bles V and VII), the average deviation is ±0.0012 in methane mole fraction and ±0.21 cc/g-mol in v. For the system containing *n*-dotriacontane (Table VI), the average deviation is ±0.0077 in methane mole fraction and ±3.41 cc/g-mol in v. The latter deviations are larger due in part to the larger x_1 and v encountered in the *n*-dotriacontane systems.

Table VIII gives some data points for the three ternary S-L-V surfaces. For these points the major unreliability is in the temperature, which is good to ±0.2 °C. The other data are at least good to the accuracies stated for Tables V–VII. Pressure could be read to ±0.07 atm. Since Table VIII is "raw" data, the temperature is tabulated to two decimals, since our Pt resistance thermometer was accurate to ±0.02 °C (*1*).

Nomenclature

P = pressure, atm
T = temp, K
v = liquid mixture molar volume, cc/g-mol
x = mole fraction

Subscripts

1 = methane
M = middle weight hydrocarbon
H = heavy hydrocarbon

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Equilibrium-Phase Properties of Carbon Dioxide–*n*-Butane and Nitrogen–Hydrogen Sulfide Systems at Subambient Temperatures

Harish Kalra, Thamra R. Krishnan,[1] and Donald B. Robinson*
Department of Chemical Engineering, University of Alberta, Edmonton, Alta., Canada T6G 2E1

Vapor and liquid equilibrium-phase compositions were determined at 50.0, 1.1, and −49.3 °F for the carbon dioxide–*n*-butane system and at −49.3 and −99.4 °F for the nitrogen–hydrogen sulfide system. The data for the 50.0 °F isotherm for the carbon dioxide–*n*-butane system were taken in a variable volume cell, and the remaining data in a constant volume cell designed for operation at low temperatures. Refractive index measurements of the equilibrium phases were made for the carbon dioxide–*n*-butane system at 50.0 and 1.1 °F. These measurements were used to determine phase densities by use of the Lorentz-Lorenz molar refractivity relationship.

To perform reliable design calculations with petroleum reservoir fluids or natural gas systems, it is desirable to have good data on all binary pairs that constitute the system. Binary data are necessary to determine the interaction parameters required in equations used to predict multicomponent phase behavior. Previous work on the carbon dioxide–*n*-butane system by Poettman and Katz (*6*), Olds et al. (*5*), and Besserer and Robinson (*1*) covered a termperature range from 80 to 280 °F. Earlier work on the nitrogen–hydrogen sulfide system by Besserer and Robinson (*2*) was in the range from 0 to 160 °F. However, increased interest in industrial processes which operate at temperatures significantly lower than those referred to above suggested that it would be useful to extend the data on these systems down to the −50 or −100 °F range.

Accordingly, the information presented in this paper is based on a study of the coexisting phase properties of the carbon dioxide–*n*-butane system between 50 and −50 °F at pressures between the vapor pressures of normal butane and carbon dioxide and of the nitrogen–hydrogen sulfide system at −50 and −100 °F to pressures of 2000 psia.

Experimental Method

The data at 50 °F for the carbon dioxide–*n*-butane system were obtained using a variable volume cell in which the vapor and liquid mixture under investigation was confined between two movable pistons. The pressure of the cell contents and the location of the phases within the cell were varied by altering the relative position of the pistons using a double-acting two-cylinder Ruska pump. The refractive index of either phase viewed in the observation port was calculated from measurements made with a special window and mirror arrangement and an autocollimating telescope. These made it possible to obtain the minimum angle of deviation of a ruby laser ray passed through the window and cell contents, reflected off the mirror, and back out through the window. The details of this equipment and the method of operation have been given by Besserer and Robinson (*1*).

The data at all other temperatures were obtained in a recently designed constant volume cell capable of operating at much lower subambient temperatures. The materials under investigation were charged to the cell at the required pressure and at a temperature determined by the surrounding cryostat. Equilibrium between phases was obtained by a magnetic stirrer coupled externally to rotating magnets. This cell was also provided with a window and mirror arrangement and an autocollimating telescope for making refractive index

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[1] Present address, Black, Sivals, and Bryson Ltd., Edmonton, Alta., Canada.

measurements. The details of this equipment and its method of operation have been described by Kalra and Robinson (*4*).

The temperature of the equilibrium phases was measured with iron constantan and copper constantan thermocouples which had been calibrated against a platinum resistance thermometer. They are believed known to within ±0.1 °F.

The pressure was measured with stainless-steel bourdon tube Heise gauges having ranges of 0–3000, 0–2000, 0–250, and 0–100 psi. These gauges had been calibrated against a Ruska dead weight gauge. The measured pressures did not normally exceed about two thirds of full scale on any gauge. They are believed known to ±0.15% of full scale or ±3 psi, whichever is the lesser.

Table I. Source and Purity of Materials Used

Material	Source	Min mol % purity
Carbon dioxide	Canadian Liquid Air	99.9
Nitrogen	Linde	99.99
n-Butane	Phillips Petroleum	99.99
Hydrogen sulfide	Matheson	99.8

Materials and Analysis

Table I gives the source and minimum purity of all the substances used during this investigation. The hydrogen sulfide was purified further by distilling the contents of the cylinder once and using the condensed liquid phase for the experiments. This procedure minimized contamination due to carbon dioxide and mercaptans.

The phase compositions were determined with a Hewlett-Packard Model 5750 gas chromatograph equipped with a thermal conductivity cell detector. The stationary column details are given for both systems in Table II together with the response factors used for converting area fractions to mole fractions. Two samples of each phase were taken, and triplicate chromatographs were run on each sample. For each point, the six analyses were generally repeatable to within ±0.2 mol %, and the accuracy was judged to be ±0.3 mol %.

Table II. Gas Chromatograph Operating Conditions

System	Column dimension	Column type	Oven temp, °F	Response factor
$n\text{-C}_4\text{–CO}_2$	0.318 x 91.4 cm	Porapak QS	284	$\frac{n\text{-C}_4}{\text{CO}_2} = \frac{1.0}{1.5466}$
$\text{H}_2\text{S–N}_2$	0.318 x 91.4 cm	Porapak QS	122	$\frac{\text{H}_2\text{S}}{\text{N}_2} = \frac{1.0}{1.1252}$

Table III. Equilibrium-Phase Properties for *n*-Butane—Carbon Dioxide System

Press, psia	Carbon dioxide concn		Equilibrium constant		Refractive index[a]		Molar vol[b]	
	x	y	K_{CO_2}	$K_{n\text{-}C_4}$	n_L	n_V	V_L	V_V
				50.0 °F				
51.9	0.0296	0.5612	18.96	0.452	1.33578	1.00309	1.55	99.0
94.9	0.0752	0.7515	9.99	0.269	1.33184	1.00460	1.52	52.9
145.2	0.1333	0.8372	6.28	0.188	1.32645	1.00637	1.48	33.7
213.9	0.2223	0.8860	3.99	0.147	1.31787	1.00888	1.42	23.4
308.9	0.3644	0.9206	2.53	0.125	1.30190	1.01279	1.32	14.7
400.5	0.5369	0.9429	1.76	0.123	1.27932	1.01714	1.20	10.5
463.2	0.6652	0.9561	1.44	0.131	1.26193	1.02007	1.10	8.77
517.3	0.7840	0.9632	1.23	0.170	1.24110	1.02340	1.02	7.42
571.0	0.8825	0.9775	1.11	0.192	1.22277	1.02652	0.941	6.38
599.5	0.9254	0.9881	1.07	0.160	1.21379	0.02834	0.908	5.84
				1.1 °F				
15.2	0.0109	0.5112	47.07	0.494	1.35098	1.00265	1.52	185.6
22.4	0.0223	0.6634	29.72	0.344	1.34980	1.00289	1.51	110.7
33.6	0.0387	0.7804	20.19	0.228	1.34957	. . .	1.50	. . .
50.4	0.0686	0.8505	12.39	0.161	1.34739	1.00316	1.49	72.6
80.3	0.1233	0.9104	7.38	0.102	1.34306	. . .	1.48	. . .
111.3	0.1888	0.9406	4.98	0.0733	1.34037	1.00406	1.43	46.0
141.3	0.2634	0.9526	3.62	0.0643	1.33500	1.00608	1.38	29.0
182.2	0.3831	0.9654	2.52	0.0560	1.32649	1.00447	1.33	38.6
216.5	0.5225	0.9716	1.86	0.0595	1.31463	1.00693	1.24	24.3
255.8	0.7387	0.9794	1.33	0.0790	. . .	1.00799	. . .	20.8
273.5	0.8150	0.9833	1.21	0.0903	1.27230	1.01102	0.950	14.8
					1.26083	1.01276	0.885	12.7
					1.23818	1.01226	0.694	12.8
				−49.3 °F				
4.8	0.00765	0.6037	78.91	0.399				
9.9	0.0223	0.8111	36.42	0.193				
20.2	0.0512	0.9103	17.79	0.0946				
38.7	0.1136	0.9577	8.43	0.0477				
53.8	0.1762	0.9704	5.51	0.0360				
72.9	0.2870	0.9806	3.42	0.0272				
90.6	0.4634	0.9918	2.14	0.0153				
104.8	0.7620	0.9928	1.30	0.0303				

[a] Relative to vacuum at 6328 Å. [b] Calculated from refractive index and composition data.

Table IV. Equilibrium-Phase Properties for Nitrogen–Hydrogen Sulfide System

Press, psia	Nitrogen concentration x	Nitrogen concentration y	Equilibrium constant K_{N_2}	Equilibrium constant K_{H_2S}
		−49.3 °F		
48.5	0.0004	0.3804	951.0	0.620
70.0	0.0008	0.5658	707.3	0.435
118.5	0.0017	0.7379	434.1	0.263
249.6	0.0033	0.8653	262.2	0.135
497	0.0066	0.9285	140.7	0.0720
802	0.0103	0.9452	91.77	0.0554
1205	0.0153	0.9540	62.35	0.0467
1605	0.0200	0.9555	47.78	0.0454
1994	0.0232	0.9564	41.22	0.0446
		−99.4 °F		
20.4	0.0005	0.6542	1308.4	0.346
74.8	0.0011	0.9022	820.2	0.0979
150.9	0.0019	0.9507	500.4	0.0494
248.1	0.0027	0.9680	358.5	0.0321
401	0.0040	0.9788	244.7	0.0213
696	0.0069	0.9858	142.9	0.0143
1017	0.0089	0.9873	110.9	0.128
1410	0.0111	0.9872	88.94	0.0129
1994	0.0135	0.9843	72.91	0.0159

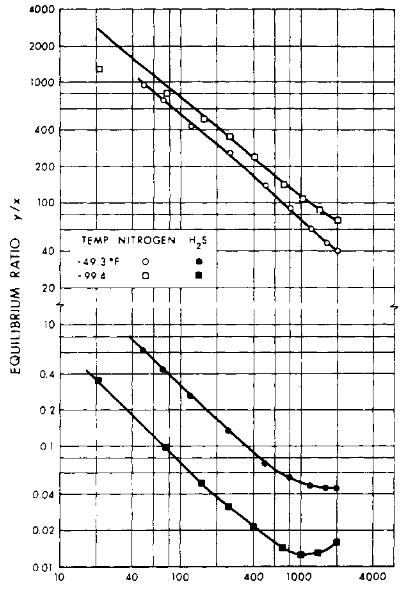

Figure 2. Equilibrium ratios for nitrogen and hydrogen sulfide in nitrogen–hydrogen sulfide binary system

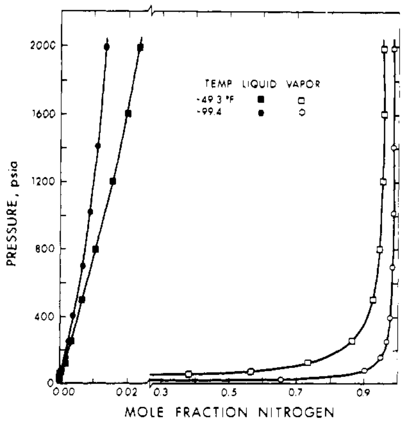

Figure 1. Pressure-composition diagram for nitrogen–hydrogen sulfide system

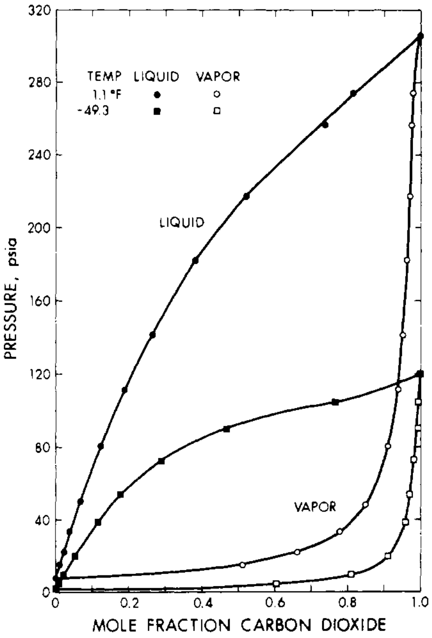

Figure 3. Pressure-composition diagram for *n*-butane–carbon dioxide system

Results

The experimental measurements of the equilibrium-phase compositions and the calculated vapor-liquid equilibrium ratios are given in Table III for the carbon dioxide–*n*-butane system and in Table IV for the nitrogen–hydrogen sulfide system. Table III also includes the refractive indices and the calculated phase densities for the 50.0 and 1.1 °F isotherms. Figure 1 shows the vapor and liquid-phase compositions as a function of pressure at −49.3 and −99.4 °F for the nitrogen–hydrogen sulfide system, and Figure 2 shows the calculated equilibrium ratios. Figure 3 shows the pressure composition relationships for the carbon dioxide–*n*-butane system at 1.1 and −49.3 °F, and Figure 4 shows the equilibrium ratios for each component at each temperature.

Discussion

The equilibrium-phase composition and refractive index data for the carbon dioxide–*n*-butane system at 50.0 and 1.1 °F were used to calculate the equilibrium-phase densities by use of the Lorentz-Lorenz refractivity relationship as explained by Besserer and Robinson (*1*). The refractivities of carbon dioxide at both temperatures and of normal butane at 50.0 °F were obtained from measured refractive indices and from densities calculated from the Benedict-Webb-Rubin

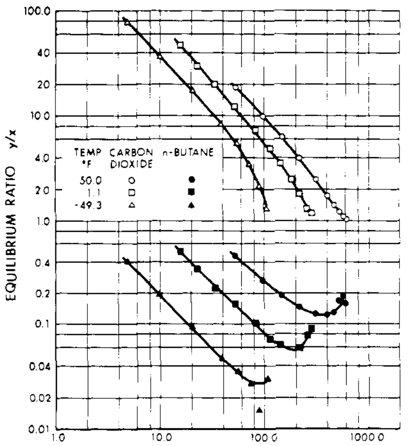

Figure 4. Equilibrium ratios for *n*-butane and carbon dioxide in *n*-butane–carbon dioxide binary system

Table V. Lorentz-Lorenz Molar Refractivities at Zero Pressure, ml/g-mol

	Temperature, °F	
Component	1.1	50.0
Carbon dioxide	6.52	6.69
n-Butane	20.49	20.43

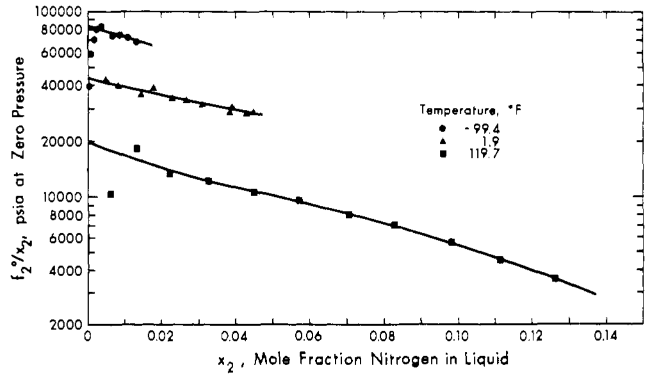

Figure 5. Typical plots for determining Henry's constant for nitrogen in hydrogen sulfide

Table VI. Henry's Constant at Zero Pressure for Nitrogen in Hydrogen Sulfide

Temp, °F	T_c/T	H°, psia
−99.4	1.867	83,300
−49.4	1.639	60,100
1.9	1.457	43,800
40.1	1.345	33,800
80.4	1.245	25,800
119.7	1.161	19,700
160.0	1.085	14,800

equation of state by use of improved coefficients (*3*). The refractivity of normal butane at 1.1 °F was determined by extrapolating data available at higher temperatures. The values of the pure component refractivities are given in Table V.

Henry's constants for nitrogen in the nitrogen–hydrogen sulfide system were obtained by extrapolating plots of ln f_2^0/x_2 vs. x_2 to zero solute concentration. The values of f_2^0/x_2 at each pressure were converted to a zero reference pressure by applying a Poynting correction, thus giving Henry's constants at zero pressure. The data obtained in the present work and also the earlier data (*2*) at 1.9, 40.1, 80.4, 119.7, and 160.0 °F were used for making the calculations. From the typical plots shown in Figure 5, the data tend to scatter at the dilute solute end, and some judgment must be exercised in performing the extrapolation. The values of the Henry's constants at each temperature are given in Table VI.

Henry's constants for carbon dioxide in *n*-butane were not calculated because at the temperatures used in this study, both carbon dioxide and *n*-butane behave as liquids.

Acknowledgment

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Nomenclature

f^0 = fugacity of solute referred to zero pressure
H^0 = Henry's constant referred to zero pressure
K = equilibrium ratio
n = refractive index
P = pressure
T = temperature
V = molar volume, ft^3/lb mol
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase

Subscripts

c = critical
L = liquid
V = vapor
2 = solute

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