

Table IV. Effective Concentration Data for Conjugated Phases with Formic Acid Distributed Between Chloroform and Water Phases at 25° C.

Formic Acid in					
Water Phase			Chloroform Phase		
<i>F</i>	<i>F</i> + <i>W</i>	$\frac{F}{F+W}$	<i>F</i>	<i>F</i> + <i>W</i>	$\frac{F}{F+W}$
17.3	97.3	0.18	0.077	99.9	0.0008
29.9	96.6	0.31	0.17	99.7	0.0017
39.4	95.7	0.41	0.31	99.6	0.0031
46.5	95.5	0.49	0.47	99.6	0.0047
51.9	95.1	0.55	0.67	99.6	0.0067
56.4	94.2	0.60	0.89	99.4	0.0090
59.3	93.6	0.64	1.12	99.2	0.011
66.9	91.0	0.72	2.48	99.0	0.024
68.9	89.3	0.77	2.98	99.3	0.030
69.6	78.6	0.89	8.32	98.3	0.084
70.6	80.1	0.89	5.40	98.5	0.055
50.0	52.0	0.96	35.00	99.0	0.35
42.6	44.0	0.97	42.60	98.6	0.43

Straight lines are shown in Figure 4 by the plot on logarithmic paper according to the equation developed by Othmer and Tobias (2).

$$\log \frac{100 - W}{W} \text{ (in water layer)} = n \log \frac{100 - C}{C} \text{ (in chloroform layer)} + \text{a constant}$$

Densities at 25° C. of the respective equilibrium layers were determined, and data are shown in Table II and in Figure 5.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Hand, D. B., *J. Phys. Chem.* **34**, 1960 (1930).
- (2) Othmer, D. F., Tobias, P. F., *Ind. Eng. Chem.* **34**, 693 (1942).
- (3) Othmer, D. F., White, R. D., Trueger, E., *Ibid.*, **33**, 1240 (1941).

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Phase Equilibria in Hydrocarbon Systems Volumetric and Phase Behavior of Ethane-*n*-Pentane System

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A KNOWLEDGE of the volumetric and phase behavior of hydrocarbon mixtures is of value in connection with the production and refining of petroleum. Equilibrium data of this nature are essential to the evaluation and application of experimental results relating to the molecular transport of components under nonequilibrium conditions. Because information appears to be available concerning the volumetric or phase behavior of mixtures of ethane and *n*-pentane, the volumetric and phase behavior of the ethane-*n*-pentane system was studied at temperatures from 40° to 460° F. and for pressures up to 10,000 p.s.i.

Ethane has been investigated experimentally in detail. The volumetric behavior was carefully studied by Beattie and coworkers (1, 3) and supplemented by other more recent investigations (15). The critical state has recently been carefully evaluated by Schmidt and Thomas (30) as well as by Beattie and coworkers (2). The phase behavior of the methane-ethane-*n*-pentane system was studied over a limited range of temperatures (4). The volumetric and phase behavior of mixtures of ethane with other hydrocarbons, as well as water, carbon dioxide, nitrogen, and hydrogen sulfide has been studied in some detail (8, 9, 11, 13, 16, 20, 22, 24). This listing of references is by no means exhaustive and has been included only to indicate the extent to which the characteristics of ethane as a pure substance and in mixtures have been investigated.

Likewise, *n*-pentane has been studied in some detail. Its volumetric and phase behavior was investigated over a reasonable range of pressures and temperatures (26). Shepard and coworkers (31) determined a number of the physical properties with accuracy at atmospheric pressure. The latent heat of vaporization (23), and the Joule-Thomson coefficients (12) and related coefficients (6, 10) have been measured along with the isobaric heat capacity of this gaseous hydrocarbon (29). The behavior of *n*-pentane

in mixtures has been the subject of some study (4, 6, 7, 10, 19, 25, 28, 32).

APPARATUS AND METHODS

The equipment employed in this investigation was described in detail (27). A mixture of ethane and *n*-pentane was confined within a stainless steel pressure vessel. The volume of the chamber available to hydrocarbons was changed by introducing or withdrawing mercury in known amounts. Attainment of equilibrium was hastened by the use of a mechanical agitator, and the molal volume and pressure were determined for a series of states for each of a number of systematically chosen temperatures. The quantity of ethane and *n*-pentane introduced into the vessel was determined by weighing bomb techniques (27) with a probable uncertainty of not more than 0.05%.

The temperature of the sample was determined from that of a strongly stirred oil bath which surrounded the stainless steel pressure vessel. A stain-free platinum resistance thermometer was employed to measure the temperature of the oil bath. This instrument was compared with a similar instrument calibrated by the National Bureau of Standards. Intercomparison of three such calibrated instruments indicates that the temperature of the sample was related to the international platinum scale with an uncertainty of less than 0.03° F.

Pressures were measured by means of a piston-cylinder combination incorporated into a balance (27) which was calibrated against the vapor pressure of carbon dioxide at the ice point (5). Experience with this equipment (17) over a period of years indicates that 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 total volume of the chamber available to hydrocarbons

was established within 0.1% at pressures up to 5000 p.s.i. and within 0.25% at the higher pressures. Measurements upon each sample were made in a series of ascending temperatures at 60° intervals from 40° to 460° F. Measurements were then repeated at 100° F. and in a few instances discrepancies of as much as 0.1% were encountered. For this reason it is believed that the volumetric data do not involve uncertainties greater than 0.25% at temperatures below 300° F. and perhaps as much as 0.35% at the higher temperatures.

The bubble point was established from the discontinuous change in the isothermal derivative of molal volume with respect to pressure at constant composition. The composition of the dew point gas was determined by withdrawal of samples of the gas phase from the heterogeneous mixture under isobaric, isothermal conditions. The composition of the samples withdrawn was obtained by a partial condensation procedure involving a partial condenser (14) which was maintained near the temperature of solid carbon dioxide and acetone. The ethane was condensed in a weighing bomb at the temperature of liquid nitrogen, and the quantity of each component determined by the gain in weight of the weighing bomb. Some measurements were made by determination of the specific weight of the gas phase at pressures near atmospheric. Satisfactory agreement was obtained between the composition of the dew-point gas as a function of pressure and temperature as measured by the partial condensation procedure and by the gas specific weight techniques. Measurements upon duplicate samples withdrawn at the same equilibrium state indicated a probable error of the order of 0.002 mole fraction *n*-pentane.

MATERIALS

The ethane and *n*-pentane were obtained from the Phillips Petroleum Co. as research grade. The ethane was said to contain not more than 0.0006 mole fraction of impurities. Partial condensation analysis showed that the sample contained less than this quantity of volatile impurities. A mass spectrographic analysis confirmed that the impurities were less than 0.0006 mole fraction and indicated that they were probably heavier aliphatic hydrocarbons. The ethane was employed without purification because it did not appear to contain measurable quantities of water, carbon dioxide, or other easily removable impurities.

The *n*-pentane was reported to contain 0.0016 mole fraction of impurities. The sample as received and after deaeration had a specific weight of 38.788 cubic feet per pound at 77° F. as compared to 38.791 cubic feet per pound reported by Rossini (21) for an air-saturated sample at the same temperature. A refractive index of 1.35476 relative to the *D*-lines of sodium was recorded at 77° F. which compares favorably with a value of 1.35472 reported by Rossini (21) for air-saturated *n*-pentane. Thus, it is believed that the sample of *n*-pentane contained less than 0.0016 mole fraction of impurities and these were probably saturated and unsaturated compounds containing five carbon atoms per molecule.

EXPERIMENTAL RESULTS

A typical set of experimental volumetric measurements at 160° F. is shown in Figure 1. The curves portraying the volumetric behavior of *n*-pentane and of ethane were based upon earlier experimental investigations (15, 26). The detailed experimental data obtained in this study are available (18). Experimental information similar to that shown in Figure 1 for temperatures between 40° and 460° F. was smoothed with respect to pressure, temperature, and composition by residual graphical methods. These smoothed data for even compositions, pressures, and temperatures are recorded in Table I. The standard error of estimate of the

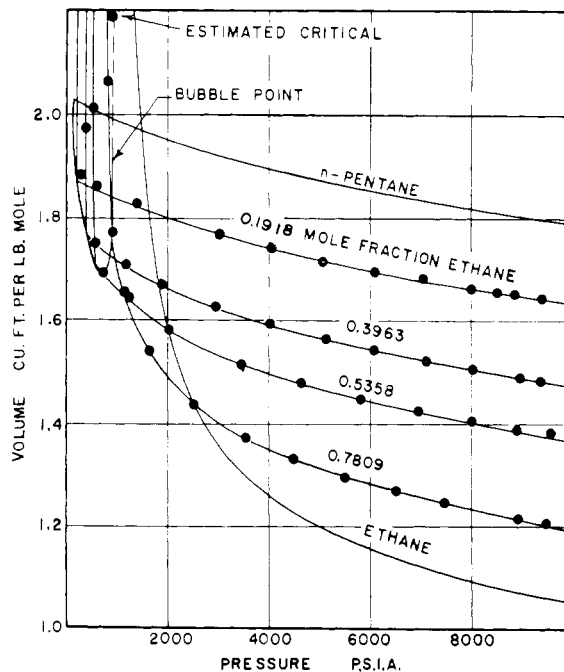


Figure 1. Experimental volumetric measurements at 160° F. experimental molal volume from the smoothed value was 0.002 cubic foot per pound mole which corresponds to an error of 0.08% of an average value of the molal volumes investigated. The corresponding volumetric behavior of pure ethane and *n*-pentane is not included, these data being otherwise available (15, 26).

The experimentally measured compositions of the coexisting gas and liquid phases are shown in Figure 2. The composition of the liquid phase was determined from the bubble point pressures of the mixtures experimentally investigated in the course of the volumetric studies. The composition of the gas phase was established, as was described, by withdrawal of samples under isobaric, isothermal conditions. These data, together with the associated volumetric measurements, were smoothed with respect to pressure, temperature, and composition and are recorded in

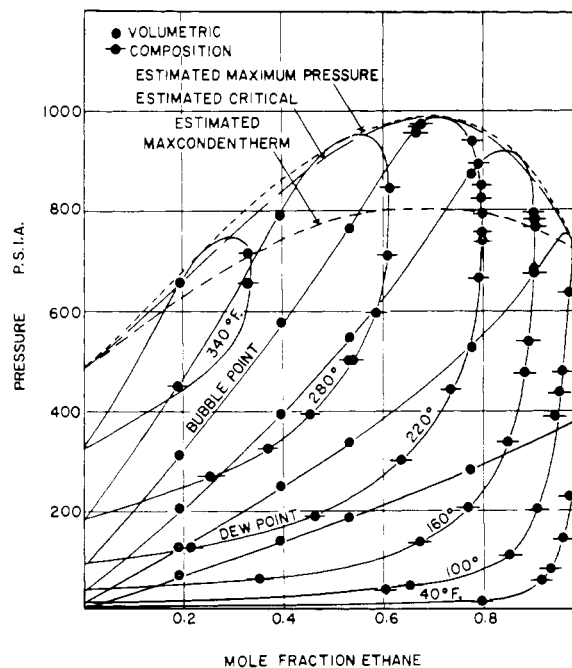


Figure 2. Compositions of coexisting gas and liquid phases

Table I. Molal Volumes for Mixtures of Ethane and n-Pentane

Pressure, P.S.I.A.	Mole Fraction Ethane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	40° F.								
DP	(8.4) ^a 634 ^b	(12.2) 436	(13.2) 403	(13.3) 399	(13.6) 390	(14.4) 368	(16.1) 328	(20.0) 263	(39.8) 129
BP	(35.5) ^a 1.724	(69.0) 1.650	(103.4) 1.577	(138.4) 1.506	(175.7) 1.438	(212.9) 1.376	(252.0) 1.322	(293.8) 1.276	(340.0) 1.236
200	1.721 ^c	1.647	1.574	1.504	1.437
400	1.718	1.643	1.570	1.500	1.433	1.371	1.317	1.271	1.232
600	1.715	1.639	1.567	1.496	1.429	1.366	1.311	1.262	1.219
800	1.711	1.636	1.563	1.492	1.426	1.362	1.304	1.253	1.207
1000	1.709	1.633	1.560	1.488	1.422	1.357	1.298	1.244	1.196
1250	1.705	1.629	1.555	1.484	1.416	1.351	1.290	1.233	1.184
1500	1.702	1.625	1.551	1.480	1.411	1.345	1.282	1.224	1.172
1750	1.698	1.622	1.547	1.475	1.406	1.399	1.275	1.214	1.162
2000	1.695	1.618	1.543	1.471	1.402	1.334	1.269	1.207	1.152
2250	1.691	1.614	1.539	1.467	1.397	1.329	1.262	1.200	1.144
2500	1.688	1.610	1.536	1.463	1.393	1.324	1.257	1.192	1.136
2750	1.684	1.607	1.532	1.458	1.388	1.319	1.251	1.186	1.129
3000	1.681	1.604	1.528	1.455	1.384	1.314	1.245	1.181	1.123
3500	1.676	1.598	1.522	1.447	1.376	1.305	1.234	1.169	1.110
4000	1.670	1.592	1.515	1.440	1.367	1.295	1.225	1.159	1.099
4500	1.664	1.586	1.508	1.432	1.359	1.287	1.217	1.151	1.090
5000	1.658	1.580	1.502	1.426	1.352	1.280	1.209	1.142	1.080
6000	1.648	1.569	1.490	1.413	1.339	1.266	1.194	1.127	1.064
7000	1.638	1.558	1.478	1.402	1.327	1.253	1.181	1.113	1.048
8000	1.627	1.546	1.466	1.390	1.315	1.241	1.170	1.100	1.034
9000	1.616	1.534	1.455	1.379	1.304	1.229	1.158	1.088	1.022
10,000	1.604	1.522	1.444	1.367	1.292	1.218	1.147	1.078	1.011
	100° F.								
DP	(47.0) ^a 129 ^b	(52.3) 116	(27.8) 206	(30.4) 188	(32.1) 178	(38.2) 149	(52.2) 109	(75.3) 74.6	(168.4) 31.6
BP	(70.1) ^a 1.829	(127.9) 1.756	(187.7) 1.686	(250.0) 1.620	(315.3) 1.560	(384.0) 1.510	(459.9) 1.472	(549.0) 1.487	(662.1) 1.599
200	1.824 ^c	1.753	1.686
400	1.819	1.746	1.678	1.614	1.558	1.509
600	1.812	1.740	1.672	1.608	1.550	1.498	1.460	1.477	...
800	1.807	1.734	1.665	1.600	1.541	1.486	1.445	1.444	1.510
1000	1.802	1.729	1.659	1.593	1.532	1.476	1.431	1.417	1.450
1250	1.796	1.723	1.651	1.585	1.522	1.463	1.414	1.391	1.397
1500	1.791	1.717	1.645	1.576	1.512	1.452	1.401	1.370	1.356
1750	1.785	1.710	1.638	1.568	1.504	1.441	1.389	1.353	1.327
2000	1.780	1.704	1.631	1.561	1.494	1.432	1.377	1.336	1.302
2250	1.775	1.699	1.625	1.553	1.486	1.423	1.367	1.321	1.281
2500	1.770	1.693	1.619	1.546	1.478	1.415	1.357	1.308	1.263
2750	1.765	1.687	1.612	1.539	1.471	1.407	1.347	1.295	1.248
3000	1.760	1.682	1.607	1.533	1.464	1.400	1.339	1.285	1.234
3500	1.750	1.671	1.595	1.522	1.452	1.386	1.321	1.263	1.211
4000	1.742	1.662	1.585	1.510	1.440	1.372	1.305	1.244	1.189
4500	1.733	1.653	1.576	1.500	1.429	1.360	1.291	1.228	1.171
5000	1.725	1.643	1.566	1.491	1.419	1.349	1.279	1.215	1.156
6000	1.707	1.627	1.548	1.473	1.401	1.329	1.259	1.193	1.131
7000	1.692	1.611	1.533	1.457	1.384	1.311	1.240	1.174	1.110
8000	1.678	1.597	1.518	1.443	1.369	1.296	1.224	1.157	1.091
9000	1.665	1.584	1.505	1.430	1.355	1.282	1.210	1.141	1.074
10,000	1.654	1.573	1.493	1.417	1.342	1.268	1.196	1.126	1.058
	160° F.								
DP	(20.0) ^a 287 ^b	(23.9) 240	(59.7) 101	(68.0) 88.6	(79.8) 75.3	(104.5) 57.2	(149.0) 39.6	(235.9) 24.0	(566.2) 7.87
BP	(121.1) ^a 1.940	(209.2) 1.868	(301.9) 1.809	(400.4) 1.760	(506.4) 1.719	(624.6) 1.695	(758.2) 1.692	(897.0) 1.854	(885.0) 3.04
200	1.937 ^c
400	1.928	1.858	1.803
600	1.920	1.849	1.792	1.744	1.710
800	1.913	1.840	1.781	1.730	1.692	1.672	1.680
1000	1.905	1.831	1.770	1.717	1.674	1.643	1.640	1.727	1.966
1250	1.896	1.821	1.757	1.701	1.653	1.615	1.599	1.631	1.778

^a Values in parentheses represent dew point or bubble point pressure expressed in p.s.i.a.

Mole Fraction Ethane

Pressure, P.S.I.A.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
160° F. Continued									
1500	1.887	1.812	1.746	1.687	1.635	1.590	1.563	1.568	1.663
1750	1.878	1.803	1.735	1.674	1.617	1.569	1.533	1.524	1.582
2000	1.870	1.794	1.724	1.661	1.603	1.550	1.507	1.490	1.520
2250	1.863	1.787	1.715	1.650	1.589	1.533	1.485	1.461	1.472
2500	1.854	1.778	1.706	1.641	1.577	1.517	1.466	1.437	1.433
2750	1.847	1.770	1.697	1.630	1.566	1.504	1.450	1.416	1.401
3000	1.840	1.763	1.689	1.622	1.557	1.492	1.435	1.397	1.374
3500	1.826	1.748	1.674	1.604	1.538	1.473	1.411	1.366	1.330
4000	1.814	1.735	1.660	1.590	1.522	1.456	1.392	1.340	1.297
4500	1.802	1.722	1.647	1.576	1.507	1.440	1.375	1.319	1.270
5000	1.791	1.710	1.635	1.563	1.494	1.426	1.359	1.301	1.248
6000	1.770	1.690	1.614	1.541	1.469	1.400	1.332	1.269	1.210
7000	1.752	1.671	1.594	1.520	1.447	1.376	1.308	1.242	1.179
8000	1.736	1.655	1.576	1.500	1.427	1.356	1.287	1.219	1.153
9000	1.721	1.640	1.560	1.484	1.410	1.337	1.266	1.198	1.132
10,000	1.706	1.627	1.546	1.470	1.395	1.320	1.248	1.179	1.113

220° F.

DP	(186.5) ^a 57.4 ^b	(121.8) 50.0	(142.3) 42.6	(167.0) 36.0	(205.0) 29.0	(267.0) 21.8	(371.4) 15.06	(693.0) 6.49	
BP	(206.2) ^a 2.101	(324.5) 2.033	(445.5) 1.980	(574.4) 1.949	(716.7) 1.948	(864.8) 2.010	(984.7) 2.276	(862.5) 4.24	
400	2.084 ^c	2.024
600	2.069	2.007	1.967	1.946
800	2.055	1.993	1.948	1.922	1.935
1000	2.042	1.979	1.930	1.897	1.902	1.964	2.168	2.971	...
1250	2.026	1.962	1.909	1.868	1.859	1.886	1.971	2.264	3.00
1500	2.010	1.946	1.888	1.842	1.821	1.822	1.862	2.008	2.297
1750	1.997	1.928	1.868	1.819	1.784	1.764	1.778	1.856	2.049
2000	1.982	1.913	1.851	1.798	1.754	1.717	1.708	1.757	1.899
2250	1.969	1.898	1.834	1.777	1.728	1.685	1.663	1.688	1.779
2500	1.956	1.886	1.820	1.760	1.706	1.657	1.630	1.638	1.690
2750	1.943	1.874	1.807	1.745	1.687	1.636	1.601	1.596	1.623
3000	1.932	1.862	1.794	1.728	1.670	1.617	1.578	1.562	1.571
3500	1.914	1.842	1.773	1.705	1.642	1.584	1.536	1.506	1.494
4000	1.897	1.823	1.753	1.684	1.617	1.557	1.504	1.464	1.436
4500	1.882	1.807	1.735	1.665	1.596	1.534	1.478	1.430	1.393
5000	1.866	1.791	1.718	1.646	1.576	1.513	1.454	1.403	1.356
6000	1.841	1.764	1.688	1.615	1.546	1.479	1.414	1.354	1.300
7000	1.818	1.738	1.661	1.588	1.516	1.448	1.381	1.317	1.259
8000	1.799	1.718	1.639	1.565	1.490	1.421	1.353	1.287	1.226
9000	1.778	1.699	1.619	1.543	1.468	1.398	1.326	1.261	1.196
10,000	1.757	1.679	1.600	1.525	1.448	1.376	1.302	1.234	1.172

280° F.

DP	(216.0) ^a 26.9 ^b	(248.6) 23.1	(288.0) 19.6	(346.0) 16.0	(443.9) 12.0	(644.8) 7.28
BP	(325.8) ^a 2.362	(471.0) 2.319	(626.6) 2.288	(802.4) 2.294	(928.0) 2.473	(935.3) 3.42
400	2.344 ^c
600	2.302	2.284
800	2.266	2.239	2.236
1000	2.234	2.202	2.186	2.218	2.379	3.13
1250	2.199	2.160	2.130	2.134	2.216	2.458	2.933	3.54	...
1500	2.171	2.121	2.084	2.065	2.101	2.217	2.475	2.877	3.39
1750	2.145	2.086	2.044	2.012	2.016	2.078	2.220	2.461	2.829
2000	2.120	2.059	2.009	1.971	1.956	1.981	2.055	2.194	2.430
2250	2.098	2.036	1.981	1.936	1.910	1.910	1.946	2.032	2.202
2500	2.078	2.015	1.956	1.907	1.873	1.855	1.867	1.922	2.043
2750	2.060	1.998	1.935	1.882	1.842	1.812	1.810	1.844	1.921
3000	2.045	1.981	1.916	1.859	1.812	1.777	1.761	1.781	1.829
3500	2.016	1.950	1.883	1.822	1.767	1.721	1.690	1.684	1.700
4000	1.991	1.924	1.855	1.789	1.730	1.679	1.636	1.613	1.609
4500	1.969	1.899	1.830	1.761	1.698	1.642	1.594	1.558	1.537
5000	1.951	1.879	1.806	1.738	1.670	1.611	1.558	1.516	1.483
6000	1.917	1.843	1.768	1.697	1.629	1.564	1.504	1.450	1.402
7000	1.889	1.812	1.736	1.663	1.592	1.526	1.462	1.402	1.347
8000	1.864	1.784	1.708	1.635	1.560	1.490	1.423	1.361	1.303
9000	1.839	1.760	1.683	1.608	1.533	1.460	1.392	1.328	1.267
10,000	1.813	1.738	1.660	1.582	1.505	1.434	1.363	1.295	1.233

^b There exist larger uncertainties in regard to dew point volumes than other states reported. ^c Volume expressed in cubic feet per pound mole. (Table I continued on next page)

Table I. Continued

Pressure, P.S.I.A.	Mole Fraction Ethane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	340° F.								
DP	(384.2) ^a 12.8 ^b	(446.0) 10.6	(533.7) 8.23
BP	(488.5) ^a 2.970	(670.3) 3.17	(749.0) 3.78
600	2.718 ^c
800	2.603	2.712	3.32
1000	2.516	2.559	2.740	3.22	4.19
1250	2.437	2.440	2.495	2.654	3.04	3.68
1500	2.376	2.357	2.371	2.444	2.629	2.932	3.33	3.77	4.23
1750	2.328	2.294	2.285	2.317	2.413	2.587	2.840	3.18	3.54
2000	2.286	2.245	2.223	2.226	2.271	2.382	2.554	2.785	3.08
2250	2.254	2.205	2.174	2.160	2.177	2.237	2.348	2.509	2.725
2500	2.227	2.173	2.133	2.106	2.103	2.133	2.196	2.306	2.470
2750	2.199	2.146	2.097	2.062	2.044	2.050	2.082	2.159	2.285
3000	2.178	2.122	2.025	2.025	1.996	1.986	2.001	2.052	2.144
3500	2.136	2.074	2.016	1.962	1.922	1.893	1.884	1.901	1.944
4000	2.102	2.036	1.974	1.914	1.863	1.824	1.798	1.793	1.807
4500	2.072	2.004	1.936	1.873	1.817	1.769	1.733	1.712	1.706
5000	2.046	1.975	1.906	1.840	1.781	1.728	1.681	1.649	1.631
6000	2.000	1.926	1.854	1.786	1.722	1.659	1.604	1.557	1.518
7000	1.965	1.888	1.813	1.741	1.674	1.607	1.546	1.492	1.443
8000	1.932	1.856	1.779	1.706	1.636	1.567	1.502	1.441	1.386
9000	1.902	1.825	1.747	1.673	1.601	1.528	1.458	1.394	1.336
10,000	1.876	1.798	1.721	1.644	1.570	1.494	1.424	1.360	1.300
	400° F.								
800	3.40 ^c	5.12
1000	3.09	3.46	4.10	4.93
1250	2.835	2.956	3.22	3.68	4.23	4.84
1500	2.682	2.736	2.868	3.09	3.41	3.76	4.14	4.53	4.94
1750	2.589	2.605	2.656	2.768	2.988	3.27	3.58	3.89	4.21
2000	2.519	2.509	2.526	2.586	2.713	2.893	3.12	3.38	3.64
2250	2.458	2.436	2.434	2.464	2.536	2.656	2.824	3.03	3.24
2500	2.413	2.382	2.364	2.370	2.406	2.477	2.597	2.748	2.924
2750	2.372	2.335	2.304	2.294	2.304	2.346	2.428	2.537	2.676
3000	2.338	2.293	2.254	2.230	2.223	2.245	2.297	2.376	2.487
3500	2.279	2.226	2.174	2.132	2.106	2.098	2.110	2.149	2.213
4000	2.231	2.168	2.112	2.062	2.022	1.997	1.986	1.997	2.028
4500	2.190	2.124	2.062	2.005	1.958	1.923	1.894	1.885	1.892
5000	2.154	2.086	2.019	1.958	1.904	1.858	1.822	1.798	1.790
6000	2.094	2.022	1.950	1.884	1.822	1.766	1.715	1.677	1.643
7000	2.046	1.972	1.898	1.828	1.762	1.699	1.641	1.591	1.546
8000	2.006	1.928	1.856	1.784	1.714	1.647	1.582	1.526	1.474
9000	1.972	1.894	1.816	1.743	1.672	1.601	1.535	1.474	1.417
10,000	1.942	1.862	1.784	1.708	1.637	1.564	1.493	1.427	1.368
	460° F.								
1000	4.25 ^c	5.38
1250	3.56	3.94	4.41	4.93	5.45	5.98
1500	3.18	3.36	3.61	3.92	4.26	4.60	4.95	5.29	5.64
1750	2.977	3.05	3.19	3.42	3.69	3.96	4.24	4.51	4.79
2000	2.834	2.865	2.944	3.09	3.29	3.51	3.74	3.96	4.19
2250	2.732	2.733	2.766	2.843	2.985	3.16	3.34	3.53	3.71
2500	2.650	2.632	2.640	2.682	2.772	2.892	3.04	3.20	3.35
2750	2.583	2.552	2.545	2.564	2.617	2.698	2.807	2.934	3.06
3000	2.528	2.487	2.466	2.466	2.494	2.548	2.622	2.720	2.831
3500	2.442	2.386	2.348	2.328	2.322	2.337	2.372	2.422	2.488
4000	2.376	2.314	2.261	2.223	2.204	2.196	2.198	2.217	2.252
4500	2.319	2.254	2.194	2.148	2.112	2.086	2.072	2.071	2.086
5000	2.270	2.203	2.138	2.086	2.041	2.002	1.976	1.962	1.958
6000	2.197	2.122	2.052	1.991	1.937	1.886	1.840	1.803	1.772
7000	2.134	2.055	1.982	1.916	1.856	1.796	1.741	1.695	1.654
8000	2.087	2.006	1.931	1.859	1.792	1.730	1.672	1.617	1.568
9000	2.048	1.968	1.890	1.818	1.747	1.678	1.613	1.554	1.498
10,000	2.010	1.928	1.849	1.773	1.700	1.632	1.564	1.502	1.442

^a Values in parentheses represent dew point or bubble point pressures expressed in p.s.i.a.

^b There exist larger uncertainties in regard to dew point volumes than other states reported.

^c Volume expressed in cubic feet per pound mole.

Table II for even values of pressure for each of the temperatures investigated. In this table, the molal volume and composition of each of the phases, and the equilibrium ratios of the two components are included. Molal volumes at dew point are more uncertain than corresponding volumes at bubble point. The standard error of estimate of the experimental composition data from the smooth curves of pressure *vs.* composition, assuming that all of the error is in the mole fraction, was 0.005 mole fraction. The product of the pressure and the equilibrium ratio, PK, is shown for both components in Figure 3. A pressure-temperature dia-

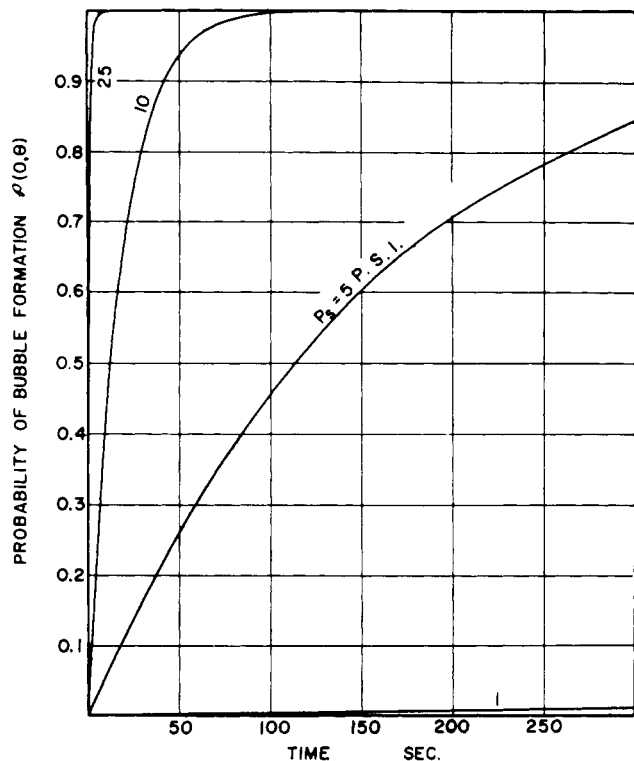


Figure 3. Equilibrium ratios for ethane and *n*-pentane

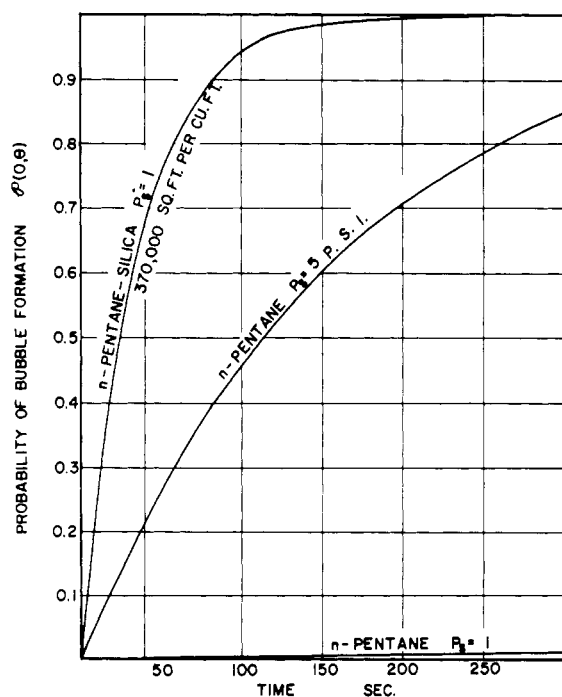


Figure 4. Pressure-temperature diagram for the ethane-*n*-pentane system

gram showing the phase behavior of each of the mixtures experimentally investigated constitutes Figure 4. The loci of unique states including those of the point of maximum pressure, the critical state, and the maxcondentherm are included on this diagram. 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 presented in Table III involves much larger uncertainties than are encountered in either Table I or II. This results from the fact that extensive interpolation of the volumetric and phase equilibrium data is required to arrive at the pressures and temperatures associated with each of these states. Uncertainties may be as large as 2% in pressure and 2° F. in temperature. The probable error in these values is much smaller but is difficult to establish with certainty.

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LITERATURE CITED

- (1) Beattie, J. A., Hadlock, C., Poffenberger, N., *J. Chem. Phys.* **3**, 93 (1935).
- (2) Beattie, J. A., Su, Gouq-Jen, Simard, G. L., *J. Am. Chem. Soc.* **61**, 924 (1939).
- (3) *Ibid.*, p. 926.
- (4) Billman, G. W., Sage, B. H., Lacey, W. N., *Trans. Am. Inst. Mining Met. Engrs.* **174**, 13 (1948).
- (5) Bridgeman, O. C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
- (6) Carter, R. T., Sage, B. H., Lacey, W. N., *Trans. Am. Inst. Mining Met. Engrs.* **142**, 170 (1941).
- (7) Dourson, R. H., Sage, B. H., Lacey, W. N., *Ibid.*, **151**, 206 (1943).
- (8) Gami, D. C., Patel, I. P., "Phase Behavior Studies: Methane-Ethane Studies," Research Conference on Phase Behavior of the Hydrocarbons, University of Michigan, Ann Arbor, Mich., July 1953.
- (9) Hanson, G. H., Hogan, R. J., Ruehlen, F. N., Cines, M. R., *Chem. Eng. Progr. Symp. Ser.* **49**, No. 6, 37 (1953).
- (10) Jessen, F. W., Lightfoot, J. H., *Ind. Eng. Chem.* **30**, 312 (1938).
- (11) Kay, W. B., Brice, D. B., *Ibid.*, **45**, 615 (1953).
- (12) Kennedy, E. R., Sage, B. H., Lacey, W. N., *Ibid.*, **28**, 718 (1936).
- (13) McKay, R. A., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ibid.*, **43**, 2112 (1951).
- (14) Reamer, H. H., Fiskin, J. M., Sage, B. H., *Ibid.*, **41**, 2871 (1949).
- (15) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ibid.*, **36**, 956 (1944).
- (16) *Ibid.*, **37**, 688 (1945).
- (17) Reamer, H. H., Sage, B. H., *Rev. Sci. Instr.* **26**, 592 (1955).
- (18) Reamer, H. H., Sage, B. H., Lacey, W. N., *Am. Doc. Inst.*, Washington 25, D. C., Document 6065 (1959).
- (19) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **45**, 1805 (1953).
- (20) Reamer, H. H., Selleck, F. T., Sage, B. H., Lacey, W. N., *Ibid.*, **44**, 198 (1952).
- (21) Rossini, F. D., Pitzer, K. S., Arnet, R. L., Braun, R. M., Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
- (22) Sage, B. H., Davies, J. A., Sherborne, J. E., Lacey, W. N., *Ind. Eng. Chem.* **28**, 1328 (1936).
- (23) Sage, B. H., Evans, H. D., Lacey, W. N., *Ibid.*, **31**, 763 (1939).
- (24) Sage, B. H., Lacey, W. N., *Ibid.*, **31**, 1497 (1939).
- (25) *Ibid.*, **32**, 992 (1940).
- (26) *Ibid.*, **34**, 730 (1942).
- (27) Sage, B. H., Lacey, W. N., *Trans. Am. Inst. Mining Met. Engrs.* **136**, 136 (1940).

Table II. Properties of Coexisting Gas and Liquid Phases

Pressure, P.S.I.A.	Dew Point		Bubble Point		Equilibrium Ratio		Pressure, P.S.I.A.	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole fraction ethane	Volume, cu. ft./lb. mole	Mole fraction ethane	Volume, cu. ft./lb. mole	Ethane	n-Pentane		Mole fraction ethane	Volume, cu. ft./lb. mole	Mole fraction ethane	Volume, cu. ft./lb. mole	Ethane	n-Pentane
	40° F.							220° F.					
4.4 ^a	0	1211.5	0	1.798	...	1.0000	94.9 ^a	0	64.5	0	2.184	...	1.0000
50	0.9158	102	0.1432	1.716	6.40	0.0983	100	0.0462	61.1	0.0048	2.181	9.62	0.9584
100	0.9504	49.2	0.2891	1.587	3.29	0.0698	150	0.3350	40.3	0.0506	2.140	6.62	0.7004
150	0.9659	31.4	0.4316	1.505	2.238	0.0600	200	0.4820	29.8	0.0947	2.102	5.09	0.5722
200	0.9763	22.4	0.5659	1.394	1.725	0.0546	250	0.5698	23.4	0.1367	2.063	4.17	0.4983
250	0.9838	17.01	0.6950	1.332	1.416	0.0531	300	0.6358	19.21	0.1796	2.040	3.54	0.4439
300	0.9901	13.36	0.8141	1.255	1.216	0.0533	350	0.6837	16.14	0.2213	2.015	3.09	0.4062
350	0.9960	10.68	0.9235	1.215	1.078	0.0523	400	0.7188	13.80	0.2630	2.002	2.733	0.3815
385 ^b	1.0000	9.20	1.0000	1.199	1.000	1.0000	450	0.7456	11.95	0.3032	1.978	2.459	0.3651
100° F.						280° F.							
15.7 ^a	0	366.0	0	1.903	...	1.0000	185.6 ^a	0	31.6	0	2.407	...	1.0000
50	0.6808	114	0.0624	1.886	10.91	0.3404	200	0.0481	29.2	0.0084	2.401	5.73	0.9600
100	0.8448	55.3	0.1519	1.796	5.56	0.1830	250	0.2042	22.9	0.0436	2.385	4.68	0.8321
150	0.8897	35.8	0.2371	1.710	3.75	0.1446	300	0.3257	18.78	0.0821	2.374	3.97	0.7346
200	0.9134	26.1	0.3201	1.661	2.854	0.1274	350	0.4050	15.82	0.1172	2.354	3.46	0.6740
250	0.9284	20.2	0.4002	1.602	2.320	0.1194	400	0.4612	13.59	0.1520	2.340	3.03	0.6354
300	0.9389	16.19	0.4774	1.562	1.967	0.1169	450	0.5046	11.84	0.1859	2.321	2.714	0.6085
350	0.9472	13.35	0.5511	1.536	1.719	0.1176	500	0.5402	10.39	0.2197	2.312	2.459	0.5893
400	0.9548	11.18	0.6219	1.508	1.535	0.1195	600	0.5874	8.12	0.2842	2.294	2.067	0.5764
450	0.9609	9.50	0.6879	1.492	1.397	0.1253	700	0.6107	6.39	0.3426	2.285	1.782	0.5922
500	0.9673	8.09	0.7465	1.474	1.296	0.1290	800	0.6165	5.02	0.3988	2.294	1.546	0.6379
600	0.9782	5.76	0.8503	1.526	1.150	0.1456	900	0.6139	3.99	0.4702	2.386	1.306	0.7288
700	0.9854	3.77	0.9274	1.675	1.062	0.2011	955 ^c	0.5630	2.866	0.5630	2.866	1.000	1.0000
756 ^c	0.9778	2.236	0.9778	2.236	1.000	1.0000	340° F ^d						
160° F.						329.2 ^a							
42.5 ^a	0	142.3	0	2.029	...	1.0000	350	0.0385	15.41	0	2.807	...	1.0000
100	0.5855	59.8	0.0755	1.948	7.76	0.4484	400	0.1274	12.12	0.0451	2.877	2.917	0.9744
150	0.7018	39.3	0.1323	1.911	5.30	0.3437	450	0.2062	10.42	0.0762	2.977	2.825	0.9138
200	0.7692	28.8	0.1900	1.865	4.05	0.2849	500	0.2698	9.02	0.1070	3.04	2.522	0.8186
250	0.8100	22.5	0.2443	1.822	3.32	0.2514	600	0.3299	6.94	0.1606	3.10	2.054	0.7983
300	0.8391	18.20	0.2982	1.798	2.814	0.2293	700	0.3359	5.03	0.2216	3.23	1.516	0.8532
350	0.8592	15.10	0.3500	1.778	2.455	0.2166	748.5 ^c	0.2946	3.72	0.2946	3.72	1.000	1.0000
400	0.8722	12.76	0.3991	1.759	2.185	0.2127							
450	0.8823	10.94	0.4471	1.745	1.973	0.2129							
500	0.8909	9.45	0.4940	1.737	1.803	0.2156							
600	0.9032	7.20	0.5804	1.714	1.556	0.2307							
700	0.9091	5.53	0.6579	1.690	1.382	0.2657							
800	0.9100	4.14	0.7295	1.706	1.247	0.3327							
900	0.8908	2.772	0.8028	1.868	1.110	0.5538							
923.5 ^c	0.8502	2.189	0.8502	2.189	1.000	1.0000							

^a Vapor pressure of n-pentane.

^b Vapor pressure of ethane.

^c Estimated critical.

^d Greater uncertainty exists in establishment of phase boundaries at 340° F. than at lower temperatures.

Table III. Properties at the Unique States in the Ethane-n-Pentane System

Mole Fraction Ethane	Pressure, P.S.I.A.	Temp., ° F.	Pressure, P.S.I.A.	Temp., ° F.	Pressure, P.S.I.A.	Temp., ° F.
	Critical		Maxcondentherm		Max. Pressure	
0.0 ^a	489.5	385.9	489.5	385.9	489.5	385.9
0.1	573.5	373.8	564.0	375.0	582.0	366.1
0.2	661.9	357.0	631.9	361.1	677.0	346.3
0.3	753.8	339.0	691.5	345.6	780.1	324.5
0.4	842.3	320.0	744.5	328.9	864.0	305.3
0.5	917.9	297.6	782.7	308.1	930.0	285.1
0.6	969.9	267.9	801.0	235.2	971.3	259.3
0.7	990.0	228.9	803.2	256.0	990.0	228.9
0.8	962.1	183.8	792.7	221.0	968.2	194.7
0.9	872.1	137.5	767.7	167.1	888.0	150.1
1.0 ^a	716.0	90.1	716.0	90.1	716.0	90.1

^a Based on Rossini (21).

- (28) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *Ind. Eng. Chem.* **34**, 1108 (1942).
- (29) Sage, B. H., Webster, D. C., Lacey, W. N., *Ibid.*, **29**, 1309 (1937).
- (30) Schmidt, Ernst, Thomas, W., *Forsch. Gebiete Ingenieurw.* **20B**, 161 (1954).
- (31) Shepard, A. F., Henne, A. L., Midgley, T., Jr., *J. Am. Chem. Soc.* **53**, 1948 (1931).
- (32) Taylor, H. S., Wark, G. W., Sage, B. H., Lacey, W. N., *Oil Gas J.* **38**, 46 (1939).

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