Methane–*n*-Butane System in the Two-Phase Region

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COMPOSITIONS of the coexisting vapor and liquid phases have previously been reported over the temperature range of 100° to 250° F. (*1*). This work extends the range from −80° to 280° F.

EXPERIMENTAL

Windowed equilibrium cells of stainless steel construction were designed to withstand 5000 p.s.i. pressure at temperatures up to 400° F. Calibrated thermocouples inserted at several places within the cells were used to measure the temperature of the equilibrium fluids. Bourdon-type gages, calibrated against a deadweight tester, were used to indicate the pressure inside the equilibrium cells. Equilibrium was attained by circulating the vapor from the top of the cells through magnetic-piston pumps and into the bottom of the cells.

The low temperature data were obtained in a 500 c.c. Penberthy cell placed in a constant temperature liquid bath. Maximum variation of the temperature was held to ±0.1° F. Circulation was maintained for at least 8 hours for each individual sample. In the critical region this time was extended to 12 hours. At the end of the recirculation period a minimum of 1 hour was allowed for the phases to separate. Samples of the phases were withdrawn from the cell and analyzed separately at each equilibrium condition of temperature and pressure.

The equilibrium data at 220° and 280° F. were obtained in a 35 c.c. Jerguson cell located in a constant temperature oil bath. The maximum variation in the bath temperature was held to ±0.2° F. A large number of equilibrium samples were obtained in the critical region to define more clearly the two-phase envelope.

A careful procedure was used to determine the critical points at these high temperatures. After the over-all composition was adjusted as closely as possible to that of the expected critical mixture, the pressure in the cell was increased by injecting mercury until the fluid content of the cell was in single phase. Then the fluid was circulated through the magnetic-piston pump for at least 12 hours. At the end of this period the mixture was sampled, and the pressure reduced very slowly, in increments of 2 p.s.i., by removing mercury from the bottom of the cell. Fluid circulation was maintained throughout. The well known critical phenomena and the appearance of a permanent liquid phase could be observed clearly through the glass windows of the cell as the pressure was gradually decreased.

The validity of the phase envelope near the critical region at 220° F. was substantiated by repeating these experiments in two other equilibrium apparatuses. One of these was a Sloan-type Ruska variable-volume cell.

This cell was comprised of a Stainless steel cylinder with a piston actuated by the injection or removal of mercury. The hydrocarbon mixture was stirred by a propeller mounted on the shaft of an electric motor which was located inside the cylinder. The cell was contained in a constant temperature oil bath. Calibrated thermocouples and Bourdon-type gages indicated the temperature and pressure of the system.

Table I. Experimental Data

Pressure P.S.I.A.	Mole Fraction Methane Liquid Phase	Mole Fraction Methane Vapor Phase
	280° F.	
535	0.038	0.113
669	0.087	0.202
824	0.158	0.227
831	0.158	...
850	[a]	0.214
798	0.143	...
787	0.127	0.231
747	0.117	0.242
735	0.115	0.234
	220° F.	
1348	...	0.452
1342	...	0.478
1339	0.389	0.496
1336	0.382	0.506
1398	[a]	0.482
1300	[a]	0.551
1125	0.287	0.552
878	0.201	0.533
	40° F.	
53	0.0330	0.6213
74	0.0317	0.7053
102	0.0547	0.7969
152	0.0768	0.8633
192	0.0887	0.8867
253	0.0914	0.9039
298	0.1157	0.9140
341	0.1484	0.9200
447	0.1806	0.9420
449	0.2061	0.9282
515	0.1979	0.9312
584	0.2232	0.9424
640	0.2424	0.9432
735	0.2887	0.9510
835	0.3139	0.9464
840	0.3193	0.9463
930	0.3453	0.9479
1060	0.3674	0.9456
1155	0.4245	0.9437
1285	0.4795	0.9381
1370	0.4842	0.9351
1480	0.5226	0.9321
1615	0.5641	0.9177
1685	0.5888	0.8937
1750	0.6369	0.9015
	40° F.	
1770	0.6275	0.8862
1835	0.6898	0.8545
1905	0.7749	0.8171
1915[b]	0.7953	0.7953
	−20° F.	
26	0.015	0.457
49	0.023	0.788
78	0.043	0.875
120	0.064	0.925
149	0.077	0.930
177	0.095	0.941
251	0.116	0.971
348	0.174	0.973
429	0.205	0.978
506	0.246	0.980
613	0.306	0.978
720	0.334	0.975
845	0.403	0.977
910	0.412	0.982
930	0.422	0.977
1075	0.504	0.973
1225	0.552	0.970
1235	0.563	0.968
1290	0.578	0.967
1295	0.580	0.970
1380	0.608	0.957
1590	0.719	0.938
1645	0.793	0.903
1724[b]	0.863	0.863
	−80° F.	
27	0.0350	0.8782
57	0.0728	0.9437
110	0.1058	0.9758
169	0.1759	0.9839
207	0.1796	0.9940
263	0.2376	0.9918
359	0.3165	0.9883
518	0.4133	0.9917
725	0.5986	0.9918
785	0.6554	0.9948
890	0.7412	0.9840
975	0.8112	0.9670
1041[b]	0.9214	0.9214

[a] Single phase. [b] Critical pressures.

The determination was started by charging the cell with a mixture somewhat richer in methane than the expected critical mixture. With the stirring motor running, the pressure was increased slowly by lowering the piston. When the dew point pressure was reached the transition into the single-phase state was observed through a window in the wall of the cell.

Next a small amount of *n*-butane at constant pressure was added to bring the mixture back into the two-phase region. Then the pressure was increased again to the dew

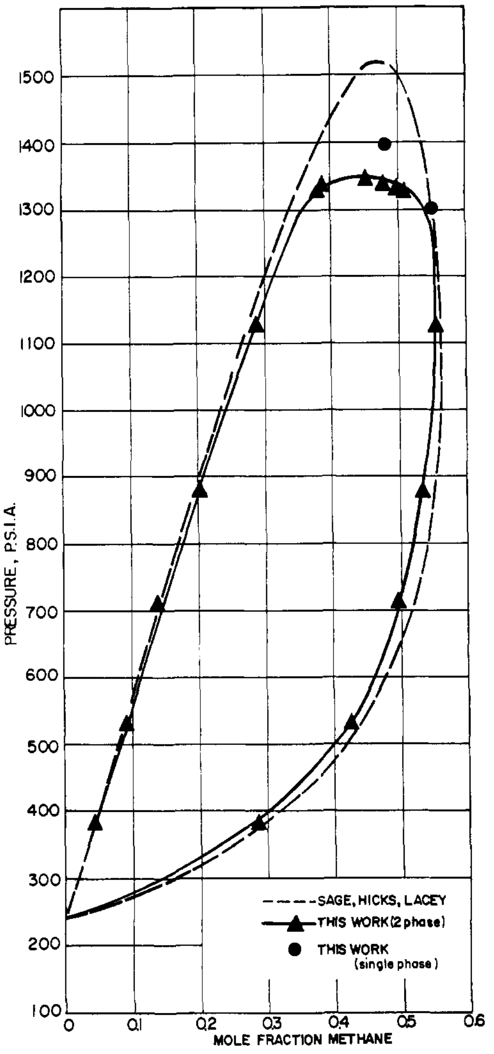

FIG. I COMPARISON OF THE DATA AT 220°F.

Figure 1. Comparison of the data at 220° F.

point pressure of the new mixture. In this manner the dew point line was followed up to the maximum pressure of the two-phase region.

In addition the 220° F. isotherm was rerun in a 400 c.c. windowed Penberthy cell contained in an air bath.

ANALYTICAL

Each equilibrium phase was sampled for analysis. The samples were withdrawn from the equilibrium cells into Stainless steel high pressure tubing connected to the cells proper. The pressure was carefully maintained in the cells by adding mercury through another port as the samples were withdrawn. Subsequently the sample was expanded into a glass flask whose volume was large compared to the volume of the sample and connecting lines. The samples were analyzed using a GC-2 Beckman chromatograph. Occasional checks were made using a mass spectrometer. At no time did the analysis with these two methods disagree more than 0.005 mole fraction.

MATERIALS

The *n*-butane was research grade with a purity of over 99.9%. The methane was also research grade with a purity of over 99.5%. The principal impurity in the methane was nitrogen.

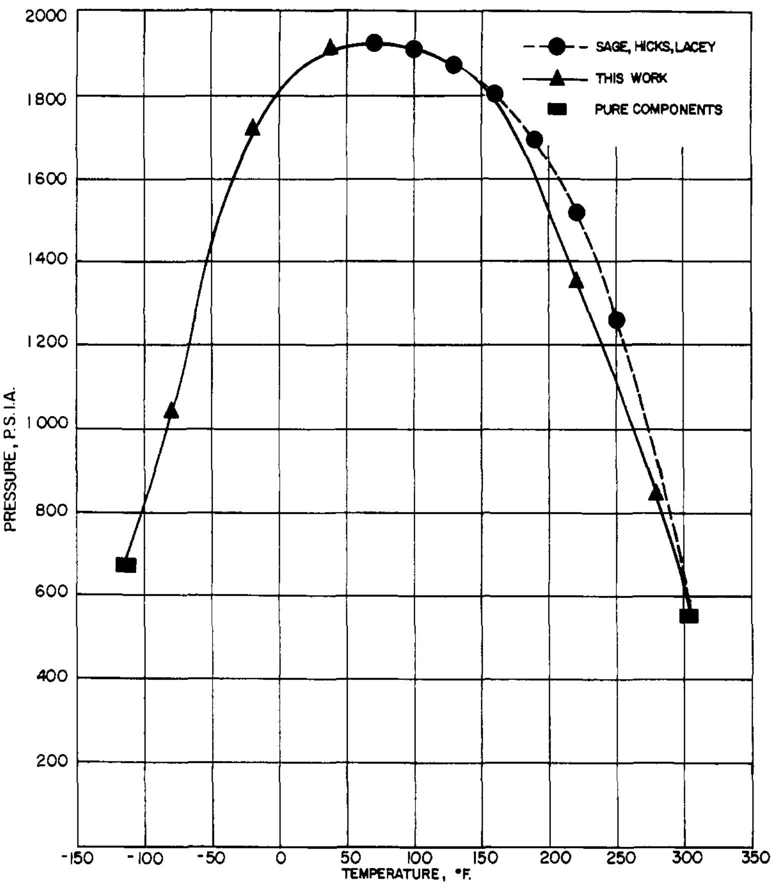

Figure 2. Critical locus

RESULTS

The analyses of the equilibrium mixtures are shown in Table I. Figure 1 shows the data obtained in this investigation compared to the corresponding data published by Sage, Hicks, and Lacey (*1*) on the same system at 220° F. The agreement with their data was excellent at 100° and 160° F. The critical locus is shown in Figure 2. The data at 220° and 280° F. were plotted as in Figure 1 to establish the critical pressure.

The accuracy of the indicated pressure is ±2 p.s.i.a. Other sources of error include temperature variations during the recirculation, sampling procedures, pressure gage readings, and analytical errors. Consideration of the analytical procedure shows that the analyses are reliable to within 0.002 mole fraction. The maximum temperature variation within the cell during recirculation was ±0.2° F. and ±0.05° F. during settling and sampling time.

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