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RECEIVED for review February 9, 1971. Accepted October 13, 1971.

Vapor-Liquid Equilibrium of Methane-Propane System at Low Temperatures and High Pressures

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Experimental techniques were developed to sample and analyze vapor-liquid equilibrium phases containing as little as 0.00001 mole fraction propane, which were used for measurements both at near-critical and at considerably dilute conditions. Binary compositions, temperature, pressure, and *K*-values are reported and graphically illustrated for ten isotherms from -75° to -225° F and pressures from 25-950 psia. Error analysis gives an average total relative error in the *K*-values of 1.6%, but for the vast majority of measurements the error is less than 1%.

No vapor-liquid equilibrium data for the methane-propane system in the low temperature range have been reported since the measurements of Price and Kobayashi (3). Increased industrial operation at these conditions and improvements in analytical techniques justify investigations at low temperature conditions.

EXPERIMENTAL APPARATUS

The apparatus was the vapor-recycle type reported by Chang et al. (2). Significant changes were made in the sampling system. A complete description of the equipment is available (5).

A simplified schematic line diagram of the apparatus is given in Figure 1. Cylinders for methane, ethane, and propane are shown. Subsequently the methane-ethane system and the ternary system were investigated, reports of which will appear

in this Journal. The gases were charged to the equilibrium cell, made from a Jerguson high-pressure liquid-level gage. The vapor was recirculated through the equilibrium cell. Phase samples were analyzed by chromatography. The Dewar flask was mounted in a Riki box, so that it could be lowered without moving the equilibrium cell or any flow lines.

Special microregulating 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 in 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 procedure for the sampling of phases into the gas chromatograph was changed after preliminary investigations of the liquid phase gave nonreproducible results. The cause was in-

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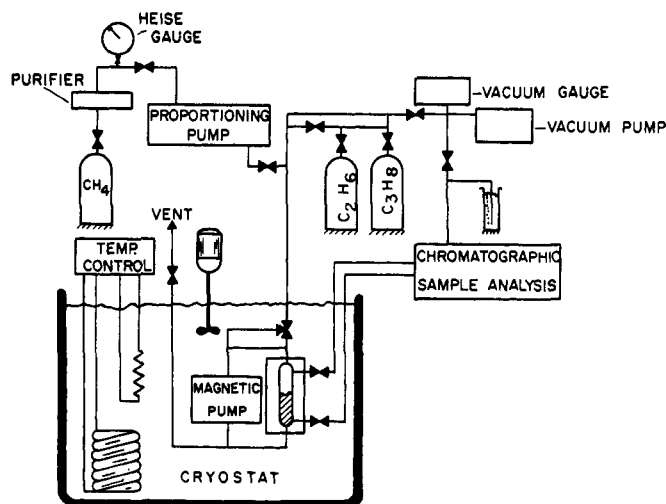


Figure 1. Flow diagram of vapor-liquid equilibrium apparatus

complete nonhomogeneous evaporation of the liquid phase in the sample line owing to a relatively high linear flow rate of fluid in a small-diameter tube. The problem was solved by an addition to the liquid sample line of an external volume. This glass tube 250 mm long and 10 mm o.d. contained a loosely fitting soft iron core intermittently moved by a ring magnet to produce a homogeneous gasified liquid for the liquid-phase sample. The gas- or liquid-phase sample was introduced into the sample loop (volume approximately 0.2 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 170-cm length of $\frac{1}{8}$ -in. o.d. stainless steel tubing coiled and packed with 80-100 mesh Porapak-Q substrate, a highly cross-linked polystyrene. A Texas Instruments integrating recorder recorded the chromatograms.

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 Ω which corresponds to a temperature accuracy of 0.01°C. The bath temperature was maintained within this limit. Liquid nitrogen was used for cooling the bath.

The pressure in the system was indicated by two (0-400 and 0-2000 psi) 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, propane 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 100-ml proportioning pump. Further adjustments of the pressure were necessary during early stages of circulation. As the equilibrium pressure was approached, the vapor sample line was opened to give a very slight withdrawal of the vapor phase from the cell. The flow rate of the gas phase was adjusted to one bubble/5-15 sec, determined as an optimal rate. (A higher flow rate would cause excessive pressure drop in the equilibrium cell; a lower flow rate would not fill the sample loop.) Above 200-600 psia (determined by the temperature), the amount of vapor phase

withdrawn did not affect the pressure in the cell. At lower pressures very small amounts of methane were added by manual operation of the proportioning pump to compensate for pressure drop in the cell.

A magnetic pump (4) was used to recycle the equilibrium cell contents. If drops of the liquid phase should enter the vapor-phase sample line, a change in the vapor-phase concentration would occur. However, this was not observed, even in the critical region. The system was circulated until the pressure was constant for at least 10 min, after which vapor-phase analyses were made. On completion of the vapor-phase analysis, the recycle pump was stopped and the vapor-phase sample valve was closed. The liquid sample system was evacuated and purged with room air several times to assure removal of previous sample from the relatively large volume of the homogenizer. For the first 5 min of liquid sampling, no manual mixing with the ring magnet was carried out to ensure that the air in the mixer was replaced by the new sample. The liquid-phase analyses were made with intermittent mixing to homogenize the "liquid" sample. At least six analyses were made of each phase. After both phases had been analyzed, the pressure was readjusted for the next run.

Material Used. Ultrahigh-purity methane was purchased from Matheson Gas Products Co. The gas was reported to analyze at least 99.97% methane, with the total amount of major impurities as 105 ppm. The methane was charged through a high-pressure molecular sieve-type cartridge for removal of oil, water, and particles down to approximately 12 μ . No impurities were detected by analysis on this gas chromatographic system.

Research-grade (99.99%) propane was donated by the Phillips Petroleum Co. No impurities were found by the investigator's gas 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. Any absolute error in the K -value due to the variable V is given by

$$\epsilon K_V = \frac{\Delta K}{\Delta V} \epsilon V \quad (1)$$

The percent error is

$$\delta K_V = \frac{\epsilon K_V}{K_{\text{mean}}} 100 \quad (2)$$

The detailed error analysis based on Equations 1 and 2 is available (5). The results are summarized in Table I.

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 Figure 2 it is evident that the maximum change of K with respect to the

Table I. Error Analysis

Composition analysis		
Mole fraction	Deviation, \pm	
0.99900	0.00001	
0.9900	0.0001	
0.900	0.0008	
0.50	0.0025	
0.100	0.0008	
0.0100	0.0001	
0.00100	0.00001	
Error source	Error range, %	Estimated av, %
Concentration	0 to 2	1
Temperature	0.05 to 0.15	0.1
Pressure	0 to 5	0.5
Total	0.05 to 7	1.6

Table II. Vapor-Liquid Equilibrium for Methane-Propane System

CH ₄ mole fraction		Pressure		K-value	
<i>x</i>	<i>y</i>	Psia	Atm	Methane	Propane
Temp = 213.71°K = -59.44°C = -75.0°F					
0.0000	0.0000	6.352 ^a	0.4322 ^a	160 ^b	1.000
0.0205	0.7669	27.5	1.87	37.4	0.238
0.0443	0.8706	51.5	3.50	19.7	0.135
0.0899	0.9288	100.0	6.80	10.3	0.0782
0.1358	0.9505	150.0	10.20	7.00	0.0573
0.2709	0.9698	300.0	20.40	3.58	0.0414
0.3656	0.9741	400.0	27.20	2.66	0.0408
0.4580	0.9760	500.0	34.00	2.13	0.0443
0.5563	0.9767	600.0	40.85	1.76	0.0525
0.6555	0.9755	700.0	47.65	1.49	0.0711
0.7573	0.9726	800.0	54.45	1.28	0.113
0.8600	0.9646	900.0	61.25	1.122	0.253
0.9053	0.9519	939.0	63.90	1.051	0.508
0.9469	0.9469	944.0 ^c	64.25 ^c	1.000	1.000
Temp = 195.2°K = -78.0°C = -108.4°F					
0.0000	0.0000	2.151 ^a	0.1464 ^a	360 ^b	1.000
0.0377	0.9244	30.5	2.08	24.5	0.0786
0.0667	0.9541	52.5	3.57	14.3	0.0492
0.0958	0.9670	75.0	5.10	10.1	0.0365
0.1263	0.9742	99.0	6.74	7.71	0.0295
0.2545	0.9845	200.0	13.60	3.87	0.0208
0.3969	0.9882	300.0	20.40	2.49	0.0196
0.5392	0.9898	400.0	27.20	1.84	0.0221
0.6947	0.9904	500.0	34.00	1.43	0.0314
0.7734	0.9905	550.0	37.45	1.28	0.0419
0.8454	0.9905	600.0	40.85	1.17	0.0614
0.9061	0.99075	650.0	44.25	1.093	0.0985
0.9546	0.9912	688.0	46.80	1.038	0.181
0.9719	0.9911	708.0	48.20	1.020	0.317
0.9856	0.9856	724.0 ^c	49.25 ^c	1.000	1.000
Temp = 192.3°K = -80.9°C = -113.6°F					
0.0000	0.0000	1.776 ^a	0.1208 ^a	420 ^b	1.000
0.0409	0.9355	30.0	2.04	22.9	0.0673
0.0692	0.9601	50.0	3.40	13.9	0.0429
0.1052	0.9718	75.0	5.10	9.24	0.0315
0.1379	0.9783	100.0	6.80	7.09	0.0251
0.2737	0.9874	200.0	13.60	3.61	0.0173
0.4207	0.9899	300.0	20.40	2.35	0.0174
0.5819	0.9913	400.0	27.20	1.70	0.0208
0.7529	0.9919	500.0	34.00	1.32	0.0328
0.8728	0.9924	575.0	39.15	1.137	0.0597
0.9578	0.9941	639.0	44.50	1.038	0.140
0.9782	0.9953	666.0	45.30	1.017	0.206
0.9844	0.9957	674.0	45.85	1.011	0.276
0.9926	0.9926	688.5 ^c	46.85 ^c	1.000	1.000
Temp = 190.95°K = -82.20°C = -116.0°F					
0.0000	0.0000	1.627 ^a	0.1107 ^a	440 ^b	1.000
0.4379	0.9915	300.0	20.40	2.26	0.0151
0.5587	0.99215	375.0	25.50	1.77	0.0178
0.6918	0.9927	450.0	30.60	1.435	0.0237
0.8157	0.9930	520.0	35.40	1.22	0.0380
0.8695	0.9932	550.0	37.45	1.142	0.0521
0.9161	0.99365	580.0	39.45	1.085	0.0757
0.9500	0.9947	610.0	41.50	1.047	0.106
0.9764	0.9960	639.0	43.50	1.020	0.169
0.9851	0.9969	651.0	44.30	1.012	0.208
0.9924	0.9981	663.0	45.10	1.006	0.250
0.9958	0.99861	669.0	45.50	1.002	0.331
(1.0000)	(1.0000)	671.0 ^{c,d}	45.65 ^{c,d}	1.000	(1.000)
Temp = 190.58°K = -82.57°C = -116.6°F					
0.9614	0.9952	615.0	41.85	1.035	0.124
0.9797	0.9967	638.0	43.40	1.017	0.163
0.9913	0.9981	654.0	44.50	1.007	0.218
0.99546	0.99890	661.0	45.00	1.0034	0.242
0.9967	0.99921	663.0	45.10	1.0025	0.239
1.0000	1.0000	667.0 ^c	45.40 ^c	1.000	(0.9 ^f)

(Continued on next page)

Table I. (Continued)

CH ₄ mole fraction		Pressure		K-value	
<i>x</i>	<i>y</i>	Psia	Atm	Methane	Propane
Temp = 187.54°K = -85.61°C = -122.3°F					
0.0000	0.0000	1.284 ^a	0.08737 ^a	520 ^b	1.000
0.0629	0.9656	41.0	2.79	15.35	0.0367
0.1506	0.9839	100.0	6.80	6.53	0.0190
0.3042	0.9907	200.0	13.60	3.26	0.0136
0.4769	0.9929	300.0	20.40	2.08	0.0136
0.6728	0.9937	400.0	27.20	1.48	0.0193
0.8450	0.9947	490.0	33.35	1.18	0.0342
0.9230	0.9958	540.0	36.75	1.08	0.0545
0.9623	0.99675	565.0	38.45	1.036	0.0862
0.9810	0.9980	586.0	39.85	1.017	0.1052
1.0000	1.0000	606.0 ^a	41.25 ^a	1.000	0.5 ^f
Temp = 172.04°K = -101.11°C = -150.0°F					
0.0000	0.0000	0.3850 ^a	0.02620 ^a	1150 ^b	1.000
0.0692	0.9862	30.8	2.10	14.25	0.0148
0.1196	0.9915	52.6	3.57	8.29	0.00965
0.2270	0.99505	100.0	6.80	4.38	0.00640
0.4909	0.9973	200.0	13.60	2.03	0.00530
0.6907	0.9979	260.0	17.70	1.44	0.00679
0.8423	0.99845	300.0	20.40	1.185	0.00983
0.9032	0.99880	320.0	21.75	1.106	0.0123
0.9650	0.99925	342.0	23.25	1.035	0.0214
1.0000	1.0000	361.5 ^a	24.60 ^a	1.000	0.035 ^f
Temp = 158.15°K = -115.00°C = -175.0°F					
0.0000	0.0000	0.09680 ^a	0.006587 ^a	2900 ^b	1.000
0.0873	0.9958	25.0	1.70	11.4	0.00460
0.1791	0.99793	51.5	3.50	5.57	0.00252
0.3510	0.99888	100.0	6.80	2.85	0.00172
0.5450	0.99921	138.5	9.42	1.83	0.00174
0.8000	0.99956	176.0	12.00	1.25	0.00220
0.8738	0.99965	187.0	12.70	1.14	0.00277
0.9135	0.99972	194.0	13.20	1.094	0.00324
0.9497	0.99979	201.5	13.70	1.053	0.00417
1.0000	1.0000	213.5 ^a	14.50 ^a	1.000	0.0053 ^f
Temp = 144.26°K = -128.89°C = -200.0°F					
0.0000	0.0000	0.01866 ^a	0.001270 ^a	8200 ^b	1.000
0.2109	0.99940	31.0	2.11	4.74	0.000760
0.3005	0.99959	48.0	3.27	3.33	0.000586
0.5258	0.99975	74.0	5.04	1.90	0.000527
0.7200	0.99986	91.0	6.19	1.39	0.000500
0.8306	0.99990	98.0	6.67	1.20	0.000590
0.9287	0.999952	108.0	7.35	1.076	0.000673
1.0000	1.0000	114.0 ^a	7.75 ^a	1.000	0.00071 ^f
Temp = 130.37°K = -142.78°C = -225.0°F					
0.0000	0.0000	0.002591 ^a	0.000176 ^a	28000 ^b	1.000
0.3924	0.999921	27.0	1.84	2.55	0.000130
0.5007	0.999935	34.0	2.31	2.00	0.000130
0.6982	0.999962	42.0	2.86	1.43	0.000126
1.0000	1.0000	54.0 ^a	3.67 ^a	1.000	0.00013 ^f

^a Saturated vapor pressure of C₃H₈. ^b K₁[∞]. ^c Critical pressure of system. ^d Extrapolated. ^e Saturated vapor pressure of CH₄. ^f K₃[∞]

pressure occurs only at very high and low pressures at constant temperature. Also, it is obvious that the error due to the pressure is zero at the minimum of the *K-P* curve. A thorough error mapping of the *K-P* plot was made, which showed that at least 80% of the results have a percent error in the *K*-values from pressure of less than 0.5%. The *K*-values for the heavier component 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 indeterminate in the region of no data near convergence pressure, where the *K*-value changes from 0.5-1.0 for a very small change in pressure.

The error from the concentration measurements arises from the calibration of the chromatograph with weighed artificially prepared samples. The accuracy of the graphically smoothed

area factor was statistically improved to an estimated value of 0.4%. The nominal error of the integrator was 0.3%. The calibration procedure for the area factors eliminated any other errors from the electrometer and recorder. The errors in the integral height determination did not exceed 0.3% for almost all of the analyses. A major advantage is the fact that this error is independent of the concentration.

The sum of these three errors in the peak area determination was reasonably estimated as 1% for the binary system. The absolute mole fraction deviations ϵ_x or ϵ_y caused by this error in the peak area determination are given in Table I. The reproducibility of the individual measurements was within these limits. In addition, from a statistical basis, the accuracy was improved by repeating the sample phase determination for each

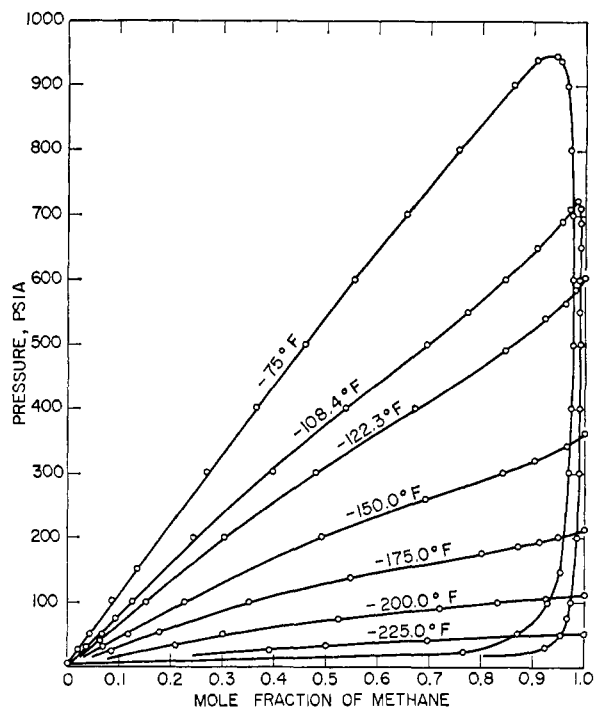


Figure 2. Pressure-composition diagram for the methane-propane system

concentration. In the midconcentration region where the relative error is larger, even more analyses were made to decrease the error. This improvement was not considered in the error analysis.

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.

All errors are summarized in Table I. For almost all of the measurements the total error was 1% or less, while a very few points had excessive deviations from unavoidable random error associated with any extensive phase equilibrium measurement.

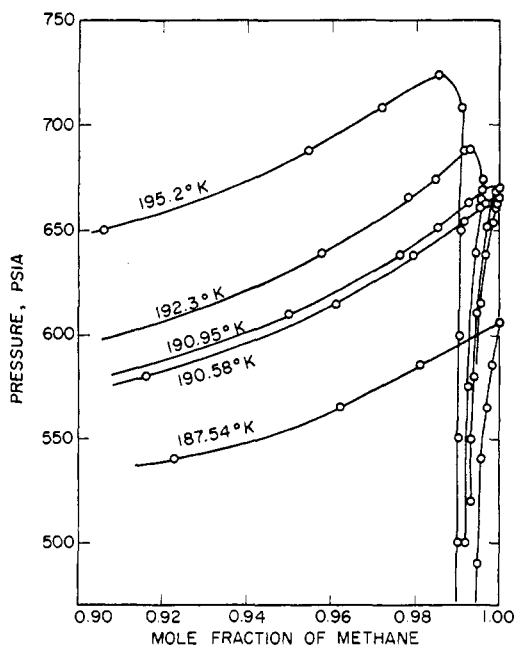


Figure 3. Pressure-composition diagram for the methane-propane system on an expanded scale

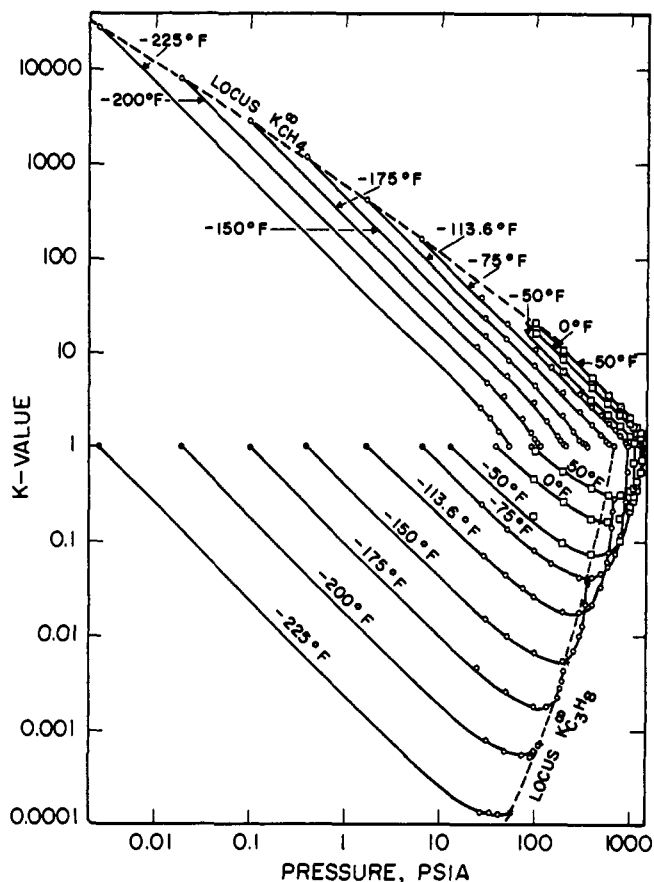


Figure 4. K -value-pressure diagram for the methane-propane system

○ = this work. □ = Price and Kobayashi (3). ● = saturated vapor pressure

RESULTS

Table II presents all of the experimental results for the methane-propane binary. Additional details for such items as calibration and procedure are available (5). A graphical illustration of the pressure-mole fraction behavior is shown in Figure 2 while Figure 3 presents the region of the methane critical on an expanded scale. This behavior in the critical region of the more volatile component is described and discussed elsewhere (6, 7).

Figure 4 gives the usual K -value-pressure representation of a binary system. The vapor pressure was obtained from Carruth (1) for the limiting condition ($K = 1.0$) for propane. The associated infinite dilution values for methane also reported in Table II were obtained by Henry's law

$$K_{\text{CH}_4} = H/P \quad (3)$$

with Henry's constant evaluated by extrapolation at a pressure of 1 atm.

The most recent data available from the literature in the range of this investigation are those of Price and Kobayashi (3). Preliminary investigation showed that their higher temperature ($-50, 0, +50^\circ\text{F}$) data could be reproduced on this equipment. These values are shown in Figure 4. However, significant deviations occur at -75°F and lower temperatures. Analysis to only 0.001 mol fraction was possible at the time of the older work; improvements in sampling and analytical chromatographic equipment now make accurate and reproducible analysis to 0.00001 possible. It is evident from the data that analysis of this range is required.

ACKNOWLEDGMENT

Phillips Petroleum Co. contributed research-grade propane for this investigation.

NOMENCLATURE

- δ = percent error
 Δ = change in quantity designated
 ϵ = absolute error
 H = Henry's constant, atm
 K = y/x
Mean = arithmetic average of the interval
 P = pressure, atm
 V = variable (pressure, temperature, composition)
 x = mole fraction in liquid phase
 y = mole fraction in vapor phase

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RECEIVED for review February 22, 1971. Accepted September 2, 1971. The National Science Foundation and the Natural Gas Processors Assoc. provided financial support.

Vapor-Liquid Equilibrium of Methane-Ethane System at Low Temperatures and High Pressures

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Vapor-liquid equilibrium data are reported for 12 isotherms from -100° to -225° F for pressures from 25–800 psia. The necessary equipment and techniques to measure concentrations of 0.00001 to 0.99999 mol fraction were developed, which gave a maximum total relative error in the K -values of 1.6%; the vast majority of the data has error less than 1%. The improved method made possible measurements of very dilute mixtures close to critical conditions. Extensive investigation near the critical temperature of methane showed that (1) the liquid-vapor (x - y) curve at the critical temperature of methane approaches 100% methane with a slope equal to 1; (2) no discontinuity at $K = 1$ is evident in isothermal curves of K -value—pressure at or above the critical temperature of methane; and (3) the pressure—composition (of either phase) curve at the critical temperature of methane approaches 100% methane with a zero slope.

Since the last investigation (4) of this system, a hundred-fold increase in the precision of measurement of equilibrium concentrations has made possible more sensitive investigations in this region of rather small concentrations. Commercial operations of natural gas processing are rapidly approaching lower and lower temperatures so that the data have immediate application.

EXPERIMENTAL

The prototype of the vapor recycle apparatus was reported by Chang et al. (3). The apparatus and improvements for the current investigation are reported in a paper (8) on the methane-propane system and in the depository document (6).

The error analysis is the same type as reported (6, 8) for the earlier investigation, but the resultant average maximum percent error is 1% in the K -values as compared to 1.6% for the

methane-propane system. This improvement in the accuracy arose from the increase in manipulatory skill of the investigator, which decreased the error in the concentration measurements.

The procedure is the same as previously reported (8).

Materials Used. The same (8) "ultrahigh purity" methane, purchased from Matheson Gas Products Co., was used. The reported analysis was at least 99.97% methane with a total amount of major impurities of 105 ppm. The charge gas passed through a molecular sieve purifier to remove water, oil, and particles down to $12\ \mu$.

Research-grade (99.99%) ethane was donated by The Phillips Petroleum Co. It was used without further purification. No impurities in the methane or ethane were detected by the investigator's gas chromatographic analysis.

RESULTS

Experimental pressures, temperatures, and compositions are reported in Table I for the 12 isotherms investigated from -100° to -225° F. The tabular limiting conditions of the vapor pressure of ethane were obtained from a recent investiga-

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