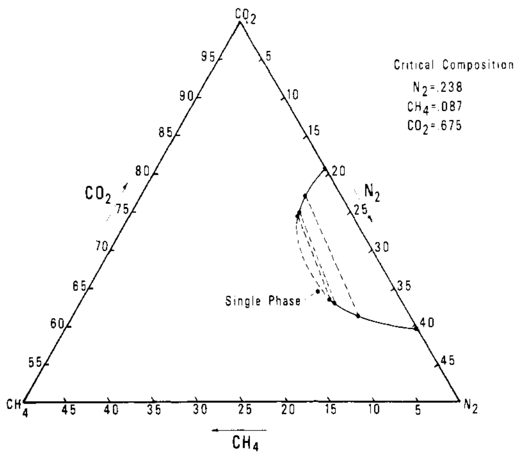

Figure 8. $N_2 + CH_4 + CO_2$, 270.00 K and 110 atm.

Table IX. Values of the Binary Interaction Parameters

system	k_{ij}	j_{ij}
$N_2 + CH_4$	+0.04	−0.00078
$N_2 + CO_2$	−0.0049	−0.0045
$CH_4 + CO_2$	+0.106	+0.0024

represent both phases, while the second uses an equation of state for the vapor phase and a liquid solution theory for the liquid phase. A historical review of methods for calculating multicomponent equilibria is given by Robinson (*14*). An extensive review of the mixing rules is given by Smith (*16*).

Based on current interest the equations of Redlich and Kwong and van der Waals in one of their modified forms and applied to both the liquid and vapor phases were selected as the most appropriate for this study. Three modified forms of the Redlich-Kwong equation, as proposed by Prausnitz (*12*, *13*), Soave (*17*), and Chaudron et al. (*2*) as well as the modified van der Waals equation of Peng and Robinson (*10*) were applied to the binary $N_2 + CO_2$ and $CH_4 + CO_2$ systems. The Peng-Robinson equation proved superior to the modified Redlich-Kwong relations in representing the data for these two binary systems, and thus all further work was done with this relation. The optimum values of the interaction parameters (k_{ij} and j_{ij}) for the Peng-Robinson relation were found by applying the method of Powell (*11*) to the binary data to minimize the value of the relation.

$$\sum(|x_{\text{exptl}} - x_{\text{calcd}}| + |y_{\text{exptl}} - y_{\text{calcd}}|)/2(\text{no. of data points})$$

The mixing rules used were

$$a = y_1^2 a_1 + 2 y_1 y_2 a_{12} + y_2^2 a_2$$

$$a_{12} = (a_1 a_2)^{1/2} (b_{12}^2 / b_1 b_2)^{1/2} (1 - k_{12})$$

$$b = y_1^2 b_1 + 2 y_1 y_2 b_{12} + y_2^2 b_2$$

$$b_{12} = \left[\left(\frac{b_1^{1/3} + b_2^{1/3}}{2}\right)(1 + j_{12})\right]^3$$

The above relations differ slightly from those proposed by Peng and Robinson but the values of *a* and *b* were obtained using the relations proposed by them (*10*). For the $N_2 + CH_4$ system the data of Kidnay et al. (*6*) and Parrish and Hiza (*9*) over the temperature range 100–170 K were used to obtain the interaction parameters, which were assumed to be independent of temperature. The values for k_{ij} and j_{ij} are given in Table IX. The negative value of k_{ij} for the $N_2 + CO_2$ system is unusual and may be due to quadrupole interactions.

The interaction parameters determined for the binary systems (Table IX) were then used to predict the behavior of the ternary $N_2 + CH_4 + CO_2$, but the results, in the opinion of the authors, were unsatisfactory in all regions near the critical of the ternary. Adjustment of the parameters, of course, forces a better fit in the critical region, but only at the expense of a poorer fit in regions removed from the critical and in the binary systems. It was not possible to obtain a set of interaction parameters that produced a satisfactory fit to both the binary and the ternary data over all regions of pressure and temperature.

Acknowledgment

The authors wish to acknowledge the assistance of R. D. McCarthy in applying the method of M. J. D. Powell to the experimental data.

Glossary

f_i	fugacity of component i
H	Henry's constant
j_{ij}	binary interaction parameter
k_{ij}	binary interaction parameter
K_i	y_i/x_i
P	total pressure
P_i°	vapor pressure of component i
T	temperature

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Received for review December 27, 1977. Accepted June 26, 1978.

Gas–Liquid Equilibrium in Mixtures of Hydrogen and Quinoline

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Gas–liquid equilibrium in hydrogen/quinoline mixtures was experimentally determined at four temperatures from 190 to 430 °C and seven pressures from 20 to 250 atm in a flow apparatus. Vapor pressure of quinoline was measured in the same apparatus. The new mixture equilibrium data are compared with general correlations that have been developed for hydrogen/hydrocarbon mixtures.

Introduction

The solubility of a light supercritical component in a heavy liquid is of both theoretical and practical interest. The theoretical interest reflects the basic nature of the solubility problem as an intermolecular force phenomenon. The practical interest stems from engineering design needs. With the recent intensified development of hydrotreating processes particularly coal liquefaction, equilibrium data of hydrogen/oil mixtures are in demand. Previous studies of phase equilibrium of hydrogen/solvent systems were mostly confined to relatively low temperatures. The literature was reviewed by Simnick et al. (*8*) and updated in ref 10. Work in this laboratory has produced data at conditions of elevated temperatures (to 430 °C) and pressures (to 250 atm). The systems studied so far include the binary mixtures of hydrogen with tetralin (*8*), bicyclohexyl (*7*), diphenylmethane (*9*), 1-methylnaphthalene (*11*), *m*-cresol, and *m*-xylene (*10*). In this work we investigate mixtures of hydrogen and a hetroatom-containing hydrocarbon. Solvents of this type have not been studied with respect to hydrogen solubility at high pressures.

The experimental apparatus and procedure of this study have been described, and the attainment of equilibrium in the apparatus at the operation conditions has been established (*8–11*). The same apparatus description and equilibrium consideration apply to this work and therefore will not be reiterated.

Materials

The hydrogen gas used in this work was supplied by Air Products Co. with a reported minimum purity of 99.95%. The quinoline purchased from Fisher Scientific Co. as certified reagent grade of 99+% purity showed a deep purple indicating presence of the air oxidation product, quinoline *N*-oxide. It was therefore purified by fractional distillation over zinc dust at reduced pressure under a helium blanket. The distillate was colorless and was stored over anhydrous sodium sulfate prior to use.

Quinoline from both the gas and liquid streams from the equilibrium cell was checked for possible chemical reactions with a gas chromatograph equipped with a thermal conductivity detector. The analysis indicated a small amount of impurities in the sample from the gas stream. However, the sum of the peak areas of these impurities never amounted to more than 1.5% of the total peak areas of the sample. The most probable impurity is isoquinoline. Quinoline from the cell effluents did show a slight coloration. Therefore, all quinoline collected from the cell effluents was distilled before reuse. The distillation yielded a colorless overhead product which was reused. A small amount of colored residue was left in the still and was discarded.

The rate of thermal decomposition of quinoline was studied by Johns and co-workers (*3*) who reported an observed rate

0021-9568/78/1723-0305$01.00/0