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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

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

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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.

The composition of the coexisting gas and liquid phases was established at 79 states distributed throughout the heterogeneous region of the methane–propane–*n*-butane system at temperatures between 40° and 220° F. These data indicate a marked variation in the equilibrium ratio of the several components with respect to the composition of the system at a fixed temperature and pressure. The critical states were not established directly, but were extrapolated or interpolated from phase equilibrium measurements carried out at some distance from that state. For this reason, it is not surprising that greater uncertainties exist near the critical state than elsewhere in the region of heterogeneous equilibrium. The results are presented in tabular form, with a limited number of graphical illustrations.

EXPERIMENTAL METHODS

Mixtures of methane, propane, and *n*-butane were brought together in a heterogeneous region in a stainless steel vessel, where they were confined over mercury. Mechanical agitation was provided by a magnetically driven stirrer. The relative volumes of the liquid and gas phases were determined by means of a "hot wire" mounted parallel to the interface (*18*). 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 (*8, 18*).

The pressure was measured by means of a piston-cylinder balance (*10, 11, 19*). This instrument was calibrated against the vapor pressure of carbon dioxide at the ice point (*2*), and experience over the past four 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 pressure balance was connected to the stainless steel pressure vessel through an oil-mercury interface. Appropriate corrections were made for variations in the specific weights of oil and mercury as a result of changes in temperature and pressure.

The temperature of the vessel, in which the heterogeneous equilibrium was obtained, was controlled by immersion within an agitated oil bath. The temperature of this bath was maintained by a modulating circuit (*9*) within 0.005° F. The temperatures were established by means of the indications of a strain-free, platinum resistance thermometer (*8*) which had been calibrated against the indications of an identical instrument standardized at the National Bureau of Standards. Experience with these strain-free, platinum resistance thermometers indicates that the temperature was related to the international practical temperature scale (international platinum scale) within 0.03° F. throughout the temperature interval between 40° and 220° F.

Gas chromatographic equipment was employed to determine the composition of the samples of the coexisting gas and liquid phases withdrawn from the heterogeneous equilibrium mixture. Conventional chromatographic equipment was employed with thermal conductivity cells to determine the quantity of each component, and automatic integration equipment was employed to determine the total quantity of each of the three components. In order to maintain a control of the performance of the chromatographic equipment, samples of known composition were periodically subjected to analysis. These samples were prepared by adding known weights of methane, propane, and *n*-butane to a weighing bomb and withdrawing samples for analysis. The results of these controlled analyses are set forth in Table I. The standard deviations of the chromatographic measurements from the gravimetrically prepared control samples have been included in Table I. The average values of the standard deviation for all of the samples investigated amount to 0.00131 mole fraction of methane, 0.00210 mole fraction of propane, and 0.00170 mole fraction of *n*-butane.

During the withdrawal of the small sample involving not more than 25 cc. of gas, as measured at atmospheric pressure, the temperature of the heterogeneous equilibrium system did not vary by more than 0.005° F. and the pressure by more than 0.05 p.s.i. Care was exercised to avoid the selective adsorption of any of the components on the tubing involved in connecting the equilibrium vessel with the sample container.

In a large number of cases, duplicate analyses were made from a single sample withdrawn, and in other cases duplicate samples were withdrawn. In the first part of Table II are set forth the results obtained upon all of the duplicate analyses which were carried out in the course of this investigation for a given sample. The average standard deviation was 0.00085 mole fraction of methane, 0.00060 mole fraction of propane, and 0.00081 mole fraction of *n*-butane. In the second part of Table II is set forth the agreement of duplicate samples withdrawn at the same state in the course of this investigation. These have been recorded for each of several temperatures.

After a careful review of the information submitted in Tables I and II, it is believed that the composition of the coexisting phases of the methane–propane–*n*-butane system were established with an uncertainty of not more than 0.005 mole fraction. At some states, the mole fraction of a given component was below 0.001 mole fraction; under these conditions, the uncertainty in the mole fraction was markedly less than the above-mentioned value. It is difficult to set forth meaningful average values of the uncertainty of measurements, since the mole fraction of a particular component varies widely over the range of states covered in this investigation.

MATERIALS

The propane and *n*-butane were obtained as research grade hydrocarbons from Phillips Petroleum Co., and after deaeration were utilized without further purification. The variation in vapor pressure with quality at two temperatures is shown in Table III. The relatively small change in vapor pressure with a large change in quality under conditions of constant temperature is an excellent indication of purity of the hydrocarbons. In addition, the deaerated sample of *n*-butane was sub-

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

Date	Methane	Propane	n-Butane
Sample 1. Gravimetrically Prepared			
9-18-67		0.49924	0.50076
Chromatographic Analysis			
10- 9-67		0.49805	0.50195
1-23-68		0.49973	0.50027
6- 5-68		0.49999	0.50001
7-19-68		0.49798	0.50202
8-27-68		0.49927	0.50073
10- 1-68		0.49756	0.50245
σ[a]		0.00105	0.00105
Sample 2. Gravimetrically Prepared			
9-18-67	0.32659	0.34868	0.32473
Chromatographic Analysis			
9-20-67	0.32718	0.34806	0.32476
10- 9-67	0.32614	0.34860	0.32526
12-20-67	0.32598	0.34983	0.32419
7-19-68	0.32691	0.34911	0.32398
10- 2-68	0.32575	0.35002	0.32424
σ[a]	0.00059	0.00085	0.00052
Sample 3. Gravimetrically Prepared			
9-25-67		0.16275	0.83725
Chromatographic Analysis			
10- 9-67		0.16185	0.83815
7-19-68		0.16205	0.83795
10- 1-68		0.16016	0.83984
σ[a]		0.00163	0.00163
Sample 4. Gravimetrically Prepared			
9-26-67		0.85870	0.14130
Chromatographic Analysis			
10- 9-67		0.85706	0.14294
σ[a]		0.00164	0.00164
Sample 5. Gravimetrically Prepared			
10-20-67	0.34493	0.32994	0.32513
Chromatographic Analysis			
10-24-67	0.34589	0.32948	0.32463
1-19-68	0.34610	0.33078	0.32312
1-22-68	0.35056	0.32821	0.32123
1-23-68	0.34675	0.33109	0.32216
1-31-68	0.34403	0.33093	0.32504
2-15-68	0.34321	0.33143	0.32537
2-23-68	0.34352	0.33093	0.32555
3-11-68	0.34449	0.33042	0.32509
3-12-68	0.34392	0.33192	0.32417
3-25-68	0.34296	0.33091	0.32613
4- 9-68	0.34422	0.32975	0.32603
6- 4-68	0.34368	0.33129	0.32502
7-19-68	0.34388	0.33053	0.32560
8-27-68	0.34310	0.33146	0.32544
10- 1-68	0.34168	0.33144	0.32688
σ[a]	0.00201	0.00119	0.00152
Sample 6. Gravimetrically Prepared			
10-26-67	0.52520	0.47480	
Chromatographic Analysis			
10-27-67	0.52528	0.47472	
12-22-67	0.52334	0.47666	
1-19-68	0.52630	0.47370	
1-23-68	0.52515	0.47486	
3-11-68	0.52427	0.47574	
3-12-68	0.52527	0.47473	
7-19-68	0.52482	0.47518	
8-27-68	0.52326	0.47674	
10- 1-68	0.52300	0.47700	
σ[a]	0.00126	0.00126	

Mole fraction: Methane, Propane, n-Butane.

[a] Standard deviation defined by:

$$\sigma = \left[\sum_{1}^{N} (G_r - G_c)^2/N\right]^{\frac{1}{2}}$$

Table II. Analysis of Samples

Temp., ° F.	Number of Duplicate Analyses[a]	Standard Deviation,[b] Mole Fraction: Methane	Propane	n-Butane	Number of Duplicate Samples[c]	Standard Deviation,[b] Mole Fraction: Methane	Propane	n-Butane
	Duplicate Analysis on a Given Sample				Duplicate Samples			
40	45	0.00082	0.00030	0.00060	1	0.00758	0.00635	0.00389
100	56	0.00076	0.00040	0.00072	7	0.00910	0.00697	0.00546
160	40	0.00111	0.00112	0.00135	4	0.00497	0.00429	0.00345
220	17	0.00071	0.00057	0.00057	1	0.01131	0.00895	0.00758
	Average	0.00085	0.00060	0.00081				

[a] Number of duplicate analyses carried out on a single sample withdrawn.

[c] Number of duplicate samples withdrawn.

[b] Standard deviation defined by: $\sigma = \left[\sum_{1}^{N} (G_r - G_e)^2/(N-1)\right]^{\frac{1}{2}}$

jected to chromatographic analysis; the result of this analysis is also included in Table III. The methane utilized was obtained through the courtesy of Texaco, Inc., from a well in the San Joaquin Valley, Calif. The methane was passed over calcium chloride, activated charcoal, Ascarite, and anhydrous calcium sulfate at pressures in excess of 500 p.s.i. After such treatment, chromatographic analysis indicated it to contain only small quantities of impurities, as is indicated in Table III. The chromatographic analysis upon the purified methane indicated that the only impurity present in measurable quantities was nitrogen with traces of

Table III. Physical Properties of Components

Quantity	Measured	Reported
Change in vapor pressure,[a] p.s.i.		
Propane, 100° F.	0.15	
n-Butane, 250° F.	0.25	
Composition, mole fraction		
Methane	0.9991[b]	0.9995[c]
Propane		0.9999[c]
n-Butane	0.9995[b]	

[a] Change in vapor pressure associated with change in quality 0.1–0.8.
[b] Chromatographic analysis.
[c] Purity reported by vendor.

oxygen. The latter impurity probably was associated with the handling of the gas in the laboratory. The information presented in Table III indicates that all three components contained less than 0.001 mole fraction of impurities.

EXPERIMENTAL RESULTS

In connection with the development of the phase equilibrium data, use was made of other measurements concerning the characteristics of the components and of the three binary systems. The vapor pressure of propane has been established with accuracy (*20*), as has its critical state. Likewise, the vapor pressure and critical properties of n-butane (*21*) have been determined with sufficient accuracy as not to contribute any uncertainty to the current experimental data for the methane–propane–n-butane system. The phase behavior of the methane-propane system has been determined with some certainty (*12*), and the phase behavior of the methane–n-butane system was also investigated (*17*). In connection with the latter binary system, the work of McKetta *et al.* (*16*) established the behavior near the critical state with much greater certainty than somewhat earlier measurements (*17*). Table IV reports the composition of the coexisting phases and the critical states chosen for the methane–n-butane system, in connection with the development of the data for the methane–propane–n-butane system. In Figure 1 is shown

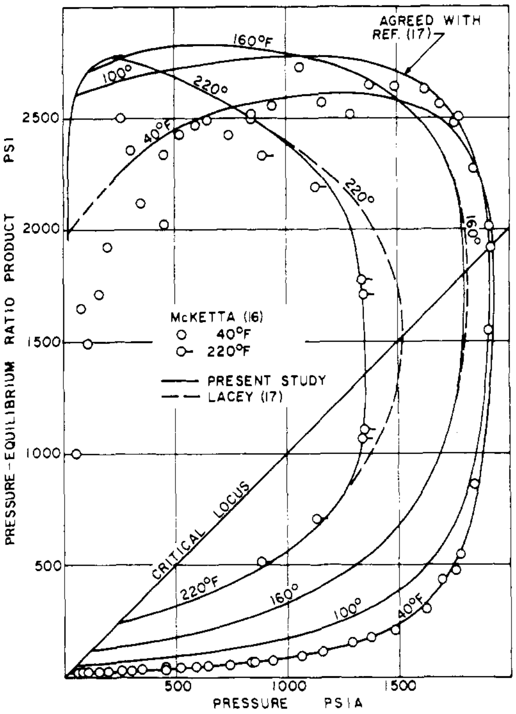

Figure 1. Pressure-equilibrium ratio product for the methane–n-butane system

Table IV. Properties of the Coexisting Phases for the Methane–n-Butane System Employed

Temp., °F.	Pressure, P.S.I.A.	Gas Phase Mole Fraction		Liquid Phase Mole Fraction		Equilibrium Ratio[a]	
		Methane	n-Butane	Methane	n-Butane	Methane	n-Butane
40	200	0.8888	0.1112	0.0808	0.9192	11.000	0.1210
	500	0.9369	0.0631	0.1913	0.8087	4.898	0.0780
	1000	0.9461	0.0539	0.3651	0.6349	2.591	0.0849
	1250	0.9407	0.0593	0.4513	0.5487	2.084	0.1081
	1500	0.9262	0.0738	0.5390	0.4610	1.718	0.1601
	1700	0.9044	0.0956	0.6194	0.3806	1.460	0.2512
	1923[b]	0.7970	0.2030	0.7970	0.2030	1.000	1.0000
100	200	0.7027	0.0530	0.2973	0.9470	13.258	0.3139
	500	0.8473	0.1556	0.1527	0.8444	5.445	0.1808
	1000	0.8809	0.3171	0.1191	0.6829	2.778	0.1744
	1250	0.8786	0.3974	0.1214	0.6026	2.211	0.2015
	1500	0.8665	0.4799	0.1335	0.5201	1.806	0.2567
	1700	0.8440	0.5586	0.1560	0.4414	1.511	0.3534
	1912[b]	0.7236	0.2764	0.7236	0.2764	1.000	1.0000
160	200	0.3517	0.6483	0.0256	0.9744	13.738	0.6653
	500	0.6796	0.3204	0.1201	0.8799	5.659	0.3641
	1000	0.7567	0.2433	0.2717	0.7283	2.785	0.3340
	1250	0.7588	0.2412	0.3482	0.6518	2.179	0.3701
	1500	0.7439	0.2561	0.4329	0.5671	1.718	0.4516
	1700	0.7036	0.2964	0.5103	0.4897	1.379	0.6053
	1792[b]	0.6165	0.3835	0.6165	0.3835	1.000	1.0000
220	500	0.4200	0.5800	0.0783	0.9217	5.365	0.6293
	1000	0.5630	0.4370	0.2361	0.7639	2.385	0.5721
	1250	0.5338	0.4662	0.3200	0.6800	1.668	0.6856
	1348[b]	0.4520	0.5480	0.4520	0.5480	1.000	1.0000

[a] Molal equilibrium ratio defined by: $K_k = \dot{y}_k/\dot{x}_k$. [b] Estimated critical.

Table V. Properties of the Coexisting Phases for

Temp., °F.	Pressure, P.S.I.A.		Gas Phase Mole Fraction			Liquid Phase Mole Fraction			Equilibrium Ratio[a]	
			Methane	n-Butane		Methane	n-Butane		Methane	n-Butane
					40° F.					
200	0.0	0.8888[c]	0	0.1112	0.0808[c]	0	0.9192	11.000	0	0.1210
	0.2	0.8273	0.0819	0.0909	0.0762	0.1848	0.7390	10.855	0.4430	0.1230
	0.4	0.7636	0.1659	0.0705	0.0710	0.3716	0.5574	10.760	0.4465	0.1265
	0.6	0.6990	0.2524	0.0486	0.0662	0.5603	0.3735	10.560	0.4505	0.1300
	0.8	0.6327	0.3422	0.0251	0.0609	0.7513	0.1878	10.390	0.4555	0.1335
	1.0	0.5627	0.4373	0	0.0549	0.9451	0	10.250	0.4627	0
500	0.0	0.9369[c]	0	0.0631	0.1913[c]	0	0.8087	4.898	0	0.0780
	0.2	0.9102	0.0391	0.0507	0.1996	0.1601	0.6403	4.560	0.2444	0.0792
	0.4	0.8825	0.0788	0.0387	0.2001	0.3200	0.4799	4.410	0.2464	0.080
	0.6	0.8523	0.1215	0.0263	0.1987	0.4808	0.3205	4.290	0.2526	0.0820
	0.8	0.8180	0.1685	0.0135	0.1962	0.6431	0.1608	4.170	0.2620	0.0842
	1.0	0.7819	0.2181	0	0.1923	0.8077	0	4.066	0.2700	0
1000	0.0	0.9461[c]	0	0.0539	0.3651[c]	0	0.6349	2.591	0	0.0849
	0.2	0.9275	0.0281	0.0444	0.3949	0.1210	0.4841	2.349	0.2318	0.0918
	0.4	0.9068	0.0574	0.0358	0.4030	0.2388	0.3582	2.250	0.2403	0.0999
	0.6	0.8835	0.0904	0.0261	0.4071	0.3557	0.2371	2.170	0.2542	0.1100
	0.8	0.8567	0.1289	0.0144	0.4119	0.4705	0.1176	2.080	0.2739	0.1226
	1.0	0.8208	0.1792	0	0.4226	0.4774	0	1.942	0.3754	0
					40° F.					
1250	0.0	0.9407[c]	0	0.0593	0.4513[c]	0	0.5487	2.084	0	0.1081
	0.2	0.9203	0.0276	0.0521	0.4918	0.1016	0.4066	1.871	0.2716	0.1282
	0.4	0.9004	0.0571	0.0426	0.5070	0.1972	0.2958	1.776	0.2894	0.1438
	0.6	0.8749	0.0923	0.0329	0.5154	0.2908	0.1939	1.698	0.3173	0.1696
	0.8	0.8470	0.1335	0.0195	0.5278	0.3778	0.0944	1.605	0.3534	0.2064
	1.0	0.8222	0.1778	0	0.5492	0.4508	0	1.497	0.3944	0
1500	0.0	0.9262[c]	0	0.0738	0.5390[c]	0	0.4610	1.718	0	0.1601
	0.2	0.9035	0.0297	0.0668	0.5970	0.0806	0.3224	1.513	0.3681	0.2073
	0.4	0.8747	0.0645	0.0608	0.6157	0.1537	0.2306	1.421	0.4197	0.2636
	0.6	0.8360	0.1114	0.0526	0.6391	0.2165	0.1444	1.308	0.5144	0.3647
1700	0.0	0.9044[c]	0	0.0956	0.6194[c]	0	0.3806	1.460	0	0.2512
	0.2	0.8585	0.0348	0.1067	0.7017	0.0597	0.2387	1.224	0.5830	0.4470
					100° F.					
200	0.0	0.7027	0	0.2973	0.0530	0	0.9470	13.259	0	0.3139
	0.2	0.5742	1.1833	0.2425	0.0452	0.1910	0.7638	12.697	0.9600	0.3175
	0.4	0.4447	0.3689	0.1864	0.0368	0.3853	0.5779	12.094	0.9575	0.3225
	0.6	0.3130	0.5574	0.1296	0.0272	0.5837	0.3891	11.516	0.9550	0.3330
	0.8	0.1823	0.7498	0.0679	0.0165	0.7868	0.1967	11.038	0.9530	0.3450
	1.0	0.0521	0.9479	0	0.0049	0.9951	0	10.633	0.9526	0
500	0.0	0.8473	0	0.1527	0.1556	0	0.8444	5.445	0	0.1808
	0.2	0.7902	0.0831	0.1267	0.1514	0.1697	0.6789	5.220	0.4898	0.1866
	0.4	0.7316	0.1700	0.0984	0.1459	0.3417	0.5125	5.016	0.4976	0.1920
	0.6	0.6653	0.2641	0.0706	0.1386	0.5168	0.3446	4.800	0.5110	0.2048
	0.8	0.5953	0.3669	0.0378	0.1304	0.6957	0.1739	4.564	0.5274	0.2176
	1.0	0.5209	0.4791	0	0.1235	0.8765	0	4.218	0.5466	0
1000	0.0	0.8809	0	0.1191	0.3171	0	0.6829	2.778	0	0.1744
	0.2	0.8430	0.0545	0.1025	0.3201	0.1360	0.5440	2.634	0.4008	0.1884
	0.4	0.8036	0.1132	0.0833	0.3209	0.2717	0.4075	2.505	0.4166	0.2043

[a] Composition parameter, C, defined by Equation 1.
[b] Molal equilibrium ratio defined by: $K_k = y_k/x_k$.
[c] Experimental study (*15*) and extrapolation from experimental data at higher temperatures (*16*). See Figure 1.

for the methane–n-butane system the product of the pressure and the equilibrium ratio from the two sets of earlier measurements (*16*, *17*), together with the critically chosen values used in this experimental work. The phase behavior of the propane–n-butane system has also been studied to a limited extent (*7*). Therefore, it appears that there is adequate information concerning the vapor pressures of the pure substances and the phase behavior of the pertinent three binary systems forming the boundaries of the ternary system, methane–propane–n-butane. The uncertainties in establishing the phase behavior of these binary systems, with the possible exception of the propane–n-butane system, have not contributed to the uncertainties in the current experimental measurements for the ternary system.

The composition of the coexisting phases in the

the Methane–Propane–*n*-Butane System

Pressure, P.S.I.A.	Composition Parameter[a]	Gas Phase Mole Fraction			Liquid Phase Mole Fraction			Equilibrium Ratio[b]		
		Methane	Propane	*n*-Butane	Methane	Propane	*n*-Butane	Methane	Propane	*n*-Butane
100° F. (Continued)										
	0.6	0.7582	0.1798	0.0621	0.3191	0.4086	0.2724	2.376	0.4400	0.2278
	0.8	0.7122	0.2525	0.0353	0.3217	0.5426	0.1357	2.214	0.4653	0.2600
	1.0	0.6635	0.3365	0	0.3271	0.6729	0	2.028	0.5001	0
1250	0.0	0.8786	0	0.1214	0.3974	0	0.6026	2.211	0	0.2015
	0.2	0.8425	0.0506	0.1069	0.4051	0.1190	0.4760	2.080	0.4254	0.2246
	0.4	0.8038	0.1055	0.0907	0.4111	0.2356	0.3533	1.955	0.4480	0.2566
	0.6	0.7604	0.1688	0.0708	0.4181	0.3492	0.2328	1.819	0.4834	0.3042
	0.8	0.7143	0.2427	0.0430	0.4276	0.4579	0.1145	1.670	0.5301	0.3756
	1.0	0.6766	0.3234	0	0.4511	0.5489	0	1.500	0.5892	0
1500	0.0	0.8665	0	0.1335	0.4799	0	0.5201	1.806	0	0.2567
	0.2	0.8249	0.0505	0.1246	0.4966	0.1007	0.4028	1.661	0.5013	0.3095
	0.4	0.7783	0.1087	0.1130	0.5152	0.1939	0.2909	1.511	0.5606	0.3883
	0.6	0.7103	0.1904	0.0993	0.5403	0.2758	0.1839	1.315	0.6903	0.5400
1700	0.0	0.8440	0	0.1560	0.5586	0	0.4414	1.511	0	0.3534
	0.2	0.7801	0.0540	0.1659	0.5910	0.0818	0.3272	1.320	0.6603	0.5071
160° F.										
200	0.0	0.3517	0	0.6483	0.0256	0	0.9744	13.738	0	0.6653
	0.2	0.1171	0.3439	0.5391	0.0091	0.1982	0.7927	12.909	1.735	0.6800
500	0.0	0.6796	0	0.3204	0.1201	0	0.8799	5.659	0	0.3641
	0.2	0.5771	0.1477	0.2753	0.1086	0.1783	0.7131	5.315	0.8282	0.3860
	0.4	0.4754	0.3032	0.2214	0.0955	0.3618	0.5427	4.978	0.8380	0.4080
	0.6	0.3702	0.4702	0.1597	0.0803	0.5518	0.3679	4.612	0.8520	0.4340
	0.8	0.2650	0.6481	0.0869	0.0634	0.7493	0.1873	4.178	0.8650	0.4640
	1.0	0.1550	0.8450	0	0.0433	0.9567	0	3.580	0.8832	0
1000	0.0	0.7567	0	0.2433	0.2717	0	0.7283	2.785	0	0.3340
	0.2	0.6944	0.0933	0.2123	0.2669	0.1466	0.5865	2.602	0.6360	0.3620
	0.4	0.6285	0.1954	0.1761	0.2622	0.2951	0.4427	2.397	0.6620	0.3978
	0.6	0.5527	0.3131	0.1342	0.2625	0.4463	0.2975	2.157	0.7015	0.4512
	0.8	0.4640	0.4547	0.0814	0.2556	0.5955	0.1489	1.815	0.7635	0.5466
	1.0	0.3558	0.6442	0	0.2800	0.7200	0	1.271	0.8947	0
1250	0.0	0.7588	0	0.2412	0.3482	0	0.6518	2.179	0	0.3701
	0.2	0.6992	0.0842	0.2166	0.3549	0.1290	0.5161	1.970	0.6524	0.4197
	0.4	0.6314	0.1795	0.1891	0.3598	0.2561	0.3842	1.755	0.7008	0.4922
	0.6	0.5377	0.3006	0.1617	0.3718	0.3769	0.2513	1.446	0.7974	0.6436
1500	0.0	0.7439	0	0.2561	0.4329	0	0.5671	1.718	0	0.4516
	0.2	0.6610	0.0814	0.2576	0.4692	0.1062	0.4246	1.409	0.7667	0.6067
1700	0.0	0.7036	0	0.2964	0.5103	0	0.4897	1.379	0	0.6053
220° F.										
500	0.0	0.4200	0	0.5800	0.0783	0	0.9217	5.365	0	0.6293
	0.2	0.2628	0.2233	0.5139	0.0554	0.1889	0.7557	4.744	1.182	0.6800
	0.4	0.1342	0.4573	0.4085	0.0328	0.3869	0.5803	4.091	1.182	0.7040
	0.6	0.0142	0.7062	0.2796	0.0042	0.5975	0.3983	3.377	1.182	0.7020
1000	0.0	0.5630	0	0.4370	0.2361	0	0.7639	2.385	0	0.5721
	0.2	0.4615	0.1375	0.4010	0.2311	0.1538	0.6151	1.997	0.8940	0.6519
	0.4	0.3560	0.2876	0.3564	0.2316	0.3074	0.4610	1.537	0.9358	0.7730
1250	0.0	0.5338	0	0.4662	0.3200	0	0.6800	1.668	0	0.6856

methane–propane–*n*-butane system at 79 states was investigated, and these detailed experimental results are available (*22*). As an indication of the nature of the measurements, Table V shows a sample of the experimental results obtained at 160° F. In some situations, duplicate or triplicate measurements of the composition of a given sample were determined by chromatographic techniques, while in other situations, duplicate or triplicate samples were withdrawn and subjected to individual chromatographic analysis. The experimental data (*22*) were first plotted upon large triangular diagrams approximately 36 inches on a side. These smooth data were then compared with values of the equilibrium ratios, K_1, K_3, and K_4, smoothed from the experimental data for each of the three components.

The composition of the heterogeneous system was

Table VI. Experimental Results for 160° F.

Pressure, P.S.I.A.	Composition Parameter[a]	Mole Fraction Gas			Mole Fraction Liquid		
		Methane	Propane	n-Butane	Methane	Propane	n-Butane
200	0.2013	0.13801	0.31994	0.54205	0.01126	0.19903	0.78972
	0.2018	0.13715	0.32023	0.54263	0.01063	0.19970	0.78967
	0.3223	0.02302	0.51026	0.46673	0.00211	0.32160	0.67630
500	0.1919	0.57391	0.14235	0.28374	0.10791	0.17123	0.72087
	0.1922	0.57394	0.14211	0.28394	0.10835	0.17137	0.72028
	0.3652	0.49399	0.27495	0.23107	0.09946	0.32886	0.57168
	0.3660	0.49215	0.27552	0.23233	0.09834	0.33002	0.57164
	0.5851	0.37388	0.46097	0.16515	0.08007	0.53830	0.38163
	0.5867	0.37499	0.46022	0.16479	0.08023	0.53960	0.38017
	0.8149	0.25304	0.66572	0.08124	0.06125	0.76502	0.17373
	0.8174	0.25249	0.66767	0.07985	0.06139	0.76722	0.17139
	0.8190	0.25264	0.66800	0.07937	0.06063	0.76931	0.17005
1000	0.1900	0.69686	0.08872	0.21442	0.26564	0.13955	0.59482
	0.1902	0.69748	0.08854	0.21398	0.26632	0.13957	0.59412
	0.3576	0.64344	0.17261	0.18395	0.26450	0.26299	0.47251
	0.3585	0.64460	0.17221	0.18319	0.26680	0.26282	0.47038
	0.5864	0.55916	0.30433	0.13651	0.25669	0.43585	0.30746
	0.5873	0.55810	0.30455	0.13736	0.25842	0.43556	0.30603
	0.8136	0.45413	0.46839	0.07749	0.25221	0.60838	0.13941
	0.8188	0.44874	0.47466	0.07660	0.25370	0.61111	0.13519
	0.8193	0.45088	0.47366	0.07546	0.25421	0.61104	0.13475
1250	0.1916	0.70228	0.08063	0.21710	0.35509	0.12358	0.52133
	0.1929	0.70074	0.08076	0.21851	0.35506	0.12438	0.52056
	0.3556	0.64679	0.15744	0.19576	0.35651	0.22882	0.41467
	0.3560	0.64621	0.15738	0.19641	0.35758	0.22872	0.41371
	0.3565	0.64657	0.15745	0.19598	0.35795	0.22892	0.41312
	0.5773	0.55043	0.28541	0.16417	0.36851	0.36454	0.26695
	0.5784	0.54997	0.28502	0.16501	0.36946	0.36472	0.26582
	0.6514	0.50076	0.34364	0.15560	0.38057	0.40350	0.21594
	0.6523	0.50139	0.34382	0.15478	0.38147	0.40348	0.21505
	0.6717	0.47760	0.36394	0.15846	0.38761	0.41136	0.20103
	0.6722	0.47977	0.36353	0.15671	0.38867	0.41094	0.20039
	0.6874	0.45276	0.38385	0.16340	0.39745	0.41420	0.18836
	0.6884	0.45206	0.38474	0.16321	0.39694	0.41513	0.18793
1500	0.1991	0.65635	0.08225	0.26140	0.46122	0.10729	0.43149
	0.1992	0.65794	0.08203	0.26004	0.46253	0.10709	0.43038
	0.3153	0.57477	0.14213	0.28310	0.50177	0.15809	0.34115
	0.3154	0.57473	0.14170	0.28357	0.49917	0.15798	0.34285
	0.3208	0.56558	0.14586	0.28855	0.50701	0.15817	0.33483
	0.3215	0.56814	0.14583	0.28603	0.50816	0.15813	0.33371

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

described in terms of parameter C, which is defined as follows.

$$C = \dot{x}_3/(\dot{x}_3 + \dot{x}_4) \tag{1}$$

The relation of the composition of each phase to the equilibrium ratios and to the composition parameter C is defined by the following expressions.

$$\dot{x}_1 = 1 - \frac{K_1 - 1}{K_1 - [CK_3 + (1 - C)\,K_4]} \tag{2}$$

$$\dot{x}_3 = C\,(1 - \dot{x}_1) \tag{3}$$

The experimental results shown for a temperature of 160° F. in Table V are depicted in Figure 2. Combining lines have been included, as well as curves representing the composition of the dew-point gas and the bubble-point liquid. For 160° F., the standard error of estimate of the experimental data from the smoothed information shown in Figure 2 was 0.0056 mole fraction of methane, 0.0048 mole fraction of propane, and 0.0027 mole fraction of n-butane. The corresponding average values are 0.0071, 0.0037, and 0.0021 mole fraction for all temperatures investigated.

The equilibrium ratios are defined in the nomenclature and are shown in Figure 3 for three pressures of the heterogeneous region for 160° F. It is of interest to note the significant influence of the composition parameter C upon the equilibrium ratio for the heterogeneous system at a given temperature and pressure. These smoothed values of the equilibrium ratios yielded a fractional deviation, without regard to sign from the experimental equilibrium ratios, of 0.0085, 0.0080, and 0.0117 for methane, propane, and n-butane, respectively.

Values of the composition of the coexisting phases and the three equilibrium ratios are given in Table VI for each of the four temperatures investigated, for the six different pressures, and for the six values of the composition parameter C, as defined by Equation 1. The curves shown in Figures 2 and 3 at 160° F. correspond to the information recorded in Table VI.

Sufficient experimental information was obtained in the course of this investigation and was coupled with that already available for the pertinent binary systems to permit some of the properties of the critical state to be estimated. There are set forth in Table VII the pressure and composition of the critical state as a function of the composition parameter for each of the temperatures investigated. These data involve markedly greater uncertainties than the information presented in Table VI. For example, it is probable that the critical pressures are not known within less than 50 p.s.i., the temperatures within 5° F., and the compositions within 0.03 mole fraction. The indirect methods of estimating the critical states used in this investigation are not considered optimum; nevertheless, the data of Table VII are considered of utility in establishing the effect of temperature and composition upon the critical pressure. The data shown in Table VII are consistent with the information recorded in Table VI within 15 p.s.i., 1° F., and 0.005 mole fraction in composition.

Table VII. Estimated Properties of the Critical State

Composition Parameter[a]	Pressure, P.S.I.A.	Mole Fraction		
		Methane	Propane	n-Butane
		40° F.		
0.0[b]	1923	0.7970	0.0000	0.2030
0.2	1786	0.7835	0.0433	0.1732
0.4	1664	0.7736	0.0906	0.1358
0.6	1561	0.7633	0.1420	0.0947
0.8	1500	0.7530	0.1976	0.0494
1.0[c]	1474	0.7459	0.2541	0.0000
		100° F.		
0.0[b]	1912	0.7236	0.0000	0.2764
0.2	1764	0.6964	0.0607	0.2429
0.4	1644	0.6653	0.1339	0.2008
0.6	1545	0.6346	0.2192	0.1462
0.8	1452	0.6097	0.3122	0.0781
1.0[c]	1353	0.5882	0.4118	0.0000
		160° F.		
0.0[b]	1792	0.6165	0.0000	0.3835
0.2	1616	0.5784	0.0843	0.3373
0.4	1458	0.5295	0.1882	0.2823
0.6	1312	0.4668	0.3199	0.2133
0.8	1166	0.3947	0.4842	0.1211
1.0[c]	1020	0.3228	0.6772	0.0000
		220° F.		
0.0[b]	1348	0.4520	0.0000	0.5480
0.2	1197	0.3880	0.1224	0.4896
0.4	1065	0.3121	0.2752	0.4127
0.6	905	0.2198	0.4681	0.3121
0.8	715	0.0832	0.7334	0.1834
	628[d]	0.0000	0.8895	0.1105

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

[b] Methane–n-butane system.

[c] Methane-propane system.

[d] Propane–n-butane system.

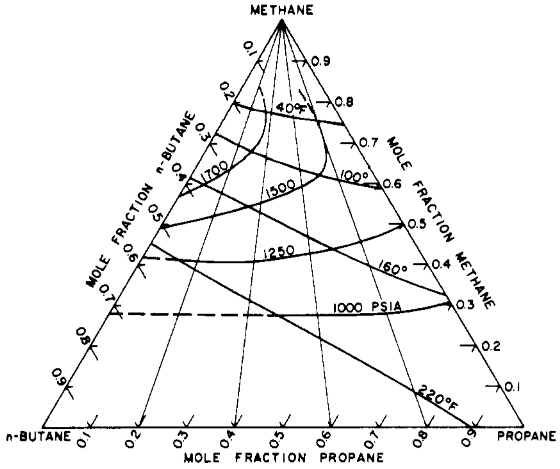

Figure 2. Composition of coexisting phases at 160° F.

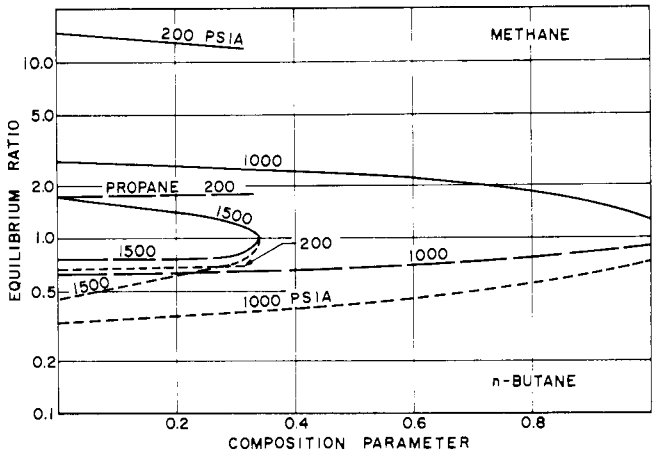

Figure 3. Equilibrium ratios at 160° F. for the methane–propane–n-butane system

BEHAVIOR OF THE SYSTEM

There are a large number of diagrams that may be drawn to illustrate the behavior of a ternary system. In the present instance, Figure 4 shows an isometric projection of the influence of pressure upon the composition of the coexisting phases at 160° F. The marked decrease in the region in which heterogeneous equilibrium exists with an increase in pressure is clearly evident.

The influence of composition upon the estimated critical temperature and pressure of the methane-propane-n-butane system is shown in Figure 5. As has been found for other ternary hydrocarbon systems, the maximum critical pressure exists at the binary system involving the components with the largest difference in molecular weight, which in this case is in the methane–n-butane system.

The product of the pressure and the equilibrium ratio for each of the components for a temperature of 160° F. is shown in Figure 6. This diagram again indicates the marked influence of composition upon the equilibrium

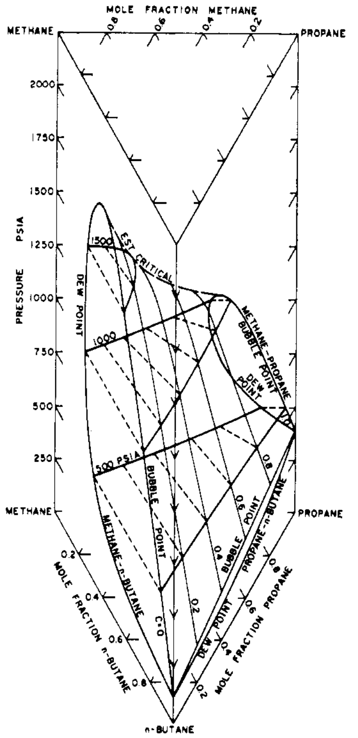

Figure 4. Pressure-composition diagram for 160° F.

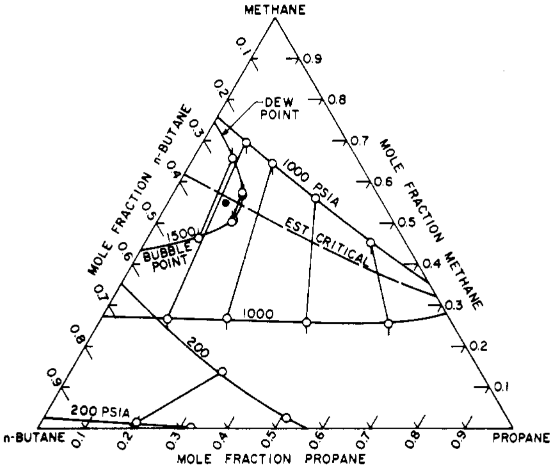

Figure 5. Estimated critical pressures and temperatures in the methane–propane–n-butane system

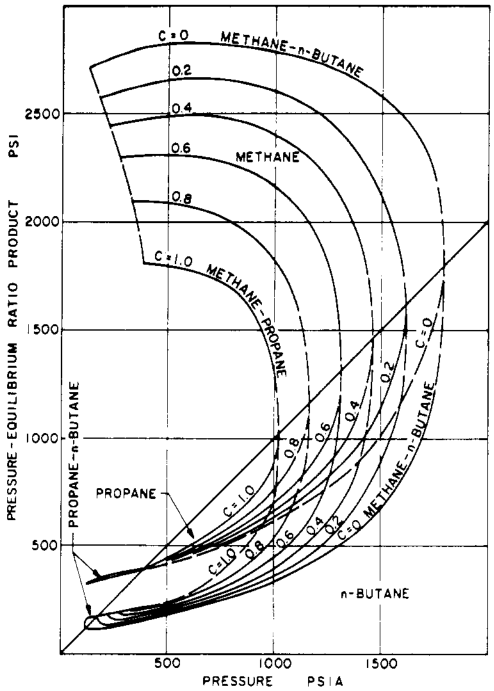

Figure 6. Effect of composition and pressure upon equilibrium ratios at 160° F.

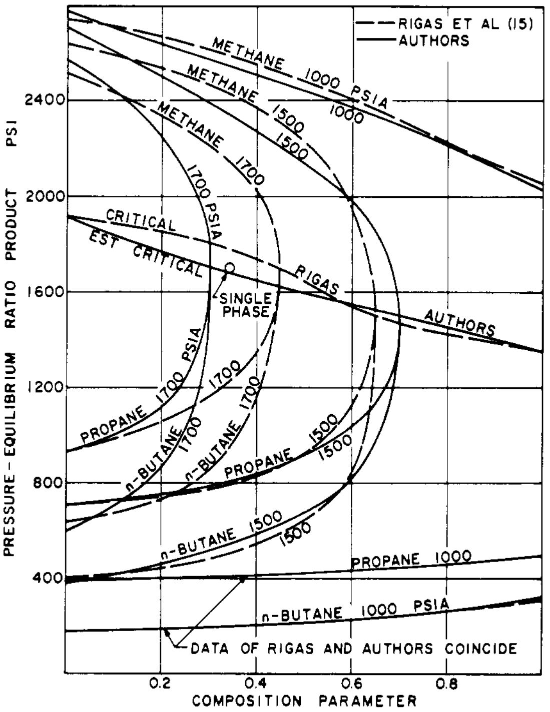

Figure 7. Comparison of pressure-equilibrium ratio products at 100° F.

ratio of each of the three components at a given pressure and temperature. Figures 4 to 6 inclusive are only illustrative in the nature of the many diagrams that may be drawn from the information presented in Table VI.

An effort has been made to reconcile the behavior of the methane–propane–n-butane system with that of the methane-propane-n-decane and methane-n-butane-n-decane systems. Some discrepancies near the critical state of the methane–n-butane system, as reported for the methane–n-butane–n-decane system, from that presented here, exist as a result of the more recent data by McKetta *et al.*, which have made some variations in the chosen value of the critical pressures for a given temperature of this binary system at temperatures above 100° F. There was an experimental investigation carried out by Rigas and coworkers (*15*) upon vapor-liquid equilibria for the methane–propane–n-butane system at 100° F. A comparison of the earlier data obtained by Rigas and coworkers (*15*) with the current investigation is presented in Figure 7. Also shown is a single-phase measurement for 1700 p.s.i.a. and 100° F., which falls well within the two-phase domain reported by

Rigas. Reasonable agreement is obtained at 1000 and 1500 p.s.i.a. However, a rather marked discrepancy in the behavior, particularly near the critical state, in the range of composition parameters from 0.3 to 0.4 was experienced. The significant disagreement near the critical state at the above-mentioned composition parameters is an indication of the need for the direct measurement of the critical pressures and temperatures as a function of composition for ternary systems by direct optical observation of the equilibrium.

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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 = fractional deviation defined by:

$$\sum_{1}^{N} \frac{|G_e - G_s|}{G_e} \Big/ N$$

x = mole fraction liquid
y = mole fraction gas
Σ = summation operator
σ = standard deviation or standard error of estimate defined by:

$$\left[\sum_{1}^{N} (G_e - G_s)^2/(N - 1) \right]^{\frac{1}{2}}$$

Subscripts

c = chromatographic analysis
e = experimental
k = component
r = reference
s = smooth
1, 3, 4 = components methane, propane, and n-butane, respectively

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