about 3500 p.s.i.a. Table 1 presents a comparison of the observed three- and four-phase conditions of the methane-toluene and methane-*n*-heptane and methane-methylcyclohexane binaries. Table II presents a complete tabulation of all binary phase compositions and *K* values determined in this investigation at the experimental conditions. Plots of *K* value *vs.* pressure for the six isotherms studied are presented in Figure 1. Minimum *K* values of toluene are at approximately 600 p.s.i.a. as shown in Figure 1. A plot of the *K* values of toluene *vs.* the reciprocal absolute temperature is shown in Figure 2. The critical locus in Figure 3 is estimated using the toluene critical point and the data of Elbishlawi and Spencer (*5*) and Sabbina and Velikovski (*10*). Great care was taken to have the experimental conditions at even temperature and pressure increments (Table II).

ACKNOWLEDGMENT

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Vapor-Liquid Equilibria of the Methane-Methylcyclohexane System at Low Temperatures and High Pressures

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The methane-methylcyclohexane system exhibits limited liquid miscibility at temperatures below the critical of methane. A quadruple point involving a gas phase, two liquid phases, and a solid phase has been located visually at −213.5° F. and 73 p.s.i.a. Experimental data on the pressure-temperature projection show that the low temperature phase behavior of this system is qualitatively similar to the methane–n-heptane system with the exception that a minimum point appears in the critical locus. Binary *K* values of methane and methylcyclohexane are reported at intervals of 20° from 0° to −100° F. for pressures from 100 p.s.i.a. to the critical of the system. The lowest *K* value of methylcyclohexane determined was 0.000044 at 100 p.s.i.a. and −100° F.

THE EQUILIBRIUM ratio and the low temperature phase behavior of the several methane-*n*-paraffin binary systems studied in the last few years have recently been reviewed (*2*). There are only a few references on the study of methane-aromatic or methane-naphthenic systems (*7, 8, 11*). The only literature data found for the methane-methylcyclohexane system was the study by Clark (*6*) in 1949.

The objectives of this study were: to obtain vapor-liquid equilibrium data on the methane-methylcyclohexane system over a temperature range comparable with that made for the methane-*n*-heptane (*4*) and the methane-toluene (*5*) systems—i.e., from 0° to −100° F. inclusive— and to reveal the effect of solvent types on the vapor-liquid equilibrium behavior of these systems; to provide basic data on binary systems which would serve as a basis for subsequent multicomponent vapor-liquid equilibrium studies at both infinitesimal and finite concentrations of the intermediate components both by classical and gas-liquid partition chromatography methods; and to provide basic data to permit theoretical studies on the effects of molecular size and structure of the solvent on the vapor-liquid equilibria behavior of hydrocarbon systems at low temperatures and elevated pressures (*2, 3*).

PHASE BEHAVIOR IN METHANE-METHYLCYCLOHEXANE BINARY SYSTEM

The binary phase behavior of methane with other *n*-paraffin hydrocarbons through *n*-decane offers three types of phase behavior: complete liquid phase miscibility, limited liquid miscibility, and the intersection of the three-phase solid-liquid-gas solubility curve locus with the gas-liquid critical locus, which causes an interruption in the latter. This study showed that the low temperature phase behavior of methane-methylcyclohexane system falls in the middle category and is qualitatively similar to methane–*n*-heptane binary system, which is characterized by liquid-liquid immiscibility and a quadruple point involving the coexistence of four phases, G-L_1-L_2-S. The four three-phase

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lines emanating from the quadruple point are L_1-L_2-G, L_1-L_2-S, L_1-S-G, and L_2-S-G, where L_1 represents the liquid phase rich in the solvent and S is substantially pure solvent. The $L_1 \equiv G$ critical locus runs from the critical of pure solvent to the "three-phase critical" in which the intensive properties of L_1 and L_2 become identical with essentially solid solvent present. The limited liquid phase immiscibility has both an upper and lower critical solution temperature for the methane-*n*-hexane (*13*) system.

A review of previous studies (*2*) indicates that all the gas-liquid critical loci for the methane-*n*-paraffin mixtures from methane-ethane to methane-*n*-decane show a maximum critical pressure. An interesting observation of the methane-methylcyclohexane system is that there is not only a maximum point in the critical locus but also a minimum point which exists at approximately −60° F. and 2722 p.s.i.a. For temperatures below −60° F. the critical pressure becomes higher as the temperature is lowered. The lowest temperature critical point which was observed was at −213.3° F. and 4225 p.s.i.a. Kohn and Kurata (*10*) reported that the methane–hydrogen sulfide system showed a similar inflection in the critical locus but found no minimum in the locus. This observed rise in the critical locus as the temperature is decreased is probably caused by the increasing role of the repulsive forces between methane and the solvent molecules in the lower temperature region.

The "Type *K* singular point" (*12*) for this system is very close to the corresponding point for the methane–*n*-heptane system (*4*). Since such a point represents the critical identity of a liquid phase rich in methane with a gas phase also rich in methane, it is expected to be very close to the critical point of pure methane. A study of the observed Type *K* singular points reported below confirms this.

	Critical, Methane	K_{singular}, Methane-*n*-Heptane	K_{singular}, Methane-Methylcyclohexane
T, ° F.	−116.6	−114.7	−113.8
P, p.s.i.a.	671.0	694.0	687.0

Table I. Observed Three-and Four-Phase Conditions of the Methane-Methylcyclohexane System

Phases	Temp., ° F.	Pressure, P.S.I.A.
L_1L_2G	−155.0	318
L_1L_2G	−177.5	190
L_1L_2G	−194.0	125
L_1SG	−216.0	66
L_1SG	−223.0	53
L_2SG	−209.5	65
L_2SG	−207.0	50
L_1L_2SG	−213.5	73
L_1L_2S	−213.5	100
L_1L_2S	−214.0	400
Type $K_{\text{singular point}}$	−113.8	687

Table II. Observed Critical Conditions of the Methane-Methylcyclohexane System

Temp., ° F.	Methane Critical Concentration[a]	Pressure, P.S.I.A.
0	0.910	3885
−20	0.910	3815
−40	0.915	3755
−60	0.920	3722
−80	0.920	3738
−100	0.930	3855
−110		3970
−115		4050
−117		4090
−123.3		4225

[a] Estimated.

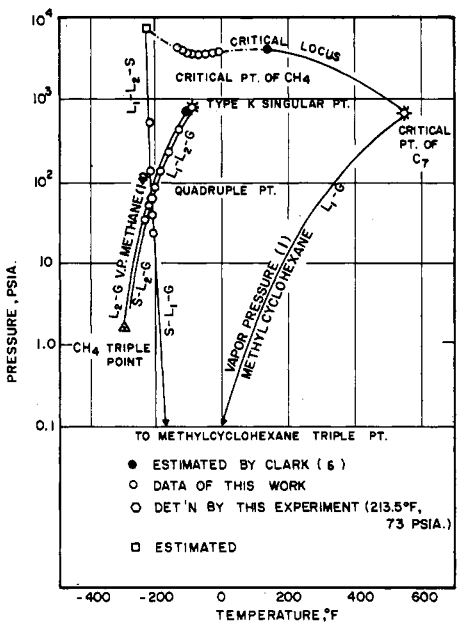

Figure 1. Pressure-temperature projection for the methane-methylcyclohexane system

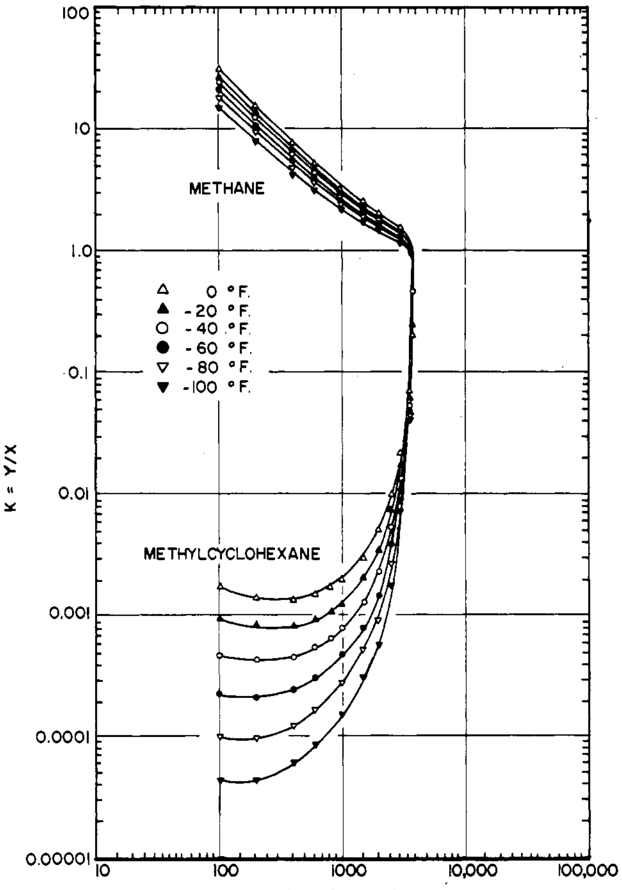

Figure 2. *K* value *vs.* pressure for methane-methylcyclohexane system

The quadruple point for the methane-methylcyclohexane system is far below the quadruple point for the methane–*n*-heptane system because of the appreciably lower freezing point of methylcyclohexane. A comparison of the pure component freezing points and of their respective quadruple points in the methane binary systems is presented below.

	Freezing Point		Quadruple Point	
	n-Heptane	Methylcyclohexane	Methane-*n*-heptane	Methane-Methyl cyclohexane
T, ° F.	−131.3	−195.6	−154.2	−213.5
P, p.s.i.a.	...	...	331.0	73.0

Table I presents the observed three- and four-phase conditions of the methane-methylcyclohexane system. Table II lists the observed critical temperatures and pressures of the methane-methylcyclohexane system together with some estimated critical compositions. The pressure-temperature projection of the methane-methylcyclohexane system in Figure 1 is a graphical summary of the general phase behavior of the system.

MATERIALS USED

The methane was purchased from the Matheson Co., Inc., and carried a certified purity of 99.99 mole %. The methane was passed through tubes packed with silica gel, activated charcoal, and Ascarite before being introduced into the equilibrium cell.

The methylcyclohexane was purchased from the Phillips Petroleum Co. and carried a reported purity of 99.96 mole %. It was used without further purification.

RESULTS AND DISCUSSION OF VAPOR-LIQUID EQUILIBRIUM DATA

The sampling procedure, the experimental equipment, and the analytical procedure have been discussed in detail (*2*) with a detailed error analysis. The expected maximum errors as summarized in a previous paper (*4*) were shown to be less than 5% of the amount present of the heavy component in the vapor phase.

The coexisting vapor and liquid compositions determined experimentally at the tabulated even values of pressure and temperature are given in Table III. Great care was taken to have the experimental conditions at even tem-

Table III. Vapor-Liquid Equilibrium Data of Methane-Methylcyclohexane System

P, P.S.I.A.	y_7	x_7	K_1	K_7
		0.0° F.		
100.0	0.00165	0.9667	29.98	0.00170
200.0	0.00131	0.9345	15.30	0.00140
400.0	0.00113	0.8726	7.85	0.00130
600.0	0.00119	0.8039	5.10	0.00148
800.0	0.00129	0.7561	4.10	0.00170
1000.0	0.00138	0.7101	3.45	0.00196
1250.0	0.00163	0.6530	2.88	0.00250
1500.0	0.00180	0.6016	2.51	0.00300
1750.0	0.00228	0.5550	2.24	0.00410
2000.0	0.00250	0.5050	2.00	0.00500
2250.0	0.00331	0.4669	1.87	0.00710
2500.0	0.00429	0.4286	1.75	0.01000
2750.0	0.00578	0.3851	1.62	0.01500
3000.0	0.00754	0.3506	1.54	0.0215
3250.0	0.01091	0.2949	1.44	0.0370
3500.0	0.01776	0.2537	1.34	0.0700
3750.0	0.03472	0.1736	1.21	0.230
		−20.0° F.		
100.0	0.00089	0.9623	26.90	0.00092
200.0	0.00074	0.9263	13.55	0.00080
400.0	0.00068	0.8553	6.91	0.00079
600.0	0.00072	0.7912	4.79	0.00091
800.0	0.00075	0.7369	3.80	0.00102
1000.0	0.00084	0.6835	3.16	0.00123
1250.0	0.00097	0.6251	2.66	0.00155
1500.0	0.00113	0.5726	2.34	0.00198
1750.0	0.00136	0.5224	2.09	0.00260
2000.0	0.00161	0.4737	1.90	0.00340
2250.0	0.00212	0.4335	1.76	0.00490
2500.0	0.00297	0.4012	1.67	0.00739
2750.0	0.00395	0.3554	1.55	0.01112
3000.0	0.00538	0.3197	1.47	0.01682
3250.0	0.00816	0.2750	1.37	0.0302
3500.0	0.01511	0.2477	1.31	0.0620
3750.0	0.04097	0.1671	1.15	0.275
		−40.0° F.		
100.0	0.00044	0.9583	24.00	0.00046
200.0	0.00039	0.9180	12.20	0.00043
400.0	0.00038	0.8412	6.30	0.00045
600.0	0.00041	0.7773	4.49	0.00053
800.0	0.00045	0.7169	3.53	0.00063
1000.0	0.000505	0.6594	2.94	0.00077
1250.0	0.000590	0.6025	2.51	0.00098
1500.0	0.000704	0.5455	2.20	0.00129
1750.0	0.000843	0.4875	1.96	0.00173
2000.0	0.00102	0.4444	1.80	0.00230
2250.0	0.00140	0.3999	1.66	0.00350
2500.0	0.00189	0.3631	1.57	0.00520
2750.0	0.00264	0.3290	1.49	0.0080
3000.0	0.00375	0.2806	1.39	0.0134
3250.0	0.00701	0.2579	1.34	0.0222
3500.0	0.01121	0.1934	1.23	0.0580
		−60.0° F.		
100.0	0.000210	0.9524	21.01	0.00022
200.0	0.000191	0.9082	10.89	0.00021
400.0	0.000198	0.8246	5.70	0.00024
600.0	0.000226	0.7531	4.05	0.00030
800.0	0.000256	0.6923	3.25	0.00037
1000.0	0.000300	0.6377	2.76	0.00047
1250.0	0.000349	0.5727	2.34	0.00061
1500.0	0.000410	0.5146	2.06	0.00078
1750.0	0.000471	0.4615	1.86	0.00102
2000.0	0.000593	0.4118	1.70	0.00144
2250.0	0.000862	0.3731	1.59	0.00231
2500.0	0.00170	0.3478	1.51	0.00380
2750.0	0.00213	0.2951	1.42	0.00722
3000.0	0.00259	0.2568	1.35	0.0101
3250.0	0.00401	0.2172	1.27	0.0185
3500.0	0.00866	0.1624	1.18	0.0533
		−80.0° F.		
100.0	0.000094	0.9445	18.01	0.00010
200.0	0.000095	0.8949	9.51	0.000095
400.0	0.000120	0.8055	5.14	0.000120
600.0	0.000119	0.7245	3.63	0.000164
800.0	0.000154	0.6997	3.00	0.00022
1000.0	0.000170	0.6078	2.55	0.00028
1250.0	0.000207	0.5454	2.20	0.00038
1500.0	0.000255	0.4819	1.93	0.00053
1750.0	0.000315	0.4253	1.74	0.00074
2000.0	0.000379	0.3827	1.62	0.00099
2250.0	0.000514	0.3428	1.52	0.00150
2500.0	0.000762	0.3048	1.43	0.00250
2750.0	0.00122	0.2647	1.36	0.00460
3000.0	0.00203	0.2344	1.30	0.00860
3250.0	0.00414	0.1937	1.24	0.0214
3500.0	0.00786	0.1540	1.17	0.0510
		−100.0° F.		
100.0	0.000041	0.9334	15.01	0.000044
200.0	0.000039	0.8762	8.08	0.000044
400.0	0.000046	0.7800	4.40	0.000060
600.0	0.000059	0.6923	3.25	0.000085
800.0	0.000070	0.6292	2.64	0.000113
1000.0	0.000084	0.5733	2.29	0.000150
1250.0	0.000107	0.5155	1.99	0.000220
1500.0	0.000136	0.4442	1.78	0.000310
1750.0	0.000168	0.3902	1.64	0.000430
2000.0	0.000216	0.3491	1.52	0.000630
2250.0	0.000292	0.3097	1.43	0.000970
2500.0	0.000472	0.2793	1.39	0.00169
2750.0	0.000920	0.2520	1.34	0.0037
3000.0	0.00159	0.2180	1.28	0.0073
3250.0	0.00384	0.1829	1.22	0.0210
3500.0	0.00719	0.1440	1.16	0.0499

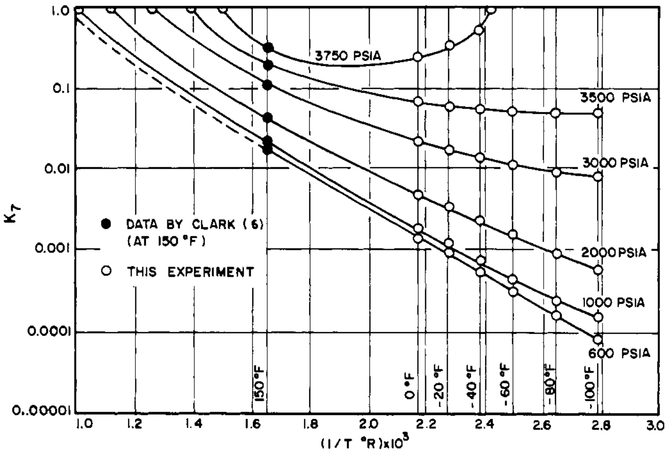

Figure 3. *K* value of methylcyclohexane *vs.* 1/*T* in the methane-methylcyclohexane system

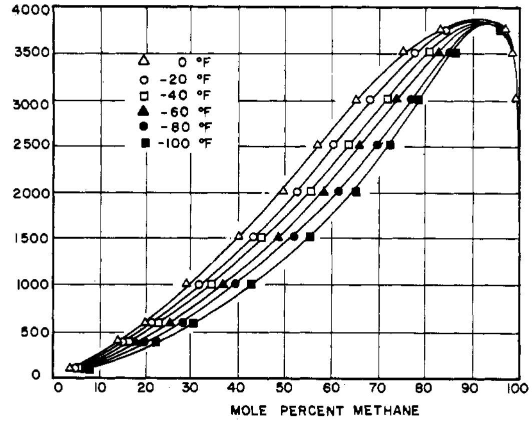

Figure 4. Pressure-composition diagram for the methane-methylcyclohexane system

perature and pressure increments (Table III). One more significant figure than is justified has been frequently, though not always, carried in presenting the methylcyclohexane concentrations in the liquid phase. The calculated *K* values for the methane and methylcyclohexane are also tabulated in Table III at the experimental temperatures and pressures. *K* values for methylcyclohexane as low as 0.000044 were measured at −100° F. and 100 p.s.i.a.

The *K* values for methane and methylcyclohexane are summarized in Figure 2 on a log-log plot of the *K* values *vs.* pressure at the isotherms studied. The plots show that Raoult-Dalton's law does not hold for even the lowest pressure and highest temperature studied. Because the experimental studies covered the range of temperatures in the region of the minimum in the critical locus, the critical pressure was observed to vary little with temperature.

The isobaric self-consistency of this work and the probable interconsistency of this work and the data of Clark are indicated in Figure 3.

The pressure-composition diagram for the methane-methylcyclohexane system in Figure 4 shows the liquid phase compositions and the approximate location of the mixture criticals. The vapor phase compositions essentially coincide with the methane axis.

A study of the comparative magnitudes of the *K* values of methane in the three solvents *n*-heptane, methylcyclohexane, and toluene at comparable values of temperatures and pressures has been presented (*9*). A comprehensive theory correlating the solubility of methane in the same three solvents has also been developed (*2*, *3*).

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