Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Vapor-Liquid Equilibrium in the *n*-Butane–Methane–Nitrogen System

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Experimental data were obtained in this hydrocarbon–nitrogen system at 100, 160, 220, and 280° F. At each temperature the two-phase diagram of the ternary system was defined at intervals of 500 p.s.i., starting at 500 and extending up to 3000 p.s.i.a. or the critical pressure, whichever was lower. K-values are presented showing quantitatively how the K-values of methane and *n*-butane change when varying amounts of nitrogen are added to mixtures of the two hydrocarbons.

BECAUSE hydrocarbon mixtures often contain appreciable amounts of nitrogen, it is interesting to know how the vapor-liquid equilibrium ratios of the hydrocarbons are affected by the presence of this impurity. This investigation shows quantitatively how the K-values of methane and *n*-butane change when varying amounts of nitrogen are added to mixtures of the two hydrocarbons.

EXPERIMENTAL

The experimental apparatus and procedures for this work have been described earlier (*3*, *6*). Essentially, equilibrium between the vapor and the liquid was attained by circulating the vapor from the upper part of a windowed high-pressure cell through a magnetic–piston pump and back into the bottom of the cell so that the vapor bubbled up through the liquid. The equilibrium fluids were allowed to stand undisturbed for 1 hr. before being sampled to ensure complete separation of the phases. The experimental work was conducted at each of four temperatures—100, 160, 220, and 280° F.—the two-phase diagram of the ternary system was defined at intervals of 500 p.s.i,, starting at 500 and extending up to 3000 p.s.i.a. or the critical pressure, whichever was lower.

The samples obtained at each different set of conditions of temperature, pressure, and composition were analyzed by either mass spectrometry or gas chromatography. Instrumental calibrations were checked frequently, and the equivalence of the two methods was also checked by comparison from time to time.

The experiments were performed at constant temperatures, and the pressure of each experiment was controlled by the amounts of the components added to the equilibrium cell. In addition, mercury could be injected into or removed from the cell to change the pressure. Over-all composition of the mixture in the cell could, of course, be varied independently of the pressure.

The *n*-butane used was instrument grade with a minimum purity of 99.5 mole per cent, the methane was pure grade with a minimum purity of 99 mole per cent, and the nitrogen was o.p. grade with a minimum purity of 99.9 mole per cent. The principal impurity of the methane was nitrogen.

RESULTS

The analyses of all the equilibrium samples obtained in this investigation are shown in Table I and Figure 1.

Two features of the diagrams of Figure 1 for this particular system are of interest. The first is the concavity exhibited by the liquid surfaces of the two-phase envelopes. The second feature is the perfectly straight isobaric outlines of the two-phase envelopes on the vapor surfaces below the critical pressures of the methane–*n*-butane binary systems.

The ternary data should of course approach the binary data as the ternary mixtures become leaner in one of the components. At 100° F. the data of this work showed excellent agreement with data published for the binary systems *n*-butane–nitrogen (*1*) and *n*-butane–methane (*5*). However, at higher temperatures some serious discrepancies were encountered.

On the *n*-butane–nitrogen side there was a general disagreement. For this reason this binary system was investigated, and data were obtained which were in excellent

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Table I. Analysis of Equilibrium Samples

Temp., °F.	Press., P.S.I.A.	Concentration, Mole Fraction: Vapor Phase n-C_4	Vapor Phase C_1	Vapor Phase N_2	Liquid Phase n-C_4	Liquid Phase C_1	Liquid Phase N_2
100	500	0.150	0.434	0.416	0.895	0.074	0.031
		0.149	0.691	0.160	0.856	0.131	0.013
		0.154	0.187	0.659	0.918	0.040	0.042
	1000	0.112	0.480	0.408	0.774	0.164	0.062
		0.110	0.327	0.563	0.809	0.113	0.078
		0.115	0.609	0.276	0.746	0.214	0.044
		0.121	0.808	0.071	0.689	0.300	0.011
	1500	0.109	0.344	0.547	0.731	0.165	0.104
		0.114	0.475	0.411	0.661	0.242	0.097
		0.128	0.708	0.164	0.567	0.384	0.049
		0.096	0.246	0.658	0.746	0.115	0.139
	2000	0.151	0.523	0.326	0.519	0.348	0.133
		0.141	0.564	0.295	0.507	0.373	0.120
		0.152	0.638	0.210	0.451	0.456	0.093
		0.183	0.720	0.097	Single phase		
		0.168	0.698	0.134	0.430	0.497	0.073
		0.143	0.624	0.233	0.462	0.434	0.104
		0.133	0.540	0.327	...	...	...
		0.113	0.233	0.654	0.663	0.137	0.200
		0.110	0.249	0.641	0.650	0.149	0.201
		0.117	0.280	0.603	...	...	...
		0.302	0.639	0.059	Single phase		
	2500	0.129	0.269	0.602	0.546	0.196	0.258
		0.146	0.399	0.455	0.456	0.302	0.242
		0.161	0.455	0.384	...	...	...
		0.191	0.536	0.273	Single phase		
		0.175	0.472	0.353	0.400	0.379	0.221
		0.163	0.464	0.373	0.404	0.371	0.225
		0.155	0.429	0.416	0.429	0.338	0.233
	3000	0.134	0.119	0.747	0.538	0.092	0.370
		0.158	0.167	0.675	0.508	0.136	0.356
		0.167	0.234	0.599	0.450	0.195	0.355
160	500	0.338	0.334	0.328	0.907	0.067	0.026
	1000	0.239	0.409	0.352	0.807	0.137	0.056
		0.228	0.132	0.640	0.869	0.039	0.092
		0.230	0.073	0.697	0.883	0.022	0.095
		0.235	0.043	0.722	0.884	0.013	0.103
	1500	0.218	0.249	0.533	0.750	0.117	0.133
		0.235	0.295	0.470	0.733	0.143	0.124
		0.228	0.386	0.386	0.699	0.192	0.109
		0.242	0.490	0.268	0.661	0.257	0.082
		0.252	0.570	0.178	0.639	0.301	0.060
		0.245	0.561	0.194	0.642	0.296	0.062
	2000	0.286	0.499	0.215	Single phase		
		0.281	0.462	0.257	0.554	0.323	0.123
		0.285	0.440	0.275	0.560	0.307	0.133
		0.281	0.432	0.287	0.578	0.291	0.131
		0.291	0.487	0.222	0.535	0.356	0.109
		0.217	0.122	0.661	0.713	0.070	0.217
		0.237	0.267	0.496	0.650	0.158	0.192
		0.267	0.376	0.357	0.600	0.245	0.155
		0.292	0.415	0.293	0.570	0.290	0.140
	2500	0.347	0.237	0.416	0.507	0.203	0.290
		0.423	0.233	0.344	Single phase		
		0.265	0.095	0.640	0.630	0.067	0.303
		0.313	0.213	0.474	0.543	0.166	0.291
		0.318	0.232	0.450	0.531	0.189	0.280
220	500	0.604	0.0	0.396	0.952	0.0	0.048
		0.588	0.273	0.139	0.934	0.051	0.015
		0.602	0.356	0.042	0.918	0.078	0.004
		0.601	0.143	0.256	0.942	0.029	0.029
	1000	0.449	0.516	0.035	0.758	0.236	0.006
		0.439	0.358	0.203	0.810	0.144	0.046
		0.444	0.284	0.272	0.834	0.098	0.068
		0.440	0.310	0.250	0.810	0.129	0.061
		0.428	0.232	0.340	0.833	0.088	0.079
	1500	0.415	0.162	0.423	0.730	0.089	0.181
		0.395	0.129	0.475	0.739	0.073	0.188
		0.417	0.218	0.365	0.720	0.122	0.158
		0.407	0.200	0.393	...	...	...
		0.466	0.353	0.181	0.639	0.254	0.107
		0.510	0.362	0.128	Single phase		
		0.401	0.218	0.381	...	...	...
		0.430	0.280	0.290	0.673	0.188	0.139
		0.470	0.354	0.176	0.628	0.265	0.107
		0.455	0.357	0.188	0.640	0.246	0.114
		0.523	0.357	0.120	Single phase		
		0.513	0.363	0.124	Single phase		
280	500	0.943	0.014	0.043	0.989	0.002	0.009
		0.940	0.016	0.044	0.987	0.004	0.009
	800	0.770	0.192	0.038	0.883	0.101	0.016
		0.769	0.106	0.125	0.904	0.046	0.050
	1000	0.754	0.080	0.166	0.849	0.052	0.099
		0.746	0.071	0.183	0.849	0.041	0.110

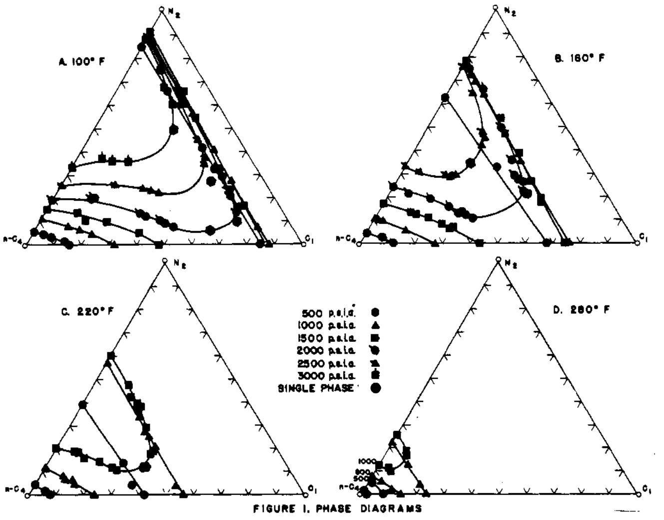

Figure 1. Phase diagrams

A. 100° F. C. 220° F.
B. 160° F. D. 280° F.

agreement with the ternary data (*4*). On the *n*-butane–methane side only one discrepancy was encountered at 220° F. in the critical region of the binary system. In Figure 1 *C*, the 1500 p.s.i.a. isobar exhibits a critical ternary mixture substantially removed from the binary surface and 20 p.s.i. below the reported critical pressure of the binary. An investigation of the *n*-butane–methane binary system produced data which substantiated the ternary data (*3*).

The data in Table I were also plotted on a *y*-*x* graph and a series of smooth curves was drawn through the data points. The smoothed values were then transferred back to triangular plots similar to those in Figure 1. From these smoothed graphs were taken the values used to produce the curves in Figures 2 through 5. Here the familiar K-value graphs are shown, with constant nitrogen content in the vapor phase serving as the parameter (*5*).

Notice in Figure 2 that the K-values of methane decrease with increasing nitrogen concentration at 500 p.s.i.a., but that they reverse this trend above 1500 p.s.i.a. The same behavior is observed at 160° F. (Figure 3) to a lesser extent but not at higher temperatures. This behavior is attributed to the difference in solubility of the methane and nitrogen in the liquid phase. As the temperature and pressure increase this difference becomes less and less, and the K-values behave more like those of mixtures of chemically similar compounds (*2*).

Accuracy. The accuracy of the indicated pressure is ±4 p.s.i.a. Other sources of error include temperature variations

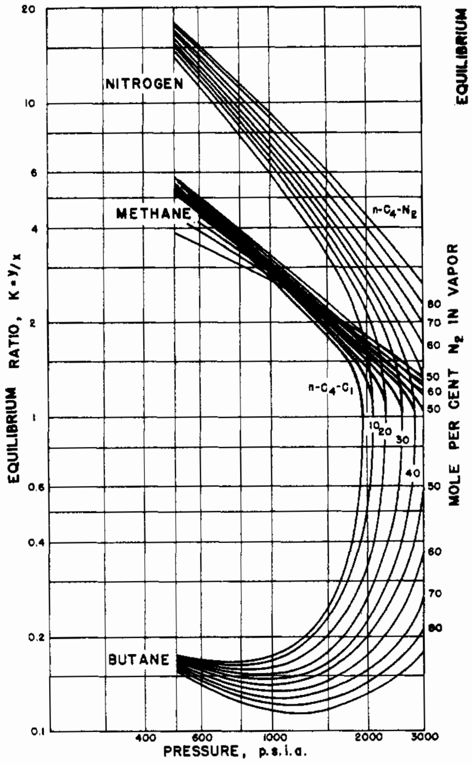

Figure 2. K values at 100° F.

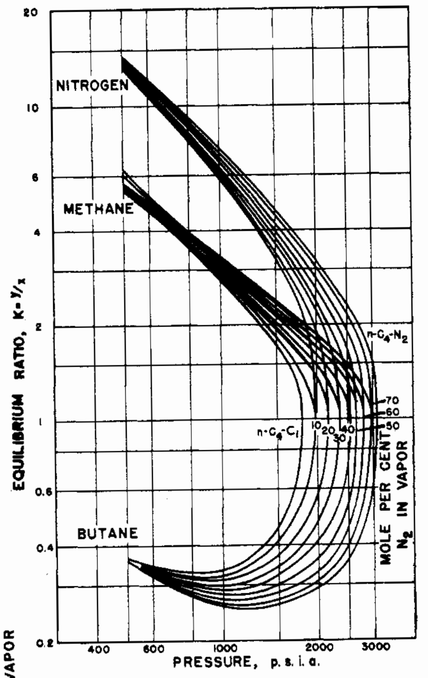

Figure 3. K values at 160° F.

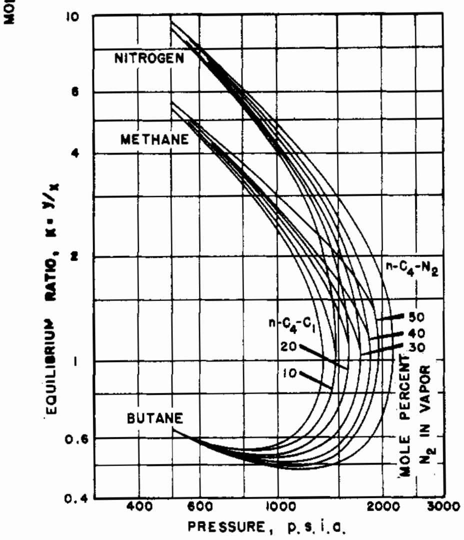

Figure 4. K values at 220° F.

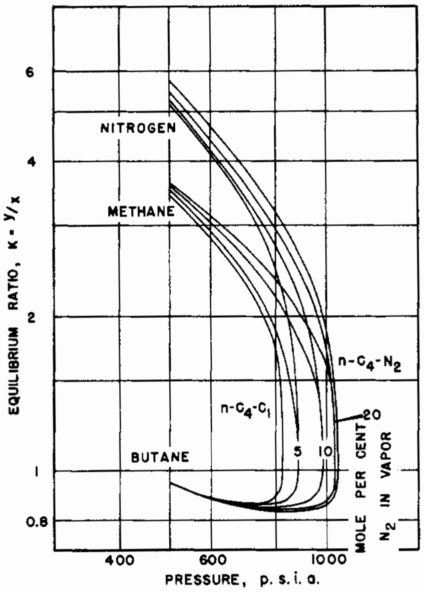

Figure 5. K values at 280° F.

during recirculation differences in sampling procedures and pressure gage readings, as well as analytical errors. Consideration of the analytical procedure shows that the anlyses are reliable to within 0.002 mole fraction. The maximum temperature variation within the cell during recirculation was ±0.2° F. and ±0.1° F. during the settling and sampling time.

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