Nomenclature

a = constant in Equation 2, mm Hg l./g-mol, °C
b = constant in Equation 2, mm Hg l./g-mol
c = concentration, g mol/l.
H = Henry coefficient, mm Hg l./g-mol
K = consistency index, g/cm sec^{2-n}
n = flow behavior index
p = partial pressure of gas, mm Hg
t = temperature, °C

Greek Letters

γ = shear rate, sec^{-1}
τ = shear stress, g/cm sec

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Dew-Point Loci for Methane-*n*-Butane Binary System

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The dew-point loci for the binary system of methane and normal butane were determined at 13 temperatures from +40° to −200°F. The pressure range covered from 20 up to near 1900 psia. A constant flow gas saturation technique was developed and used for the experimental study. The existence of triple-valued dew points in a narrow concentration range was observed for isotherms at and immediately below the critical temperature of pure methane.

Equilibrium data for binary systems of methane and heavier alkanes are important both for practical and for theoretical purposes. Accurate *K*-value data are needed for the design of process units in petroleum industries. The data can also be used to extract the interaction coefficients which are often required in the equilibrium computations for multicomponent systems. Earlier studies of equilibrium in the low temperature range for binary systems of methane with other alkanes heavier than propane are either incomplete or inconsistent. This has been caused by the difficulties in the determination of the dew-point concentrations.

The concentration of the heavier component in the vapor phase becomes small as the system temperature goes down. The ordinary chromatographic method will be inaccurate because errors are caused by adsorption on the tube wall. Also, characteristics of the packing material for the chromatographic column and the sampling technique become more significant. Calibration of the chromatographic detector becomes more difficult since it is difficult to prepare a very dilute mixture without appreciable errors.

A constant flow gas saturation technique (*1*) has been developed to measure the dew-point concentration. This method is especially useful to determine the trace amount of the heavier component in the vapor phase.

Experimental Method

The main equipment components which were used in the constant flow saturation method consisted of a 410 stainless-steel windowed cell with a pressure rating of 8000 psi, a cryostatic bath, a carrier gas metering pump, and analytic equipment. For details of the equipment and

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method, please refer to the earlier paper (*1*) by the authors.

The flow chart of the equipment layout is shown in Figure 1. Pure methane flow is metered by the carrier gas metering pump. The methane flow passes through the bypass line for a period of time to clear out impurities in the system. The equilibrium cell and presaturator are first evacuated, and then charged with normal butane. The cell and presaturator are immersed in a stirred cryogenic bath which is controlled at the desired temperature. After thermal equilibrium is attained, the bypass line is shut off, and the pure methane passes through the precooler to bring the stream temperature to the bath temperature; then it flows through a presaturator made of three 1-ft long sections of ⅛-in. stainless-steel pipes connected in series, packed with Chromopacks which were presaturated with normal butane. Finally, the gas stream enters from the bottom of the equilibrium cell, which is filled with the heavier hydrocarbon and small glass beads to disperse the gas flow through the liquid.

The effluent dew-point gas mixture is expanded to atmospheric pressure and measured continuously by a thermal conductivity cell and recorder. A steady-state condition produces a steady signal on the recorder and a constant cell pressure and pump pressure. After the steady signal voltage on the recorder has been registered, the pure methane flow is again switched to the bypass line to clear out the mixture and to recheck the base line. The concentration of the mixture is determined by a calibration curve from the signal difference between the mixture and pure methane.

The detector was calibrated in a steady flow manner to preserve the similarity to the conditions of obtaining data. A specially designed micropump (*5*) pumped normal butane at a slow rate into the mixing valve, where pure methane was metered by the carrier gas metering pump to mix with the hydrocarbon stream. The mixed gas stream was passed into the thermal conductivity cell where a signal was produced by using pure methane as the reference stream. A pressure transducer was installed at the top of the micropump. When steady state is obtained, the pressure in the carrier gas pump and micropump will stay constant, and the signal from the thermal conductivity cell will also stay at a constant value. The concentration of the mixture can be calculated from the flow rate of both pumps.
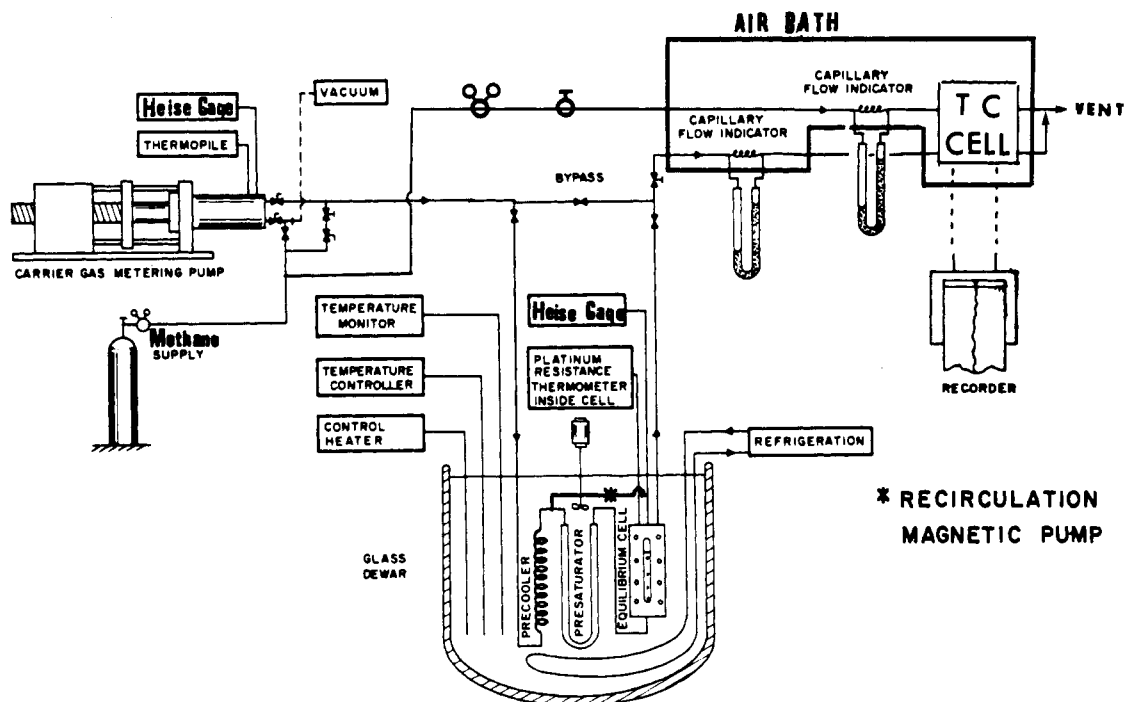
Figure 1. Schematic flow diagram for apparatus used for isothermal dew-point measurements. Equipment specially designed and calibrated for extremely low concentrations. Note methane carrier gas passes through both sides of TC cell, thus effectively canceling response from any impurities in that gas
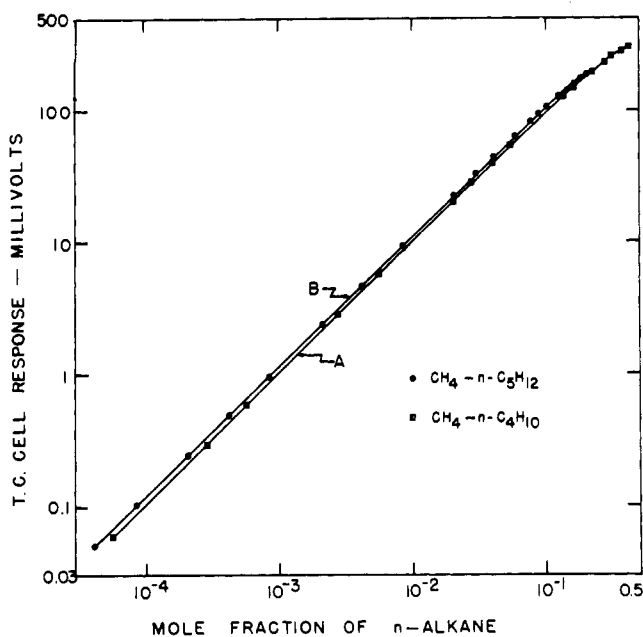

MOLE FRACTION OF n-ALKANE

Figure 2. Calibration curves for TC cell by use of micropump (5)

Both pumps were kept in thermally controlled (±0.1°C) air baths to make correct density evaluations and also to eliminate flow fluctuations. Mixtures of various concentrations can be prepared by varying the micropump speed. A mixture stream as dilute as 10^{-7} mole fraction can be prepared. The lower limitation of detection actually is restricted by the sensitivity of the detector. The lower detection limit has been about 10 ppm with the thermal conductivity cell used in this work. The calibration curve of this detector for the methane–n-butane binary system is shown as curve A in Figure 2. The concentration covered ranges from 10^{-5} to 0.4 mole fraction of n-butane in methane. The response of the detector

was linear from 6×10^{-5} to 0.1 mole fraction; concentrations more than 0.1 gave a curved response. The response curve was fit by a linear equation and a fifth-order polynomial for the respective regions by the least-squares method.

The data were taken over two time periods. In the first period, the data were taken up to 700 psia for each isotherm. At the end of this period, one cylinder of pure methane was almost exhausted; then a switch to another high-pressure cylinder was made to complete the high-pressure portions of isotherms above the critical temperature of methane. The joint points for each isotherm were redetermined; they were in good agreement with the previous determination within experimental errors.

Materials

The n-butane used in this investigation was donated by Phillips Petroleum Co. The n-butane was research grade with purity of 99.93%. The pure methane was purchased from Matheson Gas Products. It was ultra high-purity grade with purity of 99.97% minimum. No further checks for purity over these manufacturer's specifications were made. Since the signals from the thermoconductivity detector were obtained by comparing the mixture and pure methane stream which were originated from the same source, any slight effects on the signals owing to impurity would be canceled out.

Experimental Results

The experimental dew-point data for the methane–n-butane binary system are shown in Table I at temperatures from +40° down to -200°F. The pressure of the data begins at 20 psia for all temperatures except at +40°F, since at this temperature, for system pressures below 100 psia, the concentration of n-butane is so high that the output signal from the detector becomes saturated. The sensitivity of the detector will be poor in the saturation region. The upper limits of the pressure are set either at the point when the liquid and gas interface begins

Table I. Dew-Point Data for Methane–n-Butane System

T = 40.00°F = 4.44°C		T = 0.01°F = −17.77°C		T = −19.97°F = −28.87°C	
Press, psia	Mole fraction of n-butane	Press, psia	Mole fraction of n-butane	Press, psia	Mole fraction of n-butane
100.4	0.204	20.4	0.410	20.3	0.235
150.4	0.140	25.4	0.308	25.3	0.186
200.4	0.110	50.4	0.163	50.3	0.0953
300.4	0.0824	100.4	0.0839	100.2	0.0512
400.4	0.0687	150.3	0.0597	150.3	0.0370
500.4	0.0615	200.3	0.0484	200.3	0.0297
600.	0.0575	300.4	0.0361	300.3	0.0230
700.	0.0542	400.4	0.0311	400.3	0.0199
800.	0.0531	500.4	0.0284	500.3	0.0186
1000.	0.0541	600.	0.0272	600.	0.0182
1200.	0.0610	700.	0.0271	700.	0.0184
1400.	0.0706	800.	0.0272	800.	0.0191
1600.	0.0900	1000.	0.0304	1000.	0.0228
1800.	0.131	1200.	0.0375	1200.	0.0312
1865.	0.159	1400.	0.0501	1400.	0.0502
		1600.	0.0825	1500.	0.0657
		1700.	0.121	1600.	0.0986

T = −39.95°F = −39.97°C		T = −59.95°F = −51.08°C		T = −79.97°F = −62.21°C	
20.3	0.131	20.3	0.0686	20.0	0.0340
25.3	0.107	25.1	0.0562	25.1	0.0270
50.3	0.0542	50.3	0.0294	50.0	0.0144
100.3	0.0297	100.2	0.0160	100.0	0.00809
150.3	0.0213	150.3	0.0117	150.0	0.00566
200.3	0.0173	200.3	0.00966	200.0	0.00494
300.3	0.0137	300.3	0.00765	300.0	0.00408
400.3	0.0122	400.3	0.00702	400.1	0.00392
500.3	0.0116	500.3	0.00702	500.1	0.00401
600.	0.0118	600.	0.00738	600.	0.00454
.700.	0.0123	700.	0.00815	700.	0.00549
800.	0.0132	800.	0.00954	800.	0.00730
1000.	0.0178	1000.	0.0157	900.	0.0104
1200.	0.0295	1100.	0.0226	950.	0.0138
1300.	0.0392	1200.	0.0315	1000.	0.0170
1400.	0.0521			1013.	0.0184
				1025.	0.0197
				1045.	0.0243

T = −99.88°F = −73.27°C		T = −116.62°F = −82.57°C		T = −119.37°F = −84.09°C	
Press, psia	Mole fraction of n-butane	Press, psia	Mole fraction of n-butane	Press, psia	Mole fraction of n-butane
20.1	0.0154	20.1	0.00743	19.8	0.00646
25.0	0.0125	25.1	0.00596	25.0	0.00524
50.3	0.00654	50.1	0.00323	51.2	0.00278
100.1	0.00367	100.1	0.00186	101.1	0.00165
150.1	0.00280	150.1	0.00134	151.0	0.00118
200.1	0.00243	199.7	0.00120	201.0	0.00105
300.3	0.00206	299.7	0.00105	300.3	0.000917
400.3	0.00205	399.7	0.00111	400.0	0.000951
500.1	0.00230	500.1	0.00134	500.7	0.00125
600.	0.00285	600.	0.00177	550.	0.00139
700.	0.00416	625.	0.00176	600.	0.00127
750.	0.00555	650.	0.00137	615.	0.00104
763.	0.00605	660.	0.000909	631.	0.000359
779.	0.00667	665.	0.000599	636.	0.000000
800.	0.00770				
805.	0.00853				

T = −139.96°F = −95.53°C		T = −159.97°F = −106.65°C	
20.0	0.00213	20.0	0.000617
25.0	0.00172	25.1	0.000529
50.0	0.000999	50.0	0.000344
100.1	0.000609	100.0	0.000199
149.8	0.000469	150.0	0.000169
199.9	0.000403	200.0	0.000134
249.9	0.000363	250.0	0.000089
299.9	0.000349	269.9	0.000084
349.8	0.000349		
399.9	0.000329		
414.8	0.000269		
420.5	0.000233		
429.6	0.000159		
440.0	0.000000		

T = −179.99°F = −117.77°C		T = −200.01°F = −128.89°C	
20.1	0.000172	19.9	0.000043
24.9	0.000149	25.2	0.000040
50.1	0.000099	49.9	0.000029
100.1	0.000060	99.9	0.000017
150.1	0.000052		

to disappear (for temperatures above the critical point of the methane) or at the vapor-pressure point of pure methane (for temperatures below the critical point of methane). Fixed pressure intervals were used to obtain better results for interpolating and cross plotting purposes.

Figure 3 is the pressure-concentration plot for isotherms from +40° to −100°F. The points at the highest pressure for each isotherm were taken when the liquid-gas interface just begins to disappear. They were believed to be close to the critical points of the mixture. Since no bubble-point data were measured and this is the limit of the experimental method (which will be discussed later), we cannot make very accurate measurements at the critical points. The reader is referred to the associated article in this issue on the vapor-liquid equilibrium of this system.

Figure 4 is the pressure-concentration plot for isotherms below −100°F. An expanded concentration scale was used in this plot to show the smoothness of the data. The isotherm of −100°F was repeated to show the general trend of transition of the system with respect to tem-

perature. For temperatures below the critical temperature of methane, the isotherm will bend toward the vapor pressure of pure methane at the corresponding temperature. The vapor-pressure points of pure methane measured at −119.37° and −139.96°F agreed with the Vennix (7) data within experimental error.

The isobaric plots of the dew-point data are shown in Figure 5 (20–400 psia) and Figure 6 (500–1800 psia). The plots were made with the logarithm scale of the mole fraction of n-butane vs. the reciprocal of absolute temperature. The isobaric curves are almost linear in the low-pressure range; thus, scattering in the data will be easily spotted. This method can also be used to interpolate the data.

Discussion of Results

An interesting phenomenon has been discovered in this investigation. In Figure 4 the isotherms at −116.62° (essentially the critical temperature of methane) and at −119.37°F show an S-type bend on the upper part of the curve. This is a demonstration of the continuous change of the vapor-phase boundary surface as the system tem-
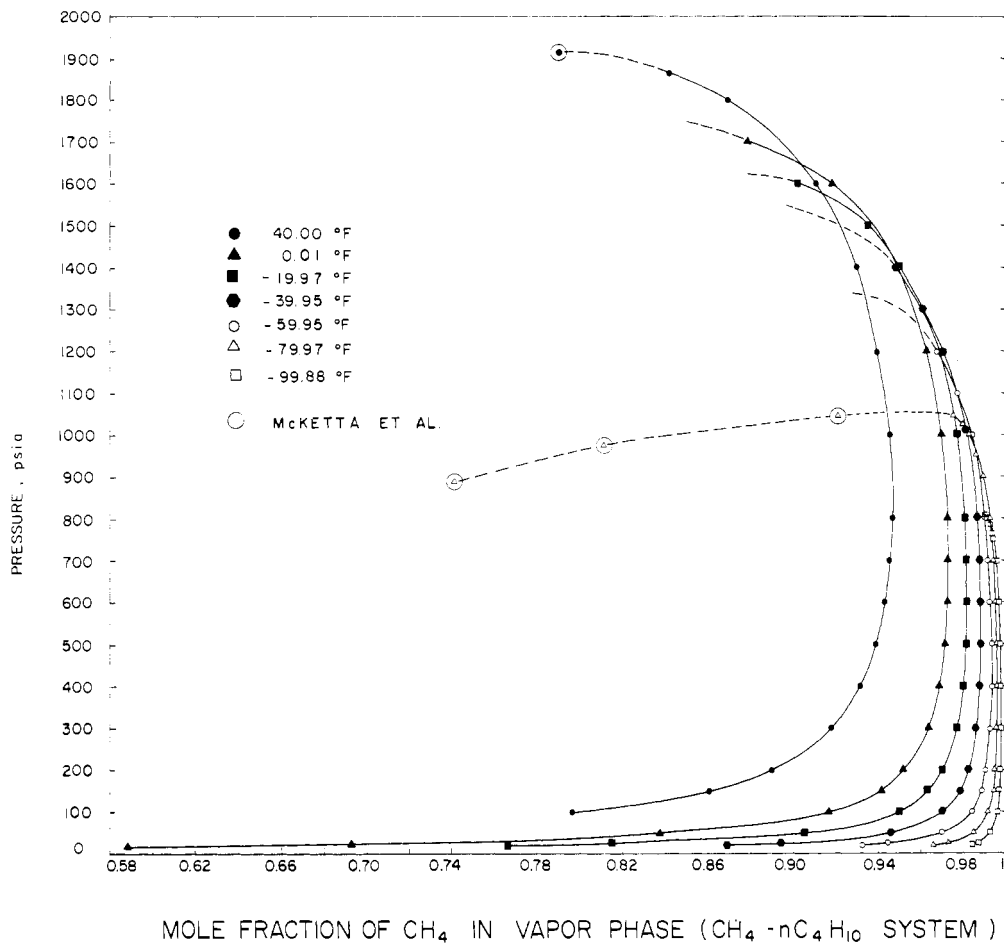
MOLE FRACTION OF CH₄ IN VAPOR PHASE (CH₄ - nC₄H₁₀ SYSTEM)

Figure 3. Isothermal dew-point data for methane–*n*-butane from +40° to −100°F
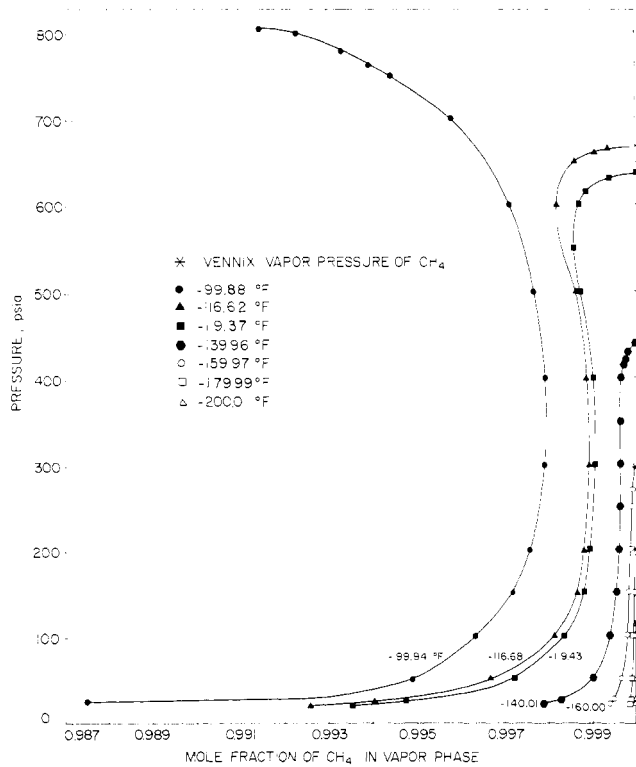

Figure 4. Isothermal dew-point data for methane–*n*-butane from −100° to −200°F. Note magnitude of mole fraction scale
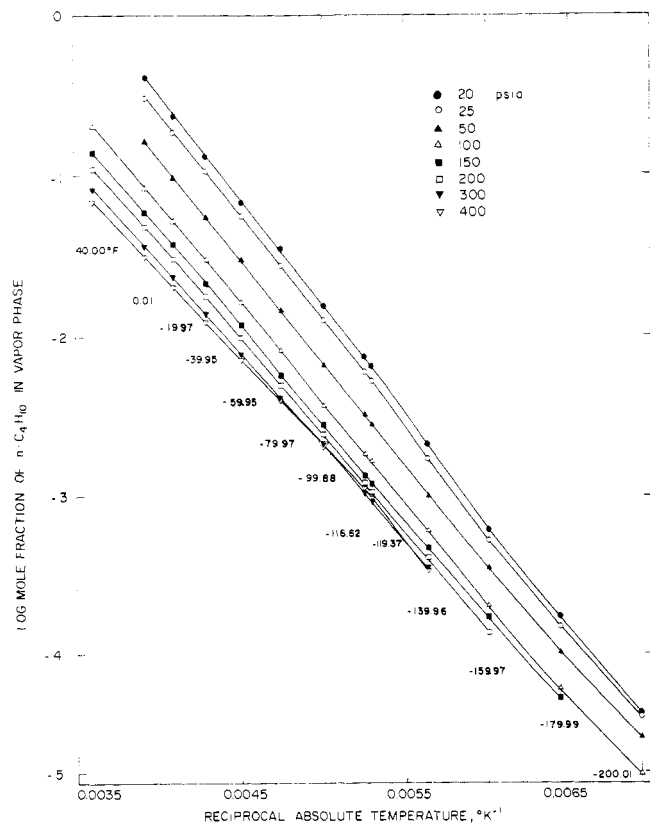

Figure 5. Isobaric dew-point data for methane–*n*-butane from 20 to 400 psia
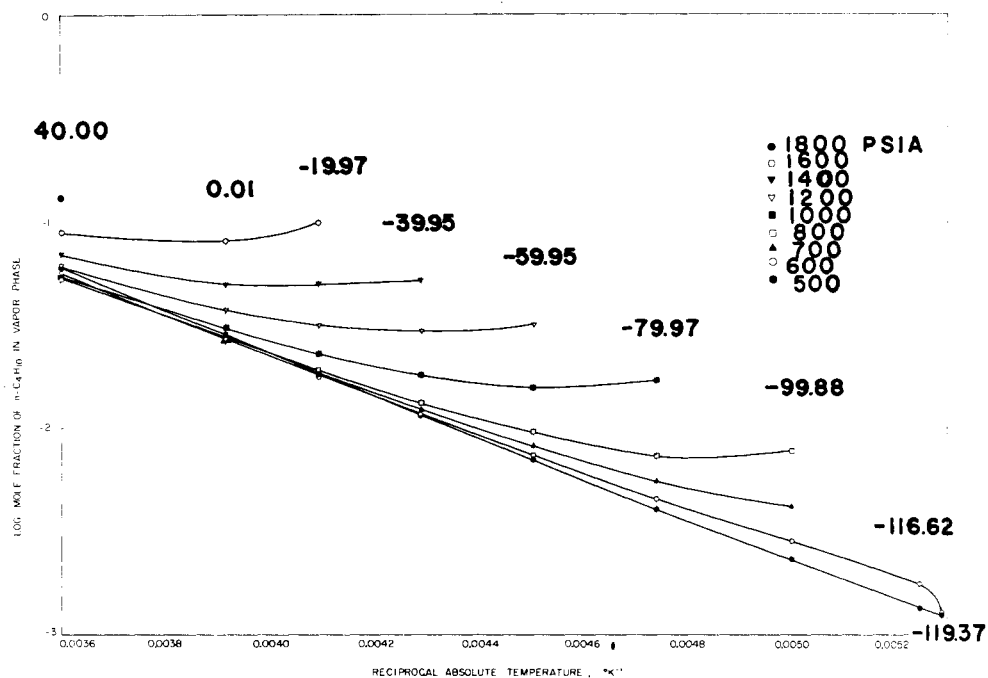
Figure 6. Isobaric dew-point data for methane–*n*-butane from 500 to 1800 psia

perature moves across the critical temperature of methane. For isotherms above the critical temperature of methane (for example, an isotherm at −100°F), the curve will bend to the left to the critical point of the mixture; the curve is convex to the right and shows the well-known retrograde condensation phenomenon. When the system temperature is changed to the critical temperature of methane (isotherm at −116.62°F), the lower part of the curve preserves the part of convex characteristic and still shows the retrograde phenomenon for a binary mixture. But as the system pressure is increased by introducing more methane into the system, it begins to be dominated by the characteristics of pure methane, and the curve will start to bend to the vapor-pressure point of pure methane; thus, an S-type bend occurs.

Because of the continuity of the vapor-phase boundary surface, isotherms immediately below the critical temperature of methane (isotherms at −119.37°F) also show the same bend, but for temperatures far below the critical (such as isotherms at −140°F), the S-type bending has disappeared. Because of this S-type pressure-concentration curve for a narrow concentration range, triple dew points will be found for the temperature at and immediately below the critical temperature of methane. The "best" value for the critical temperature of methane is 190.50K (−82.65°C), reported in 1970 (*3*). Our "critical temperature of methane" measurements were made at −82.57°C, some 0.08° higher.

The accuracy of the data points at the highest pressure for isotherms from +40° to −100°F is questionable because they were taken when the interface began to disappear. The flow method has a disadvantage; theoretically, it cannot be used to measure the concentration of critical points, because at critical point, the concentrations of both phases have the same value. If pure methane is continuously introduced into the system, then the system will no longer stay at the critical composition; but if the cell is well mixed and flow is small, the results will be close to the critical condition.

Accuracy

The pressure in the equilibrium cell was measured by a set of three Heise gages with ranges of 0–200, 0–500, and 0–2000 psi. The gages were calibrated by the manufacturer with an accuracy of 0.1% of full scale. The temperature of the system could be controlled to ±0.02°F. It was measured with a Leeds & Northrup Model 8163-B platinum resistance thermometer which is accurate to at least ±0.01°C with respect to the IPTS (1948). Temperatures were first recorded as IPTS (1948) and then converted to IPTS (1968) by using a table of differences (*2*). The uncertainty in the flow rate (*1*) of methane is ±0.18%, and *n*-butane is ±0.0177%. The read out system for the thermal conductivity cell consisted of a millivolt recorder and integrator. The error in this system is less than 0.5% of full scale.

The overall error in the dew-point data is either less than 2% or 0.00001 in mole fraction of *n*-butane, depending on which is larger.

Comparison of Data

Sage et al. (*6*) determined the vapor and liquid-equilibrium composition for methane and *n*-butane binary systems at temperatures from +70° up to 250°F. Their pressure ranges started from vapor pressures of *n*-butane up to the critical pressure of the mixture. The only low-temperature equilibrium data for this system were reported by McKetta and coworkers (*4, 8*). The lowest temperature of their data is −140°F.

A comparison between our data and those of McKetta and coworkers indicates that we are in fair agreement at +40°F (within 5%). At −20°F, the data are in good agreement in the medium pressure range (500–1300 psia), but there is about 20% difference in mole fraction of *n*-butane at the low-pressure and high-pressure ends. The disagreement becomes larger at −80°F; their data are about 80% higher in mole fraction of *n*-butane than ours. Their data show more scattering as the system

temperature gets lower. Their smoothed data at −140°F are about four times higher than ours. This is the region where the vapor phase is so dilute in n-butane (0.005 in mole fraction) that the ordinary chromatographic method approaches its limit.

Acknowledgment

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Dew-Point Loci for Methane-n-Pentane Binary System

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Dew-point loci for the binary system of methane and normal pentane were determined at nine temperatures from 0° to −100°C from 20 up to 2200 psia. A constant flow gas saturation technique was used for this experimental study. Quadruple-valued dew points in a narrow concentration range were observed for isotherms immediately above the critical temperature of pure methane.

No equilibrium-phase composition data for the methane-n-pentane binary system exist for temperatures below 0°C owing to the difficulty in the determination for the dew-point data. As shown in the previous paper on methane-n-butane (2), the errors which are inherent in pulsed chromatography become significant in the determination of the trace amount of the heavier component in the vapor phase. As the molecular size of the heavier component gets larger, its concentration becomes more dilute in the vapor phase; thus, the determination of the dew-point values for the methane-n-pentane system is more difficult than the methane-n-butane system.

The objective of this study is to determine the dew-point data for the methane-n-pentane system by the constant flow gas saturation technique which was used in the previous study. These data can then be combined with liquid-phase concentration data determined by ordinary chromatographic methods [as has been done by Elliot et al. (3) for the methane-n-butane system] to form a complete set of equilibrium data for this binary system.

Experimental Method

The experimental equipment and procedure are essentially the same as discussed in the previous paper. However, it was necessary to install a magnetic circulation pump to recycle the vapor from the top of the equilibrium cell to the inlet of the presaturator. This will accelerate the time to achieve equilibrium, particularly for high system pressures. Another Heise gage with a range of 0–4000 psia was added to the pressure measuring system for high-pressure measurements.

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The data were taken in two periods; in the first period, the dew-point values were determined up to 1000 psia for all isotherms. Since the equilibrium condition could be reached in a short time, the recycle pump was not needed in this period. In the second period, a high-pressure methane cylinder was used to determine the dew-point data above 1000 psi for temperatures at 0°, −25°, and −50°C. The recycle magnetic pump was installed and used in this period of investigation to shorten the time for reaching equilibrium. The points at 1000 psia were redetermined; they were in good agreement with the values determined in the first period.

Minor modifications were also necessary in the equipment for calibration. Because n-pentane is in the liquid state at room temperature and atmospheric pressure, it has to be gasified to insure good mixing with methane. In the previous work, the micropump and mixing valve were kept in the same temperature-controlled air bath at 32°C. The insulation material for the air bath cannot withstand higher temperature; therefore, for this study the mixing valve was placed into a separate insulated box above 70°C, which is well above the boiling point of n-pentane (36.07°C). This insures that the n-pentane becomes gasified at the valve seat. To avoid condensation, both the inlet and outlet lines of the mixing valve were insulated and heated above 70°C. The thermoconductivity detector was kept in a constant temperature air bath controlled at 74°C.

The calibration curve of the detector for this system is shown as curve B in Figure 2 of the previous paper (2). The response of the detector was linear from 4×10^{-5} to 0.05 mole fraction of normal pentane; mole fractions greater than 0.05 gave a curved response. The response curve was fit by a linear equation and a third-order polynomial for the respective regions by the least-squares method.

Materials

The n-pentane used in this investigation was donated by Phillips Petroleum Co. It was research grade with purity of 99.98 mol %. The ultra high-purity methane used in the first period was bought from Matheson Gas Products Co. The high-pressure (3500 psi) cylinder of pure meth-