Vapor-Liquid Equilibria

The System Methane-Propane–*n*-Butane at 100° F.

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The phase behavior for the ternary system methane–propane–*n*-butane at 100° F. has been investigated with the equipment tested on the methane–*n*-butane system at 100° F. (*4,5*). The cell includes a movable piston, hydraulically activated, which varies the volume of the equilibrium chamber and, consequently, the pressure of the system. Small samples of the coexisting vapor and liquid phases are withdrawn and analyzed by a mass spectrometer.

The gases were purchased from the Matheson Co., Inc. The methane was C.P. grade of 99.3% purity and the propane and *n*-butane were instrument grade of 99.9 and 99.7% purity, respectively. Mass spectrometer analyses showed the purities of these materials to be equal to or better than claimed.

The procedure for charging the cell, bringing its contents to equilibrium and withdrawing samples of the coexisting phases was essentially that described (*5*). Methane was charged into the cell as gas at 1000 p.s.i.a., while *n*-butane and propane were charged as liquids. The quantity of methane charged was accounted for by *P-V-T* data (*2*), while the densities of liquid *n*-butane and propane at the charging pressure and temperature were calculated from the liquid expansion factor correlation of Watson (*6*). Initially, methane and *n*-butane were charged in the proportion of 73 moles of methane to 27 moles of *n*-butane for the study of this binary system (*5*). To this charge, propane was added in four steps to produce overall compositions of approximately 0.09, 0.12, 0.18, and 0.27 mole fraction propane. After each charge, the pressure of the system was varied, and samples of the coexisting liquid and vapor phases were withdrawn at several pressures and analyzed. The pressure measurements were accurate within ±2 p.s.i. The temperature was known and controlled to within ±0.2° F. The analyses of the liquid and vapor phases were correct to within 0.005 mole fraction. Thermodynamic equilibrium was assumed to exist when the pressure of the system remained constant for 1 hour.

The experimental vapor-liquid equilibrium compositions resulting from the four charges are presented in Table I. The data for charge 2 are plotted in Figure 1 to produce the phase equilibrium relationships for methane, propane, and *n*-butane

Table I. Experimental Vapor-Liquid Equilibrium Data at 100° F.

Pressure, P.S.I.A.	Liquid Composition, Mole Fraction			Vapor Composition, Mole Fraction			Vapor-Liquid Equilibrium Constants			Composition Parameter, C
	Methane	Propane	*n*-Butane	Methane	Propane	*n*-Butane	Methane	Propane	*n*-Butane	
Charge 1										
735	0.228	0.133	0.638	0.830	0.059	0.111	3.64	0.442	0.173	0.173
959	0.304	0.136	0.560	0.847	0.055	0.098	2.78	0.403	0.176	0.195
1173	0.384	0.126	0.490	0.835	0.055	0.109	2.18	0.440	0.223	0.204
1368	0.459	0.120	0.421	0.835	0.056	0.109	1.82	0.465	0.260	0.221
1573	0.531	0.107	0.361	0.807	0.056	0.136	1.52	0.538	0.375	0.228
1655	0.562	0.097	0.341	0.803	0.060	0.138	1.43	0.615	0.404	0.221
Charge 2										
734	0.226	0.196	0.578	0.810	0.085	0.106	3.58	0.432	0.183	0.253
938	0.299	0.193	0.508	0.825	0.080	0.095	2.76	0.414	0.188	0.275
1135	0.362	0.184	0.454	0.823	0.081	0.096	2.27	0.439	0.211	0.288
1335	0.442	0.168	0.390	0.826	0.079	0.094	1.87	0.472	0.242	0.301
1455	0.482	0.162	0.356	0.811	0.080	0.109	1.68	0.492	0.305	0.312
1588	0.539	0.144	0.317	0.788	0.085	0.127	1.46	0.587	0.402	0.313
1623	0.558	0.145	0.297	0.786	0.087	0.127	1.41	0.596	0.429	0.328
1668	0.571	0.139	0.290	0.768	0.090	0.142	1.34	0.648	0.490	0.324
1705	0.607	0.133	0.260	0.751	0.095	0.154	1.24	0.714	0.591	0.339
1756	0.613	0.127	0.260	0.715	0.101	0.184	1.17	0.795	0.708	0.328
Charge 3										
745	0.221	0.325	0.454	0.767	0.149	0.084	3.47	0.458	0.186	0.417
993	0.315	0.319	0.366	0.782	0.138	0.080	2.49	0.433	0.218	0.466
1123	0.341	0.303	0.356	0.781	0.135	0.083	2.29	0.446	0.234	0.460
1405	0.465	0.260	0.274	0.766	0.140	0.093	1.65	0.540	0.339	0.487
1550	0.514	0.239	0.246	0.730	0.152	0.117	1.42	0.635	0.477	0.493
1595	0.550	0.224	0.227	0.712	0.159	0.128	1.30	0.714	0.565	0.496
1623	0.548	0.222	0.230	0.715	0.158	0.127	1.30	0.712	0.552	0.491
1628	0.584	0.209	0.207	0.633	0.189	0.178	1.08	0.905	0.859	0.502
Charge 4										
725	0.210	0.470	0.320	0.704	0.225	0.072	3.35	0.478	0.224	0.595
972	0.301	0.445	0.253	0.744	0.198	0.058	2.47	0.445	0.230	0.637
1256	0.408	0.381	0.211	0.736	0.198	0.066	1.80	0.519	0.316	0.644
1390	0.454	0.353	0.193	0.714	0.214	0.073	1.57	0.606	0.377	0.646
1447	0.496	0.326	0.178	0.675	0.233	0.093	1.36	0.715	0.520	0.640

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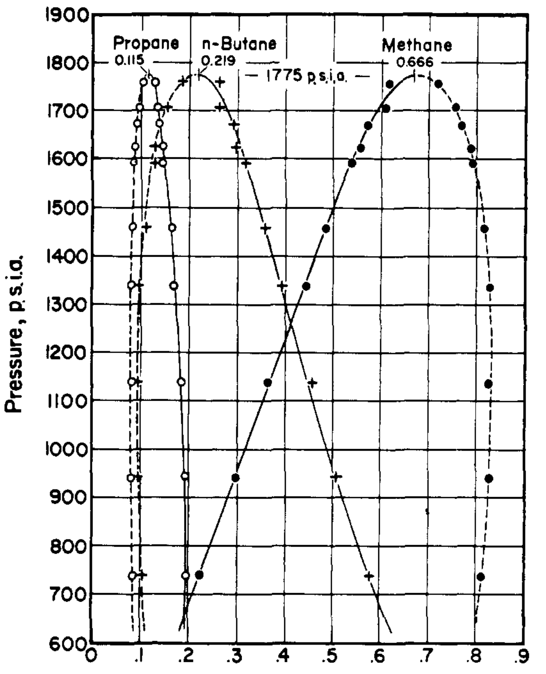

Figure 1. Vapor-liquid equilibrium compositions at 100° F. (Charge 2)

as a function of pressure. Similar plots prepared for the other three charges appear elsewhere (*4*). Values of the vapor-liquid equilibrium constant,

$$K_j = \frac{y_j}{x_j} \tag{1}$$

where x_j = mole fraction of jth component in liquid phase and y_j = mole fraction of jth component in vapor phase, resulting from the experimental data, are also presented in Table I, and are plotted against pressure in Figure 2. In this figure, the equilibrium constants obtained from each of the four charges produce separate families of curves. To present the limits of this ternary system, the binary systems methane-propane (*3*) and methane-*n*-butane (*5*) were included in Figure 2. Extrapolation of the curves of Figure 2 to $K = 1.0$ permits the estimation of the critical pressure of each charge. The compositions corresponding to these critical pressures were established from the extrapolation of the composition curves of Figure 1 and similar plots for the other charges (*4*). These critical pressures and compositions were made consistent through repeated adjustments of the smoothed composition and equilibrium constant curves and are presented in Table II. Figure 3 presents the critical composition as a function of critical pressure. The critical compositions presented in Table III were obtained for several pressures from an enlarged plot of Figure 3.

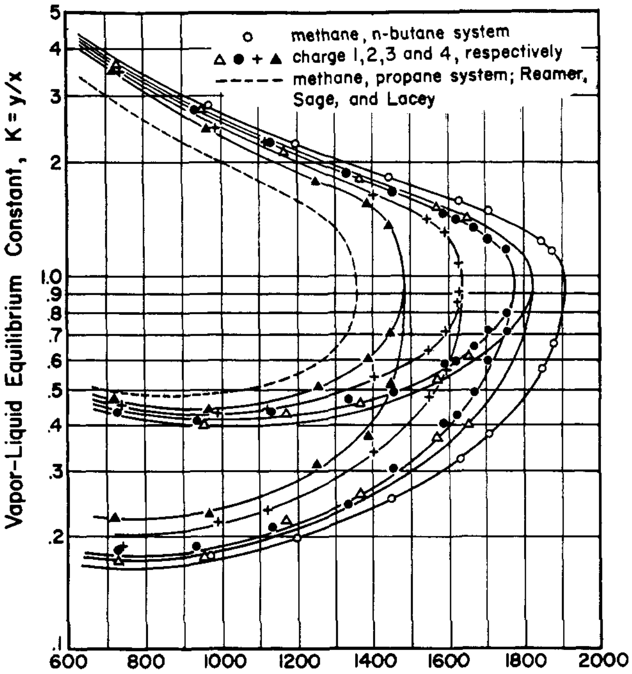

Figure 2. Vapor-liquid equilibrium constants at 100° F. resulting from five different cell charges

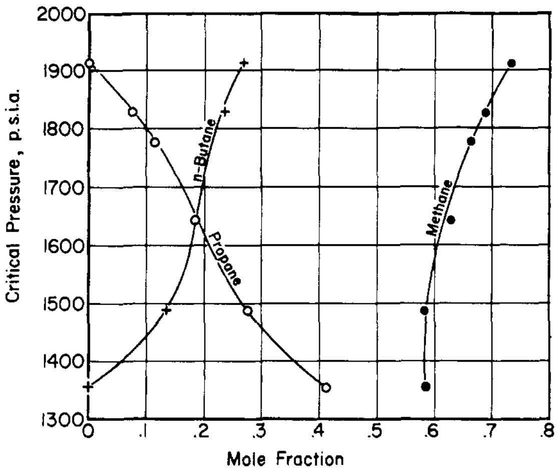

Figure 3. Critical pressure–composition relationship at 100° F.

The internal consistency of the results was satisfactory for all charges. The results for charge 2 shown in Figure 1 exhibited an average deviation from the smoothed curves of 0.003 mole fraction. The maximum deviation was found to be 0.006 mole fraction for methane in the liquid phase while the minimum deviation was 0.001 mole fraction for propane in the vapor phase.

Table II. Critical Constants at 100° F. Resulting from Four Cell Charges

Charge	Critical Pressure, P.S.I.A.	Composition at Critical Pressure, Mole Fraction			Composition Parameter, *C*
		Methane	Propane	*n*-Butane	
1	1825	0.690	0.075	0.235	0.242
2	1775	0.666	0.115	0.219	0.344
3	1640	0.630	0.185	0.185	0.500
4	1485	0.587	0.278	0.135	0.673

Table III. Critical Constants at 100° F.

Critical Pressure, P.S.I.A.	Composition at Critical Pressure, Mole Fraction			Composition Parameter, *C*
	Methane	Propane	*n*-Butane	
1353[a]	0.588	0.412	0.000	1.000
1370	0.584	0.392	0.024	0.966
1400	0.582	0.358	0.060	0.877
1450	0.585	0.308	0.107	0.742
1500	0.589	0.267	0.144	0.650
1550	0.598	0.237	0.165	0.589
1600	0.610	0.211	0.179	0.541
1650	0.623	0.188	0.189	0.500
1700	0.638	0.162	0.200	0.447
1750	0.654	0.139	0.207	0.379
1800	0.677	0.101	0.222	0.313
1850	0.702	0.059	0.239	0.198
1900	0.727	0.013	0.260	0.048
1910[b]	0.735	0.000	0.265	0.000

[a] Reamer, Sage and Lacey (*3*).

[b] Rigas, Mason and Thodos (*5*).

The application of Gibbs' phase rule to a ternary system requires, besides temperature and pressure, one more intensive property for complete definition of the system. Thus, any parameter which imposes a restriction on the composition of the vapor or liquid phase besides temperature and pressure suffices to define the system. The composition parameter of Sage, Carter, and Lacey (*1*),

$$C = \frac{x_i}{x_i + x_h} \qquad (2)$$

was adopted. In Equation (2), x_i represents the mole fraction of the component of intermediate volatility in the liquid phase while x_h represents the mole fraction of the heavy component in the liquid phase.

The curves of Figures 1 and 2 do not exactly represent lines of constant composition parameter. This is to be expected because the experimental procedure involved the successive compression of the coexisting vapor and liquid phases. During this operation, the composition and relative amounts of each phase adjusted themselves to the new pressure—the composition parameter increased slightly with pressure. The calculated composition parameters corresponding to the data are tabulated in Table I.

The composition parameters resulting from the critical compositions presented in Figure 3, are plotted against critical pressure in Figure 4. The values of these composition parameters are also included in Tables II and III. The relationship of Figure 4 is nonlinear and possesses a point of inflection at approximately $C = 0.5$.

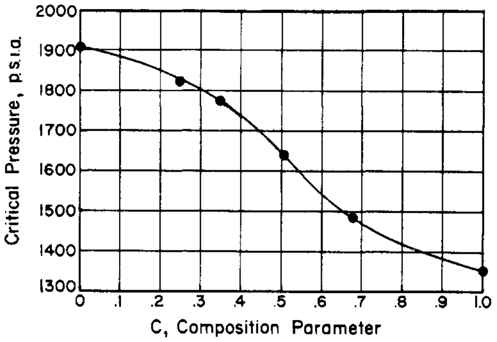

Figure 4. Critical pressure–composition parameter relationship for the methane–propane–*n*-butane system at 100° F.

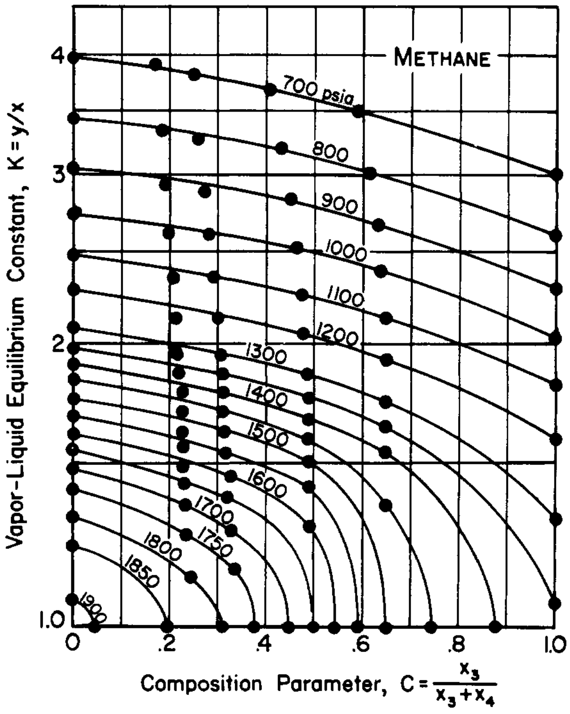

Figure 5. Relationships of vapor-liquid equilibrium constants and composition parameter for methane at 100° F.

The vapor-liquid equilibrium constants for a ternary system depend upon composition as well as temperature and pressure, so it becomes necessary to include the effect of composition for their correlation. Equilibrium compositions from the smoothed curves of Figure 1 and similar figures for charges 1, 3, and 4(*4*) were used to calculate equilibrium constants and composition parameters at fixed pressures ranging from 700 p.s.i.a. to the critical pressure of each charge. This procedure was adopted to construct the relationship of *K vs. C* with parameters of constant pressure for methane, propane, and *n*-butane. The resulting correlation for methane is presented in Figure 5. The equilibrium constant values at C = O and C = 1.0 represent the binary systems, methane-*n*-butane and methane-propane, respectively. The pressures and composition parameters corresponding to K = 1.0 represent the critical constants of the methane-propane-*n*-butane system obtained

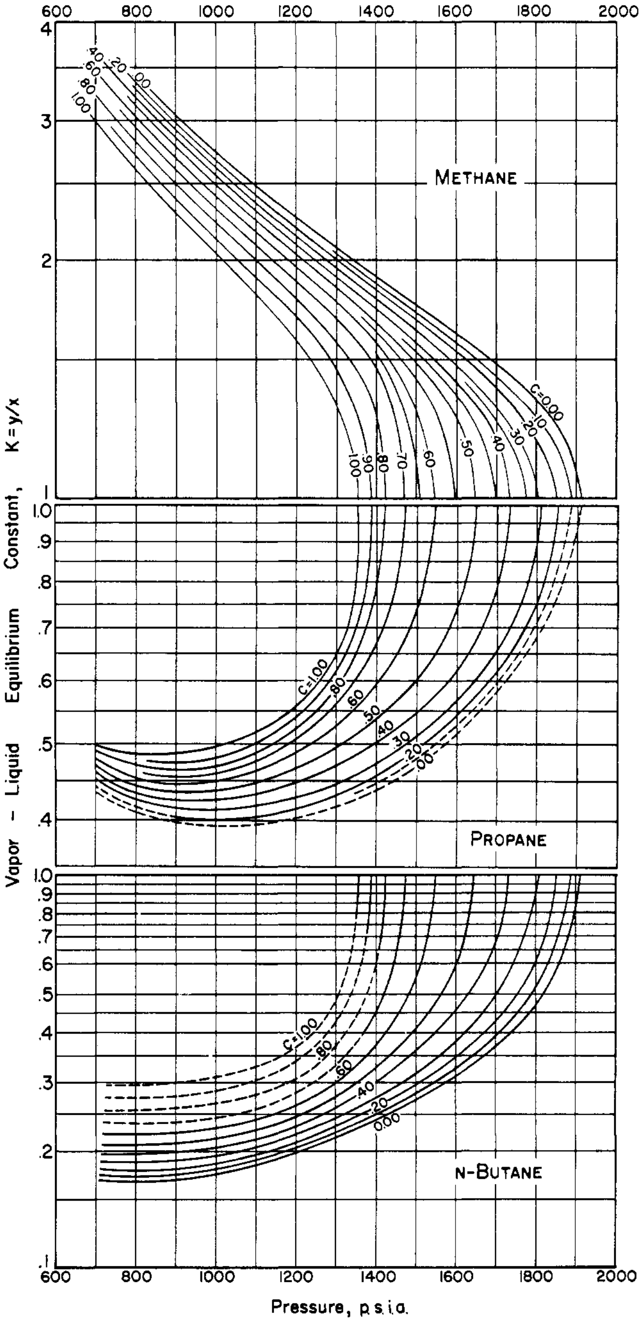

Figure 6. Vapor-liquid equilibrium constants at 100° F.

from Figure 4. The dependence of the equilibrium constant on composition is clearly shown in Figure 5. If the equilibrium constants were independent of composition, the constant pressure lines would have been horizontal. With decreasing pressure, this condition is approached. However, even the lowest pressure of 700 p.s.i.a. exhibited a marked slope. The maximum deviations obviously occur in the critical region.

Cross plots of Figure 5 and similar plots using constant composition parameters produced Figure 6. This figure presents the equilibrium constant as a function of pressure for constant composition parameters at 100° F. The extrapolated portions of Figure 6 represent regions in which the data were extrapolated to limiting compositions of zero mole fraction for propane and *n*-butane. For propane the extrapolation was made in a region where the ratio of propane to *n*-butane is small, and for *n*-butane, this extrapolation covers a range having a small *n*-butane to propane ratio. Consequently, even large errors in these extrapolated equilibrium constants will have a very small effect on the resulting vapor and liquid compositions.

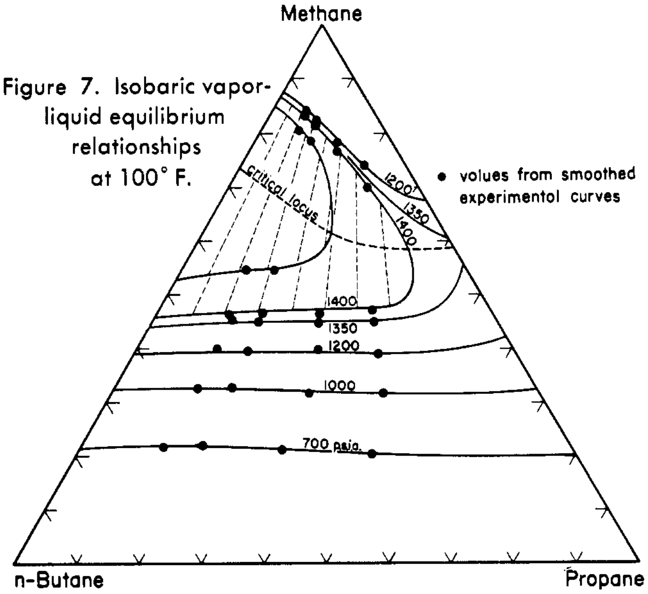

Figure 7. Isobaric vapor-liquid equilibrium relationships at 100° F.

Figure 6 was used to calculate the composition of the coexisting phases at constant pressures and varying composition parameters. Figure 7 presents on a triangular plot the phase behavior of the methane-propane-*n*-butane system at different pressures. The solid lines represent the results from the equilibrium constants of Figure 6, whereas the dots represent points obtained from the smoothed curves such as presented in Figure 1. These calculated values and smoothed experimental data are in good agreement and offer a good proof of satisfactory internal consistency and manipulation of the data.

ACKNOWLEDGMENT

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CORRECTION

In "Vapor-Liquid Equilibria: Microsampling Technique Applied to a New Variable Volume Cell" [T. J. Rigas, D. F. Mason, and George Thodos, *Ind. Eng. Chem.* **50,** 1297 (1958)] all pressures concerned with the experimental investigation should be increased by 15 p.s.i.a. This change brings the data of this study and those of Sage, Hicks and Lacey within the designated experimental error.

Partial Volumetric Behavior in Hydrocarbon Systems

Methane-Cyclohexane System in the Liquid Phase

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The concept of partial thermodynamic properties was perhaps first originated by Lewis (*4*), and it has been found that, in the course of many engineering operations, a knowledge of the partial volumetric behavior of the components of binary and multicomponent systems is useful for the prediction of the behavior of fluid systems of industrial interest (*12,13*). This is particularly true in connection with the evaluation of diffusion coefficients from experimental data (*8*) and the application of such coefficients to the prediction of material transport (*7*) under conditions involving a concentration gradient.

As a part of a study of the transport of methane in the liquid phase of the methane-cyclohexane system, measurements of the volumetric behavior of four mixtures of methane and cyclohexane were made (*10*). In addition, adequate volumetric data concerning the behavior of methane (*2,3,5,6*) and of cyclohexane (*9*) were available. These measurements were used as the basis for the evaluation of the partial volumetric behavior of methane and cyclohexane in the liquid phase of the methane-cyclohexane system.

METHODS AND PROCEDURE

The calculations were carried out using the method of graphical intercepts proposed by Roozeboom (*11*). By application of this method, curves of variation in molal volume with respect to mole fraction for isobaric, isothermal conditions were prepared for each of the several temperatures of interest. The intercept of a tangent to this curve at each of the several compositions of interest was determined, thus yielding directly the partial molal volume (hereafter referred to as partial volume) of the components. In this instance, the partial volume of each of the components may be established from

$$\overline{V}_k = V + (1 - n_k)\left(\frac{\partial V}{\partial n_k}\right)_{T,P} \qquad (1)$$

In the application of this method the uncertainties in the evaluation of the partial volumes increase rapidly as the mole fraction of the component decreases.