P = total pressure of the system, atm.
S_1 = solid n-nonane phase
T = absolute temperature of the system, ° K.
V = vapor phase; molar volume of liquid, ml. per gram mole
X = mole fraction n-nonane in the liquid phase

The standard state of the solute is the hypothetical incompressible liquid of unit mole fraction obeying Henry's Law. The standard state of the solvent is the pure liquid under its own vapor pressure.

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Vapor-Liquid Equilibrium in the Ethane–n-Butane–Nitrogen System

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Experimental data on the compositions of the conjugate phases are presented in the form of isotherms at 100°, 160°, 220°, and 280° F. For each temperature, equilibrium data were obtained at 500-p.s.i. intervals from 500 p.s.i.a. to the convergence pressure. The nitrogen concentration was varied from 0% to 100% in the vapor phase.

SINCE nitrogen is found in many natural petroleum fluids, a detailed knowledge of the phase equilibria is of importance to the petroleum industry. Although K values for nitrogen are reported in the NGSMA data book (8) and Winn, Hadden, and Grayson (5, 13) have prepared a nomograph whereby K values for nitrogen may be obtained, there is great need for more experimental data to describe the effect of nitrogen on hydrocarbon K values. This effect has been shown to be more pronounced with methane than for heavier hydrocarbon components in several experimental works (1, 9, 12).

In this investigation, experimental data were obtained for the ethane-n-butane-nitrogen system at temperatures of 100°, 160°, 220°, and 280° F. at pressure intervals of 500 p.s.i. from 500 p.s.i.a. to the convergence pressure. All possible ranges of nitrogen concentration were investigated.

EXPERIMENTAL

A Sloan-type equilibrium variable-volume cell (manufactured by Ruska Equipment Corp., Catalog No. C216), with an internal stirring motor, was used (1, 2, 3). The cell has a maximum capacity of about 3000 cc. when the piston is at the extreme top position. The internal stirring motor was driven by an electric motor which was placed in the motor chamber of the cell. Its speed was regulated with a transformer regulator placed outside the cell. The voltage to the electric motor ranged from 7 to 16 volts.

The pressurized mixture was agitated for several hours and allowed to stand an additional hour for phase separation before sampling each phase. The phase compositions were determined by gas chromatography with a Beckman GC-2

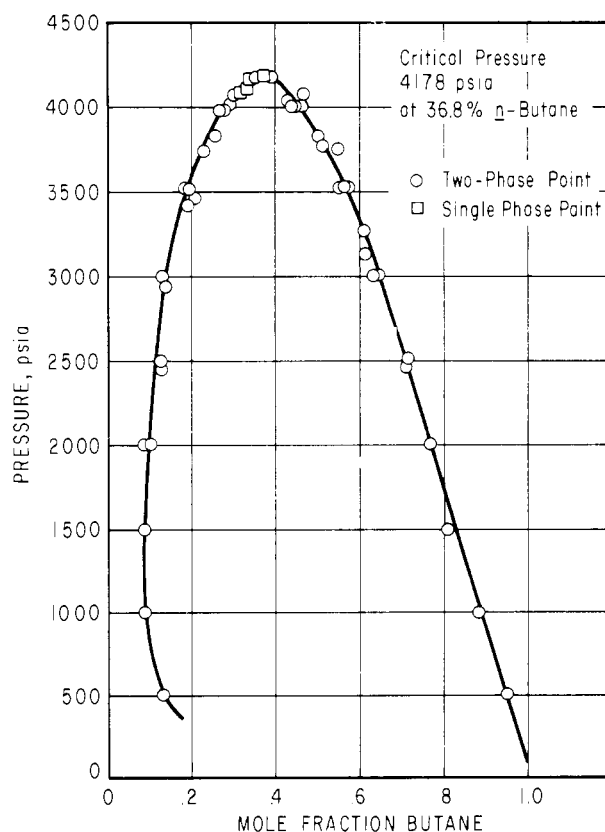[1] Present address: Mobil Chemical Co., Beaumont, Tex.

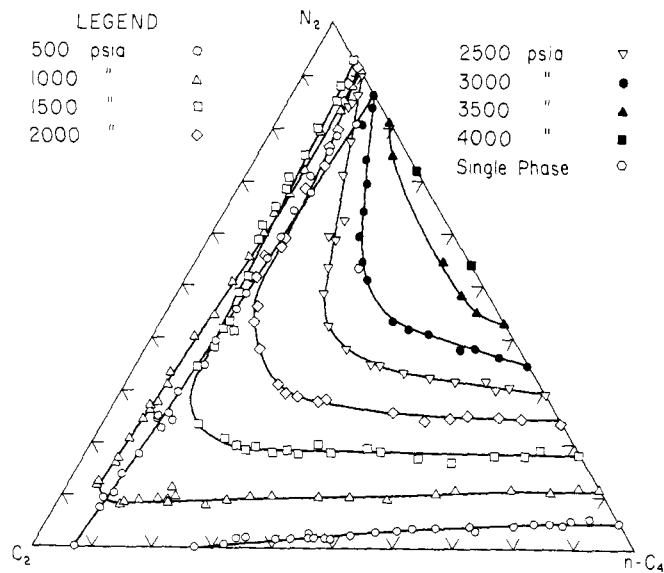Figure 1. Nitrogen–n-butane binary at 100° F.
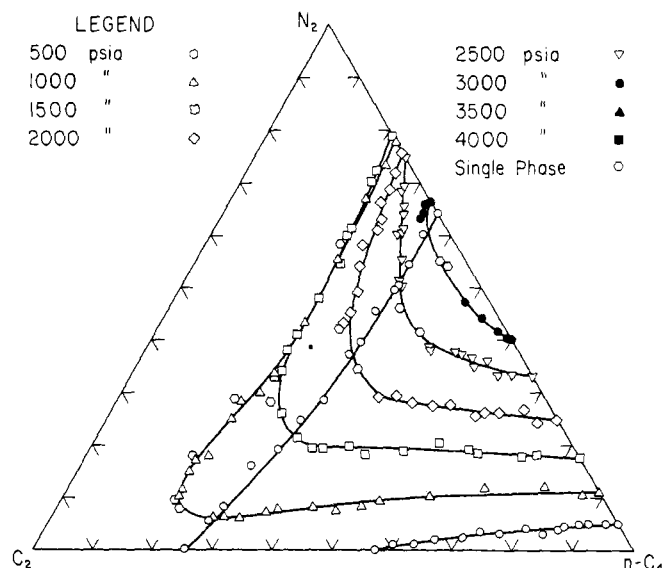
Figure 2. Phase diagram at 100° F.

Figure 3. Phase diagram at 160° F.

Table I. Nitrogen–n-Butane Equilibrium Data at 100° F.
for High Pressure

P, P.S.I.A.	Vapor N_2	Vapor $n\text{-}C_4H_{10}$	Liquid N_2	Liquid $n\text{-}C_4H_{10}$
2018	0.897^2	0.102^8	0.230^0	0.770^0
2462	0.870^1	0.129^9	0.290^8	0.709^2
2931	0.859^7	0.140^3	0.363^0	0.637^0
3000	0.871^7	0.128^3	0.367^2	0.632^8
3242	0.874^3	0.125^7	Single phase	
3430	0.806^3	0.193^7	0.455^8	0.544^2
3447	0.792^0	0.208^0	Single phase	
3510	0.800^5	0.199^5	0.432^7	0.567^3
3535	0.806^9	0.193^1	0.444^8	0.555^2
3540	0.811^3	0.188^7	0.439^7	0.560^3
3735	0.771^4	0.228^6	0.459^2	0.540^8
3825	0.740^1	0.259^9	0.496^4	0.503^6
3975	0.735^4	0.264^6	Single phase	
3985	0.724^7	0.275^3	Single phase	
4000	All liquid		0.555^0	0.445^0
4015	0.701^3	0.298^2	0.559^9	0.440^1
4040	0.685^2	0.314^2	Single phase	
4065	0.697^3	0.302^7	0.535^3	0.464^7
4110	0.677^9	0.322^1	Single phase	
4170	0.664^0	0.336^0	0.613^0	0.387^0
4178^a	0.631^8	0.368^2	Single phase	

^{a} Critical pressure.

Table IV. Comparison of Chao-Seader K-Values
with Experimental K-Values

System Temp., ° F.	Av. % Deviation, $P_r \leqq 0.8$		
$N_2\text{-}C_2\text{-}nC_4$	N_2	C_2	$n\text{-}C_4$
100	16.55	3.25	11.11
160	24.0	2.22	9.59
220	5.13	8.59	3.05
280	6.06	6.49	2.09
$N_2\text{-}C_1\text{-}nC_4$	N_2	C_1	nC_4
100	15.81	5.11	10.94
160	22.1	3.80	8.27
220	6.7	7.64	3.54
280	3.8	5.19	1.89
$N_2\text{-}C_1\text{-}nC_6$	N_2	C_1	nC_6
100	24.19	7.59	37.1
160	27.51	5.53	30.4
220	17.40	6.83	18.3
280	13.91	9.08	9.1
$N_2\text{-}C_1\text{-}nC_{10}$	N_2	C_1	
100	30.1	17.3	
160	38.6	19.5	
220	25.1	14.1	
280	19.4	8.0	

instrument. Separations were performed with 6 feet of a column containing Ansul ether on firebrick at 34° C. A complete description of the sampling and analytical techniques and calculations of the results are available (7).

Materials. The ethane used during this research project was purchased from the Phillips Petroleum Co. and the Matheson Co. The Phillips ethane was pure grade, approximately 99.35% pure. That from Matheson was C.P. grade of the same purity. The n-butane purchased from Phillips was Instrument grade of 99.5% minimum purity. Nitrogen was O.P. grade with a minimum purity of 99.9 mole %.

RESULTS

The two binary systems existing as limiting cases for the ternary system data were checked and found to agree with the reported findings of Kay (6) and Roberts and McKetta (11). The nitrogen–n-butane binary was extended up to the critical pressure at 100° F. to complete the binary system (Figure 1). The binary equilibrium data are reported in Table I.

The ternary equilibrium data are tabulated by mole fractions in Table II (Tables II and III deposited with ADI) and were plotted on triangular diagrams as shown in Figures 2 through 5. These data were smoothed by plotting the best curve through the data points on a Y-X diagram for each component of the system. Each point was adjusted so that it was consistent with all three Y-X curves as well as with the vapor and liquid composition lines on the triangular diagram. The smoothed data are tabulated in Table III. (The standard error of estimate of the major values from the smoothed data was 0.005 mole fraction of any one component.) Figure 6 shows the K values for each component as functions of pressure and per cent nitrogen in the vapor phase at 160° F.

K values for ethane and n-butane compared favorably with values predicted by the method of Chao and Seader (4) up to a reduced pressure of 0.8. By considering nitrogen as a simple fluid in the manner of Chao and Seader (4), using the solubility parameter of 2.58 (cal./ml.)$^{1/2}$ calculated for nitrogen by Prausnitz and Shair (10), and a molar volume of 36.0 ml. per gram-mole, the K values for nitrogen
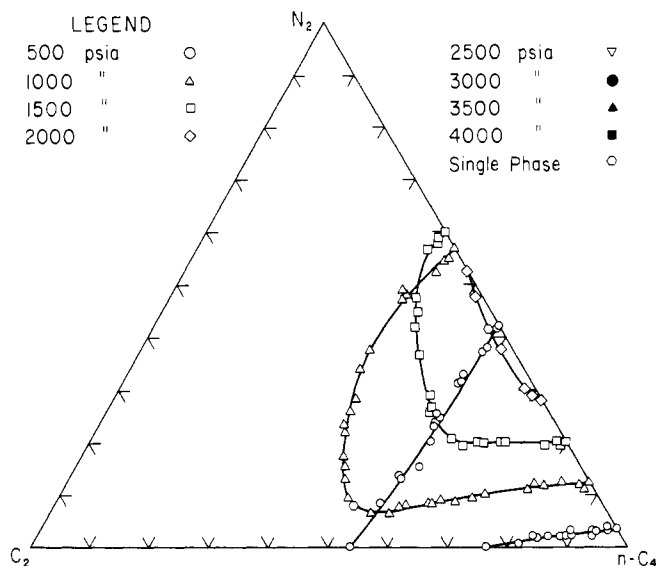
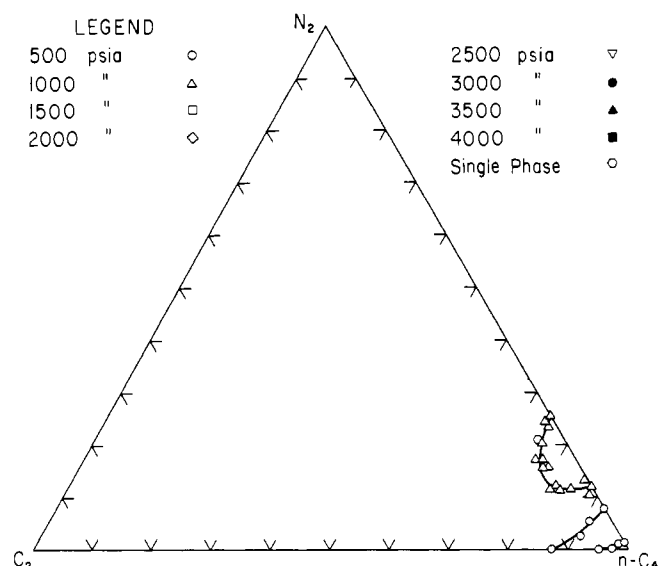Figure 4. Phase diagram at 220° F.

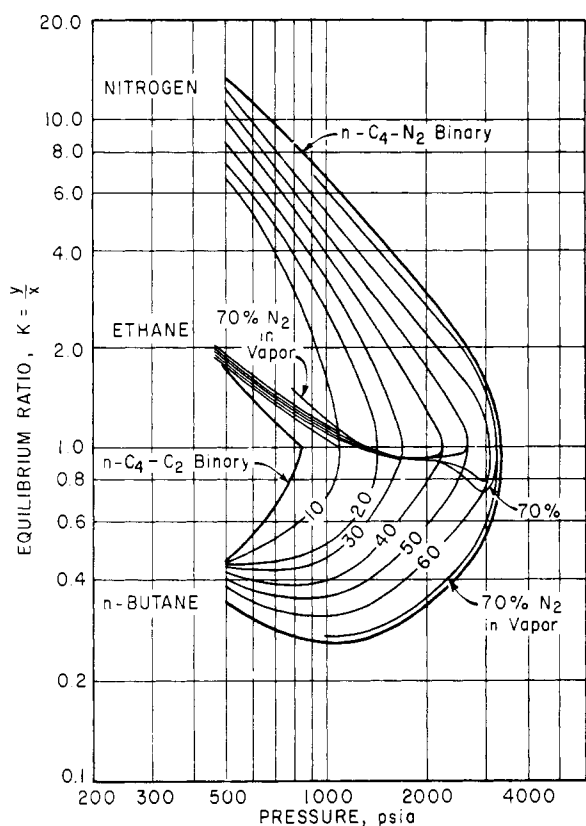

Figure 5. Phase diagram at 280° F.

Figure 6. K values at 160° F.

could also be predicted up to about $0.8P_r$ by the method of Chao and Seader by expressing the hypothetical liquid fugacity coefficient of pure nitrogen in the following form as determined by multiple linear regression analysis on the experimental data:

$$\text{Log}_{10}\nu^\circ = 0.636835 + 0.070691\ T_r +$$

$$0.050886\ P_r - 0.051284\ P_4 T_r - \log_{10}P_r$$

Table IV compares experimental K values with those determined by the above method.

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