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Low-Temperature *K* Data for Methane-*n*-Butane

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Phase-equilibrium data are presented for the methane-*n*-butane system at low temperatures and high pressures. Eight isotherms from 50° to −160°F and 20-1600 psia were obtained. The data obtained confirmed the unusual shape of the dew-point curve near the methane critical point reported by Chen et al. Observed critical pressures were significantly lower than previous measurements.

Previous low-temperature phase-equilibrium data for this system (*7, 9*) contain considerable "scatter" in the reported phase analyses. With the recent improvement in sampling and analyzing techniques and with the industrial interest in recovering light hydrocarbons from natural gas, a reinvestigation of this system is justified.

Experimental

Equipment. The 50°F isotherm was obtained with the equipment previously described (*5*). Because of pressure limitations of this equipment, a close approach to the critical pressure could not be made.

The 0°F and lower isotherms were obtained with equipment (Figure 1) manufactured by the Rice University Shop. This system is basically the same as that used by Wichterle and Kobayashi (*10*). It consists of a windowed equilibrium cell and magnetic pump, to recirculate the vapors, immersed in a suitable liquid bath. Cooling was obtained with either mechanical refrigeration or liquid nitrogen, depending on the temperature level. The bath temperature was controlled with a Bayley precision temperature controller. The temperature was measured with a platinum resistance thermometer (PRT) located in the body of the windowed cell. The pressure was measured with a calibrated 0-2000 psia Heise gage. Sample analyses were made with a bis(2-methoxyethyl) adipate (BMEA) chromatographic column and thermal conductivity detector. Helium was used as the carrier gas.

Procedure. Phillips research grade *n*-butane was charged to the evacuated cell to a level above the liquid sample point. The vapor was analyzed to assure that no noncondensables were present. If necessary, the vapor phase was evacuated until analysis showed negligible noncondensables (air). Research grade methane was added until the desired pressure was obtained. The vapor was recirculated for at least 30 min at constant temperature and pressure to assure equilibrium.

Initially, an attempt was made to sample the equilibrium phases with the method used by Wichterle (that is, to continuously bleed a small flow to the chromatographic sample valve while maintaining the pressure constant from a reservoir of methane). However, with this system this method of sampling gave unreproducible results. Also, diluting the vapor phase with pure methane during vapor sampling was philosophically unacceptable. Therefore, it was necessary to develop a new sampling technique.

The vapor circulation line was repiped to go outside the cryostat so that small samples could be taken directly into the sample loop of the chromatographic analyzer (valve 1). It was recognized that the change in temperature of the vapor phase might introduce problems if data were taken in the region where retrograde condensation existed, but the ease of sampling outweighed this disadvantage.

After much experimentation with obtaining the right liquid sample, the following procedure was adopted: the vapor circulation was stopped, and the phases were allowed to separate; with valve 3 closed, valve 2 was opened to fill the line with liquid sample; valve 2 was closed, and valve 3 was opened to admit the sample into an evacuated sample cylinder (150-cc volume) containing several glass beads; the sample cylinder was im-

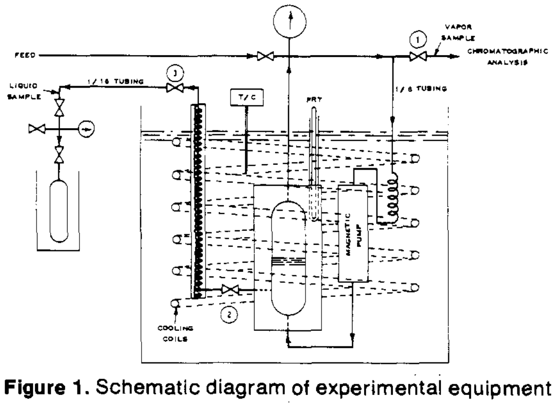

Figure 1. Schematic diagram of experimental equipment

Table I. Phase-Equilibrium Data for Methane–*n*-Butane

Pressure		Composition, mole fraction methane		Butane partial press, psia	K-value	
Psia	Atm	Liquid	Vapor		Methane	Butane
		T = 50.0°F = 10.0°C				
21.6	1.470^a	0.00	0.00	21.6	...	1.00
51	3.47	0.013	0.566	22.1	43.5	0.440
100	6.80	0.035	0.775	22.5	22.1	0.233
201	13.68	0.076	0.875	25.1	11.5	0.135
400	27.22	0.152	0.925	30.0	6.09	0.0884
600	40.82	0.232	0.939	36.5	4.05	0.0793
800	54.43	0.304	0.941	46.9	3.09	0.0842
1000	68.04	0.377	0.941	59.1	2.50	0.0949
1200	81.65	0.442	0.933	80.1	2.11	0.120
1400	95.26	0.514	0.924	106.5	1.80	0.157
		T = 0.0°F = −17.8°C				
7.26	0.494	0.00	0.00	7.26	...	1.00
20	1.36	0.0063^b	0.623	7.54	98.9	0.379
50	3.40	0.0212^b	0.846	7.69	39.9	0.157
100	6.80	0.0461^b	0.9174	8.26	19.9	0.0866
400	27.22	0.195	0.9704	11.8	4.98	0.0368
599	40.76	0.2925	0.9746	15.2	3.33	0.0359
998	67.90	0.470	0.9710	29.0	2.07	0.0547
1397	95.05	0.651	0.9531	65.7	1.46	0.134
1597	108.66	0.758	0.9317	109.2	1.23	0.282
1657	112.74	Critical opalescence observed				
		T = −50.0°F = −45.6°C				
1.77	0.120	0.00	0.00	1.77	...	1.00
50	3.40	0.034^b	0.962	1.9	28.3	0.0393
100	6.80	0.069	0.980	2.0	14.2	0.0215
200	13.61	0.139^b	0.988	2.4	7.11	0.0139
299	20.34	0.209	0.9907	2.8	4.74	0.0118
499	33.95	0.350	0.9918	4.1	2.83	0.0126
798	54.30	0.534	0.990	8.0	1.85	0.0215
998	67.90	0.656	0.985	15.0	1.50	0.0436
1197	81.44	0.805	0.972	33.5	1.21	0.144
1290	87.77	Estimated critical pressure				
		T = −80.0°F = −62.2°C				
0.62	0.042	0.00	0.00	0.62	...	1.00
20	1.36	0.019^b	0.969	0.62	51.0	0.0316
40	2.72	0.038^b	0.984	0.64	25.9	0.0166
80	5.44	0.077	0.9913	0.70	12.9	0.0094
120	8.16	0.111^b	0.9936	0.77	8.95	0.0072
160	10.89	0.148^b	0.9948	0.83	6.72	0.0061
200	13.61	0.184	0.9955	0.90	5.41	0.0055
399	27.15	0.361	0.9965	1.40	2.76	0.0055
599	40.76	0.532	0.9959	2.46	1.87	0.0088
798	54.30	0.721	0.9934	5.27	1.38	0.0237
936	63.68	...	0.9867	12.4	...	...
973	66.20	0.933	0.9802	19.3	1.05	0.296
990	67.36	Estimated critical pressure				
		T = −110.3°F = −79.05°C				
0.17	0.012	0.00	0.00	0.17	...	1.00
20	1.36	0.025^b	0.9917	0.17	39.7	0.0085
40	2.72	0.051^b	0.9955	0.18	19.5	0.0047
81	5.51	0.103	0.9975	0.20	9.68	0.0028
100	6.80	0.130	0.9979	0.21	7.68	0.0024
200	13.61	0.248	0.9986	0.28	4.03	0.0019
399	27.15	0.500	0.9988	0.48	2.00	0.0024
595	40.48	0.830	0.9980	1.19	1.20	0.0118
627	42.66	0.896	0.9977	1.44	1.11	0.0221
649	44.16	0.930	0.9975	1.62	1.07	0.0357
677	46.06	0.968	0.9972	1.90	1.03	0.0875
716	48.72	Critical opalescence observed				
		T = −125.0°F = −87.2°C				
0.084	0.0057	0.00	0.00	0.084	...	1.00
20	1.36	0.028^b	0.9956	0.088	35.6	0.0045
50	3.40	0.069	0.9981	0.095	14.5	0.0020

Table I. Continued

Pressure		Composition, mole fraction methane		Butane partial press, psia	K-value	
Psia	Atm	Liquid	Vapor		Methane	Butane
			$T = -125.0°F = -87.2°C$			
100	6.80	0.144	0.9989	0.11	6.94	0.0013
200	13.61	0.290	0.99927	0.15	3.45	0.0010
299	20.34	0.444	0.99934	0.20	2.25	0.0012
399	27.15	0.608	0.99926	0.30	1.64	0.0019
449	30.55	0.728	0.99920	0.36	1.37	0.0029
499	33.95	0.871	0.99914	0.43	1.15	0.0067
549	37.35	0.972	0.99931	0.38	1.03	0.0246
578	39.33	1.00	1.00	...	1.00	...
			$T = -140.0°F = -95.6°C$			
0.035	0.0024	0.00	0.00	0.035	...	1.00
20	1.36	0.036[b]	0.9981	0.038	27.7	0.0020
50	3.40	0.091	0.99918	0.041	11.0	0.00090
100	6.80	0.180	0.99950	0.050	5.55	0.00061
200	13.61	0.360	0.99963	0.074	2.78	0.00058
299	20.34	0.573	0.99967	0.099	1.74	0.00077
354	24.09	0.732	0.99966	0.121	1.365	0.0013
386	26.26	0.875	0.99967	0.128	1.14	0.0026
404	27.49	0.934	0.99970	0.121	1.07	0.0046
441	30.01	1.00	1.00	...	1.00	...
			$T = -160.0°F = -106.7°C$			
0.010	0.0068	0.00	0.00	0.010	...	1.00
20	1.36	0.047[b]	0.99940	0.012	21.3	0.00063
49	3.33	0.116	0.99972	0.0135	8.62	0.00032
100	6.80	0.251	0.99984	0.016	3.98	0.00021
148	10.07	0.379	0.99987	0.019	2.64	0.00021
199	13.54	0.545	0.99989	0.022	1.83	0.00024
249	16.94	0.753	0.999902	0.0245	1.33	0.00040
272	18.51	0.897	0.999920	0.022	1.115	0.00078
283	19.26	0.950	0.999943	0.016	1.05	0.00114
298	20.28	1.00	1.00	...	1.00	...

[a] *n*-Butane vapor pressures from Carruth (*1*). [b] Estimated value.

mersed in liquid nitrogen, and the sample line heated to drive the last traces of sample into the cylinder; the sample cylinder was heated to room temperature or above, mixed by rotating for at least 30 min and the sample analyzed.

The existence of only a vapor phase in the cylinder was assured by the practice of heating the sample until the pressure in the cylinder was less than *n*-butane vapor pressure (at the existing temperature). The dead space in the sample valve was flushed with two sample volumes to eliminate nonequilibrium liquid. Duplicate liquid samples were taken at each point. The volume of the liquid sample line (between valves 2 and 3) was about 0.5 cc. Since the total volume of liquid present was about 30 cm^3, sampling did not appreciably affect equilibrium.

Results

Experimental data are tabulated in Table I. The methane solubility in the liquid at low pressures was calculated by assuming a linear relationship between methane partial pressure and solubility (Henry's Law). Because of liquid sampling problems, it was felt that these calculated values were at least as good as measured values in the 5% (or less) methane concentration range. The measured methane vapor pressures agree with critically evaluated values (*11*) within 2 psi.

Pressure-composition relationships are shown in Figure 2, and Figure 3 shows the dew-point (vapor composition) curve in the near-critical region on an expanded scale. This unusual shape of the dew-point curve near the methane critical temperature confirms that recently reported (2) for the same system. Most of the vapor compositions are omitted from Figure 2 in the interest of simplicity (many of them are nearly pure methane).

The effect of total pressure on the *n*-butane partial pressure (Py) is illustrated in Figure 4. This enhancement of the vapor phase with the heavy component has been used in the past to calculate interaction virial coefficients (*3, 4, 6*), particularly for gas-solid systems. However, its value in testing the accuracy of vapor compositions in vapor-liquid systems has either not been recognized or not emphasized previously. Obviously, one end point of the curve must be the vapor pressure of the pure heavy component. For a super-critical gas-liquid system, this function increases with pressure to the critical point even though the composition (fraction butane) goes through a minimum. For temperatures below the critical point of methane, this function increased with pressure to near the methane vapor pressure and then abruptly decreased. This decrease is consistent, of course, since it must be zero at the methane vapor pressure.

This empirical testing method was used for numerous supercritical gas-liquid equilibria data in the literature. Seldom did the smoothness of the data approach the accuracy claimed by the experimenter. At times, the extrapolation of the partial pressure to the pure component vapor pressure did not agree with accepted values within an order of magnitude.

Figure 5 presents the *K* vs. pressure relationship which is quite useful in engineering work. The end point of these curves at the high pressure is either the vapor pressure of methane or the critical pressure of the mixture. The critical pressures were established by either visual observation or by extrapolation of the *K*-*P* plot to 1.0. The critical pressure-temperature relationship (Figure 6) does not agree with previously published values in the low-temperature region. Further work should be done on this relationship since it is important as an "anchor point" on the *K* curves.

Discussion of Errors

Temperature measurements with a platinum resistance thermometer are normally considered accurate to 0.01°C. However, for this work, the full potential of the PRT was not utilized for the sake of efficiency. The temperature deviations between points on the same isotherm

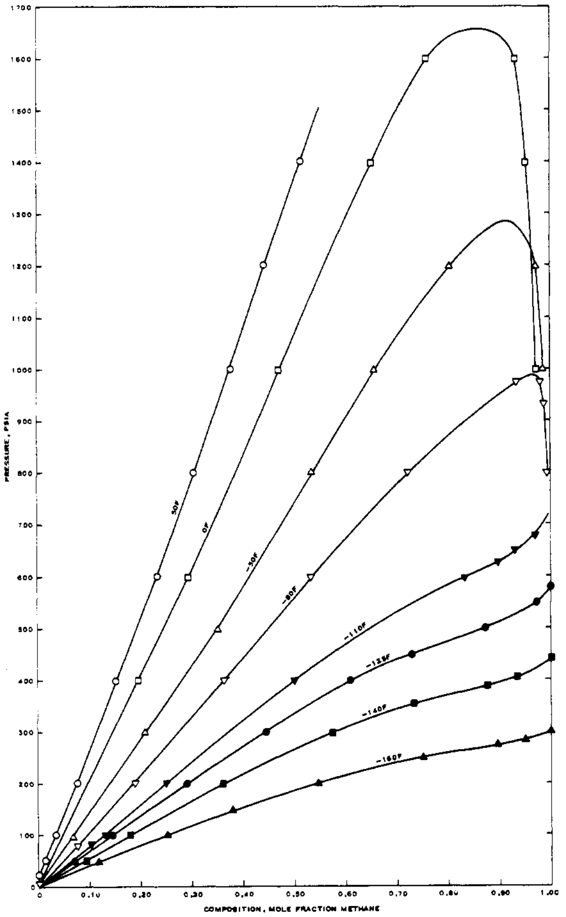

Figure 2. Isothermal pressure-composition diagram for methane–*n*-butane

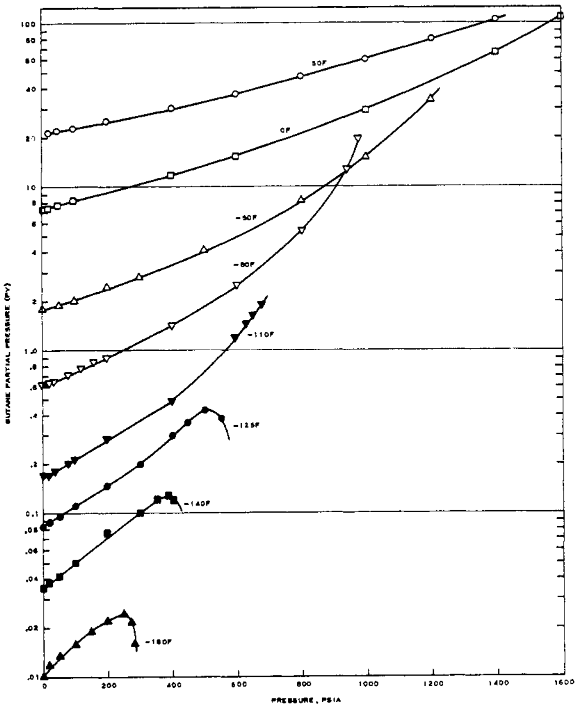

Figure 4. Enhancement of vapor phase with *n*-butane

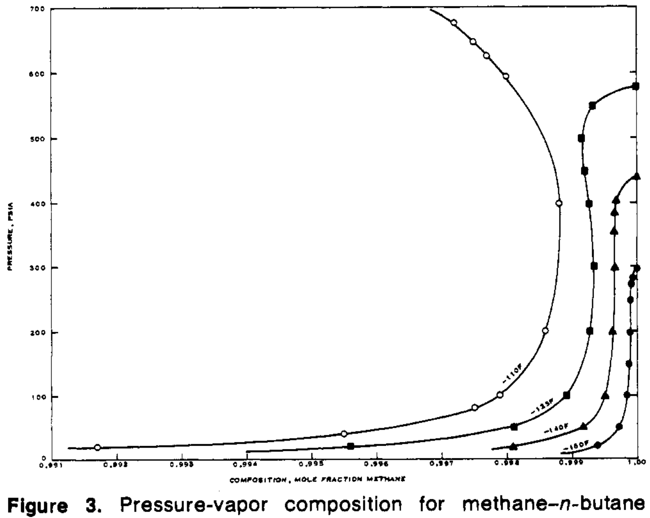

Figure 3. Pressure-vapor composition for methane–*n*-butane (expanded scale)

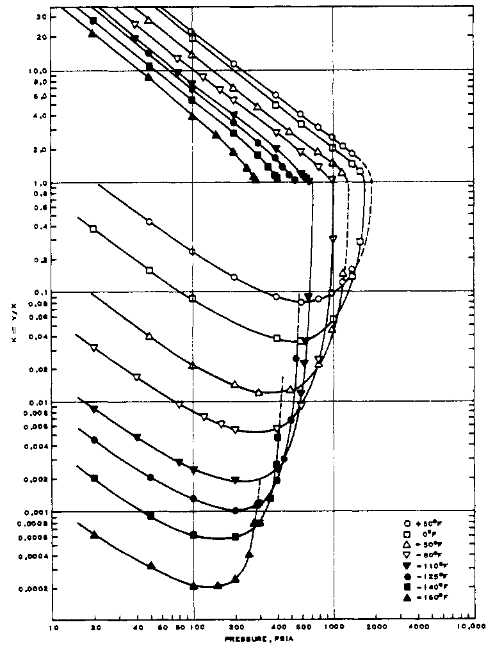

Figure 5. Isothermal *K* values for methane–*n*-butane

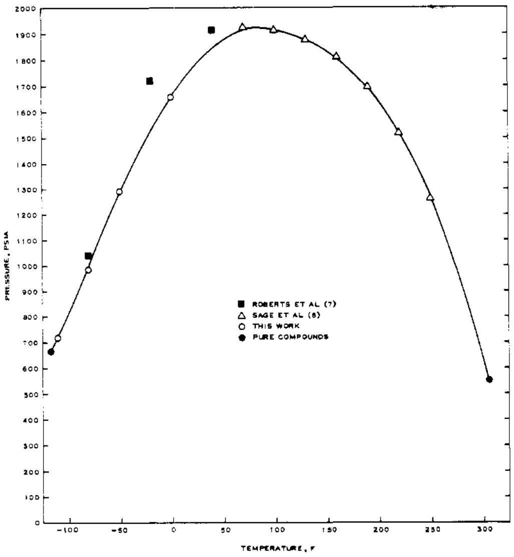

Figure 6. Critical locus for methane–*n*-butane

were within ±0.1°F. The pressure, measured with a calibrated Heise gage, could be read to the nearest pound. Based on the comparison with pure methane vapor pressure, the maximum error should be 2 psi. This error is consistent with that normally considered for a precise Bourdon tube gage (0.1% of full-scale reading).

The composition of duplicate vapor samples agreed to within 2% of the amount of minor component present even at the very low temperatures. However, based on the deviations from a smooth enhancement curve (Figure 4), several of the points are off somewhat more than that.

All of the above considerations are dwarfed to nearly insignificance by the problems involved in obtaining the right liquid sample for analysis. Once the sample is taken, it is not difficult to make the analysis to ±2% of the amount of minor component present. However, duplicate samples taken from the cell, even with the complicated sampling technique, sometimes deviated by 5–10% of the minor component present. This was particularly true when the butane concentration of the liquid was less than 10 mol %.

In view of these considerations, a somewhat subjective estimate of error in the *K* values is 2% for the bulk of the data to 10% for the butane value as the methane vapor pressure or the critical pressure is approached.

Acknowledgment

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Vapor-Liquid Equilibrium of Methane-*n*-Butane System at Low Temperatures and High Pressures

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Measurements of the bubble-point compositions are reported and combined with dew-point data to give *K*-values for the methane–*n*-butane system at 40°, 0°, −20°, −40°, −60°, −80°, −100°, −116.6°, −120°, −140°, −160°, −180°, and −200°F from the vapor pressure of *n*-butane up to the critical point or the vapor pressure of methane. Experimental conditions were selected so that direct isobaric observations were also possible.

Low-temperature *K*-values for methane–alkane binary systems with alkanes heavier than propane are scarce in the literature. Moreover, the majority of those that do exist are of such poor quality that they confuse rather than enhance correlation efforts. This is due primarily to experimental difficulties encountered in measuring dew-point concentrations at low temperatures where the concentration of the heavy component in the vapor phase is small.

A method developed to circumvent this problem was recently described by Chen et al. (*6*). This method employs the "elution" technique used by Carruth (*2*) to measure extremely low vapor pressures.

Experimental *K*-values, obtained by combining the vapor-phase measurements of the elution method with those obtained for the liquid phase by use of the more conventional gas chromatography measurements, are presented here for the CH_4-*n*-C_4H_{10} binary system.

Experimental Apparatus

In the elution technique, dew-point concentration data are determined by metering pure gaseous methane through a temperature-controlled cell containing *n*-butane. The methane stream leaving the cell (saturated with *n*-butane) is passed through a thermal conductivity

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