f° = fugacity of pure component at its vapor pressure and the temperature of the solution
$\bar{f}_i$ = partial fugacity of component in mixture
K_1 = Henry's constant for neon
$\bar{V}_i$ = partial molar volume of component i at infinite dilution
P = total pressure of the solution
P_i° = vapor pressure of pure component
m, b, c = empirical constants for Equations 3 and 7
$F(x_2)$ = a function of the concentration of helium
k_2 = a pressure dependent empirical constant for helium

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Phase Equilibria in Hydrocarbon Systems

Phase Behavior in the *n*-Butane–*n*-Decane System

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Measurements of the composition of the gas phase in heterogeneous mixture of *n*-butane and *n*-decane were made throughout the two-phase region at temperatures between 160° and 460° F. These new measurements coupled with earlier volumetric investigations serve to establish the phase behavior of this binary system pressures up to 700 pounds per square inch in the temperature interval between 160° and 460° F. The results are presented in graphical and tabular form.

STUDIES OF THE volumetric and phase behavior of hydrocarbon systems remain of importance to the petroleum industry since satisfactory methods of predicting the behavior of multicomponent hydrocarbon systems of interest to the industry continue to be based upon experimental investigation. The volumetric behavior of *n*-butane has been investigated in detail (*2, 3, 5, 6*). Similarly, the volumetric behavior of decane in the liquid phase has been studied in some detail (*8, 14*). The vapor pressures of *n*-butane (*6*) and of decane (*8*) have also been established. Measurements of the volumetric behavior of mixtures of *n*-butane and decane in the liquid phase have been carried out at pressures up to 10,000 p.s.i.a. in the temperature interval between 100° and 460° F. (*11*). The properties of the bubble-point liquid have also been studied (*11*). However, there has not been any investigation of the composition of the gas phase in heterogeneous mixtures of *n*-butane and *n*-decane at elevated pressures and temperatures. In order to complete the investigation of the phase behavior of this system, a study of the composition of the gas phase in heterogeneous mixtures of *n*-butane and *n*-decane has been carried out at pressures throughout the two-phase region at temperatures between 160° and 460° F.

APPARATUS AND PROCEDURE

The apparatus and techniques employed in this investigation are similar to those used in earlier investigations (*13*). The heterogeneous mixtures of *n*-butane and *n*-decane were confined over mercury in a stainless steel container and samples of the gas phase were withdrawn under isobaric, isothermal conditions. The composition of the material withdrawn was determined by a partial condensation technique (*7*) carried out at temperatures of solid carbon dioxide in equilibrium with acetone. After separation the relative quantities of *n*-decane and *n*-butane were determined by conventional gravimetric techniques (*7*).

The temperature of the heterogeneous equilibrium was related to the international platinum scale by use of a strain-free, platinum resistance thermometer. The behavior of this instrument was compared with the indications of a similar device calibrated by the National Bureau of Standards. Experience over a period of several decades indicates the temperature of the stainless steel container was known within 0.1° F. relative to the international platinum scale throughout the temperature interval between 160° and 460° F.

Pressure was determined by means of a balance whose construction has been described in some detail (*12*). This instrument has been calibrated at least annually against the vapor pressure of samples of carbon dioxide at the ice point. The variation in calibration of this balance over a 20-year period has been less than 0.05% (*10*). It appears that the pressures were established within 0.02% or 0.2 p.s.i. throughout the entire range of this investigation. It was not necessary to determine the volumetric behavior of the samples investigated during this series of measurements.

MATERIALS

The *n*-butane utilized in this study was obtained from the Phillips Petroleum Co. as research grade and reportedly contained less than 0.001 mole fraction of impurities. The change in vapor pressure corresponding to a change in quality from 0.1 to 0.8 was 0.06 p.s.i. at 100° F. With such a small change in vapor pressure with quality, it is believed that the reported purity is correct.

The *n*-decane was also obtained from the Phillips Petroleum Co. as research grade material with a reported purity of 99.43 mole per cent *n*-decane. The specific weight of an air-free sample was 45.335 pounds per cubic foot at 77° F. This compares with a value of 45.337 pounds per cubic foot reported (*1*) for an air-saturated sample at the same temperature. The refractive index of this sample of *n*-decane was 1.40968 relative to the D-lines of sodium at 77° F. This value of refractive index compares with a reported (*1*) value of 1.40967 for an air-saturated sample at the same temperature. The *n*-decane was dried over metallic sodium and evacuated to a pressure of the order of 0.0001 inch of mercury at liquid nitrogen temperatures.

EXPERIMENTAL RESULTS

A total of twenty-four states were investigated in the course of this study. The results of these measurements are recorded in Table I. These data represent unsmoothed, experimental values of the composition of the gas phase. It appears that the compositions were established within 0.002 mole fraction, and the pressures within 0.02% or 0.2 p.s.i., whichever was the larger measure of uncertainty. The temperatures were related to the international platinum scale with an uncertainty of not more than 0.1° F. The compositions of the gas phase were determined from samples of the latter phase withdrawn from the heterogeneous mixtures under isobaric, isothermal conditions. The compositions were determined by partial condensation techniques. In some cases, somewhat larger uncertainties than those referred to above were experienced. These were particularly important near the critical state of the system. Under these circumstances, the small perturbations in pressure associated with the withdrawal process introduced somewhat larger variations in composition than was the case with the uncertainties in the experimental determination of the composition.

There is shown in Figure 1 on a pressure-composition diagram the experimental values of the composition of the dew-point gas arising from the results of the present investigation. In addition, the experimentally established values of the composition of the coexisting liquid phase obtained from an earlier study (*11*) have been included. The estimated relationship of the critical state and that of the maxcondentherm have been shown as a function of composition on this diagram. It did not appear feasible to depict the estimated states at the point of maximum pressure since these were nearly coincident with the critical state.

In Figure 2 is presented on an enlarged scale the composition of the dew-point gas a a function of pressure. In this case it has been possible to show the estimated values of the maximum pressure, maxcondentherm, and critical state. The standard error of estimate of the experimental data from the smooth curve shown corresponded to 0.0043 mole fraction *n*-butane. This standard error of estimate was evaluated upon the basis that all of the error lay in the determination of the composition

Table I. Composition of the Coexisting Phases in the *n*-Butane–*n*-Decane System

Press. P.S.I.A.	Mole Fraction *n*-Butane Gas	Liquid
	160° F.	
96.84	0.99913	
	220° F.	
119.11	0.98876	
172.02	0.99369	
	280° F.	
72.27	0.92474	
165.34	0.96946	
293.12	0.98498	
	400° F.	
95.69	0.66070	
211.91	0.83596	
391.71	0.89728	
517.05	0.91102	
599.46	0.91143	
609.62		0.75557
609.63	0.91195	
652.05	0.90773	
663.03		0.80645
679.06		0.82538
679.19	0.89837	
	460° F.	
103.29	0.38124	
217.57	0.68379	
218.33	0.68350[a]	
443.34	0.80878	
548.64	0.83160	
648.87	0.82006	
712.81	0.75015	

[a] Duplicate withdrawal.

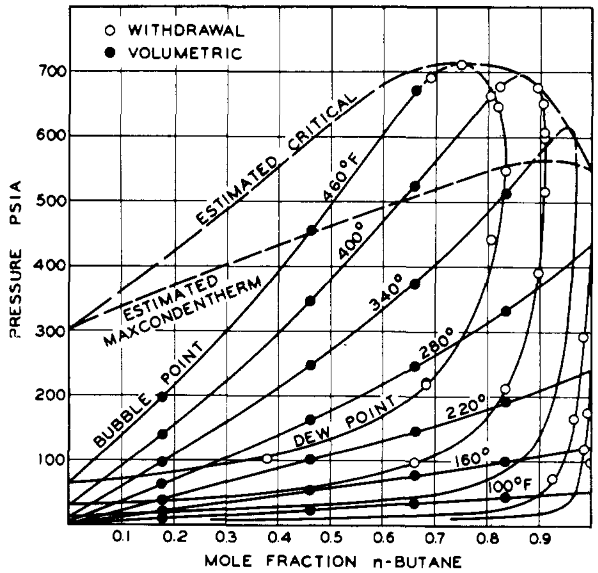

Figure 1. Pressure-composition diagram for the *n*-butane–*n*-decane system

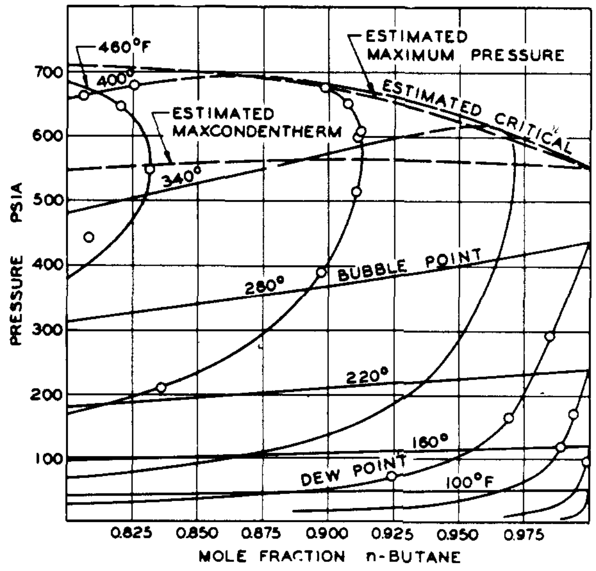

Figure 2. Composition of the dew-point gas at states near pure *n*-butane

Table II. Properties of Coexisting Gas and Liquid

	Dew Point		Bubble Point		Equilibrium Ratio	
Press. P.S.I.A.	Mole Fraction n-Butane	Volume cu. ft./lb. mole	Mole Fraction n-Butane	Volume cu. ft./lb. mole	n-Butane	n-Decane
			100° F.			
0.073[a]	0.0000	...[b]	0.0000	3.17	...	1.00000[c]
25	0.9983	...	0.4966	2.41	2.010	0.00346
50	0.9999	...	0.9751	2.18	1.025	0.00201
51.5[d]	1.0000	105.7	1.0000	1.670	1.000	...
			160° F.			
0.40[a]	0.0000	...[b]	0.0000	3.30	...	1.000[c]
25	0.9861	...	0.2162	2.94	4.561	0.0177
50	0.9944	...	0.4324	2.604	2.300	0.00987
75	0.9974	...	0.6434	2.293	1.550	0.00729
100	0.9991	...	0.8486	2.013	1.177	0.00608
120.6[d]	1.0000	45.6	1.0000	1.813	1.000	...
			220° F.			
1.59[a]	0.0000	...[b]	0.0000	3.44	...	1.0000[c]
25	0.9372	...	0.1103	3.23	8.497	0.0706
50	0.9692	...	0.2272	3.04	4.266	0.0399
75	0.9801	...	0.3435	2.860	2.853	0.0303
100	0.9857	63[e]	0.4590	2.683	2.147	0.0264
125	0.9893	49	0.5720	2.521	1.730	0.0250
150	0.9921	39.3	0.6800	2.378	1.459	0.0247
175	0.9945	32.7	0.7794	2.255	1.276	0.0249
200	0.9967	27.5	0.8706	2.155	1.145	0.0255
225	0.9987	23.7	0.9513	2.071	1.050	0.0267
241.2[d]	1.0000	21.6	1.0000	2.028	1.000	...
			280° F.			
5.08[a]	0.0000	...[b]	0.0000	3.58	...	1.000
50	0.8986	...	0.1387	3.32	6.479	0.118
100	0.9494	...	0.2870	3.10	3.308	0.0710
150	0.9664	45[e]	0.4262	2.895	2.267	0.0586
200	0.9749	31	0.5553	2.712	1.756	0.0564
250	0.9808	23.4	0.6714	2.559	1.461	0.0584
300	0.9861	18.12	0.7769	2.450	1.269	0.0623
350	0.9910	14.33	0.8682	2.392	1.141	0.0683
400	0.9960	11.45	0.9476	2.420	1.051	0.0763
436.0[d]	1.0000	9.72	1.0000	2.501	1.000	...
			340° F.			
13.49[a]	0.0000	...[b]	0.0000	3.74	...	1.000
50	0.7283	...	0.0803	3.58	9.070	0.295
100	0.8629	...	0.1865	3.43	4.627	0.169
150	0.9078	51[e]	0.2865	3.29	3.169	0.129
200	0.9303	36	0.3791	3.17	2.454	0.112
250	0.9437	26.9	0.4680	3.05	2.016	0.106

and none was associated with the determination of the pressure and temperature.

In Figure 3 is portrayed the phase behavior of the n-butane–n-decane system upon a pressure-temperature diagram. In this diagram the estimated values of the unique states have been included. The variation in the equilibrium ratio of n-decane and n-butane as a function of pressure is shown in Figure 4 for each of the several temperatures investigated. The behavior at 100° F. has been estimated. For the most part the behavior depicted in these diagrams is similar to that found for other binary hydrocarbon systems (*8, 9*).

From the experimental data which have been described the properties of the coexisting gas and liquid phases of the n-butane–n-decane system were determined and are shown in Table II. The molal volume of the bubble-point liquid was established from the earlier investigations of the volumetric behavior of this system (*11*). The molal volume of the coexisting gas phase was determined from volumetric measurements in the two-phase region of the n-butane–n-decane system (*11*). It should be recognized that the uncertainty in determining the molal volume of the coexisting gas phase is somewhat larger than that of the liquid phase. The equilibrium ratios for the two com-

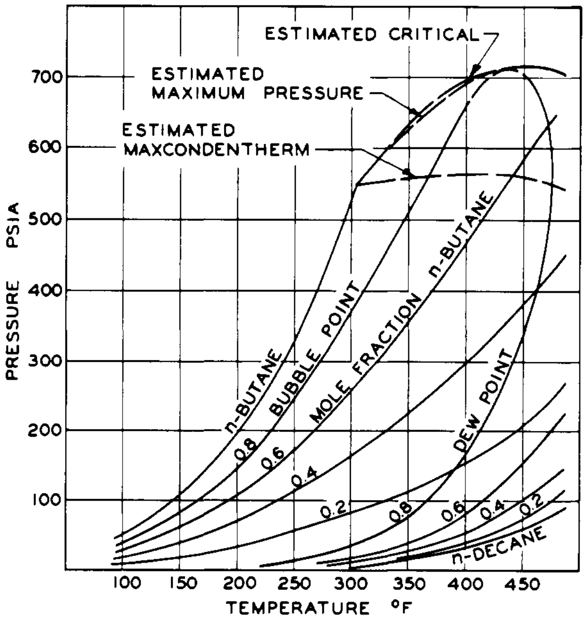

Figure 3. Pressure-temperature diagram for the n-butane–n-decane system

Phases in the *n*-Butane-*n*-Decane System

	Dew Point		Bubble Point		Equilibrium Ratio	
Press. P.S.I.A.	Mole Fraction *n*-Butane	Volume cu. ft./lb. Mole	Mole Fraction *n*-Butane	Volume cu. ft./lb. mole	*n*-Butane	*n*-Decane
			340° F.			
300	0.9527	20.9	0.5513	2.944	1.728	0.105
350	0.9591	16.67	0.6273	2.858	1.529	0.110
400	0.9639	13.39	0.6973	2.794	1.382	0.119
450	0.9677	10.82	0.7630	2.752	1.268	0.136
500	0.9704	8.75	0.8223	2.763	1.180	0.167
550	0.9713	7.05	0.8771	2.884	1.107	0.234
600	0.9696	5.35	0.9287	3.32	1.044	0.426
616.3[f]	0.956	4.00	0.956	4.00	1.000	1.000
558.2[g]	0.971	. . .				
			400° F.			
31.19[a]	0.0000	. . .	0.0000	3.96	. . .	1.000
50	0.3693	. . .	0.0324	3.90	11.40	0.652
100	0.6760	. . .	0.1160	3.78	5.828	0.367
150	0.7777	56[e]	0.1950	3.67	3.988	0.276
200	0.8279	41	0.2690	3.56	3.078	0.235
250	0.8577	31.1	0.3386	3.47	2.533	0.215
300	0.8769	24.6	0.4040	3.39	2.171	0.207
350	0.8899	19.82	0.4658	3.31	1.910	0.206
400	0.8989	16.27	0.5246	3.26	1.714	0.213
450	0.9053	13.51	0.5810	3.21	1.558	0.226
500	0.9099	11.29	0.6347	3.19	1.434	0.247
550	0.9123	9.46	0.6873	3.20	1.327	0.280
600	0.9123	7.86	0.7400	3.25	1.233	0.337
650	0.9078	6.36	0.7928	3.40	1.145	0.445
694.2[f]	0.865	4.22	0.865	4.22	1.000	1.000
565.0[g]	0.912	. . .				
			460° F.			
64.72[a]	0.0000	. . .	0.0000	4.26	. . .	1.000
100	0.3444	. . .	0.0490	4.159	7.029	0.689
150	0.5539	. . .	0.1170	4.066	4.734	0.505
200	0.6575	42[e]	0.1810	3.980	3.633	0.418
250	0.7189	33	0.2417	3.905	2.974	0.371
300	0.7595	27.0	0.2987	3.841	2.543	0.343
350	0.7877	22.6	0.3530	3.788	2.231	0.328
400	0.8075	19.22	0.4051	3.743	1.993	0.324
450	0.8209	16.45	0.4552	3.712	1.803	0.329
500	0.8290	14.07	0.5035	3.704	1.646	0.344
550	0.8317	11.96	0.5492	3.745	1.514	0.373
600	0.8297	10.06	0.5950	3.84	1.394	0.420
650	0.8199	8.23	0.6427	4.03	1.276	0.504
700	0.7830	6.18	0.6980	4.43	1.122	0.719
714.0[f]	0.739	4.97	0.739	4.97	1.000	1.000
555.0[g]	0.832	. . .				

[a] Vapor pressure of *n*-decane (*8*). [b] 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 (*4*). [c] 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. [d] Vapor pressure of *n*-butane (*6*). [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.

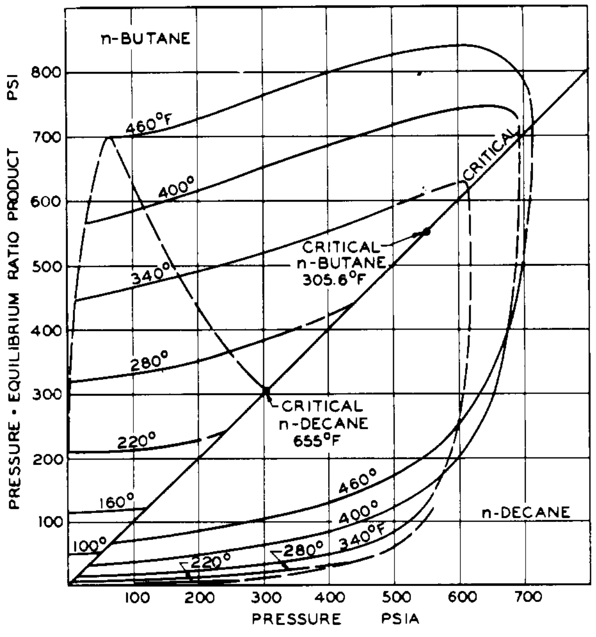

Figure 4. Equilibrium ratios for *n*-butane and *n*-decane

ponents involved are also recorded in Table II. Table III presents estimated values of the properties of the *n*-butane–*n*-decane system at the unique states of the critical maxcondentherm and maximum pressure. These results have been presented in terms of the mole fraction of *n*-butane.

ACKNOWLEDGMENT

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

Mole Fraction *n*-Butane	Critical Press. P.S.I.A.	Critical Temp., °F.	Maxcondentherm Press. P.S.I.A.	Maxcondentherm Temp., °F.	Maximum Press. Press. P.S.I.A.	Maximum Press. Temp., °F.
0.0[a]	304.0	655.0	304.0	655.0	304.0	655.0
0.1	362.0	631.7	338.3	635.3	363.2	630.0
0.2	423.0	608.3	371.5	616.0	424.7	605.2
0.3	486.0	584.7	403.0	596.8	488.5	580.3
0.4	553.8	560.0	432.5	578.0	557.2	554.0
0.5	621.5	533.7[b]	461.2	558.3	625.7	526.8[b]
0.6	683.3	505.2	490.2	536.6	685.5	499.7
0.7	710.8	474.3	520.0	510.2[b]	711.2	471.7
0.8	710.8	434.0	547.2	476.0	711.2	437.0
0.9	674.0	378.5	565.0	410.7	680.0	389.7
1.0[c]	550.7	305.6	550.7	305.6	550.7	305.6

[a] Critical state of *n*-decane (*1*). [b] Values at this and higher temperatures are subject to greater uncertainty. [c] Critical state of *n*-butane (*1*).

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Benzene-Methanol-Copper (II) Chloride System at 30.0°C.

Properties of $CuCl_2 \cdot CH_3OH$

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The phase diagram for the system $CuCl_2$-methanol-benzene at 30.0° C. was determined by the wet residue method. The solid component in the two-phase region of the diagram was $CuCl_2 \cdot CH_3OH$.

ALTHOUGH CONSIDERABLE work has been done on systems of the type inorganic solid–water–organic liquid, (*1, 2, 3, 6*) few ternary diagrams with the water replaced by another organic liquid have been published. The results reported here are the first of a planned study on systems of this type.

EXPERIMENTAL PROCEDURE

The Schreinemaker wet residue (*4*) method was employed.

Reagents. Fisher reagent grade benzene, methanol, and anhydrous copper (II) chloride were used without further purification, except for drying the $CuCl_2$ at 170° C. The Cl–Cu ratio was greater than 1.99 for the $CuCl_2$.

Mixture Preparation. Mixtures of $CuCl_2$, methanol, and benzene were prepared in 8-ounces glass bottles, fitted with caps containing polyethylene liners. The $CuCl_2$ was added to the bottles in a dry box (or very quickly in the open). Each bottle contained a Teflon-coated magnetic stirring bar. The composition of each batch of samples was adjusted (by trial and error) so that the amount of solid phase was sufficient for a wet residue analysis, but not so great as to make the mixtures too viscous to stir. The mixtures were sealed tightly, stirred for about 10 minutes at 35° to 40° C., placed in a 30.0° C. bath, and allowed to stand. Once or more daily during this equilibration period the mixtures were stirred at 30–31° C. All mixtures were equilibrated for a week or more.

Sampling Procedure. After equilibration, a sample of the liquid phase was removed (by oral suction through a coarse filter stick) into a sample bulb. Care was taken to prevent moisture from entering the sample and to prevent evaporation. Part of this sample was poured into a conical weighing bottle, and the per cent $CuCl_2$ determined. The remaining part was placed in a distillation flask. A sample of wet residue of the desired consistency (determined by trial and error in a number of runs) was put into a weighed flat-bottomed distillation flask (which had a 24/40 or a 19/24 G.S. neck so that a powder funnel could be admitted) and the weight of the wet residue was then determined.

Analyses. The EDTA method for copper was used to determine the $CuCl_2$ percentages in the liquid phase and wet residue. The distillation flask containing the liquid