urements of the conductivity increasingly more difficult. Therefore, the data in the polyphosphoric acid region would be expected to be less accurate than below 100% H_3PO_4.

Shown in Table II are some interpolated values for the conductivity of phosphoric acid which are representative of results obtained in this work and by others (5, 6, 7). The values found in this work are consistently higher than the values reported by Kakulin and Fedorchenko (5) and elsewhere (7). However, values found in this work are lower than those of Keidel (6). The limited amount of experimental detail regarding sample preparation, analysis, and thermal history in the three reports cited does not allow for a critical comparison with this work.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bell, R.N., *Ind. Eng. Chem.* 40, 1464 (1948).
(2) Clifford, J.E., Beach, J.G., Gurklis, J.A., Kolic, E.S., Gates, J.T., Faust, C.L., Battelle Memorial Institute, NASA CR-60851, 1964.
(3) Greenwood, N.N., Thompson, A., *J. Chem. Soc.* 1959, p.3485.
(4) Jones, G., Bradshaw, B.C., *J. Am. Chem. Soc.* 55, 1780 (1933).
(5) Kakulin, G.P., Fedorchenko, I.G., *Russ. J. Inorg. Chem. (Eng. Transl.)* 7, 1289 (1962).
(6) Keidel, F.A., *Anal. Chem.* 31, 2043 (1959).
(7) Monsanto Chemical Co., St. Louis, Mo., Tech. Bull No. I-239.
(8) Munson, R.A., *J. Phys. Chem.* 68, 3374 (1964).

Heterogeneous Phase and Volumetric Equilibrium in the Methane–n-Nonane System

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Vapor-liquid compositions and molar volumes are presented for eight isotherms between −50° and 150° C. The three-phase, vapor-liquid-solid behavior is presented at pressures up to 150 atm. Vapor-liquid critical temperatures are presented at five temperatures between −25° and 75° C.

THE STUDY of Savvina (13) appears to be the only one in which experimental vapor-liquid behavior on the meth-and-n-nonane binary system is reported. Savvina presents vapor-liquid isotherms at 40°, 60°, 80°, 100°, 120°, and 150° C. at pressures up to the critical. Unfortunately, the data are presented only in graphical form on a scale which lacks the accuracy necessary for most scientific and engineering purposes.

The volumetric behavior of methane has been studied extensively (1, 3, 8-11). Matthews (9) and Canjar (1) have evaluated the thermodynamic properties of methane from the P-V-T data.

The volumetric behavior of n-nonane has been established by Carmichael (2) up to 680 atm. and above 40° C. Data on the liquid density, vapor pressures, critical constants, and heat of fusion were reported by Rossini (12).

EXPERIMENTAL

The equipment and experimental techniques were described by Kohn (7) and were the same as those used in other studies of binary hydrocarbon systems (4, 6, 7, 14). Temperatures were taken on a platinum resistance thermometer which was calibrated to indicate temperature within 0.02° C. of the International Platinum Scale. Pressures were taken on bourdon tube gages which were accurate to ±0.07 atm. Each bourdon gage was checked at the start of an experimental run by use of an accurate dead weight gage. The only change was in the equilibrium cells used for the vapor-liquid study at pressures in excess of 100 atm. The
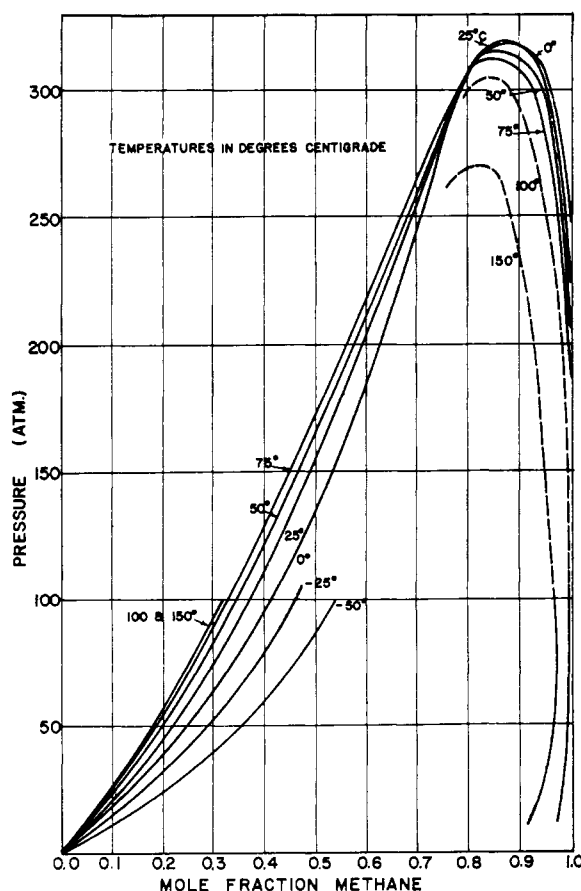
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Figure 1. Smoothed pressure-temperature diagram

equilibrium cells used at pressures below 100 atm. were made of borosilicate glass and were of the same type as those used in earlier works. Pressures up to 154 atm. were obtained in a glass capillary cell. However, the capillary cell yielded data of limited volumetric and composition accuracy and was used only for solid-liquid-vapor determinations at pressures greater than 100 atm. High pressure vapor-liquid data were obtained in a metal sight glass gage of approximately 14 cc. inside volume.

The methane and n-nonane were obtained from the Phillips Petroleum Co. Both components were pure grade materials, stated to have 99% minimum purity. The methane was processed as described by Kohn (4), and the resulting gas used in the study was thought to have a purity in excess of 99.5%. The n-nonane was deaerated before each experimental run and used without further purification.

RESULTS

The pressure-composition diagram of the system is presented in Figure 1. Eight experimental isotherms were determined in the range −50° to 150° C. at pressures to 100 atm. Each isotherm was run in a small borosilicate glass equilibrium cell of 5 ml. volume at pressures to 100 atm. and in a large borosilicate glass cell of 12 ml. volume at pressures to 70 atm. The average deviation of the experimental bubble points was ±0.0015 mole fraction, ±0.07° C. and ±0.10 atm.

The isotherms at 0°, 25°, and 75° C., were extended beyond 100 atm. to their critical pressures. This was accomplished using a Jerguson sight glass gage as an equilibrium cell. The average deviation of these high-pressure isotherms was ±0.0035 mole fraction, ±0.1° C., and ±0.7 atm.

Dew point isotherms were determined at 100° and 150° C. in a borosilicate glass equilibrium cell of 10 ml. volume. The experimental points had an average deviation of ±0.0015 mole fraction, ±0.07° C., and 0.10 atm. The metal sight glass gage was used to obtain dew points above 200 atm. at temperatures of 0°, 25°, 50°, and 75° C. The average deviation of these experimental points was ±0.003 mole fraction, ±0.1° C., and ±0.7 atm.

The critical pressures and mole fractions at 0°, 25°, 50°, and 75° C. were determined. An additional critical point was determined at −20° C., but no bubble or dew point measurements were made at this temperature. Figure 2 shows the vapor liquid critical locus.

It is believed that the critical pressures were determined to within 1 atm. The critical mole fractions were difficult to measure but are believed to be <1% in error.

The critical locus extends from the critical point of pure nonane to the type-k singular point as is shown in Figure 2. The locus passes through a maximu of 320 atm. at approximately 25° C.

Table I presents the smoothed properties of the coexisting vapor and liquid phases at temperatures between −50° and 150° C. The low pressure saturated vapor properties were not measured below 100° C. because of the difficulty of accurately measuring concentrations of n-nonane less than a few tenths of a mole fraction. The vapor volumes reported at 100° and 150° C. are reproducible to ±0.5%. Accurate vapor volumes at high pressures were not attainable in the sight glass gage. The liquid molar volumes were reproducible to ±0.1%.

Table II presents data along the solid-liquid-vapor, three-phase lines. The air saturated freezing point of n-nonane determined here is within 0.08° C. of that reported by Rossini (12). The initial slope of this line is given by the Van't Hoff law of freezing point lowering. The measured experimental solubility points were used to calculate the heat of fusion of n-nonane. The calculated heat of fusion
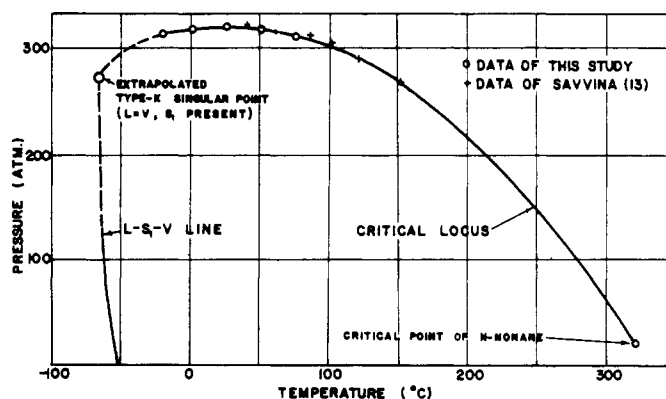

Figure 2. Vapor-liquid critical behavior

agrees closely with the literature value of 3697 cal. per gram mole (12).

Solid-liquid-vapor data of limited compositional accuracy were obtained in the 1-ml. glass cells to 154 atm. The uncertainty in the mole fraction was ±0.01. The pressure temperature diagram of the S-L-V line shows a linear character at the higher pressures. The linear approximation permits a reasonable extrapolation to the type-k singular point where the vapor phase is in critical identity with the liquid phase in the presence of a solid phase. The estimated type-k point is at 270 atm. and −67° C. It is believed that these figures are in error by less than 10 atm. and 1° C. The composition of the liquid phase is not easily estimated but is believed to be quite high in methane.

The lower solid-liquid-vapor line has a type-k singular point at −82.6° C. and 46.0 atm. The singular point is quite close in temperature and pressure to the critical point of pure methane. The three-phase solid-liquid-vapor line below −82.6° C. appears to parallel the vapor pressure curve of pure methane. The equilibrium pressures average about 0.5 atm. higher than those of pure methane when measured at the same temperature. This effect may result from using values of the vapor pressure of methane which have never been measured accurately. The small deviation in the vapor pressure of methane indicates that the composition of both the liquid and vapor phases is reasonably pure methane.

Figure 3, presenting a temperature-composition crossplot at 20 atm., shows that the vapor-liquid region is intersected by a solid-vapor region. The upper three-phase line, S_1-L-V, is at −57.6° C. The L phase is a liquid of 0.177 mole fraction methane. The solid phase, S_1, is substantially pure n-nonane, while the vapor phase is substantially pure methane. The lower S_1-L-V line is shown at −101° C. which is very close to the vapor pressure curve of methane. The L-S_1 line was not experimentally determined but is drawn as a straight line from the freezing point of nonane (−53.55° C.) to the composition of the liquid phase along the S_1-L-V line. The three-phase L-S_1-S_2 line was not experimentally determined. It is shown at a temperature of −182° C. equal to the triple point of methane which seems likely to be within 2 degrees of the true three-phase line.

Figure 4 is shown at 270 atm., the estimated pressure of the type-k singular point. The temperature is approximately −70° C. Here, the liquid-vapor region just touches the S_1-L-V line, and the liquid and vapor have the same composition. This composition is close to being pure methane. Above 270 atm., the liquid-vapor region is a non-intersected ellipse which reduces to a point at 320 atm. and 25° C.

Figure 5 shows the fugacity of methane as a function of the liquid composition along representative isotherms. As mentioned previously, the gas phase is essentially pure methane at temperatures of 75° C. and below. The fugacity values of Matthews (9) for pure methane were used to specify rigorously the fugacity of the dissolved methane.

Table I. Properties of the Coexisting Gas and Liquid Phases

Pressure, Atm.	Liquid Mole Fraction Methane	Liquid Molar Volume, Ml./Gram Mole	Vapor Mole Fraction Methane	Vapor Molar Volume, Ml./Gram Mole
		150.00° C.		
10.00	0.0329	206.23	0.9207	3460.40
20.00	0.0702	200.69	0.9360	1758.30
30.00	0.1060	195.49	0.9485	1179.70
40.00	1.1402	190.61	0.9584	882.10
50.00	0.1727	186.04	0.9656	696.90
60.00	0.2037	181.77	0.9701	567.80
70.00	0.2330	177.78	0.9719	470.80
80.00	0.2608	174.07	0.9710	393.90
90.00	0.2870	170.62	0.9674	330.40
100.00	0.3115	167.43	0.9611	276.20
		100.00° C.		
10.00	0.0362	192.06	0.9740	3003.20
20.00	0.0715	187.29	0.9824	1492.10
30.00	0.1058	182.64	0.9878	988.40
40.00	0.1392	178.15	0.9908	736.60
50.00	0.1716	173.76	0.9921	585.50
60.00	0.2030	169.51	0.9921	484.80
70.00	0.2335	165.40	0.9915	412.80
80.00	0.2630	161.41	0.9909	358.80
90.00	0.2915	157.56	0.9909	316.90
100.00	0.3190	153.84	0.9921	283.50
		75.00° C.		
10.00	0.0448	183.78	0.9999	2829.32
20.00	0.0826	178.61	0.9999	1401.83
30.00	0.1187	173.78	0.9999	926.31
40.00	0.1532	169.16	0.9999	688.93
50.00	0.1861	164.77	0.9999	546.78
60.00	0.2174	160.58	0.9999	452.26
70.00	0.2470	156.62	0.9999	384.97
80.00	0.2750	152.88	0.9999	334.70
90.00	0.3014	149.35	0.9999	295.82
100.00	0.3271	147.20	0.9999	264.90
120.00	0.3775	140.63	0.9999	219.01
140.00	0.4257	133.72	0.9999	
160.00	0.4720	126.78	0.9960	
180.00	0.5168	120.02	0.9870	
200.00	0.5605	113.61	0.9830	
220.00	0.6035	107.69	0.9800	
240.00	0.6463	102.39	0.9752	
260.00	0.6891	97.86	0.9662	
280.00	0.7324	94.28	0.9502	
300.00	0.7765	91.88	0.9270	
310.00	0.8195	89.90	0.8940	
313.00	0.8600	88.00	0.8600	
		50.00° C.		
10.00	0.0449	178.33	0.9999	2616.93
20.00	0.0860	172.95	0.9999	1291.95
30.00	0.1251	167.83	0.9999	850.77
40.00	0.1622	162.96	0.9999	630.41
50.00	0.1974	158.36	0.9999	498.47
60.00	0.2306	154.01	0.9999	410.77
70.00	0.2618	149.92	0.9999	348.39
80.00	0.2911	146.08	0.9999	301.86
90.00	0.3184	142.51	0.9999	265.89
100.00	0.3471	139.00	0.9999	237.36
120.00	0.3994	132.03	0.9999	195.22
140.00	0.4480	125.37	0.9999	
160.00	0.4935	119.09	0.9970	
180.00	0.5365	113.23	0.9906	
200.00	0.5775	107.78	0.9870	
220.00	0.6173	102.73	0.9857	
240.00	0.6562	98.05	0.9837	
260.00	0.6950	93.73	0.9783	
280.00	0.7343	89.78	0.9662	
300.00	0.7745	86.24	0.9445	
310.00	0.8003	85.08	0.9292	
315.00	0.8230	83.50	0.9120	
318.00°	0.8720	79.50	0.8720	

Pressure, Atm.	Liquid Mole Fraction Methane	Liquid Molar Volume, Ml./Gram Mole	Vapor Mole Fraction Methane	Vapor Molar Volume, Ml./Gram Mole
		25.00° C.		
10.00	0.0509	173.45	0.9999	2403.11
20.00	0.0986	167.10	0.9999	1180.64
30.00	0.1426	161.24	0.9999	773.34
40.00	0.1832	155.85	0.9999	569.96
50.00	0.2205	150.88	0.9999	448.21
60.00	0.2550	146.28	0.9999	367.31
70.00	0.2870	142.04	0.9999	309.82
80.00	0.3166	138.10	0.9999	266.99
90.00	0.3442	134.42	0.9999	233.99
100.00	0.3664	131.46	0.9999	207.88
120.00	0.4160	124.88	0.9999	169.59
140.00	0.4637	117.57	0.9999	143.45
160.00	0.5094	112.87	0.9999	
180.00	0.5533	107.42	0.9929	
200.00	0.5952	102.32	0.9883	
220.00	0.6352	97.56	0.9867	
240.00	0.6733	93.11	0.9851	
260.00	0.7094	88.97	0.9803	
280.00	0.7437	85.12	0.9695	
300.00	0.7760	81.55	0.9495	
310.00	0.8090	79.50	0.9351	
315.00	0.8320	77.30	0.9200	
319.00	0.8800	73.40	0.8800	
		0.00° C.		
10.00	0.0540	167.70	0.9999	2187.20
20.00	0.1069	161.01	0.9999	1065.90
30.00	0.1563	154.77	0.9999	691.45
40.00	0.2023	148.96	0.9999	504.88
50.00	0.2448	143.59	0.9999	393.92
60.00	0.2838	138.66	0.9999	320.41
70.00	0.3194	134.16	0.9999	268.17
80.00	0.3515	130.10	0.9999	229.32
90.00	0.3801	126.49	0.9999	199.26
100.00	0.4087	122.56	0.9999	175.58
120.00	0.4639	115.74	0.9999	141.68
140.00	0.5131	109.55	0.9999	119.08
160.00	0.5538	104.07	0.9999	103.72
180.00	0.5922	99.33	0.9999	92.96
200.00	0.6234	95.27	0.9999	85.26
220.00	0.6512	91.69	0.9990	
240.00	0.6781	88.30	0.9980	
260.00	0.7075	84.74	0.9931	
280.00	0.7434	80.71	0.9788	
300.00	0.7908	76.19	0.9572	
310.00	0.8200	72.70	0.9410	
315.00	0.8450	71.50	0.9250	
318.00	0.8850	68.60	0.8850	
		-25.00° C.		
10.00	0.0678	161.75	0.9999	1969.17
20.00	0.1288	154.20	0.9999	949.27
30.00	0.1856	147.18	0.9999	610.72
40.00	0.2381	140.69	0.9999	440.46
50.00	0.2863	134.73	0.9999	337.98
60.00	0.3302	129.30	0.9999	269.85
70.00	0.3698	124.40	0.9999	221.43
80.00	0.4051	120.03	0.9999	185.69
90.00	0.4361	116.19	0.9999	158.67
100.00	0.4629	112.88	0.9999	137.93
		-50.00° C.		
10.00	0.0989	154.68	0.9999	1746.90
20.00	0.1737	145.45	0.9999	827.64
30.00	0.2418	137.04	0.9999	520.79
40.00	0.3033	129.45	0.9999	365.62
50.00	0.3582	122.68	0.9999	271.00
60.00	0.4065	116.71	0.9999	206.61
70.00	0.4482	111.57	0.9999	160.95
80.00	0.4833	107.24	0.9999	128.76
90.00	0.5118	103.73	0.9999	106.50
100.00	0.5336	101.03	0.9999	91.40

Table II. Smoothed Solid-Liquid-Vapor, Three-Phase Lines

Pressure, Atm.	Temperature, °C.	Mole Fraction Liquid Methane	Molar Volume Liquid, Ml./Gram Mole
1.0[a]	−53.80	0.000	166
5.0	−54.68	0.046	159
10.0	−55.72	0.093	154
20.0	−57.59	0.181	143
30.0	−59.29	0.263	133
40.0	−60.80	0.343	120
60.0	−63.30	0.470	108
100.0	−64.80	0.570	
150.0	−65.4		
270.0[b]	−67.0		
30.0	−96.1		
35.0	−91.4		
40.0	−87.25		
45.0	−83.3		
46.0[b]	−82.6		

[a] Air-saturated freezing point. [b] Type-k singular point obtained by extrapolation.

Figure 4. Isobaric temperature composition diagram

Figure 3. Isobaric temperature composition diagram
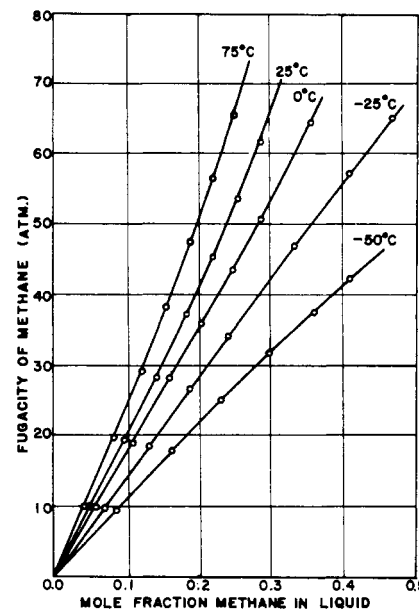
Figure 5. Fugacity-composition diagram

These isotherms show a high degree of linearity at compositions up to 0.2 fraction methane, demonstrating the applicability of Henry's law over this region.

The rigorous thermodynamic dependence of the Henry's law constants upon tenperature is given by the following equation:

$$\frac{d \ln f/x}{d\,(1)/T} = - \frac{\bar{H}_2^* - \bar{H}_2^0}{R}$$

The Henry's law constants are linear with the reciprocal absolute temperature for −50° to 25° C. This indicates that the following thermodynamic simplifications are true at concentrations of methane to 0.20 mole fraction and from 25° C. to the freezing point of n-nonane:

$$\bar{H}_2^* = \bar{H}_2^V = H_2^V$$

$$\bar{H}_2^0 = \bar{H}_2$$

$$\Delta C_p = C_{p2}^V - \bar{C}_{p2} = 0$$

From the slope of the straight line, the enthalpy change of methane on solution was

$$\Delta H = [H_2\,(\text{gas}) - \bar{H}_2] = 1117 \text{ cal. per gram mole}$$

NOMENCLATURE

$\bar{C}_{2p}^V$ = molar heat of methane in the gas phase at any temperature and pressure, cal. per gram mole × ° K.

$\bar{C}_{p2}$ = partial molar heat capacity of methane in a liquid solution of any dilution, cal. per gram mole × ° K.

f = fugacity of methane, atm.

$\bar{H}_2^*$ = partial molar enthalpy of methane in the ideal gas state at T, cal. per gram mole

$\bar{H}_2^0$ = partial molar enthalpy of methane in an infinitely dilute solution at T, cal. per gram mole

$\bar{H}_2$ = partial molar enthalpy of methane in a liquid solution of any dilution at T, cal. per gram mole

H_2^V = molar enthalpy of methane in the gas phase any T and P cal. per gram mole

L = liquid phase

LITERATURE CITED

(1) Canjar, L.N., J. CHEM. ENG. DATA 3, 185 (1958).
(2) Carmichael, L.T., Sage, B.H., Lacey, W.N., Ind. Eng. Chem. 45, 2697 (1953).
(3) Keys, F.G., Burks, H.G., J. Am. Chem. Soc. 49, 403 (1927).
(4) Kohn, J.P., A.I.Ch.E. J. 7, No. 3, 514 (1961).
(5) Kohn, J.P., Ph.D. thesis, University of Kansas, Lawrence, Kan., 1956.
(6) Kohn, J.P., Bradish, W.F., J. CHEM. ENG. DATA 9, 5 (1964).
(7) Kohn, J.P., Kurata, F., Petrol. Processing 11, 57 (1956).
(8) Kvalnes, H.M., Gaddy, V.L., J. Am. Chem. Soc. 53, 394 (1931).
(9) Matthews, C.S., Hurd, C.O., Trans. A.I.Ch.E. 42, 55 (1946).
(10) Michels, A., Nederbradt, G.W., Physics 3, 569 (1936).
(11) Olds, R.H., Reamer, N.H., Sage, R.N., Lacey, W.N., Ind. Eng. Chem. 35, 922 (1943).
(12) Rossini, F.D., Pitzer, K.S., Arnet, R.L., Brown, R.M., Pimentel, G.C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(13) Savvina, Y.O., Velikovskii, A.S., J. Phys. Chem. (U.S.S.R.) 30, 1597 (1956).
(14) Shim, J., Kohn, J.P., J. Chem. Eng. Data 7, 3 (1962).

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
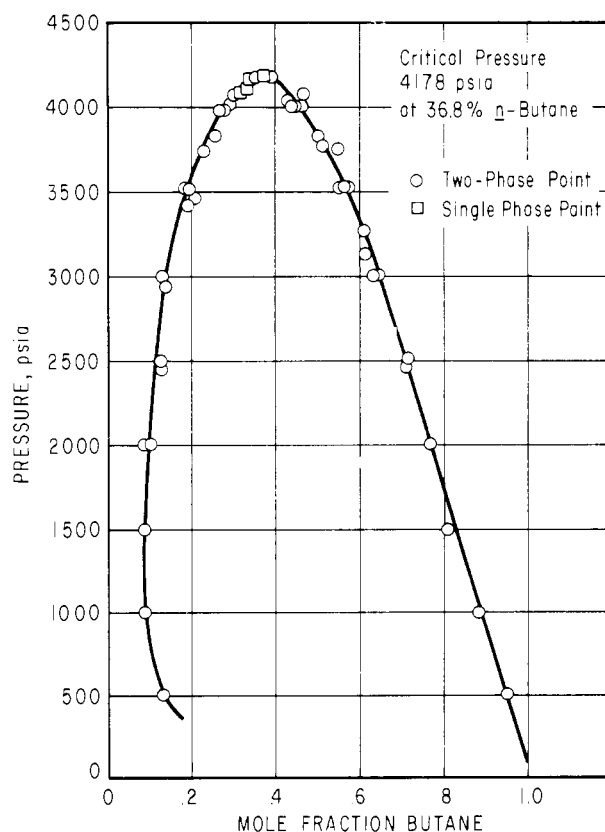
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Figure 1. Nitrogen-n-butane binary at 100° F.