Phase Equilibria in Hydrocarbon Systems

Phase Behavior in the Methane–Propane–*n*-Decane System

H. C. WIESE, H. H. REAMER, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif. 91109

Measurements of the composition of the coexisting gas and liquid phases were carried out at 73 states distributed throughout the heterogeneous region of the methane–propane–*n*-decane system at temperatures between 40° and 460° F. As would be expected, these data indicate a marked variation in the equilibrium ratio of the several components with respect to composition at a fixed temperature and pressure. The results are presented in tabular form, with a limited number of graphical examples.

EXPERIMENTAL study of the composition of the coexisting phases in ternary hydrocarbon systems is increasing. The systems investigated involving methane include the methane–propane–*n*-pentane system (*5, 6*), the methane–ethane–*n*-butane system (*7*), the methane–propane–*n*-butane system at 100° F. (*25*), the methane–*n*-butane–decane system (*13, 16, 17*), the methane–ethane–*n*-pentane system (*3*), and the methane–propane–*n*-decane system at temperatures below 70° F. (*9*). Some studies of the quaternary system, methane–ethane–propane–*n*-butane, were made by Benedict *et al.* (*2*), and limited investigations of other hydrocarbon systems have been reported. In order to complete another portion of the study of the methane–propane–*n*-butane–*n*-decane quaternary system, further measurements of the volumetric and phase behavior of the methane–propane–*n*-decane system have been carried out. The present discussion is concerned with the experimentally determined compositions of the coexisting liquid and gas phases throughout the heterogeneous region at five temperatures between 40° and 460° F. For the sake of completeness, the molal volumes of the coexisting liquid phase have been included in the tabulations. The details of the determination of the molal volume of the liquid phase will not be presented, as they are described elsewhere (*12*).

The phase behavior of the three binary systems forming the composition boundary of the methane–propane–*n*-decane system has been studied experimentally. The volumetric and phase behavior of the methane-propane system was investigated (*15*) at pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F. This experimental study included all of the heterogeneous region at temperatures above 40° F. Earlier studies (*10, 24, 25*) involving an isochoric system of variable weight gave fair agreement with the later investigation (*15*).

A rather complete set of data for the volumetric and phase behavior of the methane–*n*-decane system is available (*14, 21*). The study covered the temperature interval between 100° and 460° F. for pressures up to 10,000 pounds per square inch (*14*). The phase behavior has been investigated throughout the heterogeneous region in the temperature interval between 100° and 460° F.

The molal volumes of the liquid phase of the propane–*n*-decane system were determined experimentally (*19*) for pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F. The phase behavior throughout the temperature interval was established by direct measurement of the composition of the coexisting phases (*19*).

The above-described data suffice to establish the composition of the coexisting phases of the three binary systems associated with the methane–propane–*n*-decane system with an accuracy comparable to that realized in the current investigation. For the most part, the data for the three binary systems were used as presented in the original publications, without further smoothing.

EXPERIMENTAL METHODS

Heterogeneous mixtures of methane, propane, and *n*-decane were brought together in a stainless steel vessel, where they were confined over mercury. Agitation was provided by a magnetically-driven mechanical stirrer. The total volume of the system was established by means of a movable electrical contact and a "hot wire" mounted parallel to the interface to permit the relative volumes of liquid and gas (*22*) phases to be established. Samples of the liquid and gas phase were withdrawn under isobaric, isothermal conditions, and the compositions determined. The details of the equipment employed are available (*22, 23*) and no significant changes from the original description were found necessary or desirable during the current study.

The pressure was measured by means of a balance equipped with a piston-cylinder combination (*18, 23*). The balance was calibrated against the vapor pressure of carbon dioxide at the ice point (*4*), and experience over the past three decades leads the authors to believe that the pressures were known within an uncertainty of 0.1% or 0.1 p.s.i., whichever is the larger measure of uncertainty.

The stainless steel vessel was immersed within an agitated oil bath whose temperature was controlled by a modulating circuit (*22*) within 0.005° F. The temperature was measured by means of a strain-free, platinum resistance thermometer (*11*) which had been calibrated against the indications of a similar instrument that had been standardized at the National Bureau of Standards. It is believed that the temperature, as related to the international platinum scale, was known within 0.03° F. throughout the temperature interval between 40° and 460° F.

The compositions of the coexisting liquid and gas phases were determined by partial condensation of the *n*-decane in an especially designed condenser (*13*) maintained at a temperature of −30° C. The propane and methane were condensed in a weighing bomb (*13*) at the temperature of liquid nitrogen, at absolute pressures ranging from 0.5 to 2 cm. of mercury. Upon the completion of the partial condensation, any *n*-decane remaining in connecting lines was removed by warming the lines and evacuating through the partial condenser. The total quantity of methane and propane was determined from the change in weight of the weighing bomb after conditioning at room temperature. Corrections were made for the residual methane and propane in the sampling lines and partial condenser, and for the small sample employed for chromatographic analysis. The amount of the total correction did not exceed 1% of the total sample removed from the equilibrium vessel. The quantity of *n*-decane also was determined gravimetrically (*13*). The distribution of methane and propane was determined by partial condensation or by conventional chromatographic techniques, utilizing helium as the carrier gas. The latter technique was used for more than 80% of the measurements.

As an illustration, the results obtained on five samples which were subjected to both of the above-described analytical procedures are set forth in Table I. Good agreement between the partial condensation measurements and the chromatographic techniques was realized. On the basis of the information presented in Table I and other similar data, it is estimated that the mole fraction of methane, propane, and *n*-decane was established within 0.002 mole fraction throughout the entire range of compositions covered by the investigation. During the withdrawal process, the pressure did not change by more than 0.2 p.s.i., and the temperature remained invariant within 0.02° F. A total of 66 pairs of samples were withdrawn at five temperatures between 40° and 460° F. and at five selected pressures. The detailed experimental results are available from ASIS (*26*).

In addition, 22 selected mixtures (*12*) were investigated to establish the volumetric behavior and bubble-point pressures of the system. The measurements were made at pressures up to 10,000 p.s.i. in the temperature interval between 40° and 460° F. Extensive measurements were made throughout the two-phase region in order to permit the indirect establishment of the molal volume of the bubble-point liquid and of the dew-point gas. Difficulties were experienced in attempting the direct experimental evaluation of the molal volume of the dew-point gas, as a result of adsorption on the walls of the container of significant quantities of *n*-decane at low pressures.

The equipment employed to measure the specific volume of the homogeneous portions of the system has been described (*23*). The pressures and temperatures were known with the same accuracy as has been described. The weight of material added to the equipment was known within 0.1%, and the total volume of the equipment was known within 0.2% for pressures below 5000 p.s.i. and 0.3% at higher pressures. From these volumetric data (*12*), short extrapolations were made from the single-phase regions to the boundaries of the heterogeneous region, which were established by the phase composition measurements. This approach permitted the molal volume of the bubble-point liquid and dew-point gas in the critical region to be established directly. In addition, the discontinuity at the boundary of the heterogeneous region of the isothermal change in molal volume with pressure at constant composition was used to establish "bubble point." This independent approach yielded results in excellent agreement with the directly measured values.

Table I. Comparison of Composition of Samples as Determined by Different Methods

		Liquid Phase		Gas Phase	
Sample[a]	Component	Grav.[b]	Chr.[c]	Grav.[b]	Chr.[c]
1	Methane	0.20393	0.20473	0.76145	0.76205
	Propane	0.06898	0.06728	0.10937	0.10871
	n-Decane	0.72709	0.72799	0.12918	0.12924
2	Methane	0.17850	0.17932	0.96878	0.96890
	Propane	0.08612	0.08453	0.03092	0.03080
	n-Decane	0.73537	0.73615	0.00030	0.00030
3	Methane	0.35607	0.35607	0.57071	0.57029
	Propane	0.40648	0.40651	0.38267	0.38307
	n-Decane	0.23744	0.23745	0.04662	0.04664
4	Methane	0.05683	0.05718	0.12189	0.12147
	Propane	0.50923	0.50909	0.68636	0.68678
	n-Decane	0.43395	0.43373	0.19175	0.19175
5	Methane	0.38853	0.38956	0.60744	0.60555
	Propane	0.20378	0.20309	0.21154	0.21308
	n-Decane	0.40770	0.40735	0.18102	0.18137

[a] The samples were taken over a two-year period during the course of the investigation of the composition of the coexisting phases of the methane–propane–*n*-decane system. [b] Gravimetric determination. [c] Chromatographic analysis.

MATERIALS

The propane and *n*-decane were obtained as research grade materials from Phillips Petroleum Co., and after deaeration were employed without further purification. The methane was obtained through the courtesy of Texaco, Inc., from a well in the San Joaquin Valley, Calif., and, after passage over calcium chloride, activated charcoal, ascarite, and anhydrous calcium sulphate, contained negligible quantities of impurities. The measured physical properties of the three components are set forth in Table II, along with the measured purity of the samples as established by chromatographic methods. The small variation in vapor pressure with respect to quality is considered the best measure of purity of the propane employed. The agreement of the specific weight and the index of refraction of the *n*-decane at atmospheric pressure, as compared with published critically chosen values (*1*), is a sensitive indication of the purity of the *n*-decane. In the case of methane, the chromatographic techniques employed to detect traces of nitrogen, carbon dioxide, and hydrocarbons of higher

Table II. Physical Properties of Components

Quantity	Measured	Reference
Specific weight,[a] lb./cu. ft.		
n-Decane	45.346	45.337[b]
Index of refraction[c]		
n-Decane	1.4094	1.40967[b]
Change in vapor pressure,[d] p.s.i.		
Propane, 100° F.	0.15	
Composition, mole fraction		
Methane	0.9977[e]	
Propane		0.9999[f]
n-Decane		0.9949[f]

[a] Specific weight of liquid at 77° F. and atmospheric pressure. [b] Reference (*1*). [c] Index of refraction relative to D-lines of sodium at 77° F. and atmospheric pressure. [d] Change in quality 0.1 to 0.8. [e] Chromatographic analysis. [f] Purity reported by vendor.

molecular weight is believed to be the best measure of purity.

From the data of Table II, it appears that all three of the components contained less than 0.002 mole fraction of impurity. In the case of n-decane, the most probable impurities are saturated hydrocarbons involving the same number of carbon atoms per molecule, while nitrogen is the primary impurity in the sample of methane.

EXPERIMENTAL RESULTS

The measured compositions of the coexisting phases were plotted on large triangular diagrams, approximately 36 inches on a side, and compared with direct smoothing of the experimental values of the equilibrium ratios, K_1, K_3, and K_{10}, for each of the three components. The product of the pressure and the equilibrium ratio for the three components was also employed as an independent variable in the smoothing operations. The composition of the system was described in terms of the parameter, C, which is defined for a heterogeneous system by Equation 1.

$$C = \frac{x_3}{x_3 + x_{10}} \tag{1}$$

The relation of the composition of each phase to the equilibrium ratios, with C as the composition parameter, is as follows.

$$x_1 = 1 - \frac{K_1 - 1}{K_1 - [CK_3 + (1 - C)K_{10}]} \tag{2}$$

$$x_3 = C(1 - x_1) \tag{3}$$

The smooth data from the triangular diagrams agree with smooth values of K_1, K_3, K_{10}, and PK_1, PK_3, and PK_{10} within 0.002 mole fraction throughout the entire composition interval involved.

As an example, the experimental results for a temperature of 280° F. are recorded in Table III and the phase behavior at 280° F. is depicted in Figure 1. The remaining experimental data for 40°, 100°, 400°, and 460° F. are available from ASIS (*26*). Combining lines have been included, as have curves representing the composition of the dew-point gas and the bubble-point liquid. Interpolated values of the "bubble points" established from the volumetric measurements (*12*) have been included. The standard errors of estimate of the latter data from the smooth curves at 40°, 100°, 280°, 400°, and 460° F. were 0.0092 mole fraction methane, 0.0047 mole fraction propane, and 0.0049 mole fraction n-decane.

The standard errors of estimate of the directly measured compositions of the coexisting phases from the smooth curves for the five temperatures investigated were 0.0043 mole fraction methane, 0.0020 mole fraction propane, and 0.0031 mole fraction n-decane for the liquid phase, and 0.0110 mole fraction methane, 0.0095 mole fraction propane, and 0.0051 mole fraction n-decane for the gas phase. The somewhat larger deviations for methane and propane in the gas phase apparently results from difficulties in carrying out analyses with the same precision as for the liquid phase. The equilibrium ratios as defined in the nomenclature are shown in Figure 2 for the entire pressure interval of the heterogeneous region for 280° F. The significant effect of composition upon the equilibrium ratios for a given pressure and temperature is evident. After smoothing with respect to pressure, temperature, and parameter C, the average fractional deviation of the experimental equilibrium ratios from the smooth curves was 0.0028, 0.0098, and 0.0003 for methane, propane, and n-decane, respectively.

Koonce and Kobayashi (*9*) obtained equilibrium ratios

Table III. Experimental Results for 280° F.

Pressure, P.S.I.A.	Composition Parameter[a]	Mole Fraction, Gas			Mole Fraction, Liquid		
		Methane	Propane	n-Decane	Methane	Propane	n-Decane
400	0.0566	0.87488	0.10447	0.02065	0.08865	0.05162	0.85973
	0.4771	0.06213	0.91490	0.02297	0.01003	0.47234	0.51763
1000	0.1640	0.82969	0.15381	0.01650	0.20541	0.12210	0.67250
	0.4943	0.53613	0.44429	0.01958	0.14148	0.42440	0.43412
	0.8030	0.18349	0.78476	0.03174	0.08304	0.73635	0.18061
2000	0.1139	0.93160	0.04934	0.01906	0.38385	0.07017	0.54598
	0.3129	0.82417	0.15181	0.02402	0.36648	0.19825	0.43526
	0.4189	0.75353	0.22119	0.02528	0.35633	0.26963	0.37404
	0.6313	0.57029	0.38307	0.04664	0.35604	0.40651	0.23745
	0.7606	0.48690	0.44628	0.06682	0.37464	0.47565	0.14971
3000	...	0.93284	0.03505	0.03211	...	...	...
	0.1445	0.91889	0.04807	0.03304	0.53682	0.06694	0.39624
	0.3963	0.80363	0.14634	0.05003	0.53770	0.18320	0.27910
	0.6190	0.68350	0.22815	0.08836	0.60099	0.24698	0.15204
4000	...	0.89308	0.03663	0.07030	...	...	...
	0.2351	0.85009	0.05720	0.09271	0.71693	0.06655	0.21651

[a] Composition parameter, C, defined by Equation 1.

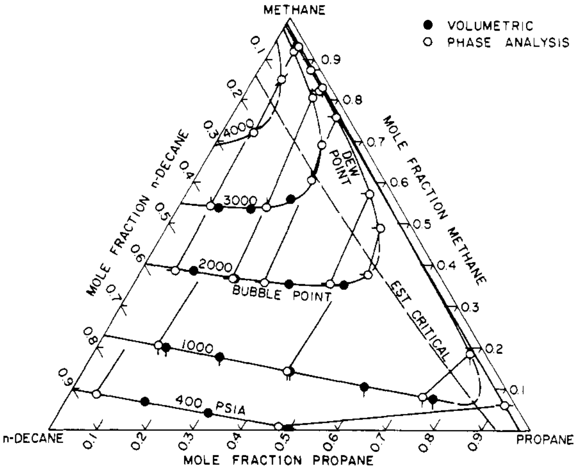


Figure 1. Composition of coexisting phases at 280° F.

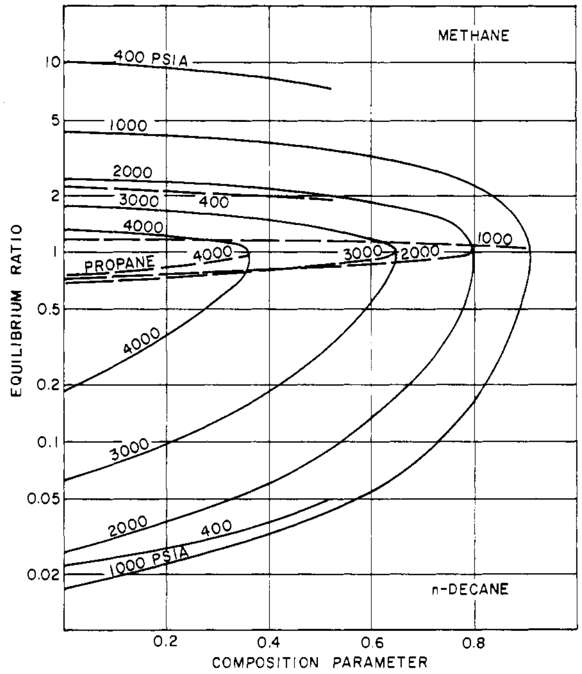


Figure 2. Equilibrium ratios for 280° F.

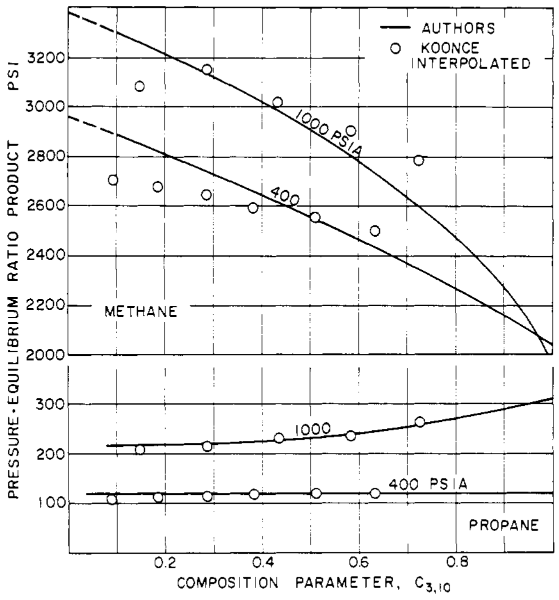


Figure 3. Comparison of phase behavior from two sources

and compositions of the coexisting phases by gas-liquid partition chromatography, utilizing radioactive retention techniques and thermal conductivity retention methods, which are shown in Figure 3. In using their data, values of the product of the pressure and the equilibrium ratio for methane and propane at 40° F. were established from interpolated values of the mole fraction of each component in the gas and liquid phases at pressures of 400 and 1000 pounds per square inch, absolute. These interpolated values show a standard error of estimate of 119 p.s.i. in the product of the pressure and equilibrium ratio for methane and 5.5 p.s.i. for propane from the smooth curves. The average deviation in the equilibrium ratio for methane, based upon the current measured compositions of the liquid and the vapor and Koonce's (*9*) values of the equilibrium ratio established from radioactive retention data, was −0.244. A similar comparison between the authors' measured vapor compositions and liquid compositions with values of the equilibrium ratios for propane calculated from radioactive retention data yielded an average deviation of −0.0005, and from thermal conductivity retention data of 0.0015. In the case of methane, Koonce's data (*9*) at the lower values of composition parameter *C*, corresponding to higher mole fractions of *n*-decane, were consistently lower than the current measurements at 400 p.s.i.a. They (*9*) were somewhat higher than the current measurements at the higher values of the composition parameter. In the case of propane, good agreement was found between Koonce's (*9*) data and the current measurements at 40° F. throughout the composition interval. The data shown in Figure 3 were at the lower end of the temperature interval currently investigated, and may involve somewhat larger uncertainties than at the higher temperatures. However, it appears that there is good agreement with the measurements of Koonce (*9*) for propane and fair agreement in the case of methane, as can be seen from comparison of the two sets of data shown in Figure 3. Koonce (*9*) did not report any *n*-decane as present in the gas phase, nor did he report any *n*-decane equilibrium ratios.

Smooth values of the composition of the coexisting phases and the three equilibrium ratios are given in Table IV for each of the five temperatures investigated for five different pressures and for a number of values of the composition parameter *C* defined by Equation 1. Table IV also includes values of the molal volume of the coexisting liquid phase.

The pressure and temperature estimated as corresponding to the critical state of a number of mixtures have been presented in Table V. These states were arrived at by suitable graphical operations on the experimental information available from ASIS (*26*), illustrated for 280° F. in Table III. It is probable that these critical states may involve absolute uncertainties of as much as 50 p.s.i., 0.02 mole fraction, and 5° F. These larger uncertainties arise from the indirect graphical methods that were employed to determine each of these states. The uncertainty in the composition of the critical state is somewhat greater at the lower temperatures corresponding to higher mole fractions of methane. The data shown in Table V are consistent with the information in Table IV within 10 p.s.i., 1° F., and 0.005 mole fraction.

Table IV. Properties of the Coexisting Phases in the Methane–Propane–*n*-Decane System

		Gas Phase			Liquid Phase						
		Mole Fraction			Mole Fraction			Volume, cu. ft./ lb.-mole	Equilibrium Ratio[a]		
Pressure, P.S.I.A.	Composition Parameter[b]	Methane	Propane	*n*-Decane	Methane	Propane	*n*-Decane		Methane	Propane	*n*-Decane
					40° F.						
400	0.0	0.9997[c]	0	0.0003	0.1350[c]	0	0.8650	2.763[c]	7.405	...	0.00035
	0.2	0.9497	0.0500	0.0003	0.1352	0.1730	0.6919	2.435	7.024	0.2890	0.00043
	0.4	0.8998	0.0999	0.0003	0.1364	0.3454	0.5181	2.128	6.598	0.2892	0.00058
	0.6	0.8485	0.1513	0.0002	0.1380	0.5172	0.3448	1.834	6.149	0.2925	0.00058
	0.8	0.7971	0.2027	0.0002	0.1411	0.6871	0.1718	1.560	5.650	0.2950	0.00116
	1.0	0.7505	0.2495	0	0.1471	0.8529	0	1.302	5.10	0.2925	...
1000	0.0	0.9994[c]	0	0.0006	0.2845[c]	0	0.7115	2.398[c]	3.513	...	0.00084
	0.2	0.9692	0.0303	0.0005	0.3017	0.1397	0.5586	2.118	3.212	0.2169	0.00090
	0.4	0.9378	0.0617	0.0005	0.3110	0.2756	0.4134	1.864	3.015	0.2239	0.00121
	0.6	0.9022	0.0973	0.0005	0.3245	0.4053	0.2702	1.622	2.780	0.2400	0.00185
	0.8	0.8579	0.1417	0.0004	0.3466	0.5227	0.1307	1.400	2.475	0.2711	0.00306
	1.0	0.8208	0.1792	0	0.4226	0.4774	0	1.274	1.942	0.3104	...
2000	0.0	0.9985[c]	0	0.0015	0.4851[c]	0	0.5149	1.954[c]	2.058	...	0.0029
	0.2	0.9671	0.0312	0.0017	0.4940	0.1012	0.4048	1.755	1.958	0.3083	0.00420
	0.4	0.9299	0.0682	0.0020	0.5109	0.1956	0.2935	1.562	1.820	0.3487	0.00681
	0.6	0.8853	0.1116	0.0030	0.5473	0.2716	0.1811	1.387	1.618	0.4109	0.01657
	0.8	0.8190	0.1734	0.0076	0.6181	0.3055	0.0764	1.254	1.325	0.5676	0.09948
3000	0.0	0.9948[c]	0	0.0051	0.6115[c]	0	0.3885	1.671[c]	1.627	...	0.0131
	0.2	0.9599	0.0338	0.0064	0.6182	0.0764	0.3054	1.521	1.553	0.4424	0.02081
	0.4	0.9160	0.0735	0.0105	0.6455	0.1418	0.2127	1.367	1.419	0.5183	0.04937
	0.6	0.8485	0.1270	0.0245	0.7100	0.1740	0.1160	1.230	1.195	0.7299	0.2112
4000	0.0	0.9863[c]	0	0.0137	0.7015[c]	0	0.2985	1.465[c]	1.406	...	0.0459
	0.2	0.9389	0.0353	0.0239	0.7181	0.0564	0.2255	1.332	1.307	0.6259	0.1060
	0.4	0.8820	0.0694	0.0485	0.7797	0.0881	0.1322	1.220	1.131	0.7877	0.3669
					100° F.						
400	0.0	0.9994	0	0.0006	0.1251	0	0.8749	2.870	7.989	...	0.00069
	0.2	0.8950	0.1044	0.0006	0.1113	0.1777	0.7110	2.584	8.045	0.5875	0.00084
	0.4	0.7850	0.2144	0.0006	0.0994	0.3603	0.5404	2.292	7.897	0.5951	0.00118
	0.6	0.6724	0.3270	0.0006	0.0918	0.5449	0.3633	2.190	7.325	0.6001	0.00165
	0.8	0.5573	0.4423	0.0004	0.0862	0.7310	0.1828	1.702	6.465	0.6051	0.00242
	1.0	0.4472	0.5528	0	0.0845	0.9155	0	1.486	5.295	0.6038	...
1000	0.0	0.9993	0	0.0007	0.2679	0	0.7321	2.536	3.730	...	0.00096
	0.2	0.9466	0.0527	0.0008	0.2579	0.1484	0.5937	2.296	3.670	0.3551	0.00135
	0.4	0.8910	0.1081	0.0008	0.2533	0.2987	0.4480	2.053	3.518	0.3619	0.00178
	0.6	0.8200	0.1791	0.0009	0.2558	0.4465	0.2977	1.800	3.206	0.4011	0.00302
	0.8	0.7351	0.2640	0.0009	0.2634	0.5893	0.1473	1.576	2.791	0.4480	0.00631
	1.0	0.6635	0.3365	0	0.3231	0.6769	0	1.511	2.028	0.4918	...
2000	0.0	0.9981	0	0.0019	0.4469	0	0.5541	2.118	2.233	...	0.00343
	0.2	0.9552	0.0427	0.0021	0.4437	0.1113	0.4450	1.935	2.153	0.3836	0.00472
	0.4	0.9038	0.0936	0.0026	0.4463	0.2215	0.3322	1.750	2.025	0.4226	0.00783
	0.6	0.8395	0.1568	0.0038	0.4619	0.3229	0.2153	1.570	1.817	0.4856	0.01765
	0.8	0.7457	0.2453	0.0090	0.5168	0.3865	0.0966	1.432	1.443	0.6347	0.09317
3000	0.0	0.9942	0	0.0058	0.5827	0	0.4173	1.803	1.706	...	0.01390
	0.2	0.9533	0.0394	0.0073	0.5824	0.0835	0.3340	1.663	1.637	0.4712	0.02186
	0.4	0.8989	0.0892	0.0119	0.5944	0.1622	0.2434	1.532	1.512	0.5499	0.04889
	0.6	0.8244	0.1528	0.0228	0.6344	0.2193	0.1462	1.408	1.300	0.6968	0.1560
4000	0.0	0.9837	0	0.0163	0.6870	0	0.3130	1.571	1.432	...	0.0521
	0.2	0.9383	0.0367	0.0250	0.6950	0.0610	0.2440	1.461	1.350	0.6016	0.1024
	0.4	0.8677	0.0819	0.0504	0.7283	0.1087	0.1630	1.344	1.191	0.7535	0.3090
					280° F.						
400	0.0	0.9798	0	0.0202	0.0974	0	0.9026	3.33	10.060	...	0.02238
	0.2	0.5872	0.3925	0.0203	0.0632	0.1874	0.7494	3.065	9.291	2.094	0.02709
	0.4	0.2081	0.7702	0.0217	0.0251	0.3900	0.5850	2.800	8.291	1.975	0.03709
1000	0.0	0.9870	0	0.0130	0.2256	0	0.7744	2.999	4.375	...	0.01679
	0.2	0.7973	0.1881	0.0146	0.1941	0.1612	0.6447	2.795	4.108	1.167	0.02265
	0.4	0.5992	0.3844	0.0164	0.1591	0.3363	0.5045	2.576	3.766	1.143	0.03251
	0.6	0.3930	0.5881	0.0189	0.1209	0.5274	0.3516	2.376	3.251	1.115	0.05375
	0.8	0.1808	0.7883	0.0309	0.0791	0.7367	0.1842	2.306	2.286	1.070	0.1678
2000	0.0	0.9845	0	0.0155	0.4028	0	0.5972	2.557	2.444	...	0.0260
	0.2	0.8871	0.0942	0.0187	0.3791	0.1242	0.4967	2.404	2.340	0.7585	0.03765
	0.4	0.7715	0.2056	0.0230	0.3588	0.2565	0.3847	2.260	2.150	0.8016	0.05979
	0.6	0.6311	0.3333	0.0356	0.3472	0.3917	0.2611	2.132	1.818	0.8509	0.1363
3000	0.0	0.9715	0	0.0285	0.5476	0	0.4524	2.214	1.774	...	0.06230
	0.2	0.8971	0.0676	0.0353	0.5381	0.0924	0.3695	2.098	1.667	0.7316	0.09553
	0.4	0.8032	0.1456	0.0512	0.5397	0.1841	0.2762	2.004	1.488	0.7909	0.1854
	0.6	0.6915	0.2205	0.0880	0.5950	0.2425	0.1625	1.944	1.162	0.9093	0.5415
4000	0.0	0.9430	0	0.0570	0.6912	0	0.3088	1.906	1.364	...	0.1846
	0.2	0.8690	0.0476	0.0834	0.7116	0.0577	0.2308	1.853	1.221	0.8250	0.3614

Table IV. Properties of the Coexisting Phases in the Methane–Propane–*n*-Decane System (*Continued*)

		Gas Phase			Liquid Phase						
		Mole Fraction			Mole Fraction			Volume, cu. ft./ lb.-mole	Equilibrium Ratio[a]		
Pressure, P.S.I.A.	Composition Parameter[b]	Methane	Propane	*n*-Decane	Methane	Propane	*n*-Decane		Methane	Propane	*n*-Decane
					400° F.						
400	0.0	0.8851	0	0.1149	0.0926	0	0.9074	3.72	9.558	. . .	0.1266
	0.2	0.3090	0.5782	0.1128	0.0364	0.1927	0.7709	3.520	8.489	3.001	0.1463
1000	0.0	0.9358	0	0.0642	0.2258	0	0.7742	3.37	4.144	. . .	0.0829
	0.2	0.6717	0.2580	0.0703	0.1768	0.1646	0.6586	3.210	3.799	1.567	0.1067
	0.4	0.4010	0.5193	0.0797	0.1228	0.3509	0.5263	3.066	3.265	1.480	0.1514
	0.6	0.1409	0.7524	0.1067	0.0579	0.5653	0.3767	3.072	2.434	1.331	0.2825
2000	0.0	0.9351	0	0.0649	0.4119	0	0.5881	2.907	2.270	. . .	0.1104
	0.2	0.7963	0.1274	0.0763	0.3815	0.1237	0.4948	2.798	2.087	1.030	0.1542
	0.4	0.6375	0.2638	0.0987	0.3571	0.2572	0.3857	2.740	1.785	1.026	0.2559
	0.6	0.4425	0.3968	0.1607	0.3485	0.3909	0.2606	2.860	1.270	1.015	0.6167
3000	0.0	0.9030	0	0.0970	0.5912	0	0.4088	2.513	1.527	. . .	0.2373
	0.2	0.7843	0.0745	0.1413	0.5984	0.0803	0.3213	2.475	1.311	0.9278	0.4265
					460° F.						
400	0.0	0.7928	0	0.2072	0.0937	0	0.9063	3.96	8.461	. . .	0.2286
	0.2	0.1626	0.6184	0.2190	0.0223	0.1955	0.7822	3.825	7.300	3.162	0.2800
1000	0.0	0.8803	0	0.1197	0.2378	0	0.7622	3.57	3.702	. . .	0.1570
	0.2	0.5935	0.2687	0.1378	0.1759	0.1648	0.6593	3.491	3.375	1.630	0.2090
	0.4	0.2947	0.5406	0.1647	0.1080	0.3568	0.5352	3.464	2.729	1.515	0.3077
	0.6	0.0583	0.7192	0.2225	0.0333	0.5800	0.3867	3.740	1.748	1.240	0.5754
2000	0.0	0.8815	0	0.1185	0.4280	0	0.5720	3.14	2.060	. . .	0.2072
	0.2	0.7230	0.1282	0.1489	0.4062	0.1188	0.4751	3.104	1.780	1.079	0.3134
	0.4	0.5396	0.2536	0.2068	0.3899	0.2440	0.3661	3.156	1.384	1.039	0.5649

[a] Molal equilibrium ratio defined by $K_k = y_k/x_k$. [b] Composition parameter, C, defined by Equation 1. [c] Values tabulated are extrapolated from experimental data at higher temperatures.

Table V. Properties of the Critical State

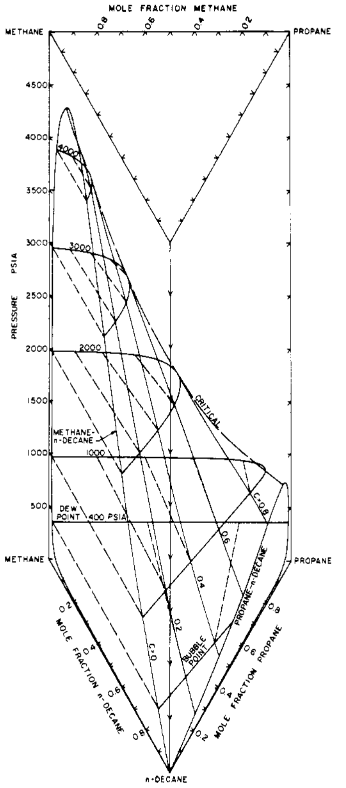
		Mole Fraction			Volume, Cu. Ft./ Lb.-Mole
Composition Parameter[a]	Pressure, P.S.I.A.	Methane	Propane	*n*-Decane	
		40° F.			
0.0[b]	5240	0.905	0.0	0.095	1.055
0.2	4756	0.882	0.024	0.094	1.076
0.4	4185	0.844	0.062	0.094	1.107
0.6	3438	0.784	0.130	0.086	1.160
0.8	2548	0.752	0.198	0.050	1.254
1.0[c]	1474	0.746	0.254	0.0	1.634
		100° F.			
0.0[b]	5310	0.898	0.0	0.102	1.180
0.2	4872	0.872	0.026	0.102	1.205
0.4	4352	0.832	0.067	0.101	1.236
0.6	3676	0.767	0.140	0.093	1.296
0.8	2725	0.683	0.254	0.063	1.400
1.0[c]	1353	0.588	0.412	0.0	2.106
		280° F.			
0.0[b]	4580	0.857	0.0	0.143	1.716
0.2	4297	0.823	0.035	0.142	1.762
0.4	3402	0.768	0.093	0.139	1.832
0.6	3245	0.661	0.203	0.136	1.977
0.8	1981	0.401	0.479	0.120	2.390
	873[d]	0.	0.928	0.072	3.22
		400° F.			
0.0[b]	3605	0.798	0.0	0.202	2.377
0.2	3350	0.744	0.051	0.205	2.449
0.4	2985	0.653	0.139	0.208	2.574
0.6	2300	0.474	0.316	0.210	2.869
	1028[d]	0.0	0.799	0.201	3.78
		460° F.			
0.0[b]	2911	0.739	0.0	0.261	2.954
0.2	2680	0.667	0.067	0.266	3.06
0.4	2345	0.539	0.184	0.277	3.25
0.6	1539	0.276	0.434	0.290	3.81
	988[d]	0.0	0.712	0.288	4.50

[a] Composition parameter defined by Equation 1. [b] Methane–*n*-decane system. [c] Methane-propane system. [d] Propane–*n*-decane system.

BEHAVIOR OF SYSTEM

There are a large number of illustrative diagrams that can be developed from the information available in Tables IV and V. For example, in Figure 4 is shown, in isometric projection, a pressure-composition diagram for a temperature of 280° F. Combining lines for indicated values of the composition parameter, C, have been included to depict the behavior encountered in the heterogeneous region. The maximum two-phase pressure occurs in the methane–*n*-decane binary system. Since 280° F. is above the critical temperatures of methane and propane, no heterogeneous region is found for the methane-propane binary system. The loci of the critical temperatures and pressures are depicted in Figure 5. Using the reported behavior of the methane-propane system (*15*), substantial curvature of the critical temperature with change in composition upon a conventional ternary diagram was encountered at the lower temperatures, as was reported for the methane–ethane–*n*-butane system by Forman and Thodos (*7*). However, the critical temperature locus in Figure 5 has been indicated as an estimate only for 100° and 40° F. Hadden's suggestion

Figure 4. Pressure-composition diagram for 280° F.



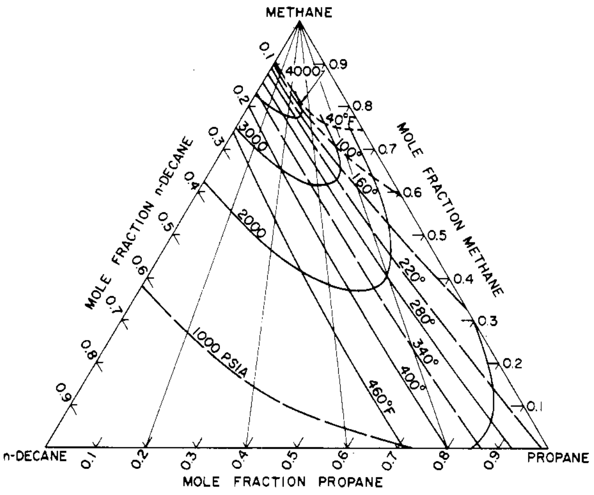


Figure 5. Critical pressures and temperatures in the methane–propane–*n*-decane system

(*8*) may be correct, but the current trend of evidence would indicate some curvature of the isothermal variation in critical composition on a conventional ternary molal composition diagram for lower temperatures corresponding to higher mole fractions of methane. It remains for further direct investigations of the critical state of ternary hydrocarbon systems containing methane to determine the extent to which Hadden's (*8*) simple suggestion is valid.

The molal volume of the coexisting liquid phase for 280° F. is presented in Figure 6. The increase in the molal volume with increasing mole fraction methane at high values of the composition parameter, *C*, is of interest.

The variation in the product of the pressure and the equilibrium ratio is shown in Figure 7 as a function of pressure at 280° F. for the three components. The marked influence of the composition parameter *C*, defined by Equation 3, is evident.

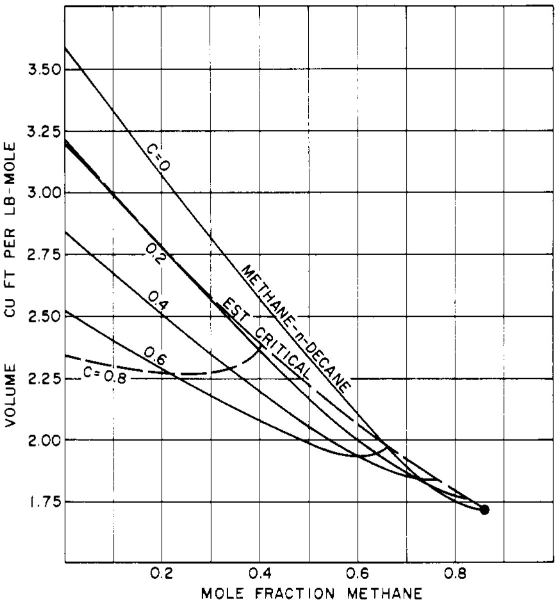


Figure 6. Molal volume of bubble-point liquid at 280° F.

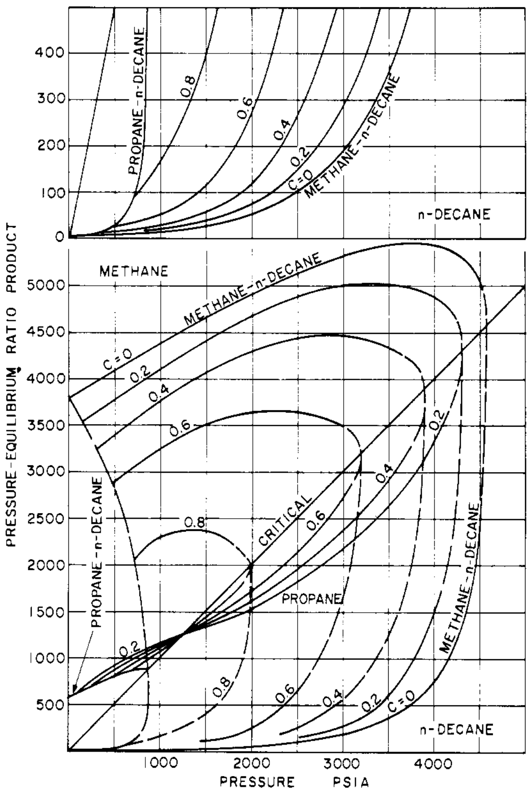


Figure 7. Effect of composition and pressure upon equilibrium ratios

Figures 4 to 7, inclusive, are only examples of the large number of diagrams which can be prepared to illustrate the effect of state upon the properties of the coexisting liquid and gas phases in the methane–propane–*n*-decane system.

ACKNOWLEDGMENT

A. H. Rijkschroeff assisted with the experimental work, while Lorine Faris and Virginia Berry were responsible for the reduction of the experimental results to a form suitable for publication.

NOMENCLATURE

C = composition parameter defined by Equation 1
G = variable
K_k = molal equilibrium ratio of component k, $K_k = y_k/x_k$
N = number of points
P = pressure, p.s.i.a.
s = average deviation defined by $\sum_1^N (G - G_s)/N$
s' = average fractional deviation defined by $\sum_1^N [(G - G_s)/G]/N$
x = mole fraction liquid
y = mole fraction gas
$\sum$ = summation operator
σ = standard deviation or standard error of estimate, defined by $[\sum_1^N (G - G_s)^2/(N - 1)]^{1/2}$

Subscripts

e = experimental
k = component
s = smoothed
1, 3, 10 = components methane, propane, and n-decane, respectively

LITERATURE CITED

(1) Am. Petroleum Inst. Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Chemical Thermodynamic Properties Center, Texas A & M University, College Station, Tex.
(2) Benedict, Manson, Webb, George B., Rubin, Louis C., *J. Chem. Phys.* **10**, 747 (1942).
(3) Billman, G.W., Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **174**, 13 (1948).
(4) Bridgeman, O.C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
(5) Carter, R.T., Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **42**, 170 (1941).
(6) Dourson, R.H., Sage, B.H., Lacey, W.N., *Ibid.*, **151**, 206 (1943).
(7) Forman, J. Charles, Thodos, George, *A.I.Ch.E. J.* **8**, No. 2, 209 (1962).
(8) Hadden, S.T., *Chem. Eng. Progr. Symposium Ser.* No. 7, **49**, 53 (1953).
(9) Koonce, K.T., Kobayashi, Riki, J. CHEM. ENG. DATA **9**, 494 (1964).
(10) Lacey, W.N., *Proc. Calif. Natl. Gasoline Assoc.* **9**, No. 1, 2 (1934); *Petrol. World (Calif.)* **31**, No. 3, 41 (1934).
(11) Meyers, C.H., *Bur. Std. J. Res.* **9**, 807 (1932).
(12) Reamer, H.H., Berry, V.M., Sage, B.H., J. CHEM. ENG. DATA **14**, 447 (1969).
(13) Reamer, H.H., Fiskin, J.M., Sage, B.H., *Ind. Eng. Chem.* **41**, 2871 (1949).
(14) Reamer, H.H., Olds, R.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **34**, 1526 (1942).
(15) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **42**, 534 (1950); *Fundamental Research on Occurrence and Recovery of Petroleum*, 14–9, Am. Petroleum Inst., New York (1950–51).
(16) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ibid.*, **43**, 1436 (1951).
(17) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ibid.*, **44**, 1671 (1952).
(18) Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **26**, 592 (1955).
(19) Reamer, H.H., Sage, B.H., J. CHEM. ENG. DATA **11**, 17 (1966).
(20) Rigas, T.J., Mason, D.F., Thodos, George, J. CHEM. ENG. DATA **4**, 201 (1959).
(21) Sage, B.H., Lavender, H.M., Lacey, W.N., *Ind. Eng. Chem.* **32**, 743 (1940).
(22) Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **174**, 102 (1948).
(23) Sage, B.H., Lacey, W.N., *Ibid.*, **136**, 136 (1940).
(24) Sage, B.H., Lacey, W.N., Schaafsma, J.G., *Proc. Am. Petrol. Inst.* **14**, No. 4, 119 (1933); *Oil Gas J.* **32**, No. 27, 12 (1933).
(25) Sage, B.H., Lacey, W.N., Schaafsma, J.G., *Ind. Eng. Chem.* **26**, 214 (1934).
(26) Weise, H.C., Reamer, H.H., Sage, B.H., Document NAPS-00524, American Society for Information Science, New York.

RECEIVED for review December 13, 1968. Accepted April 28, 1969. For additional experimental results, order NAPS Document NAPS-00524 from ASIS National Auxiliary Publications Service, 22 West 34th St., New York, N. Y. 10001; remit $1.00 for microfiche or $3.00 for photocopies. This experimental work was carried out as part of the activities of Project 37 of the American Petroleum Institute. This paper was accepted as a contribution to this journal by R. L. Pigford, editor of *Ind. Eng. Chem. Fundamentals*.

Phase Equilibria in the Hydrocarbon Systems. Phase Behavior in the Methane–Propane–*n*-Butane System

H. C. WIESE, JOAN JACOBS, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif. 91109

A NUMBER of experimental investigations of the composition of the coexisting phases in ternary paraffin hydrocarbon systems has been made at elevated pressures. The systems involving methane include the methane-propane-n-pentane system (*3, 4*), the methane-n-butane-n-decane system (*8, 13, 14*), the methane-ethane-n-pentane system (*1*), and the methane-propane-n-decane system (*5, 23*). As a part of an investigation of the quaternary methane-propane-n-butane-n-decane system, measurements of the volumetric and phase behavior of the methane-propane-n-butane system have been carried out. These studies have been limited to temperatures between 40° and 220° F., and cover the heterogeneous region in this temperature interval.