Equilibrium Phase Properties of the *n*-Butane–Hydrogen Sulfide and Isobutane–Hydrogen Sulfide Binary Systems

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Vapor and liquid equilibrium phase compositions were determined at 93.3, 103.3, 107.2, 121.1, 135.0, and 145.0 °C for the *n*-butane–hydrogen sulfide system and at 71.1, 90.0, 98.0, 99.0, 110.0, and 125.0 °C for the isobutane–hydrogen sulfide system. Measurements were made at pressures from the vapor pressure of the butanes to the critical pressure for the binary systems at each temperature. Equilibrium ratios for each component were calculated at each temperature from the phase composition data. The critical temperatures and corresponding critical pressures were measured and the critical loci were constructed for both binary systems.

Introduction

Hydrogen sulfide is present in many natural gases and crude oils. In the processing of these materials it is of interest to have the liquid–vapor equilibrium relations of mixtures of this compound with the various hydrocarbons.

The phase behavior of hydrogen sulfide–hydrocarbon binary systems has been the subject of extensive study over the past three decades. Data on these binaries can be found in the literature for methane (*1*), ethane (*2*), propane (*3*), *n*-butane (*4*), isobutane (*5*), *n*-pentane (*6*), *n*-decane (*7*), methylcyclohexane (*8*), toluene (*9*), *n*-heptane (*9*), *m*-xylene (*10*), mesitylene (*10*), ethylcyclohexane (*11*), and *n*-propylcyclohexane (*11*). As a continuation of a program to provide data on binary systems of interest to the petroleum and natural gas industry, the behavior of the *n*-butane- and isobutane–hydrogen sulfide systems was studied at temperatures up to the critical region of the butanes for both binary systems.

The primary object of the work was to verify the quality and extend the temperature range covered by the earlier work on the *n*-butane–hydrogen sulfide (*4*) and isobutane–hydrogen sulfide (*5*) binaries. A further objective was to complete the delineation of the binary critical locus for each system.

Previous work on the *n*-butane–hydrogen sulfide binary covered a temperature range from 37.8 to 135 °C in 13.9 increments. Since the critical temperature for *n*-butane is 152 °C, a significant gap existed in the information in the critical region.

Similarly, the earlier work on the isobutane–hydrogen sulfide binary covered a range from 4.4 to 104.4 °C whereas the critical temperature of isobutane is 134.7 °C. This left an unacceptably large temperature gap, particularly since the data showed a definite trend toward a temperature minimum in the critical locus but were insufficient to clarify the point.

In view of the above considerations, it was decided to verify the earlier work at one or two temperatures, to repeat the measurements where discrepancies showed up, and to extend the temperature toward the hydrocarbon critical temperatures for both systems.

Experimental Equipment and Methods

The experiments were carried out in a variable-volume vapor–liquid equilibrium cell consisting of a transparent sapphire cylinder mounted between two steel headers. This has been described in detail by Robinson et al. (*12*). The method of operation was basically the same as that described recently by Leu and Robinson (*13*).

Prior to commencing an experimental run, the equipment was thoroughly cleaned and evacuated. Equilibrium was attained by mechanically rocking the entire assembly about a horizontal axis. The gas phase was sampled first by continuously drawing off a vapor stream through the sample valve under isobaric isothermal conditions. The sample was mixed with a stream of helium and circulated through the chromatographic switching valve. Samples were taken for analysis at periodic intervals. When the analysis of the vapor phase had been completed, the remainder of the vapor phase plus a small interface portion of the liquid was removed. The liquid phase was then sampled and analyzed by using a similar procedure.

At the completion of each pressure point, a new set of conditions was established by adjusting pressure and/or adding more material. The equilibration and sampling sequence was then repeated.

The critical region was approached isothermally by using an iterative experimental procedure involving changes in pressure and/or composition. After the equilibration process had been completed, the critical pressure corresponding to a given experimental temperature was determined by performing isothermal compression and expansion on either side of the critical point to observe both the phase boundary and the color changes taking place within the system. The critical composition was determined by taking a sample as described above, but the isobaric sampling pressure was kept at least 0.14 MPa higher than the observed critical pressure.

Temperatures were measured with iron–constantan thermocouples that had been calibrated against a platinum resistance thermometer. Each temperature was read out on a digital voltmeter, such that temperatures are believed known to within ±0.1 °C or better. Pressures were measured by a strain gauge pressure transducer (Druck PTX-150/HP-4000), calibrated with a precision dead-weight gauge. Each pressure was read out on a digital voltmeter. The pressures are believed known to within ±0.1% of full scale.

The phase compositions were determined with a Hewlett-Packard (HP) Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used for both binary systems. A calibration was made for each component by gravimetrically preparing standard mixtures. The response factors for converting from area fraction to mole fraction for hydrogen sulfide were 1.9810 and 1.7484 for *n*-butane and isobutane, respectively.

The column used was a 2.44 m × 3.18 mm diameter stainless steel tube packed with Propak-QS. It was maintained at 120 °C for the *n*-butane–hydrogen sulfide system and at 110 °C for the isobutane–hydrogen sulfide system. Helium gas at a flow rate of 25 cm^3/min was used as carrier gas for both systems.

At least eight samples of each phase were taken for analysis, and the reported compositions are the result of averaging at least six determinations. The precision of the analyses was generally within better than 2% of the relative standard deviation.

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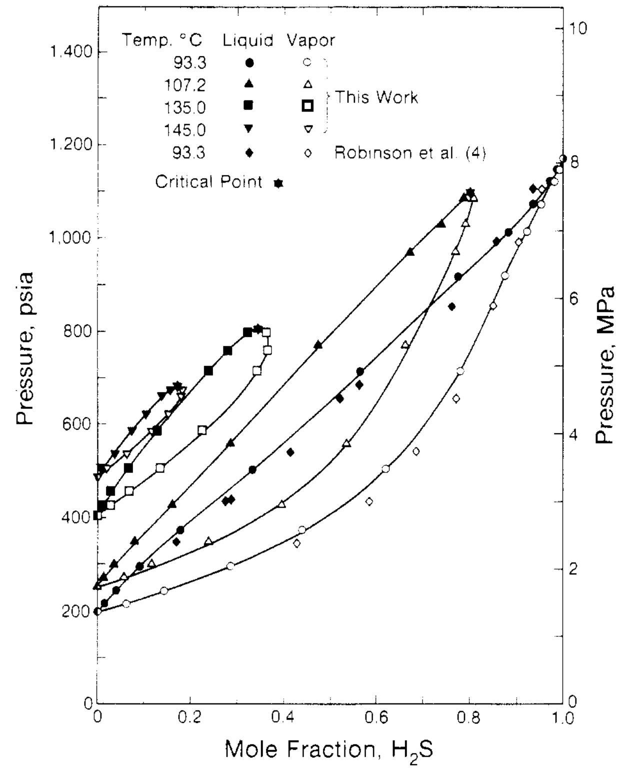

Figure 1. Pressure-equilibrium phase composition diagram for the *n*-butane-hydrogen sulfide binary system.

In determining the physical properties in the critical region, the given experimental temperature was considered as the critical temperature. The corresponding critical pressure was determined by averaging the two values obtained isothermal compression and expansion observations. The associated composition was determined as above.

Materials

Research grade *n*-butane of 99.9+ mol % purity, instrument grade 2-methylpropane (isobutane) of 99.5+ mol %, and chemically pure grade hydrogen sulfide of 99.5+ mol % were used for the experimental work. All of the gases were obtained from Matheson Gas Products Canada Inc.

The butanes were used without further purification, but the hydrogen sulfide was distilled twice to minimize the contamination from carbon dioxide and mercaptans. Gas chromatograms were run on these compounds, but no detectable impurities were found. The butanes were degassed in the equilibrium cell before the addition of hydrogen sulfide.

Results and Discussion

The experimentally measured equilibrium liquid and vapor compositions for the *n*-butane-hydrogen sulfide system are given in Table I. The first measurements were made at 93.3 °C (200 °F). These are shown graphically in Figure 1 where they are compared to the earlier work of Robinson et al. (*4*) at the same temperature. The discrepancies between the two data sets are obvious, and because of the improved experimental procedures used for the present work, the new data are considered to be the more reliable. The scattering of the earlier data causes rather large discrepancies in the equilibrium ratios. For example, at a pressure of about 6.2 MPa, the data of Robinson et al. (*4*) give an equilibrium ratio for *n*-butane of 0.68 whereas the present data give a value of 0.55, a difference of about 24%.

In view of the above, it was decided to repeat the earlier data on *n*-butane at temperatures of 107.2, 121.1, and 135 °C

Table I. Equilibrium Phase Properties of the *n*-Butane-Hydrogen Sulfide System

	composition[a]		equilib ratio	
P/MPa	x	y	K_{H_2S}	K_{nC_4}
		T = 93.3 °C		
1.351	0.000	0.000		1.000
1.482	0.0151	0.0637	4.216	0.951
1.682	0.0386	0.146	3.771	0.889
2.041	0.0906	0.288	3.175	0.783
2.579	0.180	0.440	2.437	0.684
3.482	0.334	0.620	1.856	0.570
4.923	0.562	0.777	1.383	0.509
6.322	0.775	0.875	1.129	0.555
6.991	0.884	0.924	1.046	0.653
7.398	0.938	0.953	1.017	0.752
7.729	0.978	0.982	1.004	0.837
7.894	0.993	0.994	1.001	0.912
8.067	1.000	1.000	1.000	
		T = 103.3 °C		
1.613	0.000	0.000		1.000
1.772	0.0145	0.0555	3.822	0.958
1.993	0.0448	0.154	3.440	0.886
2.303	0.0928	0.285	3.077	0.788
2.923	0.183	0.438	2.390	0.688
3.751	0.309	0.557	1.802	0.641
5.185	0.524	0.708	1.351	0.613
6.578	0.717	0.807	1.125	0.684
7.246	0.802	0.850	1.061	0.754
7.515	0.831	0.858	1.032	0.841
7.805	0.868	0.879	1.013	0.912
7.874	0.875[b]	0.875	1.000	1.000
		T = 107.2 °C		
1.731	0.000	0.000		1.000
1.868	0.0149	0.0580	3.891	0.956
2.062	0.0345	0.118	3.433	0.913
2.406	0.0771	0.237	3.079	0.826
2.958	0.161	0.395	2.450	0.721
3.854	0.286	0.534	1.866	0.653
5.316	0.472	0.661	1.399	0.643
6.695	0.670	0.767	1.144	0.707
7.102	0.738	0.790	1.069	0.804
7.488	0.787	0.807	1.025	0.908
7.536	0.796[b]	0.796	1.000	1.000
		T = 121.1 °C		
2.206	0.000	0.000		1.000
2.337	0.00994	0.0330	3.317	0.977
2.565	0.0304	0.0924	3.044	0.936
2.882	0.0710	0.187	2.640	0.875
3.454	0.134	0.300	2.246	0.808
4.337	0.259	0.439	1.693	0.758
5.667	0.425	0.547	1.287	0.788
6.088	0.494	0.575	1.165	0.839
6.481	0.547	0.588	1.075	0.909
6.543	0.569[b]	0.569	1.000	1.000
		T = 135.0 °C		
2.792	0.000	0.000		1.000
2.937	0.0100	0.0260	2.600	0.984
3.151	0.0294	0.0693	2.357	0.959
3.489	0.0646	0.135	2.092	0.925
4.040	0.128	0.225	1.758	0.889
4.930	0.239	0.342	1.431	0.865
5.233	0.280	0.365	1.304	0.882
5.495	0.322	0.362	1.123	0.942
5.543	0.345[b]	0.345	1.000	1.000
		T = 145.0 °C		
3.344	0.000	0.000		1.000
3.475	0.0104	0.0195	1.876	0.991
3.696	0.0362	0.0633	1.747	0.972
4.033	0.0736	0.116	1.575	0.954
4.295	0.105	0.154	1.461	0.946
4.557	0.137	0.179	1.303	0.952
4.640	0.156	0.182	1.168	0.969
4.716	0.173[b]	0.173	1.000	1.000

[a] Mole fraction hydrogen sulfide. [b] Critical composition.

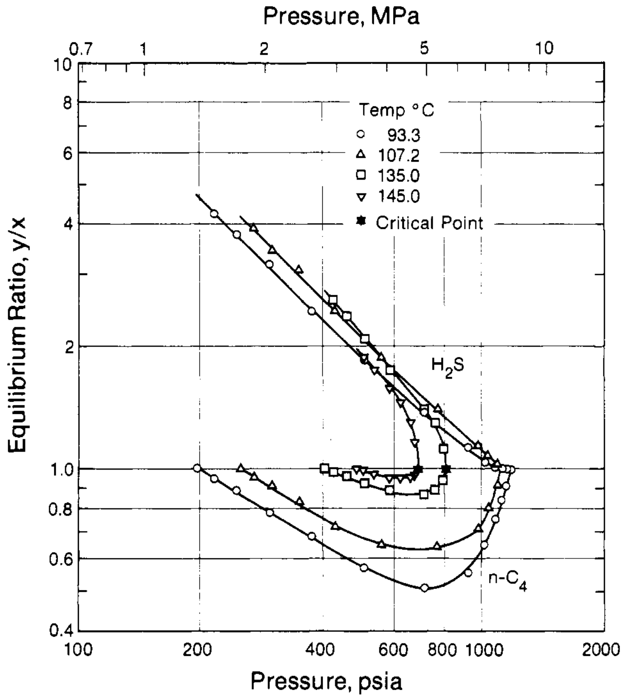

Figure 2. Equilibrium ratios for *n*-butane and hydrogen sulfide in the *n*-butane–hydrogen sulfide binary system.

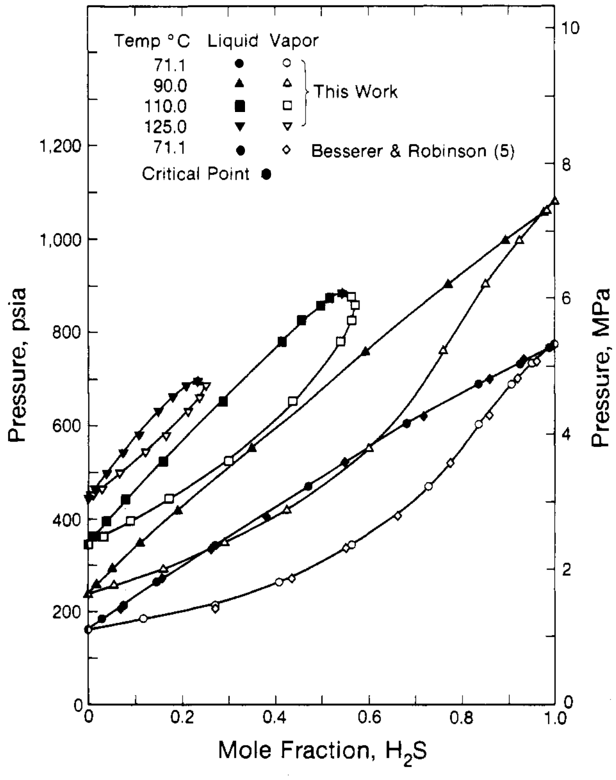

Figure 3. Pressure–equilibrium phase composition diagram in the isobutane–hydrogen sulfide binary system.

and to obtain new data at temperatures of 103.3 and 145 °C. The data at 107.2, 135, and 145 °C are also shown in Figure 1.

The calculated equilibrium ratios for each component in the binary system at each of the six temperatures are also included in Table I. The values for four temperatures are shown in Figure 2.

The first measurements on the isobutane–hydrogen sulfide system were made at 71.1 °C (160 °F), and excellent agreement was found with the earlier work of Besserer and Robinson (*5*) at the same temperature. A comparison of the two data sets is shown in Figure 3. In view of this agreement, no further work was repeated at the previous temperatures but new data were obtained at temperatures 90, 110, and 125 °C.

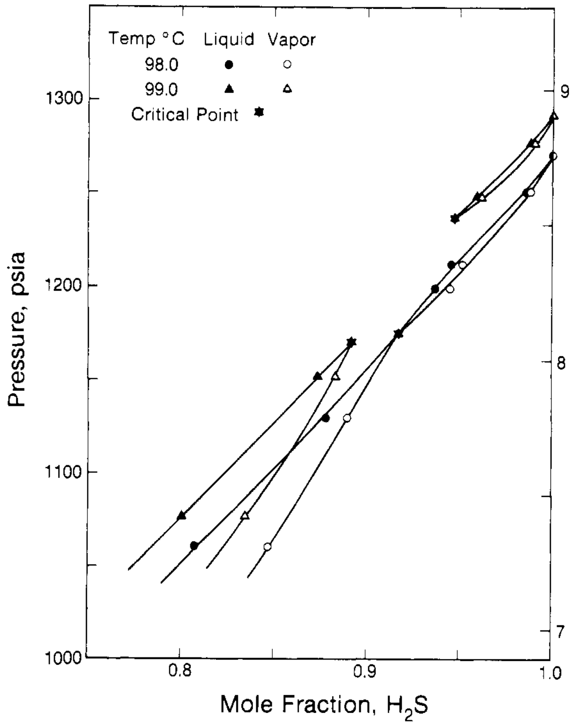

Figure 4. Equilibrium phase composition for the isobutane–hydrogen sulfide binary system in the critical region at 98.0 and 99.0 °C.

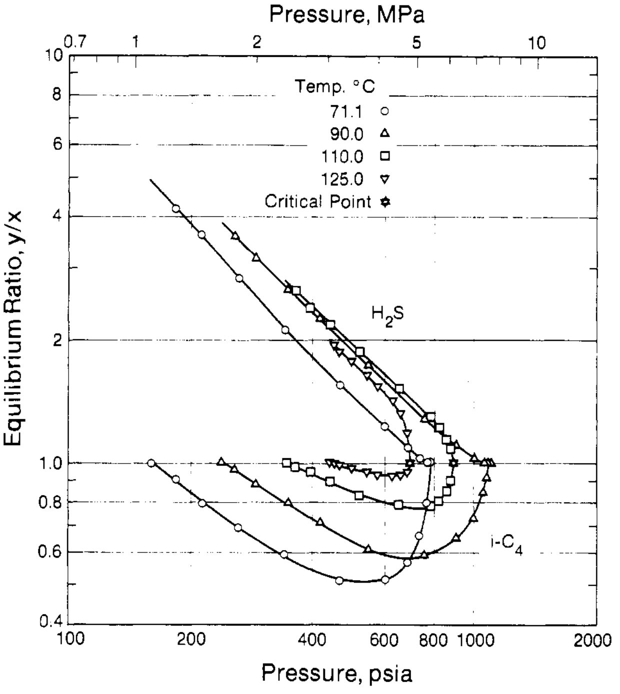

Figure 5. Equilibrium ratios for isobutane and hydrogen sulfide in the isobutane–hydrogen sulfide binary system.

A graphical representation of the critical locus for the isobutane–hydrogen sulfide binary system based on all of the available data at this time still left an uncertainty as to the configuration of the critical locus between 95 and 100 °C. Consequently, additional isotherms were then run at 98 and 99 °C.

The equilibrium phase compositions at each of the above five temperatures are given in Table II and are shown graphically

Table II. Equilibrium Phase Properties of the Isobutane–Hydrogen Sulfide System

	composition[a]		equilib ratio	
P/MPa	x	y	K_{H_2S}	K_{iC_4}
T = 71.1 °C				
1.110	0.000	0.000		1.000
1.269	0.0283	0.118	4.175	0.908
1.469	0.0750	0.270	3.600	0.789
1.813	0.144	0.407	2.832	0.692
2.358	0.268	0.564	2.101	0.596
3.234	0.470	0.728	1.550	0.513
4.151	0.681	0.836	1.228	0.515
4.737	0.835	0.906	1.085	0.568
5.061	0.927	0.952	1.027	0.661
5.281	0.985	0.988	1.003	0.800
5.337	1.000	1.000	1.000	
T = 90.0 °C				
1.648	0.000	0.000		1.000
1.772	0.0151	0.0535	3.543	0.961
2.006	0.0508	0.161	3.169	0.884
2.399	0.110	0.291	2.653	0.796
2.882	0.189	0.425	2.250	0.709
3.785	0.347	0.600	1.730	0.612
5.219	0.593	0.759	1.281	0.592
6.212	0.770	0.851	1.106	0.647
6.846	0.893	0.922	1.032	0.732
7.295	0.978	0.981	1.004	0.847
7.412	0.9967	0.9969	1.000	0.922
7.439	1.000	1.000	1.000	
T = 98.0 °C				
1.917	0.000	0.000		1.000
2.006	0.0123	0.0404	3.283	0.972
2.730	0.1078	0.2705	2.507	0.818
3.820	0.2766	0.4985	1.802	0.693
5.488	0.5376	0.6798	1.265	0.692
7.308	0.8077	0.8475	1.049	0.793
7.784	0.8786	0.8897	1.013	0.909
8.094	0.9168^b	0.9168	1.000	1.000
8.260	0.9367	0.9449	1.009	0.871
8.350	0.9458	0.9516	1.006	0.894
8.618	0.9860	0.9866	1.001	0.957
8.756	1.000	1.000	1.000	
T = 99.0 °C				
1.951	0.000	0.000		1.000
7.419	0.8089	0.8353	1.033	0.862
7.936	0.8735	0.8833	1.011	0.923
8.067	0.8913^b	0.8913	1.000	1.000
8.522	0.9472^b	0.9472	1.000	1.000
8.598	0.9590	0.9616	1.002	0.951
8.812	0.9881	0.9893	1.001	0.905
8.887	0.9988	0.9989	1.000	0.918
8.908	1.000	1.000	1.000	
T = 110.0 °C				
2.372	0.000	0.000		1.000
2.503	0.0130	0.0344	2.644	0.978
2.723	0.0377	0.0898	2.386	0.946
3.047	0.0796	0.173	2.171	0.899
3.599	0.161	0.301	1.872	0.833
4.502	0.287	0.437	1.519	0.791
5.371	0.416	0.541	1.300	0.786
5.681	0.457	0.565	1.235	0.802
5.916	0.498	0.571	1.147	0.854
6.026	0.518	0.564	1.089	0.905
6.088	0.542^b	0.542	1.000	1.000
T = 125.0 °C				
3.054	0.000	0.000		1.000
3.116	0.0048	0.0093	1.944	0.996
3.206	0.0148	0.0278	1.873	0.987
3.434	0.0373	0.0660	1.769	0.970
3.751	0.0739	0.121	1.641	0.949
3.992	0.108	0.167	1.538	0.935
4.351	0.149	0.212	1.416	0.927
4.557	0.180	0.238	1.322	0.929
4.723	0.211	0.251	1.189	0.949
4.785	0.234^b	0.234	1.000	1.000

[a] Mole fraction hydrogen sulfide. [b] Critical composition.

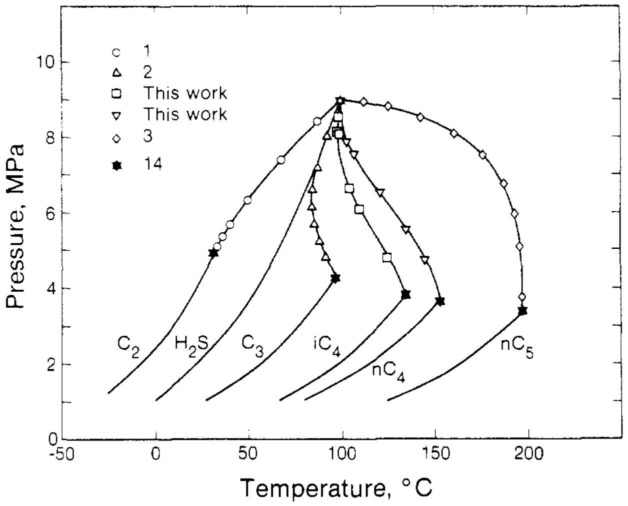

Figure 6. Critical loci for the methane–, ethane–, propane–, isobutane–, *n*-butane–, and *n*-pentane–hydrogen sulfide binary systems.

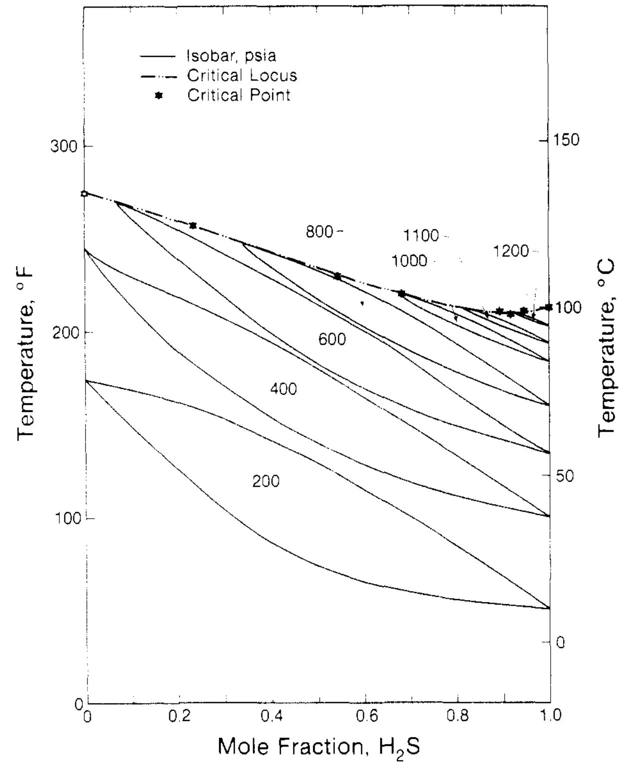

Figure 7. Temperature–equilibrium phase composition diagram in the isobutane–hydrogen sulfide binary system.

in Figure 3 for temperatures of 71.1, 90.0, 110.0, and 125.0 °C. Figure 4 is an expanded version of the critical region of this system at 98.0 and 99.0 °C. The calculated equilibrium ratios for each component in this binary system at each of the six isotherms are also given in Table II. The values for four temperatures are shown in Figure 5.

The measured critical temperatures and corresponding pressures for these two binary systems are presented in Table III. The vapor pressure curves for the pure components, the critical properties at the conditions investigated in this work, and the critical properties determined in earlier studied for the methane (*1*)-, ethane (*2*)-, propane (*3*)-, and *n*-pentane (*6*)-hydrogen sulfide systems are shown graphically in Figure 6.

An examination of Figures 1, 3, 4, and 6 indicates that hydrogen sulfide does not form an azeotrope with either *n*-butane or isobutane. However, it is interesting and considered rather

J. Chem. Eng. Data **1989**, *34*, 319-323

Table III. Critical Temperatures and Corresponding Critical Pressures on the Critical Locus of the Binary Systems

system	T/°C	P/MPa
i-C_4-H_2S	98.0	8.094
	99.0	8.067
	99.0	8.522
	104.4[a]	6.642[a]
	110.0	6.088
	125.0	4.785
n-C_4-H_2S	103.3	7.874
	107.2	7.536
	121.1	6.543
	135.0	5.543
	145.0	4.716

[a] Reference 5.

unusual to find a minimum in the critical locus without an azeotrope as in the case of the isobutane-hydrogen sulfide system. This behavior leads to the configuration of the isobars on a temperature-composition diagram as shown on Figure 7. All of the data obtained in this study together with the earlier data of Besserer and Robinson (*5*) were used in obtaining this cross-plot.

Glossary

K	equilibrium ratio, y/x
K_{H_2S}	equilibrium ratio for hydrogen sulfide
K_{nC_4}	equilibrium ratio for n-butane
K_{iC_4}	equilibrium ratio for isobutane
P	pressure, MPa
T	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Registry No. H_2S, 7783-06-4; butane, 106-97-8; isobutane, 75-28-5.

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Received for review September 9, 1968. Accepted April 4, 1989.

Vapor-Liquid Equilibrium in the System Carbon Dioxide + *n*-Pentane from 252 to 458 K at Pressures to 10 MPa

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Equilibrium pressures and compositions for the binary mixture carbon dioxide/*n*-pentane were measured on 10 isotherms from 252 K to the *n*-pentane critical temperature. On each isotherm, the entire pressure range of phase coexistence was covered. The mixture critical line has been located and is shown to be continuous in *P-T-x* space between the critical points of the pure components. Comparisons are made between the experimental results and predictions of the Soave-Redlich-Kwong, Peng-Robinson, Kubic-Martin, and Adachi-Lu-Sugie cubic equations of state. None was able to correlate the data within our estimated experimental error.

Introduction

This study of the binary system carbon dioxide/*n*-pentane is a continuation of experimental investigations of CO_2/X systems designed to explore patterns of phase behavior in fluid systems and to obtain accurate data for testing empirical and theoretical methods of data correlation (*1*, *2*). Although there have long been some data for the system of CO_2/*n*-pentane available (*3*), a considerable discrepancy was found between the phase compositions measured by Besserer and Robinson (*4*) and the earlier data of Poettman and Katz (*5*). Recently two new studies of this system were reported by Leu and Robinson (*6*) at 135, 160, and 180 °C and by Wu et al. (*7*) at 38 and 56 °C. The results reported here are distinguished from the other studies by the completeness with which they cover the vapor-liquid equilibrium region of this system.

Experimental Method

Two vapor-recirculating equilibrium apparatuses, designed for use at temperatures from -40 to 70 °C and from 40 to 250 °C and pressures to 200 MPa, have been used. They are described by Pozo and Streett (*8*) and by Streett and Calado (*9*), respectively. A schematic diagram of the apparatus for higher temperature measurements is shown in Figure 1. The temperature in the oven is controlled within ±0.02 °C. The apparatus for lower temperature measurements (not shown) is similar. It contained a water/antifreeze bath which was controlled by a Braun Model 1480 BKU proportional temperature controller. Subambient temperatures were obtained by circulating cold water or liquid nitrogen through a heat-exchange coil in the bath. Temperatures in this apparatus could be controlled to within ±0.01 °C. Pressures in both apparatuses were measured with an uncertainty of ±0.007 MPa or ±0.5% (whichever is greater) by using an Autoclave Engineers Model DPS-0021P digital pressure gauge, calibrated in this laboratory against a Ruska dead-weight gauge.

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0021-9568/89/1734-0319$01.50/0