

Phase Equilibria in Hydrocarbon Systems

Volumetric and Phase Behavior of the Propane-*n*-Decane System

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The volumetric behavior of four mixtures of propane and *n*-decane was investigated at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. The compositions of the coexisting gas and liquid phases were established throughout the two-phase region within the above-indicated range of temperature. The results are in good agreement with the volumetric and phase behavior of propane and of *n*-decane.

THERE CONTINUES to be a need for measurements of the volumetric and phase behavior of binary mixtures of the aliphatic hydrocarbons, since entirely adequate methods of prediction of such properties of binary systems are not as yet available. Furthermore, such measurements add to the background of experimental data necessary for the more extensive studies associated with ternary and more complicated systems. Experimental measurements concerning the volumetric or the phase behavior of the propane-*n*-decane system are not available, and for this reason, studies of the behavior of this binary system were carried out at temperatures between 40° and 460° F. for pressures from 200 to 10,000 p.s.i.a. The volumetric behavior of propane has been studied in detail by Beattie, Kay, and Kaminsky (2), and the critical properties have also been determined by Beattie and others (3). These measurements are in good agreement with studies of the volumetric and phase behavior of propane (10) which were carried out somewhat later than the studies of Beattie, and are also in fair agreement with the earlier studies (6, 13) upon this hydrocarbon. The available information concerning the volumetric and phase behavior of propane is believed to be adequate for the purposes of this study. *n*-Decane has also been studied in some detail (9). The volumetric behavior and the vapor pressure of this compound were investigated as part of the study of the binary system methane and *n*-decane (9, 12). Since difficulty in

determining the specific volume of the dew-point gas is experienced with materials of low volatility such as *n*-decane, measurements of the latent heat of vaporization (5) together with the vapor pressure of *n*-decane and appropriate thermodynamic relations were employed to establish the specific volume of the dew-point gas. Young (14) was perhaps the first to investigate the volumetric and phase behavior of decane, and the more recent measurements (9, 12) are in good agreement with his earlier classical studies. No further reference to the behavior of propane or *n*-decane will be made except to indicate in a semi-quantitative way the agreement of the volumetric and phase behavior for the components with the mixtures investigated.

APPARATUS AND METHODS

The equipment employed in this study has been described in detail (11). Mixtures of propane and *n*-decane were confined in a stainless steel vessel over mercury. The effective volume of the system could be varied by the introduction and withdrawal of mercury. Mechanical agitation was provided to hasten the attainment of physical equilibrium. The molal volume and associated pressure were determined for a series of states at each of eight systematically chosen temperatures between 40° and 460° F.

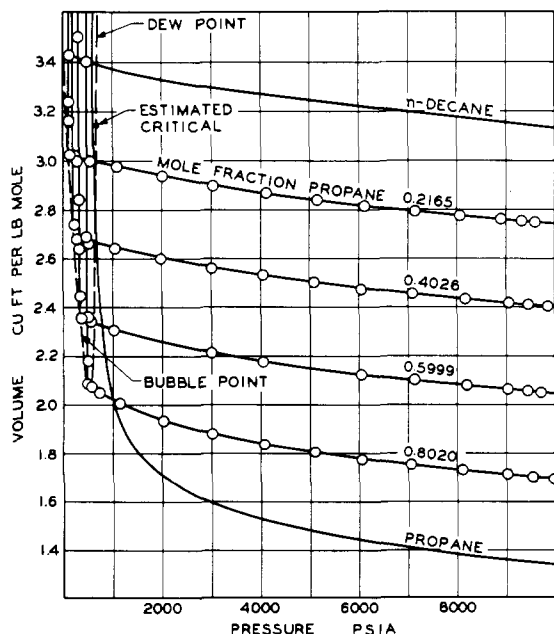


Figure 1. Volumetric measurements at 220° F.

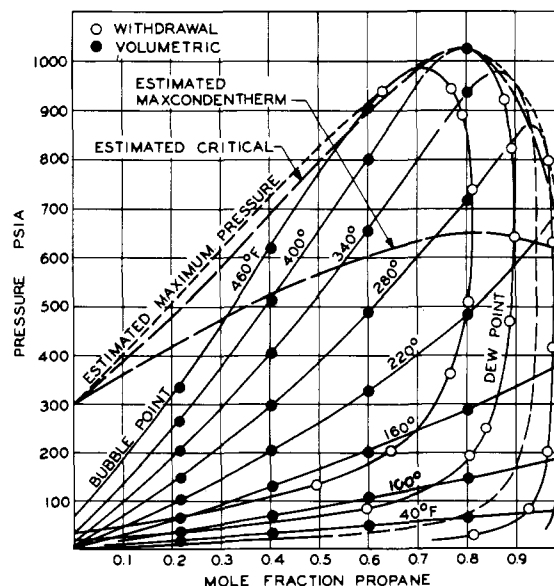


Figure 2. Pressure-composition diagram for the propane-*n*-decane system

The quantity of *n*-decane introduced into the equipment was established from volumetric measurements made upon the sample after its introduction, and the results agreed within 0.15% of the quantity of decane measured into the apparatus. The quantity of propane introduced into the variable-volume vessel was determined by weighing bomb techniques (11) with a probable uncertainty of not more than 0.05%.

The pressure of the system was established by means of a piston-cylinder combination utilized in connection with a balance (11). The over-all device has been periodically calibrated against the vapor pressure of carbon dioxide at the ice point (4). Experience over nearly three decades with this equipment indicates that the pressure of the sample was established with a probable uncertainty of 0.05% or 0.1 p.s.i., whichever is the larger measure of uncertainty. Temperatures of the sample

under investigation were determined from that of a vigorously stirred oil bath surrounding the stainless steel pressure vessel. A strain-free, platinum resistance thermometer (?) measured the temperature of the oil bath. This instrument was periodically compared with the indications of a similar platinum resistance thermometer which had been calibrated by the National Bureau of Standards. Comparisons of at least three such calibrated resistance thermometers indicated that the temperature of the sample was related to that of the international platinum scale with an uncertainty of less than 0.03° F. The total volume of the pressure vessel filled with hydrocarbon was established within 0.1% at pressures up to approximately 5000 p.s.i. and within 0.25% at the higher pressures. Variations in the calibration of the equipment at pressures above 5000 p.s.i. with respect to time introduced the uncertainty enumerated.

Table I. Molal Volumes for Mixtures of

Pressure, P.S.I.A.	Mole Fraction Propane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	40° F.								
	(8)*	(16)	(25)	(33)	(41)	(49)	(56)	(64)	(72)
BP	2.878	2.701	2.526	2.351	2.177	2.005	1.835	1.662	1.497
200	2.874 ^b	2.697	2.521	2.347	2.173	2.001	1.831	1.659	1.494
400	2.870	2.693	2.516	2.341	2.168	1.997	1.826	1.656	1.491
600	2.865	2.689	2.511	2.336	2.164	1.993	1.822	1.653	1.488
800	2.861	2.685	2.507	2.332	2.159	1.989	1.818	1.649	1.484
1000	2.857	2.680	2.502	2.327	2.155	1.985	1.814	1.645	1.480
1250	2.853	2.676	2.497	2.322	2.150	1.980	1.809	1.640	1.476
1500	2.848	2.671	2.493	2.317	2.145	1.975	1.805	1.636	1.472
1750	2.844	2.667	2.488	2.312	2.140	1.971	1.801	1.632	1.467
2000	2.839	2.662	2.484	2.308	2.135	1.966	1.796	1.628	1.462
2250	2.834	2.658	2.480	2.304	2.131	1.962	1.792	1.624	1.457
2500	2.830	2.653	2.476	2.299	2.127	1.958	1.788	1.620	1.452
2750	2.826	2.649	2.471	2.295	2.123	1.954	1.784	1.616	1.448
3000	2.822	2.645	2.467	2.292	2.120	1.950	1.781	1.612	1.443
3500	2.814	2.637	2.459	2.284	2.113	1.943	1.773	1.603	1.434
4000	2.807	2.629	2.452	2.277	2.105	1.936	1.765	1.595	1.425
4500	2.799	2.621	2.444	2.271	2.099	1.928	1.757	1.586	1.416
5000	2.793	2.614	2.438	2.265	2.092	1.921	1.749	1.577	1.408
6000	2.779	2.601	2.426	2.254	2.079	1.908	1.733	1.562	1.392
7000	2.766	2.590	2.416	2.244	2.069	1.896	1.721	1.549	1.379
8000	2.756	2.580	2.406	2.233	2.060	1.886	1.711	1.539	1.367
9000	2.747	2.570	2.396	2.223	2.051	1.876	1.701	1.527	1.355
10,000	2.739	2.562	2.388	2.215	2.042	1.867	1.692	1.518	1.344
	100° F.								
	(16) ^a	(34)	(51)	(68)	(86)	(105)	(124)	(145)	(166)
BP	2.986	2.805	2.625	2.447	2.273	2.103	1.935	1.771	1.620
200	2.980 ^b	2.799	2.620	2.443	2.270	2.100	1.933	1.769	1.619
400	2.975	2.793	2.614	2.439	2.265	2.094	1.927	1.763	1.611
600	2.969	2.788	2.609	2.433	2.260	2.088	1.921	1.757	1.604
800	2.964	2.783	2.604	2.428	2.254	2.083	1.915	1.752	1.596
1000	2.959	2.777	2.599	2.423	2.249	2.077	1.910	1.747	1.589
1250	2.952	2.772	2.593	2.417	2.243	2.070	1.903	1.739	1.580
1500	2.947	2.766	2.587	2.412	2.236	2.064	1.896	1.731	1.571
1750	2.941	2.761	2.581	2.406	2.230	2.057	1.888	1.724	1.562
2000	2.935	2.755	2.575	2.400	2.224	2.051	1.882	1.716	1.553
2250	2.928	2.748	2.570	2.394	2.218	2.045	1.877	1.709	1.546
2500	2.924	2.743	2.564	2.388	2.212	2.039	1.869	1.702	1.538
2750	2.918	2.737	2.559	2.382	2.207	2.034	1.863	1.695	1.531
3000	2.912	2.732	2.554	2.377	2.201	2.029	1.858	1.689	1.525
3500	2.901	2.721	2.544	2.368	2.192	2.019	1.847	1.677	1.512
4000	2.891	2.711	2.534	2.359	2.183	2.009	1.837	1.667	1.500
4500	2.881	2.702	2.525	2.351	2.174	2.000	1.828	1.658	1.489
5000	2.874	2.694	2.516	2.343	2.165	1.992	1.820	1.649	1.478
6000	2.859	2.680	2.501	2.327	2.150	1.977	1.804	1.632	1.460
7000	2.845	2.667	2.489	2.312	2.136	1.962	1.789	1.617	1.442
8000	2.832	2.655	2.477	2.300	2.124	1.949	1.775	1.603	1.427
9000	2.819	2.642	2.465	2.287	2.112	1.936	1.762	1.591	1.412
10,000	2.806	2.628	2.451	2.273	2.098	1.922	1.748	1.575	1.399

Measurements upon each of the samples were made at a series of ascending temperatures at intervals of 60° throughout the previously indicated temperature interval. Experience indicates that the molal volumes do not involve uncertainties greater than 0.25% at temperatures below 300° F. and may be as large as 0.3% at the higher temperatures.

The composition of the dew-point gas withdrawn from heterogeneous mixtures under isobaric, isothermal conditions was established by partial condensation procedures (8). The condenser was maintained near the temperature of solid carbon dioxide and acetone. The propane, carried as overhead, was condensed in a weighing bomb (11) at the temperature of liquid nitrogen. After the completion of the condensation procedure, the *n*-decane was permitted to warm to room temperature and then recooled again several times to ensure a relatively complete

separation of the propane from the *n*-decane which was condensed in the above-mentioned weighing bomb. The gains in weight of the partial condenser and of the weighing bomb were employed to determine the composition of the gas phase sample. Duplicate samples withdrawn at the same equilibrium state indicate a probable error of the order of 0.002 mole fraction of *n*-decane in these procedures.

MATERIALS

The propane and *n*-decane were obtained from the Phillips Petroleum Co. The propane was of research grade and was reported to contain not more than 0.001 mole fraction of materials other than propane. A mass spectrographic analysis indicated that the sample employed in this investigation contained as much as 0.004 mole fraction of materials other than

Propane and *n*-Decane in the Liquid Phase

Pressure, P.S.I.A.	Mole Fraction Propane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
160° F.									
BP	(30) ^a 3.107	(61) 2.920	(94) 2.738	(129) 2.559	(166) 2.384	(204) 2.215	(244) 2.053	(288) 1.901	(333) 1.793
200	3.100 ^b	2.915	2.734	2.556	2.382
400	3.091	2.908	2.726	2.548	2.374	2.206	2.044	1.894	1.785
600	3.083	2.901	2.719	2.541	2.366	2.198	2.034	1.883	1.761
800	3.076	2.895	2.712	2.534	2.359	2.189	2.024	1.872	1.742
1000	3.068	2.888	2.706	2.527	2.352	2.181	2.014	1.862	1.725
1250	3.060	2.880	2.698	2.519	2.344	2.171	2.004	1.849	1.708
1500	3.052	2.872	2.691	2.511	2.335	2.161	1.993	1.837	1.692
1750	3.044	2.865	2.683	2.503	2.327	2.152	1.984	1.826	1.679
2000	3.036	2.857	2.676	2.496	2.319	2.143	1.975	1.816	1.666
2250	3.028	2.849	2.668	2.489	2.311	2.135	1.965	1.806	1.653
2500	3.021	2.841	2.661	2.482	2.302	2.127	1.957	1.796	1.641
2750	3.014	2.834	2.654	2.476	2.294	2.120	1.950	1.788	1.629
3000	3.007	2.827	2.647	2.469	2.287	2.112	1.943	1.780	1.619
3500	2.992	2.814	2.635	2.457	2.274	2.099	1.928	1.764	1.599
4000	2.980	2.801	2.622	2.444	2.263	2.087	1.916	1.750	1.583
4500	2.968	2.789	2.610	2.431	2.251	2.076	1.904	1.737	1.568
5000	2.958	2.778	2.598	2.419	2.240	2.066	1.894	1.725	1.554
6000	2.940	2.760	2.580	2.399	2.221	2.044	1.874	1.705	1.529
7000	2.923	2.743	2.563	2.384	2.205	2.027	1.856	1.685	1.509
8000	2.908	2.727	2.548	2.367	2.190	2.012	1.840	1.666	1.490
9000	2.892	2.710	2.533	2.352	2.174	1.996	1.823	1.648	1.473
10,000	2.874	2.694	2.517	2.337	2.158	1.982	1.807	1.630	1.453
220° F.									
BP	(46) ^a 3.239	(94) 3.049	(146) 2.865	(202) 2.684	(262) 2.512	(327) 2.353	(400) 2.205	(482) 2.082	(580) 2.135
200	3.230 ^b	3.044	2.863
400	3.219	3.034	2.854	2.675	2.505	2.347	2.205
600	3.208	3.024	2.845	2.666	2.494	2.331	2.186	2.065	2.115
800	3.197	3.015	2.836	2.657	2.484	2.317	2.168	2.041	2.001
1000	3.188	3.005	2.827	2.649	2.474	2.304	2.151	2.019	1.941
1250	3.176	2.995	2.816	2.639	2.462	2.289	2.133	1.996	1.892
1500	3.166	2.984	2.805	2.627	2.450	2.276	2.117	1.975	1.857
1750	3.155	2.975	2.795	2.616	2.439	2.263	2.102	1.956	1.827
2000	3.145	2.965	2.785	2.606	2.427	2.251	2.088	1.939	1.802
2250	3.135	2.955	2.775	2.595	2.416	2.240	2.075	1.923	1.781
2500	3.125	2.945	2.765	2.585	2.406	2.228	2.063	1.909	1.763
2750	3.116	2.935	2.756	2.575	2.396	2.218	2.051	1.895	1.746
3000	3.108	2.926	2.746	2.565	2.385	2.208	2.040	1.882	1.731
3500	3.091	2.910	2.730	2.549	2.368	2.190	2.020	1.860	1.703
4000	3.076	2.895	2.714	2.534	2.352	2.174	2.002	1.839	1.679
4500	3.062	2.880	2.700	2.520	2.337	2.159	1.987	1.821	1.657
5000	3.048	2.867	2.685	2.505	2.323	2.145	1.973	1.805	1.638
6000	3.025	2.843	2.660	2.479	2.299	2.120	1.948	1.778	1.606
7000	3.004	2.821	2.639	2.457	2.277	2.098	1.926	1.755	1.581
8000	2.984	2.803	2.620	2.438	2.258	2.078	1.905	1.733	1.558
9000	2.965	2.784	2.602	2.420	2.239	2.060	1.884	1.710	1.534
10,000	2.945	2.763	2.583	2.401	2.227	2.041	1.864	1.687	1.511

(Continued on page 20)

Table I. Molal Volumes for Mixtures of

Pressure, P.S.I.A.	Mole Fraction Propane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
280° F.									
	(68) ^a	(136)	(211)	(295)	(386)	(487)	(598)	(718)	(850)
BP	3.386	3.195	3.014	2.841	2.676	2.523	2.403	2.343	2.78
200	3.375 ^b	3.191
400	3.359	3.177	3.001	2.832	2.674
600	3.344	3.164	2.988	2.818	2.655	2.506	2.402
800	3.330	3.152	2.976	2.803	2.636	2.480	2.358	2.309	...
1000	3.317	3.140	2.963	2.790	2.619	2.458	2.323	2.248	2.42
1250	3.302	3.122	2.947	2.772	2.599	2.433	2.290	2.193	2.248
1500	3.287	3.108	2.931	2.755	2.581	2.412	2.263	2.152	2.143
1750	3.273	3.093	2.916	2.739	2.564	2.393	2.241	2.117	2.066
2000	3.261	3.080	2.902	2.724	2.547	2.376	2.220	2.088	2.007
2250	3.248	3.067	2.888	2.709	2.532	2.360	2.201	2.060	1.959
2500	3.237	3.055	2.875	2.695	2.517	2.345	2.183	2.036	1.921
2750	3.226	3.043	2.863	2.681	2.503	2.331	2.167	2.014	1.890
3000	3.216	3.032	2.851	2.669	2.491	2.318	2.151	1.995	1.863
3500	3.196	3.011	2.829	2.646	2.466	2.292	2.122	1.962	1.819
4000	3.178	2.992	2.810	2.625	2.445	2.270	2.096	1.934	1.784
4500	3.162	2.976	2.792	2.608	2.425	2.247	2.074	1.910	1.756
5000	3.145	2.960	2.775	2.592	2.408	2.230	2.056	1.889	1.731
6000	3.117	2.931	2.744	2.561	2.379	2.198	2.024	1.856	1.691
7000	3.090	2.904	2.719	2.534	2.352	2.173	1.999	1.828	1.658
8000	3.065	2.879	2.696	2.511	2.328	2.149	1.973	1.802	1.628
9000	3.041	2.856	2.674	2.488	2.306	2.126	1.947	1.774	1.599
10,000	3.018	2.834	2.652	2.467	2.283	2.102	1.923	1.749	1.572
340° F.									
	(96) ^a	(188)	(289)	(402)	(522)	(654)	(794)	(934)	(962) ^c
BP	3.558	3.376	3.201	3.031	2.867	2.750	2.706	2.799	3.72
200	3.546 ^b	3.374
400	3.524	3.350	3.186
600	3.503	3.328	3.161	3.002	2.855
800	3.484	3.308	3.139	2.976	2.824	2.711	2.703
1000	3.467	3.288	3.117	2.952	2.797	2.667	2.612	2.713	3.45
1250	3.447	3.367	3.093	2.925	2.766	2.623	2.533	2.529	2.810
1500	3.428	3.246	3.071	2.901	2.738	2.587	2.476	2.420	2.550
1750	3.409	3.228	3.051	2.879	2.713	2.555	2.428	2.347	2.391
2000	3.395	3.210	3.032	2.858	2.688	2.528	2.388	2.291	2.275
2250	3.380	3.193	3.014	2.837	2.666	2.503	2.355	2.242	2.188
2500	3.365	3.178	2.997	2.819	2.644	2.479	2.327	2.203	2.122
2750	3.352	3.163	2.981	2.800	2.626	2.459	2.302	2.168	2.069
3000	3.339	3.149	2.966	2.783	2.608	2.439	2.280	2.138	2.026
3500	3.312	3.124	2.937	2.753	2.578	2.406	2.239	2.087	1.961
4000	3.288	3.101	2.912	2.726	2.550	2.376	2.204	2.047	1.913
4500	3.266	3.078	2.890	2.703	2.524	2.348	2.176	2.013	1.871
5000	3.246	3.058	2.870	2.682	2.502	2.324	2.152	1.985	1.837
6000	3.210	3.019	2.832	2.647	2.462	2.283	2.110	1.941	1.781
7000	3.178	2.988	2.801	2.616	2.431	2.250	2.074	1.904	1.738
8000	3.148	2.962	2.774	2.590	2.401	2.219	2.043	1.872	1.701
9000	3.120	2.935	2.748	2.564	2.375	2.192	2.015	1.842	1.667
10,000	3.097	2.909	2.722	2.537	2.349	2.167	1.989	1.814	1.637

propane. The sample employed was subjected to partial condensation followed by several evacuations at liquid nitrogen temperature. It was introduced into the volumetric equipment by conventional weighing-bomb techniques.

The *n*-decane was reported to contain not more than 0.0062 mole fraction of impurities. After deaeration and drying over metallic sodium, the *n*-decane had a specific weight of 45.3356 pounds per cubic foot at 77° F. and atmospheric pressure. This value compares with 45.337 pounds per cubic foot reported by API 44 (1) for an air-saturated sample at the same temperature. A refractive index of 1.4097 relative to the D-lines of sodium was obtained at 77° F. for the deaerated sample. This value compares favorably with a value of 1.40967 reported (1) for

air-saturated *n*-decane at the same temperature. On the basis of the above comparisons with critically chosen values of the properties of *n*-decane at atmospheric pressure, it appears that the sample of *n*-decane utilized contained less than 0.0062 mole fraction of materials other than *n*-decane and that these impurities are probably saturated hydrocarbons involving 10 carbon atoms per molecule.

EXPERIMENTAL RESULTS

Illustrative volumetric measurements obtained upon each of the four mixtures investigated are shown in Figure 1. For comparison, the corresponding influence of pressure on the molal

Propane and *n*-Decane in the Liquid Phase (Continued)

Pressure, P.S.I.A.	Mole Fraction Propane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	400° F.								
BP	(134) ^a 3.779	(249) 3.601	(375) 3.433	(512) 3.273	(655) 3.136	(802) 3.085	(948) 3.169	(1028) ^c 3.81	
200	3.765 ^b
400	3.728	3.567	3.426
600	3.695	3.529	3.379	3.250
800	3.667	3.497	3.340	3.202	3.092
1000	3.642	3.469	3.306	3.160	3.036	2.980	3.094
1250	3.615	3.439	3.271	3.115	2.979	2.888	2.876	3.18	...
1500	3.590	3.414	3.240	3.075	2.930	2.819	2.760	2.861	3.24 ^d
1750	3.568	3.388	3.210	3.040	2.887	2.763	2.679	2.691	2.873
2000	3.547	3.363	3.182	3.009	2.850	2.715	2.614	2.571	2.639
2250	3.526	3.340	3.156	2.981	2.817	2.675	2.558	2.490	2.501
2500	3.505	3.318	3.132	2.955	2.789	2.640	2.509	2.424	2.396
2750	3.487	3.298	3.111	2.932	2.764	2.610	2.471	2.369	2.314
3000	3.468	3.279	3.092	2.911	2.741	2.582	2.435	2.322	2.248
3500	3.435	3.244	3.056	2.872	2.699	2.532	2.376	2.248	2.149
4000	3.406	3.214	3.024	2.840	2.663	2.490	2.328	2.189	2.075
4500	3.379	3.187	2.996	2.810	2.631	2.454	2.288	2.140	2.013
5000	3.354	3.163	2.971	2.785	2.603	2.423	2.256	2.101	1.960
6000	3.309	3.117	2.925	2.739	2.553	2.373	2.201	2.038	1.881
7000	3.273	3.079	2.888	2.699	2.512	2.332	2.157	1.989	1.824
8000	3.238	3.047	2.856	2.666	2.478	2.296	2.119	1.947	1.778
9000	3.207	3.018	2.825	2.636	2.446	2.264	2.084	1.910	1.738
10,000	3.179	2.988	2.795	2.606	2.416	2.235	2.056	1.878	1.700
	460° F.								
BP	(183) ^a 4.058	(315) 3.887	(463) 3.727	(621) 3.615	(775) 3.619	(908) 3.741	(987) ...	(866) ...	
200	4.052 ^b
400	3.995	3.856
600	3.944	3.792	3.668
800	3.898	3.739	3.598	3.525	3.594
1000	3.859	3.692	3.542	3.446	3.440	3.539	3.88 ^d
1250	3.815	3.643	3.485	3.367	3.302	3.286	3.452	4.27 ^d	...
1500	3.776	3.600	3.436	3.304	3.200	3.137	3.200	3.54	4.41 ^d
1750	3.741	3.563	3.394	3.249	3.121	3.030	3.034	3.186	3.580
2000	3.710	3.529	3.356	3.201	3.060	2.949	2.915	2.960	3.176
2250	3.681	3.497	3.320	3.157	3.007	2.885	2.816	2.806	2.909
2500	3.655	3.468	3.287	3.119	2.963	2.831	2.735	2.692	2.740
2750	3.631	3.442	3.257	3.084	2.925	2.784	2.668	2.603	2.616
3000	3.608	3.417	3.230	3.055	2.891	2.743	2.615	2.535	2.520
3500	3.565	3.372	3.184	3.005	2.831	2.672	2.531	2.427	2.366
4000	3.528	3.334	3.147	2.965	2.784	2.615	2.468	2.347	2.251
4500	3.495	3.300	3.111	2.928	2.743	2.570	2.416	2.280	2.163
5000	3.468	3.271	3.081	2.895	2.709	2.533	2.372	2.226	2.093
6000	3.416	3.220	3.024	2.834	2.646	2.470	2.302	2.141	1.991
7000	3.372	3.176	2.979	2.786	2.597	2.420	2.246	2.078	1.916
8000	3.332	3.134	2.940	2.747	2.557	2.378	2.200	2.027	1.859
9000	3.296	3.097	2.904	2.713	2.523	2.342	2.160	1.984	1.811
10,000	3.260	3.062	2.869	2.681	2.492	2.309	2.125	1.945	1.767

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

^b Volume expressed in cubic feet per pound-mole.

^c Retrograde dew point.

^d Estimated.

volume of propane and *n*-decane at a temperature of 220° F. has been included in the figure. Experimental information in all respects comparable with that depicted in Figure 1 was obtained for temperatures between 40° and 460° F. The detailed experimental data are available through ADI. Smoothed values of the molal volume for even values of composition, pressure, and temperature are recorded in Table I. The standard error of estimate of these experimental values of the molal volume from the smoothed data recorded in Table I was 0.003 cubic foot per pound mole, corresponding to an error of 0.12% as related to the average value of the molal volumes.

Figure 2 shows a pressure-composition diagram for the propane-*n*-decane system. The solid points represent values of the bubble-point pressure as established from discontinuities in the first derivative of the isothermal change in molal volume with pressure under conditions of constant composition. The open circles correspond to values of the composition of the coexisting gas phase as measured by the partial condensation techniques described (8). The estimated loci of the maxcondens-therm, critical, and maximum pressure have been included in Figure 2. A record of the experimentally determined compositions of the coexisting gas phase is available through ADI.

Table II. Properties of Coexisting Gas and Liquid Phases

Pressure, P.S.I.A.	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole fraction propane	Volume cu. ft./lb. mole	Mole fraction propane	Volume cu. ft./lb. mole	Propane	n-Decane
40° F.						
0.004 ^a	0.0000	...	0.0000	3.055	...	1.000000 ^b
25	0.9996	...	0.3042	2.517	3.286	0.000568
50	0.9998	...	0.6172	1.977	1.620	0.000538
75	0.9999	...	0.9463	1.425	1.057	0.000596
79 ^c	1.0000	63.0	1.0000	1.347	1.000	1.000000
100° F.						
0.073 ^a	0.0000	... ^d	0.0000	3.166	...	1.00000 ^b
50	0.9979	...	0.2973	2.630	3.356	0.00300
100	0.9989	...	0.5746	2.146	1.738	0.00249
150	0.9996	33. ^e	0.8253	1.732	1.211	0.00252
189 ^c	1.0000	24.5	1.0000	1.494	1.000	1.00000
160° F.						
0.40 ^a	0.0000	... ^d	0.0000	3.302	...	1.0000 ^b
50	0.9910	...	0.1652	2.985	5.999	0.0108
100	0.9948	...	0.3178	2.705	3.130	0.00767
150	0.9961	39. ^e	0.4584	2.456	2.173	0.00718
200	0.9969	28.0	0.5899	2.232	1.690	0.00749
300	0.9985	16.14	0.8275	1.865	1.207	0.00864
384 ^c	1.0000	10.70	1.0000	1.761	1.000	1.0000
220° F.						
1.59 ^a	0.0000	... ^d	0.0000	3.443	...	1.00000 ^b
50	0.9652	...	0.1077	3.223	8.962	0.0390
100	0.9810	...	0.2110	3.028	4.649	0.0241
150	0.9863	45. ^e	0.3070	2.852	3.213	0.0197
200	0.9890	33.	0.3971	2.690	2.490	0.0183
300	0.9915	20.3	0.5591	2.416	1.773	0.0193
400	0.9923	13.59	0.7003	2.204	1.417	0.0257
600	0.9929	6.78	0.9167	2.182	1.083	0.0850
678 ^f	0.9870	3.21	0.9870	3.21	1.000	1.0000
618 ^g	0.993
280° F.						
5.08 ^a	0.0000	... ^d	0.0000	3.585	...	1.0000
50	0.8903	...	0.0732	3.439	12.17	0.1184
100	0.9403	...	0.1488	3.292	6.320	0.0701
150	0.9571	50. ^e	0.2195	3.160	4.360	0.0550
200	0.9654	36.	0.2856	3.041	3.380	0.0484
300	0.9737	22.8	0.4057	2.831	2.400	0.0442
400	0.9766	16.07	0.5139	2.654	1.900	0.0481
600	0.9770	8.94	0.7023	2.400	1.391	0.0773
800	0.9671	5.02	0.8629	2.464	1.121	0.2400
873 ^f	0.9283	3.22	0.9283	3.22	1.000	1.0000
622 ^g	0.977
340° F. ^h						
13.49 ^a	0.0000	... ^d	0.0000	3.742	...	1.0000
50	0.7147	...	0.0459	3.657	15.57	0.2990
100	0.8469	...	0.1051	3.548	8.058	0.1711
150	0.8914	52. ^e	0.1606	3.446	5.550	0.1294
200	0.9128	39.	0.2128	3.353	4.290	0.1108
300	0.9343	24.8	0.3099	3.184	3.015	0.09520
400	0.9427	17.85	0.3988	3.034	2.364	0.09531
600	0.9463	10.54	0.5595	2.790	1.691	0.1219
800	0.9420	6.77	0.7043	2.707	1.338	0.1961
980 ^f	0.8673	3.27	0.8673	3.27	1.000	1.0000
628 ^g	0.946
400° F.						
31.19 ^a	0.0000	...	0.0000	3.962	...	1.0000
50	0.3637	...	0.0190	3.926	19.12	0.6486
100	0.6647	...	0.0679	3.838	9.789	0.3597
150	0.7645	55. ^e	0.1144	3.753	6.683	0.2659
200	0.8145	41.	0.1588	3.674	5.129	0.2205

(Continued on page 23)

Table II. Properties of Coexisting Gas and Liquid Phases (Continued)

Pressure, P.S.I.A.	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole fraction propane	Volume cu. ft./lb. mole	Mole fraction propane	Volume cu. ft./lb. mole	Propane	<i>n</i> -Decane
300	0.8624	26.7	0.2419	3.530	3.565	0.1815
400	0.8827	19.32	0.3188	3.402	2.769	0.1722
600	0.8990	11.66	0.4615	3.182	1.948	0.1876
800	0.8945	7.72	0.5988	3.085	1.494	0.2630
1000	0.8456	4.013	0.7450	3.274	1.135	0.6055
1028 ^f	0.7993	3.78	0.7993	3.78	1.000	1.0000
640 ^a	0.900	...				
460° F.						
64.72 ^a	0.0000	...	0.0000	4.229	...	1.0000
100	0.3382	...	0.0311	4.177	10.88	0.6830
150	0.5416	55. ^e	0.0731	4.105	7.407	0.4946
200	0.6432	41.	0.1136	4.035	5.662	0.4025
300	0.7379	27.1	0.1890	3.906	3.904	0.3232
400	0.7803	19.86	0.2586	3.791	3.017	0.2963
600	0.8129	12.23	0.3867	3.623	2.102	0.3051
800	0.8104	8.04	0.5168	3.630	1.568	0.3924
988 ^f	0.7120	4.50	0.7120	4.50	1.000	1.0000
650 ^a	0.814	...				

^a Vapor pressure of *n*-decane (9).

^b As a result of the number of significant figures reported for dew-point gas compositions, some discrepancies in values of the equilibrium ratio, computed from the compositions reported and depicted in Figure 4, may exist at this temperature.

^c Vapor pressure of propane (10).

^d Dew-point volumes of *n*-decane expressed in cubic feet per pound-mole: at 100° F. = 82,200; at 160° F. = 16,600; at 220° F. = 4339; at 280° F. = 1447; at 340° F. = 591. Values based upon calorimetric vaporization measurements (5).

^e Dew-point volumes involve a somewhat larger uncertainty since they were established from volumetric measurements in the two-phase region.

^f Estimated critical state.

^g Estimated maxcondentherm.

^h Data at 340° F. interpolated.

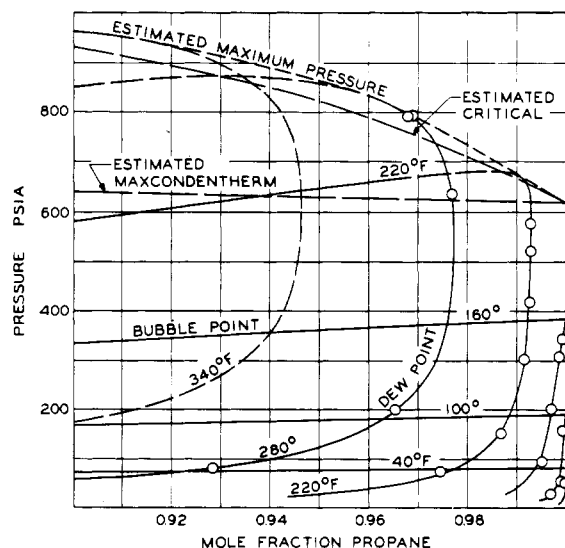


Figure 3. Experimental composition of dew-point gas

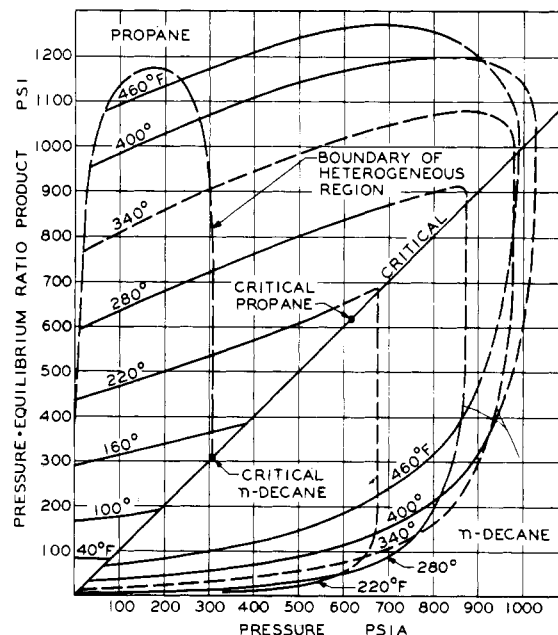


Figure 4. Equilibrium ratios for propane and *n*-decane

In the interest of depicting the behavior in somewhat greater detail at compositions near pure propane, an enlarged portion of Figure 2 is presented in Figure 3. From the information depicted in Figures 2 and 3, the equilibrium ratios have been

evaluated and are reported in a part of Table II along with the compositions and molal volumes of the dew-point gas and bubble-point liquid. The information presented in Table II has been smoothed with respect to pressure and temperature. The

Table III. Properties at the Unique States in the Propane-*n*-Decane System

Mole Fraction Propane	Critical		Maxcondentherm		Maximum Pressure	
	Pressure, p.s.i.a.	Temp., ° F.	Pressure, p.s.i.a.	Temp., ° F.	Pressure, p.s.i.a.	Temp., ° F.
0.0 ^a	304.0	655.0	304.0	655.0	304.0	655.0
0.1	387.5	641.3	361.0	642.8	406.0	633.5
0.2	477.0	625.1	418.0	628.5	511.5	610.0
0.3	580.5	604.8	472.0	611.7	618.0	582.8
0.4	688.0	580.4	521.5	592.0	724.0	552.6
0.5	793.5	551.7	562.0	570.0	824.0	519.6
0.6	892.5	515.6	600.0	543.8	918.0	483.0 ^b
0.7	979.0	466.8 ^b	632.0	510.7	996.0	444.2
0.8	1028.0	399.5	649.5	467.0 ^b	1028.0	400.2
0.9	932.0	308.5	639.0	399.5	962.0	342.0
1.0 ^c	617.4	206.3	617.4	206.3	617.4	206.3

^a Critical state of *n*-decane (1).

^b Values at this and higher temperatures are subject to greater uncertainty.

^c Critical state of propane (1).

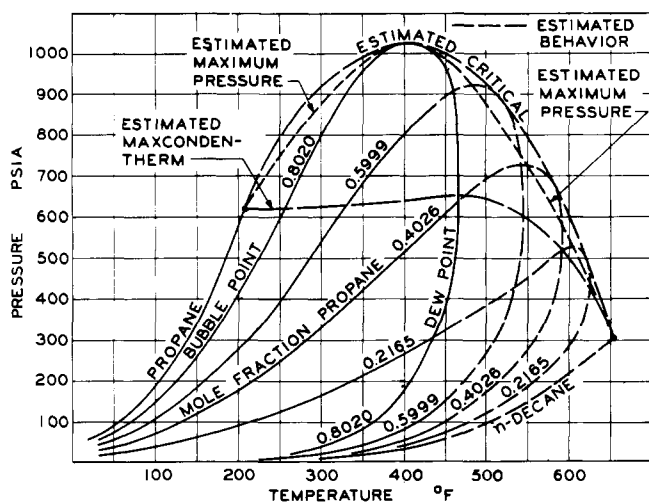


Figure 5. Pressure-temperature diagram for the propane-*n*-decane system

standard error of estimate of the experimentally determined composition data from the information presented in Table II was 0.0028 mole fraction.

As a matter of interest, Figure 4 shows the product of the pressure and the equilibrium ratio for both components as a function of pressure for each of the several temperatures investigated. The critical states of the components have been included also. There exists a larger measure of uncertainty in the equilibrium ratios for propane when present in dilute solution in *n*-decane than at other states. This has been indicated by the dashed boundary curve shown in Figure 4. The behavior depicted in this diagram is similar to that found for other paraffin hydrocarbon systems containing propane.

A pressure-temperature diagram showing the behavior of the bubble-point liquid and dew-point gas for each of the mixtures experimentally investigated constitutes Figure 5. The loci of the unique states have been included. The diagram has been extended to the critical temperature of *n*-decane. Since uncertainty exists as to the behavior of this system at temperatures significantly above those covered by this investigation, the curves have been dashed at temperatures beyond the range of experimental investigation. Estimated values of the unique states which include the critical, maxcondentherm, and loci of maximum pressure are set forth in Table III. Much larger uncertainties exist in the values reported for these states than in the case of the information presented in Tables I and II. Extensive interpolation of the volumetric and phase equilibrium data was required to arrive at the pressures and temperatures recorded in Table III. For this reason, uncertainties as large as

4% in pressure and 5° F. in temperature are to be expected. The probable error in the temperatures and pressures is somewhat smaller but was not established with certainty.

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