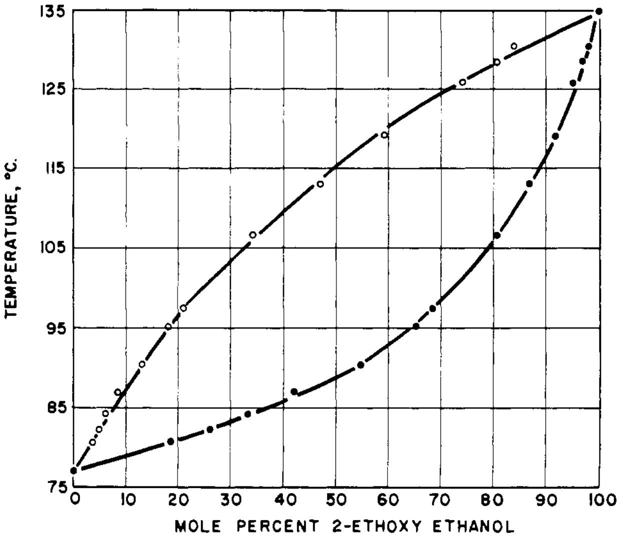

Figure 1. Boiling point–composition diagram for system 2-ethoxyethanol–ethyl acetate

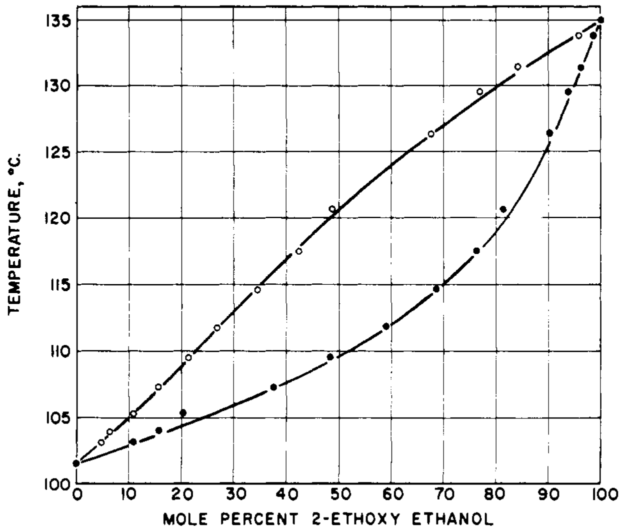

Figure 2. Boiling point–composition diagram for system 2-ethoxyethanol–propyl acetate

a manostat similar to that previously described (*6*). Positive pressure on the still was provided by dry nitrogen. The thermometer was calibrated against several pure liquid standards.

RESULTS

The experimental results are shown in Tables I and II and graphically in Figures 1 and 2. The activity coefficient, γ, of 2-ethoxyethanol in ethyl and propyl acetate has been calculated using the relation

$$\gamma = \frac{p y_1}{p_1 x_1}$$

where p signifies total gas pressure, 760 mm., y_1 the mole fraction of 2-ethoxyethanol in the vapor phase, x_1 the mole fraction of 2-ethoxyethanol in the liquid phase, and p_1 the vapor pressure of pure 2-ethoxyethanol. Values for p_1 were calculated using the Antoine equation,

$$\log p_1 = A - B/t + C$$

with constants approximated from the experimental data of Gardner (*2*).

The average value for γ in 2-ethoxyethanol-ethyl acetate solutions above 82.3° is calculated as 1.09 with the average deviation from the mean in this range ± 0.05. The average value for γ in 2-ethoxyethanol-propyl acetate solutions above 105.3° is calculated as 0.99 with average deviation from the mean in this range ± 0.02. In both of these systems there is a gradual increase in activity coefficient of 2-ethoxyethanol in the high acetate concentration range. Although there are no azeotropes in these systems, appreciable deviation from ideality does exist in dilute solutions of 2-ethoxyethanol in ethyl and propyl acetate, as indicated by the increase in the activity coefficient in this concentration range.

The refractive index-composition curve for the 2-ethoxyethanol-propyl acetate system gives a curve bowed slightly downward; in the 2-ethoxyethanol-ethyl acetate system a straight-line relation was obtained.

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Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the Methane-Cyclohexane System

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Quantitative information concerning the volumetric and phase behavior of hydrocarbon mixtures is often of value in connection with the production and refining of petroleum. Such equilibrium data are also essential to the evaluation and application of information concerning molecular transport in which deviations from equilibrium are encountered. No information was found by the authors concerning the volumetric or phase behavior of mixtures of methane and cyclohexane. Because of the absence of such experimental information, a study was made of the volumetric behavior of four mixtures of methane and cyclohexane at pressures up to 10,000 p.s.i. and at temperatures between 70° and 340° F. Significant thermal rearrangement of the cyclohexane occurred at higher temperatures, thus limiting the range of temperatures investigated.

The volumetric behavior of cyclohexane has been studied in detail near atmospheric pressure and was critically reviewed by Rossini (*14*). More recently the effect of pressure and temperature upon the molal volume of cyclohexane liquid has been determined (*9*). The latter investigation included measurements of vapor pressure of cyclohexane which were in good agreement with the critically chosen values of Rossini (*14*). The critical properties of cyclohexane were established by Meissner and Redding (*5*), who reported a critical temperature of 538° F. and a critical pressure of 593.7 p.s.i.

The volumetric behavior of methane has been well established (*3,4,6*) and the data are in good agreement with available Joule-Thomson (*2*) and heat capacity measurements (*18*). These data, together with some supplemental measurements at higher pressures, have been summarized (*7*). It is believed that the volumetric and phase behavior of meth-

Table I. Molal Volumes for Mixtures of Methane and Cyclohexane

Pressure, P.S.I.A.	Mole Fraction Methane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
70° F.									
DP[b]	(2)[a] ...	(3) ...	(4) ...	(6) ...	(8) ...	(10) ...	(12) ...	(14) ...	(15) ...
BP	(458)[a] 1.639	(958) 1.545	(1488) 1.451	(2058) 1.360	(2645) 1.276	(3260) 1.202	(3810) 1.142	(4080)[c] 1.123	(3825)[c] 1.186
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	1.636[d]	...	...	...	...	...	...	...	...
800	1.632	...	...	...	...	...	...	...	...
1,000	1.629	1.543	...	...	...	...	...	...	...
1,250	1.625	1.538	...	...	...	...	...	...	...
1,500	1.621	1.534	1.450	...	...	...	...	...	...
1,750	1.617	1.530	1.444	...	...	...	...	...	...
2,000	1.614	1.526	1.439	...	...	...	...	...	...
2,250	1.610	1.522	1.434	1.355	...	...	...	...	...
2,500	1.607	1.518	1.430	1.349	...	...	...	...	...
2,750	1.604	1.514	1.426	1.343	1.271	...	...	...	...
3,000	1.600	1.511	1.422	1.338	1.265	...	...	...	...
3,500	1.596	1.506	1.416	1.332	1.257	1.196	...	...	...
4,000	1.591	1.502	1.411	1.326	1.249	1.184	1.134	...	...
4,500	1.587	1.497	1.407	1.321	1.242	1.173	1.119	1.090	1.110
5,000	1.583	1.493	1.402	1.315	1.234	1.162	1.106	1.073	1.068
6,000	1.574	1.484	1.393	1.305	1.221	1.145	1.084	1.040	1.013
7,000	1.567	1.476	1.384	1.296	1.210	1.130	1.066	1.014	0.974
8,000	1.558	1.469	1.376	1.287	1.199	1.117	1.050	0.992	0.941
9,000	1.552	1.462	1.368	1.278	1.189	1.106	1.033	0.971	0.912
10,000	1.546	1.455	1.361	1.270	1.180	1.098	1.017	0.950	0.888
100° F.									
DP	(6)[a] ...	(9) ...	(12) ...	(16) ...	(20) ...	(23) ...	(26) ...	(29) ...	(31) ...
BP	(494)[a] 1.679	(1013) 1.584	(1575) 1.491	(2170) 1.401	(2778) 1.317	(3378) 1.245	(3890) 1.204	(4028)[c] 1.202	(3750)[c] 1.320
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	1.675[d]	...	...	...	...	...	...	...	...
800	1.671	...	...	...	...	...	...	...	...
1,000	1.667	...	...	...	...	...	...	...	...
1,250	1.663	1.578	...	...	...	...	...	...	...
1,500	1.659	1.573	...	...	...	...	...	...	...
1,750	1.655	1.568	1.486	...	...	...	...	...	...
2,000	1.651	1.564	1.481	...	...	...	...	...	...
2,250	1.648	1.560	1.476	1.398	...	...	...	...	...
2,500	1.644	1.555	1.471	1.391	...	...	...	...	...
2,750	1.641	1.553	1.466	1.385	...	...	...	...	...
3,000	1.637	1.548	1.462	1.379	1.309	...	...	...	...
3,500	1.631	1.542	1.453	1.370	1.297	1.241	...	...	...
4,000	1.626	1.536	1.446	1.362	1.287	1.226	1.196	...	...
4,500	1.620	1.530	1.440	1.356	1.278	1.213	1.168	1.156	1.190
5,000	1.614	1.525	1.434	1.348	1.269	1.199	1.149	1.126	1.137
6,000	1.604	1.513	1.423	1.336	1.253	1.177	1.121	1.087	1.060
7,000	1.595	1.503	1.412	1.324	1.238	1.159	1.098	1.052	1.017
8,000	1.586	1.494	1.403	1.313	1.225	1.145	1.079	1.024	0.980
9,000	1.576	1.485	1.392	1.303	1.215	1.134	1.062	0.998	0.945
10,000	1.570	1.477	1.384	1.294	1.205	1.123	1.045	0.973	0.914
160° F.									
DP	(19)[a] ...	(27) ...	(35) ...	(44) ...	(53) ...	(62) ...	(70) ...	(80) ...	(123) ...
BP	(540)[a] 1.755	(1108) 1.663	(1693) 1.572	(2309) 1.487	(2898) 1.411	(3470) 1.345	(3830) 1.337	(3845) 1.399	(3500) 1.599
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	1.752[d]	...	...	...	...	...	...	...	...
800	1.747	...	...	...	...	...	...	...	...
1,000	1.743	...	...	...	...	...	...	...	...
1,250	1.740	1.657	...	...	...	...	...	...	...
1,500	1.736	1.652	...	...	...	...	...	...	...
1,750	1.732	1.648	1.569	...	...	...	...	...	...
2,000	1.727	1.644	1.562	...	...	...	...	...	...
2,250	1.723	1.638	1.556	...	...	...	...	...	...
2,500	1.720	1.634	1.551	1.478	...	...	...	...	...
2,750	1.716	1.629	1.546	1.471	...	...	...	...	...
3,000	1.710	1.624	1.541	1.464	1.404	...	...	...	...
3,500	1.702	1.615	1.530	1.451	1.382	1.343	...	...	...
4,000	1.691	1.606	1.520	1.440	1.368	1.318	1.312	1.370	1.465
4,500	1.684	1.599	1.511	1.428	1.356	1.298	1.264	1.278	1.346
5,000	1.676	1.589	1.502	1.418	1.343	1.280	1.240	1.240	1.280
6,000	1.665	1.575	1.485	1.399	1.319	1.250	1.200	1.183	1.186
7,000	1.652	1.561	1.472	1.384	1.299	1.226	1.166	1.128	1.109
8,000	1.641	1.548	1.457	1.368	1.284	1.206	1.138	1.088	1.055
9,000	1.629	1.537	1.446	1.355	1.270	1.189	1.113	1.054	1.011
10,000	1.618	1.527	1.436	1.345	1.258	1.174	1.092	1.025	0.975

Pressure, P.S.I.A.	Mole Fraction Methane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
220° F.									
DP	(40)[a] ...	(53) ...	(68) ...	(82) ...	(98) ...	(115) ...	(131) ...	(157) ...	(365) ...
BP	(587)[a] 1.850	(1170) 1.759	(1772) 1.669	(2390) 1.586	(2958) 1.523	(3450) 1.483	(3685) 1.512	(3587)[c] 1.625	(2950)[c] 2.114
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	...
800	1.843[d]	...	...	...	...	...	...	...	...
1,000	1.837	...	...	...	...	...	...	...	...
1,250	1.828	1.756	...	...	...	...	...	...	...
1,500	1.821	1.745	...	...	...	...	...	...	...
1,750	1.816	1.736	...	...	...	...	...	...	...
2,000	1.810	1.728	1.658	...	...	...	...	...	...
2,250	1.803	1.720	1.649	...	...	...	...	...	...
2,500	1.797	1.714	1.639	1.579	...	...	...	...	...
2,750	1.792	1.708	1.630	1.568	...	...	...	...	...
3,000	1.785	1.702	1.622	1.558	...	...	...	...	...
3,500	1.773	1.688	1.607	1.538	1.490	1.481	...	...	...
4,000	1.763	1.677	1.595	1.522	1.465	1.432	1.444	1.530	1.656
4,500	1.753	1.666	1.584	1.507	1.442	1.400	1.393	1.434	1.524
5,000	1.744	1.655	1.570	1.490	1.420	1.372	1.356	1.372	1.425
6,000	1.726	1.638	1.550	1.466	1.389	1.330	1.294	1.285	1.299
7,000	1.711	1.621	1.533	1.446	1.365	1.296	1.244	1.214	1.207
8,000	1.697	1.604	1.515	1.425	1.342	1.270	1.206	1.162	1.138
9,000	1.683	1.591	1.500	1.410	1.323	1.245	1.176	1.122	1.084
10,000	1.669	1.578	1.487	1.397	1.309	1.227	1.150	1.087	1.040
280° F.									
DP	(75)[a] ...	(90) ...	(105) ...	(121) ...	(140) ...	(171) ...	(233) ...	(400) ...	... ...
BP	(627)[a] 1.962	(1219) 1.869	(1821) 1.784	(2430) 1.716	(2932) 1.686	(3283) 1.695	(3341)[c] 1.794	(3114)[c] 2.054	... ...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	...
800	1.949[d]	...	...	...	...	...	...	...	...
1,000	1.938	...	...	...	...	...	...	...	...
1,250	1.928	1.868	...	...	...	...	...	...	...
1,500	1.919	1.853	...	...	...	...	...	...	...
1,750	1.908	1.838	...	...	...	...	...	...	...
2,000	1.898	1.825	1.771	...	...	...	...	...	...
2,250	1.889	1.814	1.753	...	...	...	...	...	...
2,500	1.881	1.804	1.742	1.710	...	...	...	...	...
2,750	1.873	1.795	1.729	1.690	...	...	...	...	...
3,000	1.864	1.786	1.717	1.671	1.679	...	...	...	...
3,500	1.849	1.767	1.698	1.641	1.622	1.643	1.733	1.884	2.066
4,000	1.832	1.749	1.678	1.618	1.579	1.568	1.614	1.720	1.863
4,500	1.819	1.735	1.660	1.594	1.539	1.515	1.538	1.606	1.712
5,000	1.807	1.722	1.643	1.571	1.512	1.478	1.479	1.519	1.593
6,000	1.787	1.700	1.617	1.540	1.471	1.421	1.394	1.398	1.430
7,000	1.769	1.679	1.590	1.509	1.438	1.376	1.329	1.309	1.312
8,000	1.751	1.660	1.571	1.487	1.408	1.339	1.282	1.245	1.227
9,000	1.735	1.644	1.555	1.469	1.384	1.308	1.242	1.195	1.164
10,000	1.720	1.629	1.540	1.452	1.364	1.283	1.212	1.154	1.114
340° F.									
DP	(136)[a] ...	(157) ...	(181) ...	(214) ...	(270) ...	(355) ...	(524) ...	(1215) 6.35[b]	... ...
BP	(668)[a] 2.100	(1215) 6.35[b]	(1858) 1.940	(2410) 1.878	(2790) 1.866	(2910) 1.983	(2753)[c] 2.363	(2065)[c] 3.50	... ...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	...
800	2.086	...	...	...	...	...	...	...	...
1,000	2.067	...	...	...	...	...	...	...	...
1,250	2.050	...	...	...	...	...	...	...	...
1,500	2.032	1.990	...	...	...	...	...	...	...
1,750	2.017	1.965	...	...	...	...	...	...	...
2,000	2.002	1.944	1.920	...	...	...	...	...	...
2,250	1.987	1.925	1.896	...	...	...	...	...	..
2,500	1.973	1.907	1.873	1.866	...	...	...	...	...
2,750	1.959	1.890	1.850	1.836	...	...	...	...	...
3,000	1.946	1.874	1.830	1.811	1.832	1.979	2.193	2.425	2.655
3,500	1.924	1.846	1.794	1.763	1.766	1.833	1.970	2.139	2.320
4,000	1.905	1.822	1.760	1.722	1.715	1.737	1.815	1.938	2.075
4,500	1.887	1.802	1.738	1.688	1.660	1.659	1.702	1.791	1.901
5,000	1.868	1.785	1.716	1.662	1.620	1.604	1.620	1.676	1.757
6,000	1.843	1.758	1.682	1.615	1.555	1.518	1.505	1.519	1.557
7,000	1.823	1.736	1.654	1.580	1.514	1.458	1.424	1.412	1.419
8,000	1.806	1.716	1.632	1.554	1.480	1.411	1.362	1.333	1.321
9,000	1.789	1.699	1.613	1.529	1.449	1.374	1.313	1.272	1.247
10,000	1.771	1.683	1.594	1.509	1.424	1.344	1.276	1.225	1.188

[a] Values in parentheses represent dew point or bubble point pressures, p.s.i.a.

[b] Values at dew point estimated.

[c] Retrograde dew point.

[d] Molal volumes expressed in cubic feet per pound mole.

Table II. Properties of Coexisting Gas and Liquid Phases

Pressure, P.S.I.A.	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole Fraction Methane	Volume, Cu.Ft./Lb. Mole	Mole Fraction Methane	Volume, Cu.Ft./Lb. Mole	Methane	Cyclohexane
			At 70° F.			
1.58^{a}	0	...	0	1.73^{b}	...	1.0000
200	0.9891	...	0.0440	1.693	22.480	0.0114
400	0.9924	...	0.0870	1.651	11.407	0.0083
600	0.9934	8.6^{c}	0.1288	1.612	7.713	0.0076
800	0.9938	6.3	0.1693	1.574	5.870	0.0075
1,000	0.9938	4.95	0.2086	1.537	4.764	0.0078
1,250	0.9931	3.80	0.2560	1.492	3.879	0.0093
1,500	0.9920	3.10	0.3022	1.448	3.283	0.0115
1,750	0.9901	2.619	0.3468	1.407	2.855	0.0152
2,000	0.9873	2.243	0.3901	1.368	2.531	0.0208
2,250	0.9844	1.989	0.4331	1.331	2.273	0.0275
2,500	0.9805	1.768	0.4750	1.296	2.064	0.0371
2,750	0.9740	1.589	0.5170	1.263	1.884	0.0538
3,000	0.9661	1.451	0.5581	1.232	1.731	0.0767
3,500	0.9390	1.253	0.6392	1.177	1.469	0.1691
4,000	0.8489	1.133	0.7350	1.124	1.155	0.5702
4,090^{d}	0.765	1.121	0.765	1.121	1.000	1.0000
			At 100° F.			
3.2^{a}	0	...	0	1.775	...	1.0000
200	0.9793	...	0.0414	1.736	23.655	0.0216
400	0.9860	...	0.0820	1.695	12,024	0.0152
600	0.9876	9.3	0.1217	1.658	8.115	0.0141
800	0.9883	6.8	0.1601	1.621	6.175	0.0139
1,000	0.9885	5.34	0.1977	1.585	5.000	0.0143
1,250	0.9876	4.16	0.2430	1.543	4.064	0.0164
1,500	0.9860	3.40	0.2870	1.502	3.436	0.0196
1,750	0.9840	2.871	0.3300	1.462	2.982	0.0239
2,000	0.9810	2.473	0.3720	1.425	2.637	0.0302
2,250	0.9770	2.185	0.4129	1.390	2.366	0.0392
2,500	0.9710	1.950	0.4540	1.356	2.139	0.0531
2,750	0.9640	1.770	0.4959	1.320	1.944	0.0714
3,000	0.9539	1.616	0.5365	1.289	1.778	0.0995
3,500	0.9270	1.398	0.6201	1.234	1.495	0.1922
4,000	0.8263	1.214	0.7274	1.197	1.136	0.6372
4,040^{d}	0.758	1.194	0.758	1.194	1.000	1.0000
			At 160° F.			
10.9^{a}	0	...	0	1.851	...	1.0000
200	0.9380	...	0.0365	1.814	25.700	0.0644
400	0.9616	...	0.0740	1.779	12.995	0.0415
600	0.9671	10.5	0.1103	1.745	8.768	0.0370
800	0.9700	7.7	0.1462	1.712	6.635	0.0351
1,000	0.9709	6.1	0.1812	1.680	5.358	0.0355
1,250	0.9712	4.79	0.2244	1.640	4.328	0.0371
1,500	0.9700	3.93	0.2670	1.601	3.633	0.0409
1,750	0.9678	3.34	0.3086	1.564	3.136	0.0466
2,000	0.9649	2.882	0.3505	1.529	2.753	0.0540
2,250	0.9598	2.550	0.3911	1.495	2.454	0.0660
2,500	0.9540	2.257	0.4323	1.462	2.207	0.0808
2,750	0.9459	2.042	0.4746	1.429	1.993	0.1030
3,000	0.9370	1.859	0.5180	1.398	1.809	0.1307
3,500	0.9002	1.598	0.6070	1.341	1.483	0.2540
3,880^{d}	0.737	1.354	0.737	1.354	1.000	1.0000

ane and of cyclohexane were known with sufficient accuracy so as not to contribute significantly to the uncertainty of the current investigation of mixtures of these two components.

APPARATUS AND METHODS

The equipment employed in this investigation has been described in detail (*17*). A stainless steel pressure vessel was used to contain known quantities of methane and cyclohexane. The volume of the chamber available to hydrocarbons was varied by the introduction and withdrawal of mercury. Equilibrium was hastened by a mechanical agitator, and the equilibrium volume and pressure were determined for a series of systematically chosen temperatures. The quantity of cyclohexane introduced into the vessel was determined by weighing bomb techniques (*17*) with a probable uncertainty of not more than 0.03%. The methane was added from another pressure vessel by a displacement technique at constant pressure. It is probable that the weight of methane introduced was known with an uncertainty not larger than 0.15%, which is comparable to that with which the volumetric behavior of methane is known.

Pressures were measured by means of a balance (*17*) which was calibrated against the vapor pressure of carbon dioxide at the ice point (*1*). The pressure of the sample was established with a probable error of 0.05% or 0.1 p.s.i., whichever was the larger measure of uncertainty. The temperature of the sample was determined from that of an agitated oil bath surrounding the stainless steel pressure vessel measured by means of a strain-free platinum resistance thermometer of the coil-filament type which was compared with a similar instrument calibrated by the National Bureau of

Table II. (Continued)

Pressure, P.S.I.A.	Dew Point: Mole Fraction Methane	Dew Point: Volume, Cu.Ft./Lb. Mole	Bubble Point: Mole Fraction Methane	Bubble Point: Volume, Cu.Ft./Lb. Mole	Equilibrium Ratio: Methane	Equilibrium Ratio: Cyclohexane
			At 220° F.			
28.4[a]	0	...	0	1.945	...	1.0000
200	0.8437	...	0.0318	1.915	26.531	0.1625
400	0.9065	...	0.0677	1.880	13.390	0.1003
600	0.9249	11.5	0.1028	1.847	8.997	0.0837
800	0.9334	8.6	0.1373	1.816	6.798	0.0772
1,000	0.9381	6.7	0.1714	1.786	5.473	0.0747
1,250	0.9417	5.34	0.2134	1.747	4.413	0.0741
1,500	0.9410	4.40	0.2548	1.709	3.693	0.0792
1,750	0.9399	3.74	0.2963	1.673	3.172	0.0854
2,000	0.9370	3.23	0.3374	1.637	2.777	0.0951
2,250	0.9310	2.843	0.3780	1.604	2.463	0.1109
2,500	0.9220	2.527	0.4191	1.572	2.200	0.1343
2,750	0.9109	2.291	0.4610	1.543	1.976	0.1653
3,000	0.8960	2.068	0.5079	1.518	1.764	0.2113
3,500	0.8270	1.691	0.6090	1.481	1.358	0.4425
3,690[d]	0.711	1.520	0.711	1.520	1.000	1.0000
			At 280° F.			
62.0[a]	0	...	0	2.055	...	1.0000
200	0.6520	...	0.0248	2.032	26.290	0.3568
400	0.7990	...	0.0603	1.999	13.250	0.2139
600	0.8464	12.3	0.0951	1.966	8.900	0.1697
800	0.8709	9.3	0.1295	1.934	6.725	0.1483
1,000	0.8853	7.3	0.1634	1.904	5.418	0.1371
1,250	0.8939	5.77	0.2054	1.866	4.352	0.1335
1,500	0.8967	4.79	0.2471	1.828	3.629	0.1372
1,750	0.8961	4.04	0.2886	1.793	3.105	0.1460
2,000	0.8918	3.50	0.3297	1.760	2.705	0.1614
2,250	0.8829	3.07	0.3708	1.732	2.381	0.1861
2,500	0.8690	2.718	0.4134	1.710	2.102	0.2233
2,750	0.8501	2.420	0.4615	1.692	1.842	0.2784
3,000	0.8210	2.162	0.5141	1.683	1.597	0.3684
3,350[d]	0.667	1.750	0.667	1.750	1.000	1.0000
			At 340° F.			
120[a]	0	...	0	2.190	...	1.0000
200	0.3653	...	0.0148	2.176	24,682	0.6442
400	0.6354	...	0.0512	2.144	12.410	0.3843
600	0.7236	...	0.0870	2.112	8.317	0.3027
800	0.7673	9.9	0.1224	2.080	6.269	0.2652
1,000	0.7891	7.7	0.1566	2.052	5.039	0.2501
1,250	0.8019	6.0	0.1984	2.017	4.042	0.2471
1,500	0.8059	4.92	0.2392	1.984	3.369	0.2551
1,750	0.8079	4.17	0.2820	1.952	2.865	0.2675
2,000	0.8031	3.63	0.3250	1.923	2.471	0.2917
2,250	0.7886	3.15	0.3697	1.894	2.133	0.3354
2,500	0.7644	2.756	0.4193	1.868	1.823	0.4057
2,750	0.7000	2.363	0.4781	1.860	1.464	0.5748
2,910[d]	0.608	2.020	0.608	2.020	1.000	1.0000

[a] Vapor pressure of cyclohexane.
[b] Extrapolated.
[c] Volumes at dew point calculated.
[d] Critical state.

Standards. The intercomparison of these instruments indicates that the temperature of the sample was related to the international platinum scale with an uncertainty of less than 0.03° F.

After a series of measurements at ascending temperatures, the volumetric behavior of each mixture was again measured at 100° F. In the case of measurements extended to temperatures higher than 340° F. significant differences were observed. In such cases the initial measurements were adopted. However, even at 340° F. the variation between the initial and final measurements was as much as 0.2%. For this reason it is believed that the data at temperatures above 280° F. may involve uncertainties of as much as 0.35%. For the lower temperatures the probable error is about 0.25%.

The bubble point was determined by the discontinuous change in the isothermal derivative of molal volume with respect to pressure at constant composition. The composition at dew point was obtained by withdrawal of samples of the gas phase from a heterogeneous mixture under isobaric-isothermal conditions. The composition of the samples withdrawn was determined by a partial condensation procedure. The gas sample was passed through a partial condenser (*8*) which was maintained near the temperature of solid carbon dioxide and acetone and near the vapor pressure of methane at liquid nitrogen temperatures. The methane was condensed in a weighing bomb at the temperature of liquid nitrogen and the quantity of each component was determined by the gain in weight of the weighing bomb. The quantity of cyclohexane accumulating in the weighing bomb was found to be negligible, which permitted a somewhat simpler technique to be followed than was used in the case of the methane–*n*-heptane system (*11*). Measurements upon duplicate samples withdrawn at the same equilibrium states indicate a probable error of the order of 0.002 mole fraction of cyclohexane.

MATERIALS

The methane used in this investigation was obtained from a field in the San Joaquin Valley. As received, it contained traces of carbon dioxide and was saturated with water. The sample was passed over calcium chloride, potassium hydroxide, activated charcoal, anhydrous calcium sulfate, and Ascarite at pressures in excess of 500 p.s.i. A mass spectrographic analysis of methane from this source, which had been purified as described, indicated that the sample contained less than 0.001 mole fraction of material other than methane and negligible amounts of other hydrocarbons.

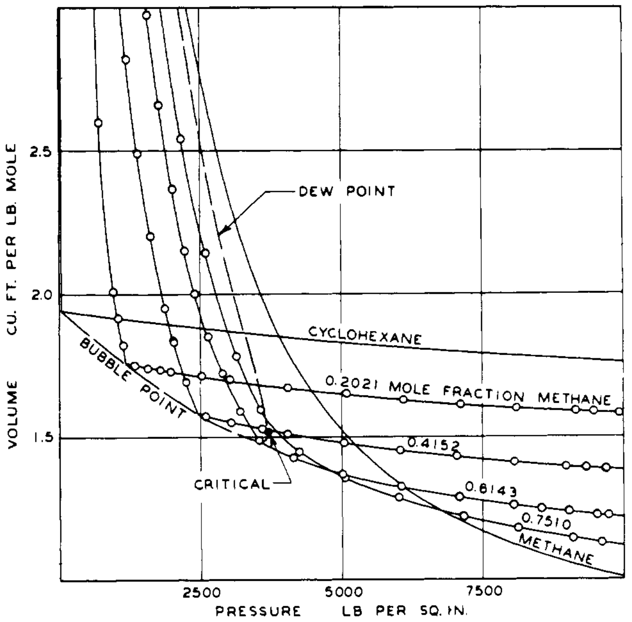

Figure 1. Experimental volumetric measurements at 220° F.

The cyclohexane was obtained from the Phillips Petroleum Co. as research grade which was said to contain 0.0002 mole fraction of impurities. As a result of earlier difficulties with regard to the purity of this material (*9*) the sample was dried over metallic sodium and fractionated in a column containing 16 glass plates at a reflux ratio greater than 30. The initial and final 5% fractions of the overhead were discarded. After deaeration by extended refluxing at reduced pressure, the cyclohexane had a specific weight of 48.306 pounds per cubic foot and a refractive index of 1.4235 relative to the *D*-lines of sodium at 77° F. These values compare favorably with the specific weight of 48.311 pounds per cubic foot and a refractive index of 1.42354 reported by Rossini (*14*) for air-saturated cyclohexane.

EXPERIMENTAL RESULTS

The experimental volumetric measurements obtained at a temperature of 220° F. are shown in Figure 1. The density of experimental points shown there for each of the four mixtures is typical of that obtained at the other four temperatures investigated. The detailed experimental data obtained in the course of this study are available (*10*).

Experimental information of the type shown in Figure 1 was smoothed by residual graphical methods (*12, 15*). These smoothed data for even compositions, pressures, and temperatures are recorded in Table 1. It is believed that the probable error in molal volume is 0.25% over the range of conditions between 70° and 280° F. but uncertainties as large as 0.35% may be encountered at the higher temperature. The standard error of estimate of the smoothed data from the experimental information was less than 0.0022 cubic foot per pound mole, corresponding to 0.15% average deviations. Corresponding volumetric behaviors for pure methane and cyclohexane are not included, as these data are available (*8*, *9*).

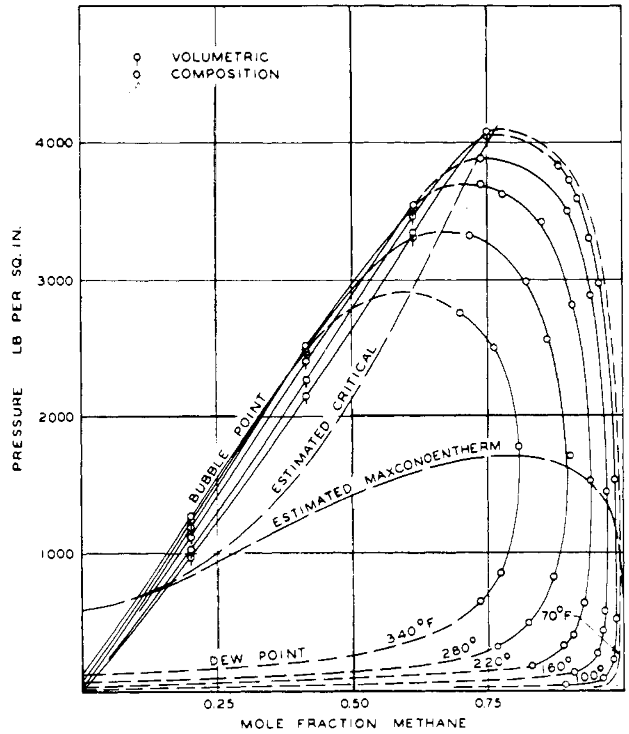

Figure 2. Composition of coexisting gas and liquid phases

The compositions of the coexisting liquid and gas phases obtained from experimentally measured composition of the gas phase, and the composition at bubble-point state determined from the volumetric data are shown in Figure 2. The

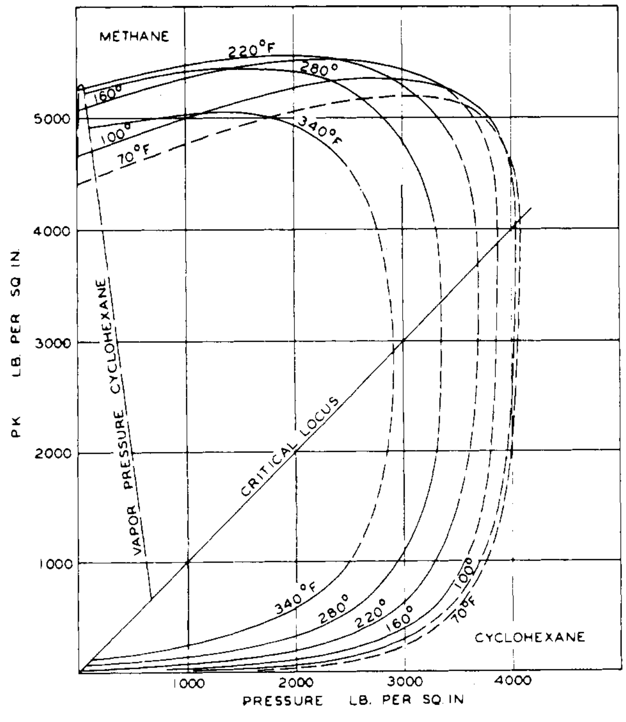

Figure 3. Equilibrium ratios for methane and cyclohexane

properties of the bubble-point and dew-point states are recorded in Table II for even values of pressure for each of the temperatures investigated. The molal volume, composition, and the equilibrium ratios of the two components are included. The standard error of estimate of the experimental data from the smooth curves of pressure *vs.* composition was 0.003 mole fraction. This assumes that all of the uncertainty existed in composition and that none was associated with the measurement of pressure or temperature. The product of the pressure and the equilibrium ratio is shown in Figure 3. The behavior is similar to that found for other binary systems containing methane (*11, 13, 16*). The maximum two-phase pressures and temperatures and those for the critical state are presented for a series of even valued compositions in Table III. The information of Table III involves much larger uncertainties than those associated with values recorded in Table I or II because it results from extensive interpolation of the volumetric and phase equilibrium data. Uncertainties may be as large as 5% in pressure and 30° F. in temperature. The probable error in these values is much smaller but is difficult to establish with certainty.

Table III. Properties at the Unique States in the Methane-Cyclohexane System[a]

Mole Fraction Methane	Pressure, P.S.I.A.	Temp., °F.	Pressure, P.S.I.A.	Temp., °F.	Pressure, P.S.I.A.	Temp., °F.
	Critical		Maxcondentherm		Maximum Pressure	
0.0	596.26[b]	536[b]	596.26	536	596.26	536
0.1	695	530	680	531	750	464
0.2	885	520	850	521	1,250	395
0.3	1,167	503	1,054	508	1,858	339
0.4	1,568	474	1,240	490	2,430	290
0.5	2,133	425	1,418	467	2,957	243
0.6	2,845	350	1,570	433	3,470	183
0.7	3,605	237	1,682	393	3,890	114
0.8	3,980[c]	123[c]	1,708	345	...	...
0.9	2,240[c]	− 77[c]	1,618	274	...	...
1.0	673[b]	− 116[b]	673	− 116	673	− 116

[a] These data are much more uncertain than directly measured quantities

[b] Based on Rossini (*14*).

[c] Estimated.

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Volumetric and Phase Behavior in Part of the Nitric Acid – Nitrogen Dioxide – Water System

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Experimental information concerning the volumetric and phase behavior of the nitric acid-nitrogen dioxide-water system at physical equilibrium is available. Klemenc and Rupp (*8*) and Taylor (*22*) contributed data on the volumetric behavior of the liquid phase and on the bubble point pressures of mixtures of nitric acid and water. McKeown and Belles (*11*) reported data on the two-phase pressure of nitric acid solutions with water and nitrogen dioxide. The freezing point of the ternary system was studied by Gordon (*5*) and Küster and Kremann (*9*). Sprague (*19*) proposed an analytical expression to describe the specific weight of the liquid phase of the ternary system at physical equilibrium for atmospheric pressures.

For conditions of physicochemical equilibrium little work had been done until recently when interest was aroused by the desire to store fuming nitric acid in closed containers. The behavior of pure nitric acid (*14*) and of samples of commercial red and white fuming nitric acid (*15*) was established. In addition studies of the nitric acid-nitrogen dioxide (*2*) and the nitric acid-water (*3*) systems were made. A limited study of the volumetric and phase behavior at physicochemical equilibrium of three mixtures of nitric acid, nitrogen dioxide, and water containing approximately a fixed ratio of the weight fraction of water to the sum of the weight fractions of water and nitric acid was completed (*13*). This study at physicochemical equilibrium extended from temperatures of 190° to 340° F. and pressures up to 5000 p.s.i. Kay (*6, 7*) and Sprague (*20*) studied the pres-