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 μ.

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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Table I. Vapor-Liquid Equilibrium for Methane–Ethane System

CH_4 mole fraction		Pressure		K-Value	
x	y	Psia	Atm	Methane	Ethane
Temp = 199.92°K = −73.23°C = −99.8°F					
0.0000	0.0000	31.45[a]	2.140[a]	20.5[b]	1.000
0.0214	0.3005	45.0	3.62	14.1	0.715
0.0512	0.5098	65.0	4.42	9.95	0.517
0.1039	0.6800	100.0	6.80	6.54	0.357
0.1875	0.7957	160.0	10.90	4.24	0.251
0.3100	0.8679	250.0	17.00	2.80	0.191
0.4526	0.9052	350.0	23.80	2.00	0.173
0.6601	0.9337	500.0	34.00	1.41	0.195
0.7852	0.9461	600.0	40.80	1.20	0.251
0.8942	0.9562	700.0	47.65	1.069	0.414
0.9126	0.9584	719.0	48.90	1.050	0.476
0.9175	0.9578	726.0	49.40	1.044	0.512
0.9222	0.9575	732.0	49.80	1.038	0.546
0.9319	0.9577	740.0	50.35	1.028	0.621
0.9520	0.9520	748.0[c]	50.90[c]	1.000	1.000
Temp = 195.44°K = −77.71°C = −107.9°F					
0.7648	0.9546	522.0	35.50	1.248	0.193
0.8539	0.9627	591.0	40.20	1.127	0.255
0.9007	0.9680	634.0	43.15	1.075	0.322
0.9437	0.9755	680.0	46.25	1.034	0.435
0.9529	0.9764	693.0	47.15	1.025	0.501
0.9613	0.9770	704.0	47.90	1.016	0.594
0.9641	0.9756	708.0	48.20	1.012	0.680
0.9706	0.9706	713.0[c]	48.50[c]	1.000	1.000
Temp = 193.92°K = −79.23°C = −110.6°F					
0.9007	0.9715	612.0	41.65	1.079	0.287
0.9469	0.9787	660.0	44.90	1.034	0.401
0.9590	0.98145	675.0	45.95	1.023	0.452
0.9671	0.98316	685.0	46.60	1.017	0.512
0.9724	0.98352	692.0	47.10	1.011	0.597
0.9756	0.98371	696.0	47.35	1.008	0.668
0.98214	0.98214	698.0[c]	47.50[c]	1.000	1.000
Temp = 192.39°K = −80.76°C = −113.4°F					
0.0000	0.0000	22.05[a]	1.500[a]	25.5[b]	1.000
0.0308	0.4339	39.0	2.65	14.1	0.584
0.0681	0.6358	61.5	4.18	9.34	0.391
0.1364	0.7755	100.0	6.80	5.69	0.260
0.2299	0.8605	160.0	10.90	3.74	0.181
0.3854	0.9087	250.0	17.00	2.36	0.149
0.5512	0.9372	350.0	23.80	1.70	0.140
0.7885	0.9607	500.0	34.00	1.23	0.186
0.9154	0.9755	600.0	40.85	1.066	0.290
0.9529	0.9822	640.0	43.55	1.031	0.378
0.9715	0.9862	662.0	45.05	1.015	0.484
0.9813	0.98973	675.0	45.95	1.009	0.555
0.9858	0.99100	682.0	46.40	1.005	0.634
0.99125	0.99125	685.0[c]	46.60[c]	1.000	1.000
Temp = 190.94°K = −82.31°C = −116.1°F					
0.0000	0.0000	20.41[a]	1.389[a]	26.5[b]	1.000
0.0340	0.4724	39.5	2.69	13.9	0.546
0.0714	0.6513	60.5	4.12	9.12	0.376
0.1386	0.7907	100.0	6.80	5.70	0.243
0.2384	0.8709	160.0	10.90	3.65	0.170
0.3955	0.9181	250.0	17.00	2.32	0.135
0.5687	0.9425	350.0	23.80	1.66	0.133
0.8150	0.9647	500.0	34.00	1.18	0.191
0.9007	0.9750	563.0	38.30	1.082	0.252
0.9474	0.9832	612.0	41.65	1.038	0.319
0.9646	0.9869	630.0	42.85	1.023	0.370
0.9749	0.9898	642.0	43.70	1.015	0.406
0.9819	0.99187	651.0	44.30	1.010	0.449
0.9882	0.99445	660.0	44.90	1.006	0.470
0.99160	0.99579	664.0	45.20	1.0042	0.501
0.99383	0.99693	668.0	45.45	1.0031	0.498
0.99561	0.99765	670.0	45.60	1.0020	0.535
1.0000	1.0000	671.0[d]	45.65[d]	1.0000	1.000
Temp = 189.65°K = −83.50°C = −118.3°F					
0.0000	0.0000	19.22[a]	1.308[a]	27.5[b]	1.000
0.0320	0.4600	35.8	2.44	14.4	0.552
0.0752	0.6741	60.0	4.08	8.96	0.352
0.1380	0.7964	95.5	6.50	5.77	0.236
0.2138	0.8626	140.0	9.53	4.03	0.175
0.3202	0.9026	200.0	13.60	2.82	0.143
0.4975	0.9369	300.0	20.40	1.88	0.126
0.6816	0.9550	400.0	27.20	1.40	0.141
0.8403	0.9706	500.0	34.00	1.155	0.184
0.9214	0.9803	562.0	38.25	1.064	0.251
0.9580	0.9876	600.0	40.80	1.031	0.295
0.9729	0.99084	615.0	41.85	1.018	0.338
0.9819	0.99338	625.0	42.50	1.012	0.366
0.9893	0.99626	634.0	43.15	1.007	0.370
1.0000	1.0000	648.0[e]	44.10[e]	1.000	0.58[f]
Temp = 188.04°K = −85.11°C = −121.2°F					
0.8403	0.9719	477.0	32.45	1.157	0.176
0.8970	0.9789	518.0	35.25	1.091	0.205
0.9413	0.9849	556.0	37.85	1.046	0.257
0.9643	0.9898	580.0	39.50	1.026	0.286
0.9819	0.99448	598.0	40.70	1.013	0.305
0.9887	0.99661	606.0	41.25	1.008	0.300
1.0000	1.0000	616.0[e]	41.90[e]	1.000	0.44[f]
Temp = 186.11°K −87.04°C = −124.7°F					
0.0000	0.0000	16.00[a]	1.089[a]	31.0[b]	1.000
0.0417	0.5585	36.7	2.50	13.4	0.461
0.0897	0.7358	61.5	4.18	8.20	0.290
0.1707	0.8471	104.0	7.08	4.96	0.184
0.3100	0.9116	180.0	12.25	2.94	0.128
0.5019	0.9435	275.0	18.70	1.88	0.113
0.7486	0.9674	400.0	27.20	1.29	0.130
0.8844	0.9792	482.0	32.80	1.107	0.180
0.9395	0.9866	524.0	35.65	1.050	0.221
0.9684	0.99187	550.0	37.40	1.024	0.257
0.9802	0.99495	562.0	38.25	1.015	0.255
0.9877	0.99730	568.0	38.65	1.010	0.220
1.0000	1.0000	579.0[e]	39.40[e]	1.000	0.35[f]
Temp = 172.04°K = −101.11°C = −150.0°F					
0.0000	0.0000	7.099[a]	0.4831[a]	51.0[b]	1.000
0.0685	0.7681	30.8	2.10	11.2	0.249
0.1087	0.8469	45.5	3.10	7.79	0.172
0.2050	0.9161	81.0	5.51	4.47	0.106
0.3164	0.9434	120.0	8.17	2.98	0.0828
0.5042	0.9656	180.0	12.25	1.92	0.0694
0.7082	0.9788	247.5	16.85	1.38	0.0727
0.8609	0.9878	299.0	20.35	1.15	0.0877
0.9175	0.99209	324.0	22.05	1.081	0.0959
0.9513	0.99531	339.5	23.05	1.046	0.0963
1.0000	1.0000	361.5[e]	24.60[e]	1.000	0.105[f]
Temp = 158.15°K = −115.00°C = −175.0°F					
0.0000	0.0000	2.715[a]	0.1847[a]	86[b]	1.000
0.1090	0.8990	25.8	1.76	8.25	0.113
0.1230	0.9089	28.8	1.96	7.39	0.104
0.1640	0.9354	40.0	2.72	5.70	0.0773
0.2186	0.9485	50.0	3.40	4.34	0.0659
0.2953	0.9645	70.0	4.76	3.27	0.0504
0.4382	0.9767	100.0	6.80	2.22	0.0415
0.6528	0.9864	140.0	9.53	1.51	0.0392
0.8107	0.99221	170.0	11.55	1.22	0.0412
0.8650	0.99420	181.0	12.30	1.15	0.0429
0.9407	0.99740	199.0	13.55	1.061	0.0438
1.0000	1.0000	213.5[e]	14.50[e]	1.000	0.045[f]

(*Continued on next page*)

Table I. (Continued)

CH_4 mole fraction x	CH_4 mole fraction y	Pressure Psia	Pressure Atm	K-Value Methane	K-Value Ethane
Temp = 144.26°K = −128.89°C = −200.0°F					
0.0000	0.0000	0.841[a]	0.0572[a]	155[b]	1.0000
0.1965	0.9716	27.3	1.86	4.94	0.0353
0.2702	0.9796	37.0	2.52	3.63	0.0279
0.3241	0.9834	43.0	2.93	3.03	0.0245
0.4385	0.9880	56.0	3.81	2.25	0.0213
0.5314	0.99100	66.0	4.49	1.86	0.0192
0.6882	0.99433	81.0	5.51	1.44	0.0182
0.8581	0.99728	98.0	6.67	1.16	0.0192
1.0000	1.0000	114.0[c]	7.75[c]	1.00	0.0195[f]
Temp = 130.37°K = −142.78°C = −225.0°F					
0.0000	0.0000	0.186[d]	0.0127[d]	330[b]	1.000
0.4319	0.99479	28.0	1.91	2.30	0.00917
0.5989	0.99654	35.0	2.38	1.66	0.00863
0.7788	0.99845	43.3	2.95	1.28	0.00701
0.8935	0.99919	48.6	3.31	1.118	0.00761
1.0000	1.0000	54.0[e]	3.67[e]	1.000	0.007[f]

[a] Saturated vapor pressure of C_2H_6. [b] K_1^∞. [c] Critical pressure of system. [d] Saturated vapor pressure and critical pressure of CH_4. [e] Saturated vapor pressure of CH_4. [f] K_2^∞.

tion in this laboratory (*2*) and the vapor pressure of methane from earlier works (*1*, *5*).

Most of the isotherms are in the region about the critical temperature of methane. These data led to a theoretical discussion (*9*) of equilibrium behavior near the critical point of the more volatile component. After investigation of the ternary methane–ethane–propane system subsequent to this study, four additional isotherms at 191.20, 193.37, 194.61, and 197.21°K were investigated for the methane–ethane binary for a methane K-value less than 1.05. These data, reported elsewhere (*7*), are entirely consistent with the wide-range study presented here.

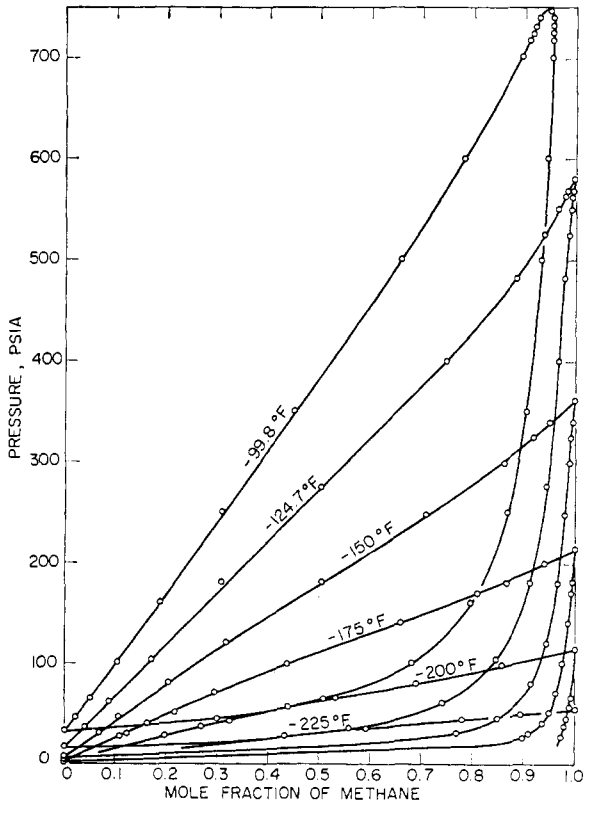

Figure 1. Pressure-composition diagram for methane–ethane system

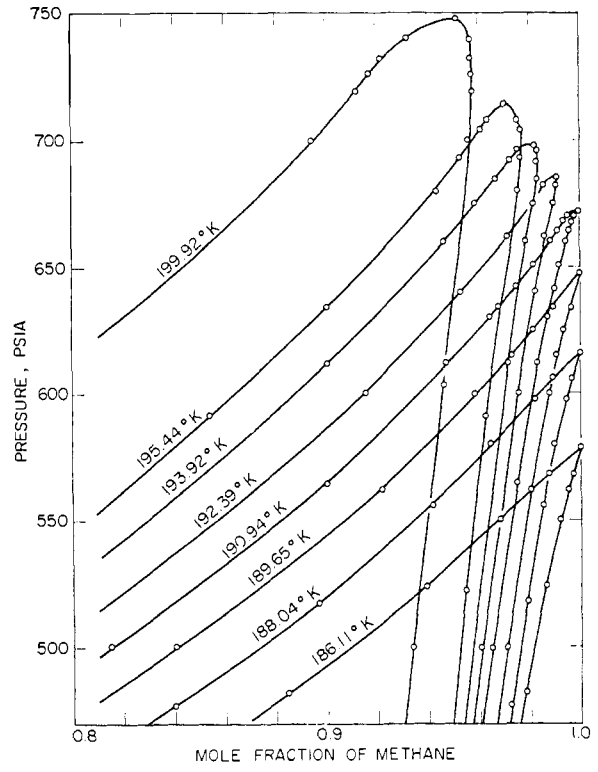

Figure 2. Pressure-composition diagram for the methane–ethane system on an expanded scale

Two conditions which are true at the critical temperature of methane, the more volatile component of the binary, are (*9*):

(1) The x-y curve approaches 100% methane with a slope equal to 1,

$$\lim_{x \to 1} \frac{dy}{dx} = 1 \qquad (1)$$

(2) The pressure-composition (P-x,y) curves approach 100% methane with a slope equal to zero,

$$\left(\frac{dP}{dx}\right)_T = \left(\frac{dP}{dy}\right)_T = 0 \qquad \text{at } x = y = 1 \qquad (2)$$

The measurements of small concentrations, where the methane K-value is less than 1.0, also show there is no evident discontinuity between the components in the usual engineering logarithmic representation K-value to pressure

$$\frac{d \ln P}{d \ln K_1} = \frac{d \ln P}{d \ln K_2} = 0 \qquad \text{at } K_1 = K_2 = 1 \qquad (3)$$

A graphical representation of the data as pressure to composition is given in Figures 1 and 2. Figure 1 shows representative isotherms spaced about 25°F apart for the entire concentration region. Figure 2 shows the high methane content region about the critical temperature of methane. These curves are labeled in °K, which corresponds to the primary unit of the actual temperature measurement, °C. The curves in Figure 1 and Figure 3 are labeled in °F, the usual engineering unit. Figure 3, the usual log K-log P plot, includes the −50° and 0°F data of Price and Kobayashi (*4*), which were verified in the preliminary stages of this investigation.

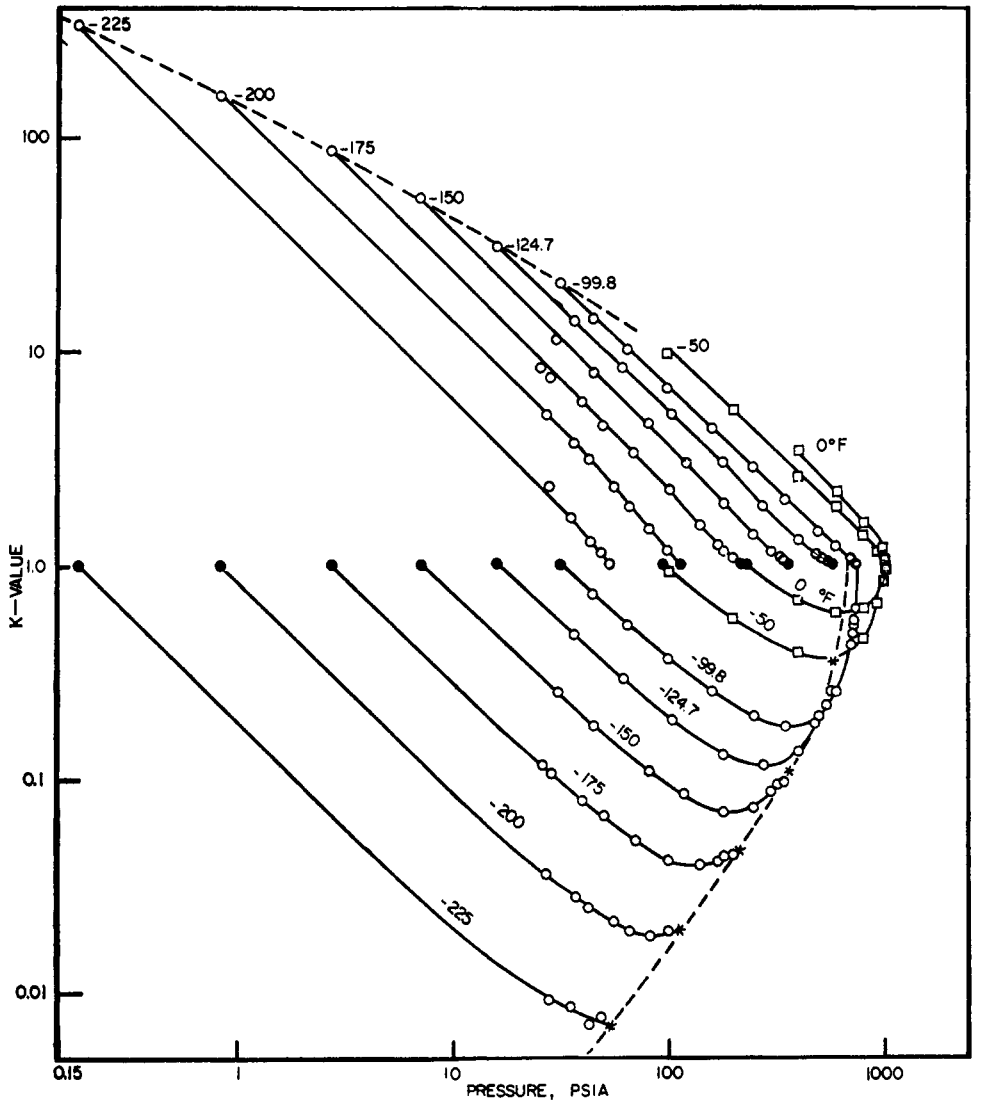

Figure 3. *K*-Value *vs.* pressure diagram for the methane–ethane system

○ = This work. □ = Price and Kobayashi (4). ● = Saturated vapor pressure

ACKNOWLEDGMENT

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

NOMENCLATURE

$K = y/x$
P = pressure, absolute
x = mole fraction in liquid phase
y = mole fraction in vapor phase

SUBSCRIPTS

1 = methane
2 = ethane

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RECEIVED for review February 22, 1971. Accepted September 9, 1971. The National Science Foundation and the Natural Gas Processors Assoc. provided financial support.