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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detector where its concentration is measured differentially with respect to a metered pure methane stream. Concentration measurements as low as 10^{-5} in the mole fraction of n-butane were accurately detected by use of this technique. A more detailed description of this procedure is presented elsewhere (6).

The applicability of the elution technique was restricted to mixture concentrations less than 3% n-butane owing to detector sensitivity limitations. Accordingly, bubble-point concentrations (and some dew-point concentrations) were measured with the more conventional gas chromatography technique. The apparatus used was an improved version of the vapor-recycle type similar to that previously reported by Chang et al. (3) and later by Wichterle and Kobayashi (12). This was the first investigation performed with this equipment.

A simplified schematic line diagram of the apparatus is given in Figure 1. The equilibrium cell was constructed by the Mechanical Engineering Machine Shop and has a volume of approximately 80 ml. The vapor was recirculated through the cell with a Ruska magnetic pump (9) which was connected to a variable speed motor. The Dewar flask was mounted in a Riki box (12) so that it could be lowered without moving the equilibrium cell or any flow lines.

Special sampling valves with a temperature-compensated packing gland were mounted directly on the equilibrium cell body with a temperature-compensated seal arrangement. These sampling valves were used simultaneously for expansion of the high-pressure sample to atmospheric pressure and for sample flow rate control. The liquid-phase sample line capillary ended close to the center of the equilibrium cell at the lowest possible position to ensure that samples were drawn from the condensed phase. The vapor-phase capillary tube protruded from the cell wall into the equilibrium chamber near the top of the cell window. The dead volume for both sampling systems from the orifice of the capillary to the needle of the valve was approximately 0.06 ml. The sample lines were insulated and heated to prevent condensation between the sample valve and the chromatograph.

A sampling procedure similar to that employed by Wichterle was used. The problem of nonhomogeneous evaporation of the liquid phase in the sample line which he encountered was more pronounced with the methane–n-butane mixture. Various combinations of mixer volumes and configurations were tried in the liquid sample line to homogenize the sample. The optimum mixer configuration was a stirred pot with a volume of approximately 200 ml.

The gas or liquid phase sample was introduced into the sample loop (volume approximately 0.25 ml) of the gas chromatograph and then bubbled through a small column of water to indicate the flow rate of the sample. Thus, the apparatus always had atmospheric pressure at the end of the sample line.

A Barber-Colman gas chromatograph Series 5000 Selecta system with flame ionization detection was used for analysis. The chromatographic column was made from a 2-ft length of ⅛-in. o.d. stainless-steel tubing packed with 80–100 mesh fire brick loaded with 10 wt % squalene. The signal from a flame ionization detector was integrated by an Autolab Model 6300 digital integrator and recorded on an L&N strip chart recorder. Temperature was measured by a Leeds & Northrup certified platinum resistance thermometer calibrated against a National Bureau of Standards reference. The resistance was measured by a Mueller bridge with an accuracy of 0.001 ohms which corresponds to a temperature accuracy of 0.01°C. The bath temperature was automatically controlled to ±0.02°C. Liquid nitrogen cooled the isohexane bath.

Temperatures are reported on the IPTS (1968) scale.

The pressure in the system was indicated by two (0–300 and 0–2000 psia) Heise gages calibrated against a dead-weight gage certified by the National Bureau of Standards. The accuracy of Heise gages is 0.1% of the full scale reading.

Procedure

The entire system was evacuated initially and then flushed with methane. After adjustment of the bath temperature, n-butane was charged into the cell directly from the cylinder. The desired pressure was set by addition of methane, with fine adjustment achieved by means of a 100-ml proportioning pump. Further adjustments of the pressure were necessary during early stages of circulation. As the equilibrium pressure was approached, the sample line was opened to give a slight withdrawal of the phase from the cell. The flow rate of the sample was ad-
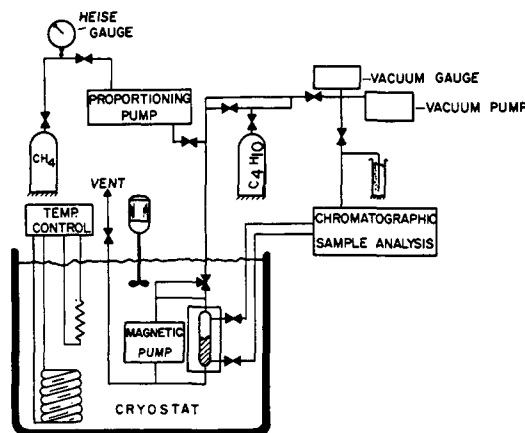

Figure 1. Schematic diagram for recycle vapor-liquid equilibrium apparatus

Table I. Experimental Data Not Included in Table II

Temp, °F	Press, psia	Methane mole fraction		
		x	y	y^a
+40.00	40.0		0.54374	
	60.0		0.68136	
	80.0		0.75222	
	100.0	0.04258	0.80151	0.79640
	200.0	0.08986	0.89032	0.88958
	400.	0.17594	0.93559	0.93127
	600.	0.25365	0.94784	0.94248
0.01	20.4		0.63609	0.58966
	25.4		0.70048	0.69215
	50.4		0.84281	0.83704
	100.4		0.91824	0.91608
	900.	0.42659		
	1300.	0.58570		
	1500.	0.68110		
−19.97	1300.	0.65795		
	1300.	0.66139		
	1350.	0.68961		
−99.88	650.	0.73466		
	780.	0.96868		
−116.62	550.	0.82698		
−159.97	30.0	0.08219		
−179.99	174.0	0.91735		
−200.01	75.0	0.47812		

^{a} Experimental "elution" dew-point data.

Table II. Vapor-Liquid Equilibrium of Methane–n-Butane System

x Methane	y Methane	Psia	Atm	K methane	K n-butane
		$T = 40.00°F = 499.67°R = 4.44°C = 277.59K$			
0.0000	0.0000	17.66[a]	1.202[a]	101.0[b]	1.000
0.04258	0.796	100.4	6.832	18.7	0.213
0.08986	0.890	200.4	13.636	9.90	0.121
0.1339	0.9176	300.4	20.440	6.852	0.0952
0.1759	0.9313	400.	27.217	5.293	0.08340
0.2152	0.9385	500.	34.022	4.361	0.07833
0.2536	0.9425	600.	40.826	3.716	0.07707
0.3262	0.9469	800.	54.435	2.903	0.07881
0.3976	0.9459	1000.	68.044	2.379	0.08983
0.4651	0.9390	1200.	81.652	2.019	0.1139
0.5331	0.9294	1400.	95.261	1.743	0.1512
0.6078	0.9100	1600.	108.870	1.497	0.2296
0.6558	0.8967[c]	1700.	115.674	1.367	0.3002
0.7278	0.8460[c]	1800.	122.478	1.162	0.5659
0.7828	0.7828[c]	1822.[d]	123.975[d]	1.000	1.000
		$T = 0.01°F = 459.68°R = -17.77°C = 255.38K$			
0.0000	0.0000	7.25[a]	0.493[a]	22.5[b]	1.000
0.02570	0.837	50.4	3.429	32.6	0.167
0.05591	0.9161	100.4	6.832	16.38	0.08889
0.1124	0.9516	200.3	13.629	8.467	0.05448
0.1643	0.9639	300.4	20.440	5.867	0.04325
0.2135	0.9689	400.	27.217	4.538	0.03948
0.2580	0.9716	500.	34.022	3.766	0.03831
0.3455	0.9729	700.	47.630	2.816	0.04143
0.3905	0.9728	800.	54.435	2.491	0.04458
0.4651	0.9696	1000.	68.044	2.084	0.05692
0.5466	0.9625	1200.	81.652	1.761	0.08261
0.6326	0.9499	1400.	95.261	1.502	0.1363
0.7498	0.9175	1600.	108.870	1.224	0.3299
0.8543	0.8543[c]	1652.[d]	112.408[d]	1.000	1.000
		$T = -19.97°F = 439.70°R = -28.87°C = 244.28K$			
0.0000	0.0000	4.326[a]	0.294[a]	320.[b]	1.000
0.06304	0.9488	100.2	6.818	15.05	0.05463
0.1237	0.9703	200.3	13.629	7.846	0.03388
0.2335	0.9801	400.	27.217	4.197	0.02598
0.3325	0.9818	600.	40.826	2.953	0.02726
0.4223	0.9809	800.	54.435	2.323	0.03307
0.5101	0.9772	1000.	68.044	1.916	0.04650
0.6062	0.9688	1200.	81.652	1.598	0.07911
0.7189	0.9498	1400.	95.261	1.321	0.1785
0.8059	0.9150[c]	1500.	102.065	1.135	0.4382
0.8605	0.8605[c]	1515.[d]	103.086[d]	1.000	1.000
		$T = -39.95°F = 419.72°R = -39.97°C = 233.18K$			
0.0000	0.0000	2.439[a]	0.1660[a]	530.[b]	1.000
0.07208	0.9703	100.3	6.825	13.46	0.03200
0.1400	0.9827	200.3	13.629	7.021	0.02016
0.2655	0.9878	400.	27.217	3.721	0.01655
0.3739	0.9882	600.	40.826	2.643	0.01881
0.4804	0.9868	800.	54.435	2.054	0.02548
0.5875	0.9822	1000.	68.044	1.672	0.04326
0.6948	0.9705	1200.	81.652	1.397	0.09661
0.7886	0.9608	1300.	88.457	1.218	0.1853
0.8549	0.9318[c]	1350.	91.859	1.090	0.4699
0.9097	0.9097[c]	1355.[d]	92.199[d]	1.000	1.000
		$T -59.95°F = 399.72°R = -51.08°C = 222.07K$			
0.0000	0.0000	1.285[a]	0.0874[a]	905.[b]	1.000
0.08202	0.9840	100.2	6.818	12.00	0.01746
0.1586	0.99034	200.3	13.629	6.246	0.01149
0.2981	0.99298	400.	27.217	3.331	0.01001
0.4284	0.99262	600.	40.826	2.317	0.01290
0.5564	0.99046	800.	54.435	1.780	0.02150
0.7056	0.9843	1000.	68.044	1.395	0.05342
0.8001	0.9774	1100.	74.848	1.221	0.1132
0.8637	0.9648[c]	1150.	78.250	1.117	0.2579
0.9326	0.9326[c]	1169.[d]	79.543[d]	1.000	1.000

Table II. Continued

x Methane	y Methane	Psia	Atm	K methane	K n-butane
		$T = -79.97°F = 379.70°R = -62.21°C = 210.94K$			
0.0000	0.0000	0.625[a]	0.04253[a]	1635.[b]	1.000
0.1889	0.99506	200.0	13.609	5.267	0.006094
0.3523	0.99608	400.	27.217	2.828	0.006049
0.5104	0.99546	600.	40.826	1.950	0.009275
0.6954	0.99271	800.	54.435	1.428	0.02395
0.8232	0.9896	900.	61.239	1.202	0.05863
0.9036	0.9862	950.	64.641	1.091	0.1431
0.9591	0.9591[c]	973.[d]	66.206[d]	1.000	1.000
		$T = -99.88°F = 359.79°R = -73.27°C = 199.88K$			
0.0000	0.0000	0.276[a]	0.0188[a]	3000.[b]	1.000
0.2267	0.99757	200.1	13.616	4.400	0.003146
0.3261	0.99794	300.3	20.433	3.060	0.003060
0.4267	0.99795	400.	27.217	2.339	0.003579
0.5322	0.99770	500.	34.022	1.875	0.004921
0.6591	0.99715	600.	40.826	1.513	0.008372
0.8296	0.99584	700.	47.630	1.200	0.02441
0.9257	0.99445	750.	51.033	1.074	0.07465
0.9829	0.9829[c]	792.[d]	53.890[d]	1.000	1.000
		$T = -116.62°F = 343.05°R = -82.57°C = 190.58K$			
0.0000	0.0000	0.12506[a]	0.0085[a]	5700.[b]	1.000
0.1466	0.99814	100.1	6.811	6.808	0.002181
0.2773	0.99880	199.7	13.588	3.601	0.001661
0.3988	0.99895	299.7	20.393	2.505	0.001748
0.5314	0.99889	400.	27.197	1.880	0.002367
0.7031	0.99866	500.	34.029	1.420	0.004513
0.9469	0.99823	600.	40.826	1.054	0.03333
1.000	1.000	671.[e]	45.657[e]	1.000	1.000
		$T = -119.37°F = 340.30°R = -84.09°C = 189.06K$			
0.0000	0.0000	0.109[a]	0.0074[a]	6500.[b]	1.000
0.1526	0.99835	101.1	6.879	6.540	0.001948
0.2860	0.99896	201.0	13.677	3.493	0.001463
0.4150	0.999083	300.3	20.433	2.408	0.001567
0.5521	0.999049	400.	27.217	1.810	0.002123
0.7511	0.99875	501.	34.069	1.330	0.005021
0.9009	0.99861	550.	37.424	1.108	0.01400
0.9808	0.99873	600.	40.826	1.018	0.06619
1.000	1.000	636.[e]	43.276[e]	1.000	0.310[f]

justed to approximately 1 bubble/sec, determined as an optimal rate. (A higher flow rate would cause excessive pressure drop in the equilibrium cell.) Above 200–600 psia (determined by the temperature), the amount withdrawn did not affect the pressure in the cell. At lower pressures, small amounts of methane were added by manual operation of the proportioning pump to compensate for pressure drop in the cell. The recycle pump was operated continuously at a slow speed during sampling of both phases. At least six analyses were made of each sample. Where experimental conditions dictated mixing of the liquid sample, a minimum of 10 analyses were made.

The bubble-point data were taken after completion of the dew-point investigation (4), and several experimental dew points were measured chromatographically to check the consistency of both experimental procedures. These points, which agreed within the combined accuracy of both experimental procedures, are tabulated in Table I along with bubble-point data taken at conditions where no experimental dew-point data were taken. At conditions near the critical point of the mixtures, the elution dew-point data deviated largely from the chromatographically determined values. This deviation has been ascribed to the absence of equilibrium conditions in the elution cell, and the chromatographically determined dew points have

been used to calculate the corresponding K-values (Table II, footnote c). The subsequent addition of a vapor recirculating magnetic pump to the elution cell appears to have resolved this problem for a recently completed dew-point investigation of the methane–n-pentane system (5).

Previous studies in this laboratory have shown that experimental difficulties increase as the temperature decreases; therefore, this investigation began with the +40°F isotherm followed by 0°, −20°, −40°, −60°, −80°, −100°, and −140°F studies. The problem of the liquid sample mixing increased as the temperature decreased, and various mixer configurations were tried during this time. After the −140°F study, the optimum 200-ml stirred pot mixer was installed, and the calibration of the chromatograph repeated. Sequentially, the −180°, −200°, −120°, and −116.62°F studies were made. Finally, about 20 experimental points at the higher temperatures were repeated. Additional experimental points were also taken to check the consistency of the measurements and to fill in regions of uncertainty or rapid change, principally in the high-pressure region.

Material Used

Ultra high-purity methane was purchased from Matheson Gas Products Co. The gas was reported to analyze at

Table II. Continued

x Methane	y Methane	Psia	Atm	K methane	K n-butane
		$T = -139.96°F = 319.71°R = -95.53°C = 177.62K$			
0.0000	0.0000	0.0360[a]	0.00245[a]	14800.[b]	1.000
0.09796	0.999001	50.0	3.402	10.20	0.001107
0.1879	0.999391	100.1	6.811	5.319	0.0007499
0.2804	0.999531	149.8	10.193	3.564	0.0006520
0.3716	0.999597	199.9	13.602	2.690	0.0006413
0.5812	0.999651	299.9	20.406	1.720	0.0008333
0.7288	0.999651	350.	23.815	1.372	0.001287
0.9370	0.999671	400.	27.217	1.067	0.005225
0.9793	0.999767	420.	28.578	1.021	0.011236
0.9841	0.999767	420.	28.578	1.016	0.01462
1.000	1.000	440.[e]	29.939[e]	1.000	0.025[f]
		$T = -159.97°F = 299.70°R = -106.65°C = 166.50K$			
0.0000	0.0000	0.0106[a]	0.0007[a]	34000.[b]	1.000
0.1370	0.999656	50.0	3.402	7.299	0.0003986
0.2640	0.999801	100.0	6.804	3.787	0.0002704
0.3930	0.999831	150.0	10.207	2.544	0.0002784
0.5451	0.999866	200.0	13.609	1.834	0.0002946
0.7910	0.999911	250.0	17.011	1.264	0.0004258
1.000	1.000	296.[e]	20.141[e]	1.000	0.0040[f]
		$T = -179.99°F = 279.68°R = -117.77°C = 155.38K$			
0.0000	0.0000	0.00264[a]	0.0002[a]	77000.[b]	1.000
0.08016	0.999828	20.1	1.368	12.47	0.0001870
0.1925	0.999901	50.1	3.409	5.194	0.0001226
0.3860	0.999940	100.1	6.811	2.591	0.0000977
0.6678	0.999948	150.1	10.213	1.497	0.0001565
1.000	1.000	187.[e]	12.724[e]	1.000	0.00086[f]
		$T = -200.01°F = 259.66°R = -128.89°C = 144.26K$			
0.0000	0.0000	0.0005	0.00004	160000.[b]	1.000
0.1492	0.999960	25.2	1.715	6.701	0.0000470
0.3006	0.999971	49.9	3.395	3.326	0.0000415
0.8173	0.999983	99.9	6.798	1.223	0.0000931
1.0000	1.000	115.[e]	7.825[e]	1.000	0.00022[f]

[a]Saturated vapor pressure of n-butane. [b]$K_{CH_4}{}^\infty$. [c]Bubble-point analysis by gas chromatography. [d]Critical pressure. [e]Saturated vapor pressure of methane. [f]$K_{nC_4H_{10}}{}^\infty$.

least 99.97% methane, with the total amount of major impurities as 105 ppm. Research grade n-butane (99.93%) was also purchased from Matheson Gas Products Co. No impurities were detected in either gas on chromatographic analysis.

Error Analysis

The error in the K-values was not constant, because the errors in the temperature, pressure, and composition varied over the wide range of this investigation. The error analysis is further complicated by the fact that most of the K-values are determined from two mutually independent experiments. Any absolute error in the K-value owing to a variable v is given by

$$\epsilon K_v = \frac{\Delta K}{\Delta v} \epsilon v \tag{1}$$

The percent error is

$$\delta K_v = \frac{\epsilon K_v}{K_{mean}} 100 \tag{2}$$

The error from any variable is maximal where the largest change of K with that variable occurs. For temperature this occurs between the two lowest isotherms. From Figures 3–5, the maximum change of K with respect to the pressure occurs only at very high or low pressures at constant temperature. Also, it is obvious that the error owing to the pressure is zero at the minimum of the log K–log P curve. It is estimated that at least 80% of the results have an error in the K-values owing to pressure of 0.5% or less. The n-butane K-values have larger errors from pressure in the region where the K-curve is essentially vertical. These errors are 3–5% at the end of the data and become indeterminant in the region of no data near convergence pressure, where the K-value approaches 1.0 or K^∞.

The error introduced from the concentration measurements arises from several sources. The overall error in the dew-point concentration measurements is reported (6) to be the larger of 2% or 0.00001 in the mole fraction of n-butane. The error in the bubble-point measurements arises from a combination of both sampling problems and uncertainties in the chromatographic analysis.

The ratio of the mole fraction of methane, x_1, to that of n-butane, x_4, was determined from the following equation:

$$x_1/x_4 = \frac{f_{14} (A_1/A_4)}{1 + f_{14} (A_1/A_4)} \tag{3}$$

The peak area factor, f_{14}, was found by calibrating the chromatograph with gravimetrically prepared samples for
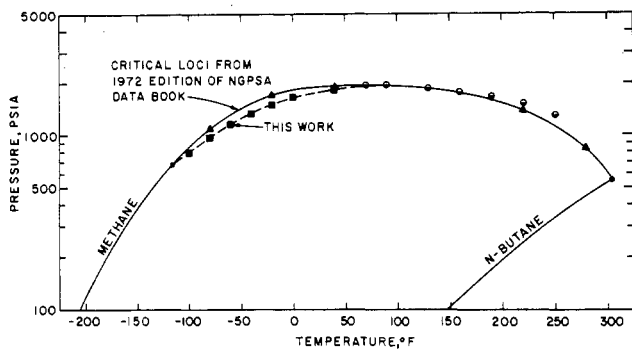
Figure 2. Comparison of NGPSA methane–n-butane critical loci to that determined in this study. ● Critical point of pure component, ■ this work, ▲ McKetta and coworkers, ◓ Sage et al.
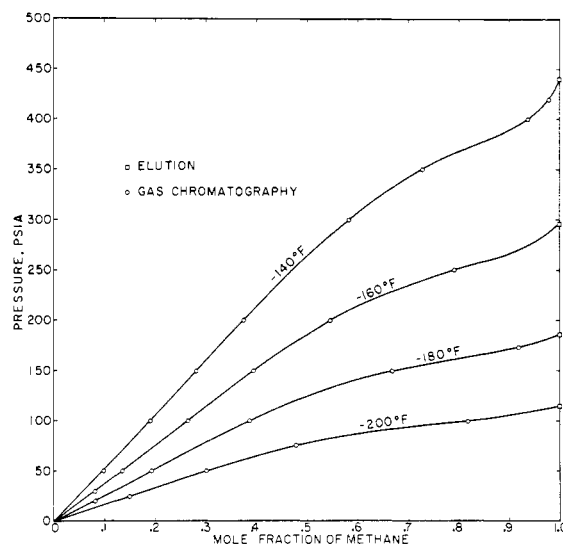

Figure 5. Pressure-composition diagram for methane–n-butane system at lowest temperatures: −140°, −160°, −180°, −200°F
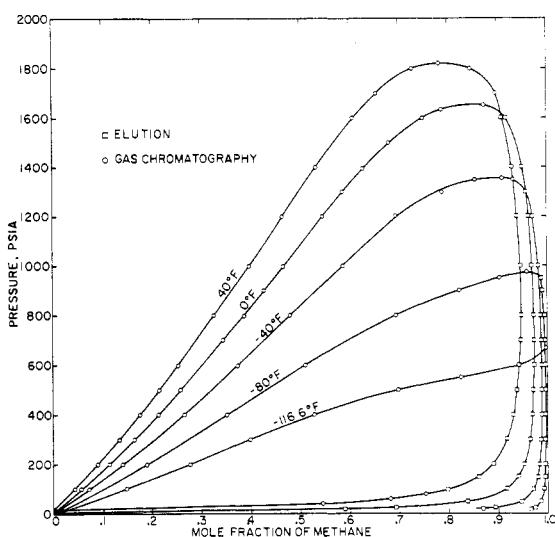

Figure 3. Pressure-composition diagram for methane–n-butane system at five temperatures: 40°, 0°, −40°, −80°, −116.6°F
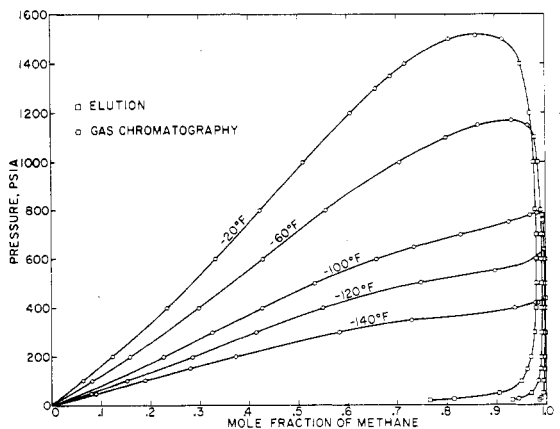

Figure 4. Pressure-composition diagram for methane–n-butane system at five temperatures: −20°, −60°, −100°, −120°, −140°F
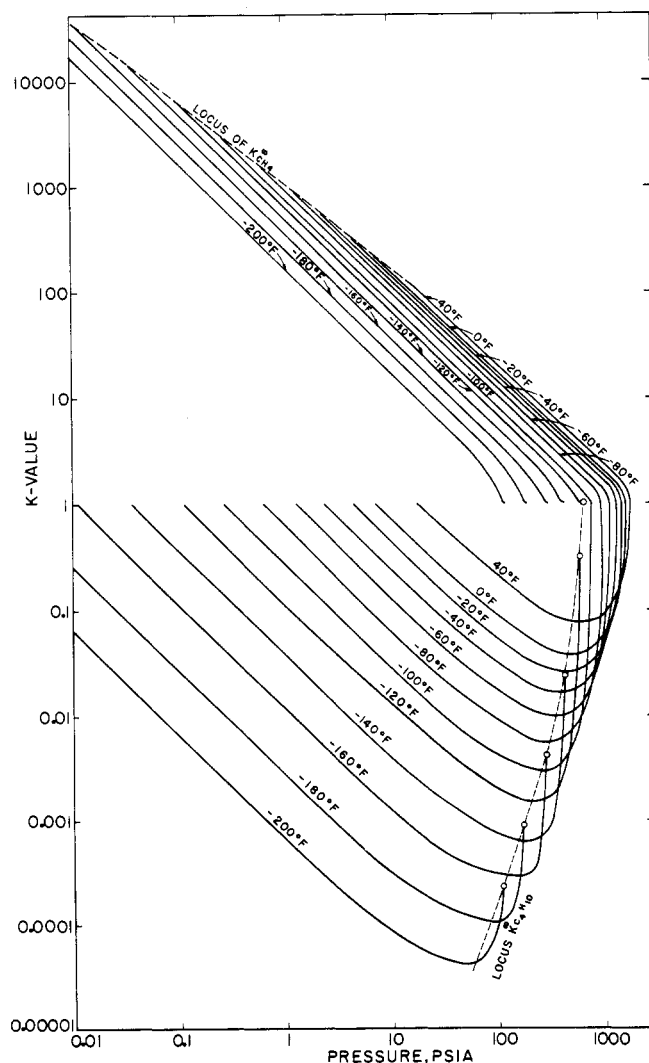

Figure 6. K-value vs. pressure along isotherms for methane–n-butane system from 40° to −200°F

peak area ratios, A_1/A_4, corresponding to a 1–98 mol % methane concentration range.

The peak area ratio was determined by the digital integrator to an accuracy of better than 1% for most of the points. Larger errors in the area ratio occurred for some low-temperature liquid-phase samples where the sample line mixer performance was not entirely adequate. The uncertainty associated with all points was statistically reduced by repetition of the analyses. Errors introduced by the chromatograph calibration are estimated to be 0.4% of the area factor.

The sum of these errors in the absolute mole fraction is estimated to be 2% or a maximum error of 0.005 in the mole fraction. The reproducibility of the individual measurements was within these limits. The resulting error in the K-value from the concentration measurements was calculated positive in y and negative in x, to give a maximum possible error. However, the vast majority of the data are good to four significant figures.

Results

The experimental results for the methane–n-butane binary are tabulated in Table II. The experimental measurements were made in °F and psia. The computer computations included conversion to other units given in Table II. Only those points where both x and y were experimentally determined are shown. Additional dew-point data are available (4). A comparison of the critical loci determined in this study with that which is widely used in industry (7) is shown in Figure 2. The results of this investigation indicate significant deviations in the low-temperature range. This range of the NGPSA critical loci is based on the experimental results of McKetta and coworkers (8, 11) from +40° to −140°F. The results of the work presented herein appear to be consistent with the high-temperature range which is based on the data of Sage et al. (10) from 70° up to 250°F. Figures 3–5 illustrate the pressure vs. composition behavior of the methane–n-butane system. Thirteen isotherms are shown ranging from +40° to −200°F with the curves constructed from data obtained by both experimental procedures.

Figure 6 gives the usual K-value vs. pressure representation of a binary system. The vapor pressures used for the limiting conditions (K = 1.0 for n-butane and the limiting conditions ($K = 1.0$ for n-butane and $K^\infty CH_4$) were obtained from the API table (1) and Carruth (2). The region below 0.01 psia is not shown, but the vapor-pressure data for this region were used in constructing the figure.

Acknowledgment

This is the first investigation to be made on a newly constructed equilibrium apparatus. The late W. E. A. Ruska designed many features, including the temperature compensation packings and the submersible magnetic pump. Ray Martin of the University Machine Shop constructed the equipment in an innovative fashion.

Nomenclature

A = peak area from chromatograph
f_{14} = peak area factor for A_1/A_4
K = ratio of vapor concentration to liquid concentration
v = variable
x = liquid concentration, mole fraction
y = vapor concentration, mole fraction
∞ = superscript denoting limiting value for the subscripted component at the limiting other pure component vapor pressure

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