Phase Equilibria in Hydrocarbon Systems

n-Butane–Decane System in the Condensed Region

H. H. REAMER, B. H. SAGE, AND W. N. LACEY

California Institute of Technology, Pasadena, Calif.

The volumetric behavior of four mixtures of n-butane and decane was experimentally determined at seven temperatures from 100° to 460° F. for pressures up to 10,000 pounds per square inch. The results establish the volumetric properties of the mixtures in the single-phase region for pressures greater than bubble point. One mixture was studied at pressures sufficiently low to permit the determination of the dew-point pressure and volume at 340°, 400°, and 460° F. An equilibrium still was used in determining the composition of the bubble-point liquid at 100° and 160° F. for pressures below 30 pounds per square inch absolute. The results indicate that at the lower temperatures and higher pressures the system approaches the volumetric behavior of ideal solutions, but at the higher temperatures and intermediate pressures the volume may differ from such behavior by more than 50%.

IN THE course of a study of the ternary system composed of methane, n-butane, and decane, no information was found in the literature regarding the volumetric properties of the n-butane–decane system. For this reason an investigation of this binary system was undertaken, and the behavior of four mixtures was determined experimentally throughout the liquid region at the lower temperatures and throughout the gaseous or single-phase fluid region at the higher temperatures for pressures up to 10,000 pounds per square inch.

Pure n-butane has been studied by many investigators, and the more recent data from different laboratories seem to be in good agreement (1, 2, 5, 8). The specific volume of liquid n-decane and its boiling point at atmospheric pressure were reported by Shepard, Henne, and Midgley (12). Young (13) determined the boiling point of n-decane at several pressures. Sage, Lavender, and Lacey measured the specific volume of liquid decane at pressures up to 3500 pounds per square inch for temperatures between 70° and 250° F. (11). Later Reamer and others (9) extended these measurements to 10,000 pounds per square inch and 460° F.

MATERIALS AND METHODS

The n-butane was obtained from the Phillips Petroleum Company with an analysis which indicated the presence of less than 0.3 mole % isobutane and negligible amounts of other impurities. This material was distilled twice with a reflux ratio of about 50 in a fractionating column, 4 feet long; it was packed with glass helices, each consisting of slightly more than one turn. The initial and final tenths of the charge in the distillation column were discarded each time, and the middle fraction was condensed at liquid air temperature with continuous removal of noncondensable gases by a high-vacuum mercury diffusion pump. A sample prepared in this manner showed a difference of less than 0.25% in its vapor pressure at 280° F. when 5% of the sample was in the gas phase and when 50% was vaporized.

The decane used in this study was obtained from the Eastman Kodak Company and was distilled at reduced pressure to remove dissolved gas and, possibly, other impurities. The resulting material had a density of 0.7178 gram per cc. at atmospheric pressure and 37.8° C. and a refractive index of 1.4100 at 77° F., referred to the D line of the sodium spectrum. When compared with information concerning n-decane (12) and several decane isomers (3, 7), these data indicate that the material used in this work was composed primarily of paraffin hydrocarbons consisting of ten carbon atoms per molecule but probably was not pure n-decane.

A detailed description of the volumetric apparatus and procedures has been published (10). The method consisted essentially in the introduction of measured weights of n-butane and decane into a stainless-steel pressure vessel whose effective volume could be varied by the injection or withdrawal of mercury, which was used as the confining liquid. The total volume of the sample was determined by measurements indicating the elevation of the mercury surface with an uncertainty of 0.1% at the largest volumes and 0.25% at the smallest. Pressure was measured by a piston-and-cylinder fluid pressure balance with an uncertainty of about 0.1%. The temperature was maintained at known values by immersing the system in a thermostatic oil bath whose temperature was indicated by a platinum resistance thermometer with an uncertainty of 0.02° F. The thermostat controls were kept in such adjustment that the temperature of the oil bath was maintained within 0.05° F. of the desired value throughout the course of an experiment. The gravimetric techniques employed in the preparation of the experimentally studied mixtures probably did not involve uncertainties greater than 0.001 mole fraction in the compositions of the mixtures.

Difficulty was experienced in obtaining consistent bubble-point data from the volumetric apparatus at pressures below 2 or 3 atmospheres. The trouble apparently resulted from traces of air, which may have reached the equilibrium cell by way of the
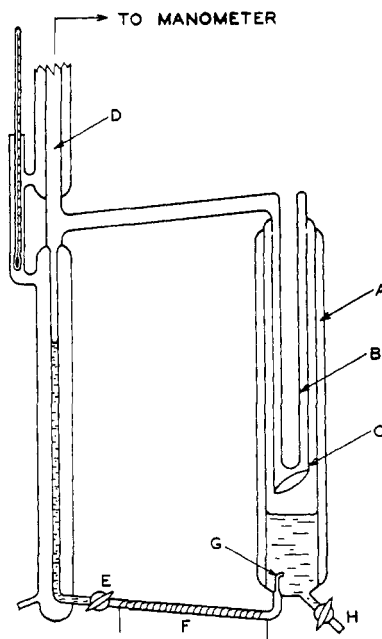

Figure 1. Equilibrium Still

TABLE I. MOLAL VOLUMES FOR MIXTURES OF n-BUTANE AND DECANE

Molal Volume, Cubic Feet per Pound Mole

Pressure, Lb./Sq. In. Abs.	Mole Fraction n-Butane, 0.1787							Mole Fraction n-Butane, 0.6617						
	100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.	100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
	(9.1)a	(21.3)	(39.9)	(63.6)	(96.1)	(140)	(198)	(33.4)a	(76.8)	(145)	(245)	(374)	(525)	(671)
B.P.	2.895	2.999	3.124	3.278	3.471	3.700	3.985	2.159	2.270	2.402	2.573	2.824	3.196	3.836
200	2.890	2.992	3.115	3.266	3.456	3.687	3.983	2.154	2.265	2.399	...	...	...	...
400	2.884	2.984	3.105	3.251	3.431	3.649	3.922	2.148	2.257	2.386	2.556	2.815	...	...
600	2.879	2.977	3.095	3.236	3.409	3.614	3.868	2.143	2.250	2.374	2.535	2.766	3.142	...
800	2.874	2.970	3.085	3.222	3.388	3.582	3.820	2.137	2.242	2.363	2.515	2.723	3.033	3.602
1,000	2.869	2.964	3.076	3.208	3.369	3.553	3.778	2.132	2.235	2.352	2.496	2.689	2.960	3.390
1,250	2.863	2.956	3.065	3.193	3.348	3.522	3.731	2.125	2.226	2.338	2.474	2.652	2.892	3.230
1,500	2.857	2.948	3.054	3.179	3.328	3.494	3.690	2.119	2.217	2.325	2.454	2.621	2.839	3.123
1,750	2.851	2.941	3.044	3.166	3.310	3.470	3.654	2.113	2.209	2.312	2.435	2.595	2.791	3.043
2,000	2.846	2.934	3.035	3.153	3.293	3.447	3.622	2.107	2.201	2.301	2.419	2.572	2.756	2.975
2,250	2.840	2.927	3.025	3.142	3.278	3.426	3.593	2.101	2.193	2.289	2.405	2.550	2.723	2.923
2,500	2.835	2.920	3.017	3.130	3.263	3.407	3.567	2.096	2.185	2.280	2.391	2.531	2.693	2.874
2,750	2.830	2.914	3.008	3.119	3.249	3.388	3.542	2.090	2.178	2.270	2.379	2.512	2.665	2.830
3,000	2.825	2.908	3.000	3.108	3.236	3.371	3.519	2.085	2.170	2.262	2.368	2.496	2.640	2.793
3,500	2.816	2.896	2.984	3.088	3.210	3.338	3.476	2.075	2.157	2.245	2.347	2.464	2.594	2.733
4,000	2.807	2.885	2.970	3.069	3.186	3.308	3.439	2.065	2.144	2.231	2.328	2.438	2.556	2.680
4,500	2.798	2.874	2.956	3.051	3.163	3.280	3.405	2.056	2.132	2.218	2.310	2.414	2.524	2.639
5,000	2.790	2.863	2.943	3.033	3.141	3.253	3.374	2.047	2.121	2.205	2.294	2.392	2.492	2.602
6,000	2.773	2.844	2.918	3.003	3.101	3.204	3.317	2.031	2.101	2.181	2.264	2.353	2.443	2.539
7,000	2.757	2.825	2.896	2.977	3.065	3.161	3.269	2.017	2.082	2.159	2.236	2.319	2.402	2.488
8,000	2.742	2.807	2.876	2.954	3.034	3.124	3.227	2.003	2.065	2.138	2.210	2.287	2.363	2.445
9,000	2.727	2.791	2.857	2.934	3.008	3.092	3.192	1.991	2.050	2.117	2.186	2.257	2.330	2.410
10,000	2.713	2.776	2.840	2.916	2.985	3.066	3.161	1.979	2.036	2.097	2.163	2.230	2.302	2.379

Pressure, Lb./Sq. In. Abs.	Mole Fraction n-Butane, 0.4631							Mole Fraction n-Butane, 0.8358						
	(23.3)a	(53.8)	(101)	(164)	(247)	(348)	(458)	(42.6)a	(98.4)	(191)	(331)	(511)		
B.P.	2.454	2.557	2.675	2.843	3.059	3.317	3.709	1.911	2.031	2.191	2.405	2.764	...	...
200	2.449	2.552	2.670	2.838	...	...	...	1.906	2.024	2.190	...	...	...	...
400	2.444	2.545	2.661	2.818	3.031	3.294	...	1.900	2.014	2.171	2.391	...	...	...
600	2.439	2.538	2.652	2.800	3.000	3.239	3.603	1.893	2.007	2.153	2.354	2.701	...	9.985
800	2.434	2.532	2.643	2.783	2.973	3.193	3.501	1.886	1.997	2.136	2.322	2.614	3.293	5.725
1,000	2.429	2.526	2.634	2.769	2.948	3.155	3.428	1.880	1.988	2.120	2.293	2.547	2.989	4.067
1,250	2.423	2.518	2.623	2.752	2.922	3.115	3.355	1.874	1.977	2.102	2.262	2.484	2.819	3.415
1,500	2.417	2.511	2.613	2.736	2.898	3.080	3.297	1.867	1.967	2.085	2.234	2.432	2.716	3.132
1,750	2.412	2.503	2.603	2.722	2.875	3.050	3.246	1.860	1.956	2.070	2.209	2.391	2.634	2.967
2,000	2.406	2.496	2.593	2.709	2.855	3.022	3.203	1.854	1.947	2.055	2.187	2.355	2.571	2.850
2,250	2.401	2.489	2.584	2.696	2.836	2.996	3.166	1.848	1.937	2.042	2.168	2.326	2.519	2.763
2,500	2.396	2.482	2.575	2.684	2.818	2.971	3.134	1.842	1.929	2.030	2.151	2.300	2.480	2.693
2,750	2.391	2.476	2.566	2.673	2.802	2.949	3.104	1.836	1.922	2.019	2.134	2.277	2.442	2.637
3,000	2.386	2.469	2.558	2.662	2.787	2.928	3.078	1.831	1.914	2.009	2.120	2.255	2.411	2.587
3,500	2.377	2.456	2.542	2.642	2.759	2.889	3.029	1.820	1.898	1.990	2.096	2.219	2.358	2.508
4,000	2.367	2.444	2.527	2.623	2.734	2.854	2.982	1.809	1.885	1.973	2.073	2.187	2.314	2.444
4,500	2.359	2.433	2.513	2.605	2.712	2.824	2.941	1.799	1.873	1.958	2.053	2.160	2.275	2.393
5,000	2.351	2.422	2.500	2.589	2.691	2.796	2.904	1.790	1.860	1.944	2.035	2.134	2.239	2.348
6,000	2.334	2.401	2.475	2.559	2.654	2.747	2.843	1.774	1.841	1.917	2.001	2.089	2.180	2.275
7,000	2.320	2.383	2.453	2.532	2.620	2.706	2.794	1.760	1.823	1.895	1.970	2.050	2.132	2.219
8,000	2.305	2.366	2.433	2.508	2.588	2.670	2.753	1.747	1.808	1.875	1.945	2.016	2.091	2.173
9,000	2.292	2.351	2.415	2.486	2.560	2.638	2.717	1.734	1.795	1.859	1.924	1.991	2.059	2.133
10,000	2.279	2.338	2.399	2.465	2.533	2.608	2.684	1.723	1.782	1.842	1.905	1.969	2.034	2.101

a Figures in parentheses represent bubble-point pressures expressed in pounds per square inch absolute.

mercury injection system. The volumetric method of determining bubble-point pressures would be expected to yield increasingly erratic results as the temperature and pressure decreased because the effect of small amounts of a noncondensable and difficultly-soluble gas upon the bubble-point pressure would become relatively greater as the vapor pressures of the hydrocarbon components of the system decreased.

For this reason an equilibrium still, resembling in principle the apparatus described by Jones, Schoenborn, and Colburn (4), was constructed. The primary advantage of the equilibrium still is its property of self-purification in so far as the more volatile impurities are concerned; the noncondensable gases are continuously swept out of the active portion of the system by the vaporization-condensation process. Figure 1 shows some of the details of the still. The kettle is provided with a vacuum jacket, A, the inner surfaces of which are silvered to reduce the transfer of energy by radiation. A platinum resistance thermometer is inserted in thermometer well B. A small amount of mercury in the bottom of the well serves to improve the thermal conductivity between the wall of the well and the thermometer and, thus, to reduce the time lag in the temperature measurements. The purpose of shield C surrounding the thermometer well is to provide additional thermal insulation by preventing the gas which is flowing

around the thermometer well from coming in contact with the walls of the kettle. The gas passes from the kettle to condenser D, which is maintained at a temperature between −20°
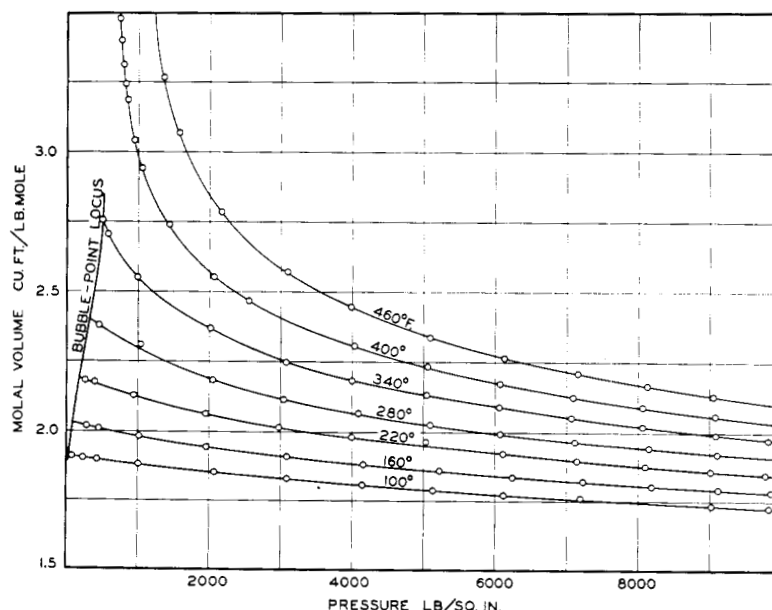

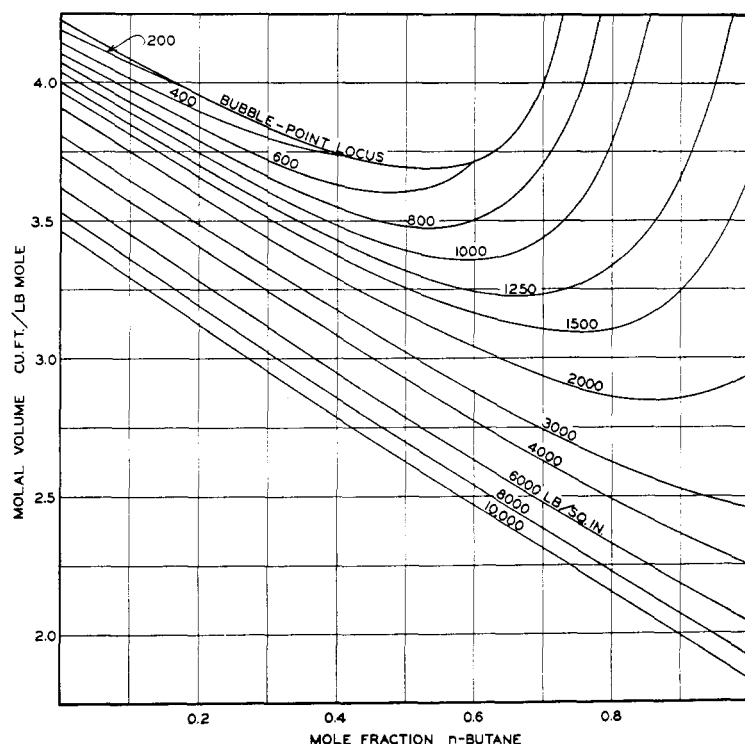Figure 2. Experimental Results for Mixture Containing 0.8358 Mole Fraction n-Butane

Figure 3. Isobaric Molal Volume Curves for 460° F., Showing Result of Varying Composition

and −40° F. by circulating chilled acetone through the condenser jacket. A column of liquid is permitted to accumulate in the lower portion of the condenser until sufficient hydrostatic pressure is developed so that the liquid can be throttled through stopcock E into heater F. Energy is supplied to the heater by means of a spirally wound Nichrome ribbon connected to a manually controlled, alternating-current power supply. The gas from the heater enters the kettle through jet G which is bent over so as to avoid impingement of liquid on the base of the thermometer well. By carefully adjusting throttle E and the heat input at F, the distillation system can be made to operate for extended periods under steady-state conditions. The pressure of the system is maintained at fixed values by a large ballast bottle which contains air and is connected to the upper end of the condenser.

Constancy of the temperature indicated by the resistance thermometer was used as a criterion of equilibrium. When equilibrium had been maintained for about half an hour, a sample of the liquid phase was withdrawn from

the kettle through sample port H. The compositions of the samples withdrawn were easily determined by fractional distillation because of the marked difference in volatility betweeen n-butane and decane. The results obtained from the equilibrium still were much more consistent than those obtained from PVT determinations of bubble points at pressures of the order of 30 or 40 pounds per square inch absolute.

RESULTS

Figure 2 shows the volumetric results obtained from the study of a mixture containing 0.8358 mole fraction n-butane. The circled points represent the experimentally observed equilibrium states of the system. Of the points shown in this representative figure, only two deviated noticeably from the smooth curves drawn when the data were correlated isothermally. Large scale plots of the data from all four of the mixtures were prepared, and isotherms drawn through the data points were used to obtain values interpolated to even pressures. The results are recorded in Table I.

The useful expansion ratio of the PVT apparatus is limited by the smallest volume which can be measured by it with satisfactory accuracy. Thus, if a large range of molal volume is to be observed, samples of various sizes must be prepared and studied at the various temperatures for different intervals of pressure. This process is time consuming and, hence, not always feasible. However, a mixture of small enough weight to permit observation of the dew-point region at 340°, 400°, and 460° F. was prepared. The results from the study of this mixture are recorded in Table II. Because of the small size of the sample it is estimated that the results in Table II involve an uncertainty of about 0.3 cubic foot per pound mole.

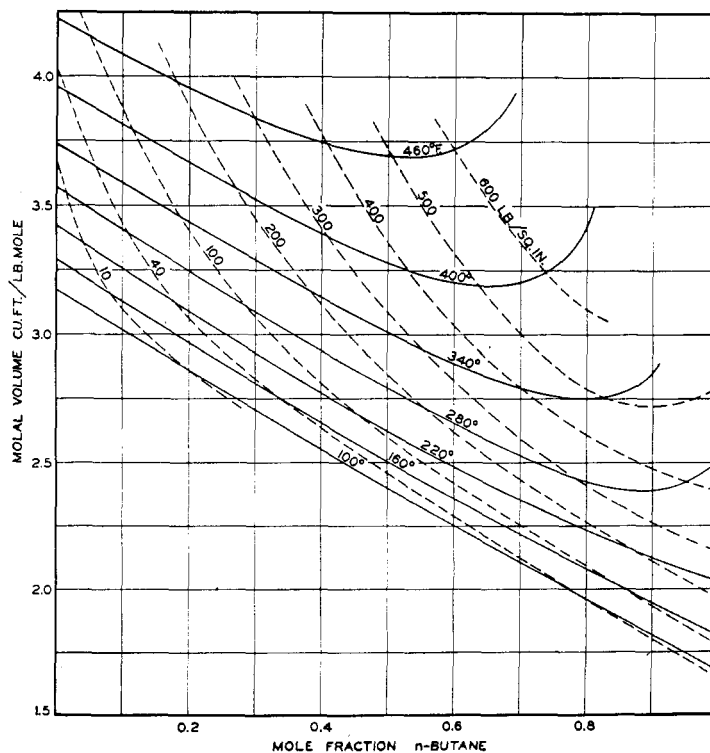Figure 3 shows isobaric curves relating the volume to the com-

TABLE II. MOLAL VOLUMES FOR A MIXTURE OF n-BUTANE AND DECANE (MOLE FRACTION n-BUTANE, 0.6599)

Pressure, Lb./Sq. In. Abs.	Molal Volume, Cu. Ft./Lb. Mole		
	340° F. (39)[a]	400° F. (99)	460° F. (219)
Dew point	211.3	83.5	36.1
20	420	454	487
40	204.3	222.8	239.8
60	116.1	145.5	157.6
80	78.6	106.4	116.2
100	58.2	82.2	91.4
150	33.2	45.1	57.9
200	21.4	29.5	40.7
300	9.3	15.7	22.0
400	...	9.0	13.6
500	...	...	8.9

[a] Figures in parentheses represent dew-point pressures in pounds per square inch absolute.

Figure 4. Effects of Pressure and Temperature on Relation between Bubble-Point Volume and Composition

TABLE III. PROPERTIES[a] OF BUBBLE-POINT LIQUID

Mole Fraction n-Butane	100° F. Pressure	100° F. Vol.	160° F. Pressure	160° F. Vol.	220° F. Pressure	220° F. Vol.	280° F. Pressure	280° F. Vol.	340° F. Pressure	340° F. Vol.	400° F. Pressure	400° F. Vol.	460° F. Pressure	460° F. Vol.
0.0	0.07	3.176	0.40	3.292	1.59	3.423	5.1	3.571	13.5	3.742	31.2	3.962	64.7	4.229
0.1	5.1	3.017	12.1	3.126	22.8	3.254	37.5	3.406	59.0	3.589	90.3	3.814	137.5	4.087
0.2	10.1	2.860	23.8	2.966	44.3	3.089	70.5	3.243	106.6	3.440	154.3	3.669	215.5	3.959
0.3	15.1	2.706	35.3	2.808	65.9	2.927	104.8	3.087	157.2	3.291	222.0	3.526	301	3.841
0.4	20.1	2.550	46.6	2.652	87.5	2.771	140.5	2.936	211.2	3.147	297	3.393	395	3.748
0.5	25.1	2.398	58.0	2.503	109.1	2.622	178.2	2.790	269	3.009	379	3.279	496	3.695
0.6	30.2	2.249	69.5	2.357	131.2	2.483	218.8	2.652	331	2.888	467	3.205	602	3.724
0.7	35.4	2.103	81.4	2.217	154.8	2.353	263	2.527	402	2.791	562	3.210	700	4.002
0.8	40.7	1.961	93.9	2.078	180.7	2.231	312	2.429	481	2.751	657	3.431	...	...
0.9	46.1	1.818	107.0	1.944	209.3	2.121	369	2.391	571	2.854	...	...	...	...
1.0	51.5	1.671	120.6	1.813	241.2	2.028	436	2.501	...	...	...	...	...	...

[a] Pressures in pounds per square inch absolute, volumes in cubic feet per pound mole.
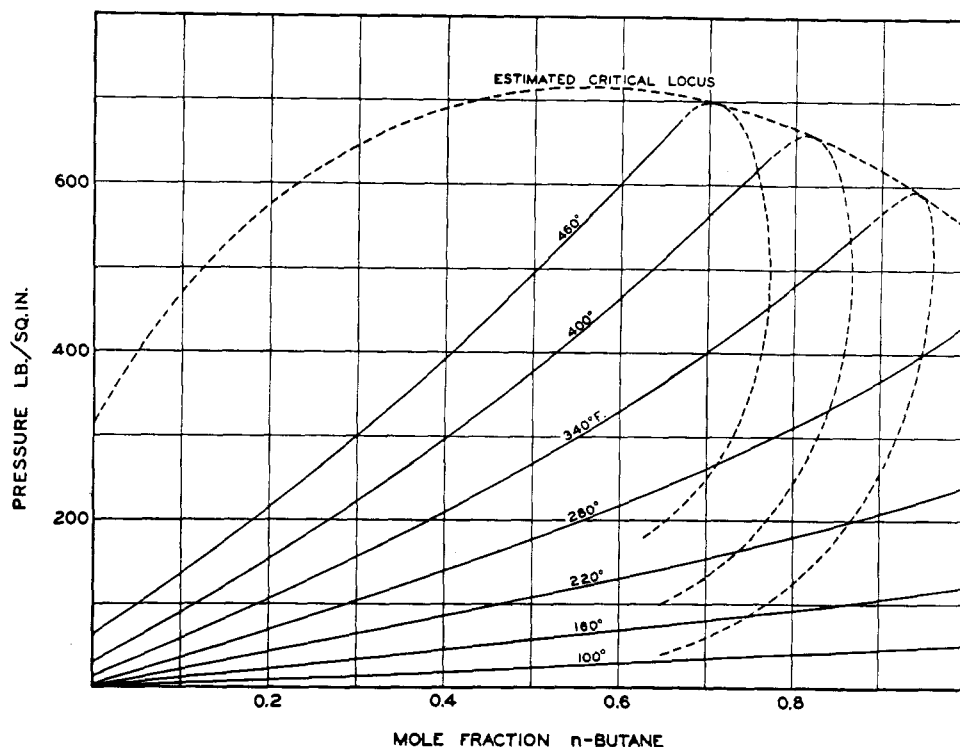
Figure 5. Bubble-Point Pressure as Influenced by Composition at Several Temperatures

as hardly more than qualitative estimates. At 100°, 160°, 220°, and 280° F. the maximum deviations of the bubble-point pressure from that predicted by Raoult's law are 3, 5, 11, and 23%, respectively. At the higher temperatures the curvature in the bubble-point pressure curves is large over the entire range of the composition, so that not even Henry's law can be used to describe the behavior of the system.

It may be concluded from the results given that at low temperatures and high pressures, mixtures of n-butane and decane approach the volumetric behavior of ideal solutions, but at elevated temperatures and intermediate pressures the system deviates so greatly from the volumetric behavior of ideal solutions as to render such an idealized concept of little value in application to this system.

position of the system at 460° F. At the highest pressures the relation between molal volume and mole fraction n-butane is nearly linear. At 3000 pounds per square inch the maximum deviation from the volumetric behavior of an ideal solution (6) is less than 5%. However, at lower pressures the deviations rapidly become very large, so that at 1000 pounds per square inch a mixture containing 0.5 mole fraction n-butane occupies a volume at 460° F. which is less than half the sum of the total volumes of its components measured separately at that pressure and temperature.

Table III gives values of pressure and molal volume at the bubble point for even values of temperature and mole fraction n-butane. Figure 4 shows the bubble-point volume in relation to the composition of the system; the isothermal curves are drawn as solid lines and the isobaric curves are dotted. Figure 5 illustrates the isothermal effect of composition upon the bubble-point pressure. The locus of critical states and portions of the dew-point isotherms for the three highest temperatures are shown as dotted lines to indicate that these curves are merely estimates of the behavior of the system. Because determinations of dew-point states were obtained for only one mixture at only three temperatures, the dotted curves in Figure 5 should be regarded

ACKNOWLEDGMENT

LITERATURE CITED

(1) Beattie, Simard, and Su, J. Am. Chem. Soc., 61, 24 (1939).
(2) Ibid., 61, 26 (1939).
(3) Calingaert and Soroos, Ibid., 58, 635 (1936).
(4) Jones, Schoenborn, and Colburn, IND. ENG. CHEM., 35, 666 (1943).
(5) Kay, Ibid., 32, 358 (1940).
(6) Lewis and Randall, "Thermodynamics", p. 221, New York, McGraw-Hill Book Co., 1923.
(7) Marker and Oakwood, J. Am. Chem. Soc., 60, 2598 (1938).
(8) Olds, Reamer, Sage, and Lacey, IND. ENG. CHEM., 36, 282 (1944).
(9) Reamer, Olds, Sage, and Lacey, Ibid., 34, 1526 (1942).
(10) Sage and Lacey, Trans. Am. Inst. Mining Met. Engrs., 136, 136 (1940).
(11) Sage, Lavender, and Lacey, IND. ENG. CHEM., 32, 743 (1940).
(12) Shepard, Henne, and Midgley, J. Am. Chem. Soc., 53, 1948 (1931).
(13) Young, Proc. Roy. Irish Acad., B38, 65 (1928).