Vapor-Liquid Equilibria for the Ethane-Propane System

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PHASE BEHAVIOR of the ethane-propane system has been experimentally examined at six temperatures between 100° and 200° F. and at pressures ranging up to the critical locus (*3*). Price (*4*) reports experimental equilibria data for this system at 0° and 50° F. To provide a complete presentation, the data of Price have been included with the present study.

The experimental equipment used in this investigation has been described (*5, 6, 7*). The basic feature of the equipment resides in an equilibrium cell, which includes a mercury-driven piston that can be made to vary the volume of the equilibrium chamber and thereby control the pressure of the system. Because of a special sampling design, coexisting vapor and liquid microsamples were obtained, thus permitting an extensive experimental coverage from a single charge. The samples were analyzed with a mass spectrometer.

To minimize temperature gradients in the air bath surrounding the equilibrium cell, two electrically driven high-speed fans were provided, which allowed the maximum over-all temperature gradient on the cell to be held within 0.4° F. Temperatures within the cell were controlled to ±0.2° F. The pressure could be read to ±2 p.s.i. The accuracy of the mass spectrograph analysis was calculated, based on the minimum reliabilities of the recorded peak values, to be within 0.005 mole fraction.

The ethane and propane used were research grade hydrocarbons supplied by the Phillips Petroleum Co. The certified purities were 99.9% for ethane and 99.99% for propane.

The equilibrium constants resulting from the experimental data were related to the pressure of the system to obtain smoothed equilibrium-constant (K) values. This was accomplished by establishing plots of log PK *vs.* P for each temperature, as well as plots of log K *vs.* log P. Both of these methods of representation have advantages from the standpoint of aligning data. The first of these methods produces curves with small slopes which tend to approach zero as the pressure approaches zero, while the second method of representation produces relationships with slopes approaching −1 as the pressure again approaches zero. These plots were then both applied to the alignment of the K values subsequently herein reported. This information was in turn used to adjust the experimental vapor-liquid equilibrium compositions to maintain internal consistency. These aligned results are listed in Table I and are also presented graphically in Figures 1, 2, and 3. The critical temperatures and pressures established in this study are given in Table II and also appear in Figures 1 and 2. The critical pressure locus was approved along a constant temperature path by carefully adjusting the over-all cell composition and pressure. The resulting data were then analyzed to show where the bubble point and dew point lines converged, thus establishing both the critical pressure and composition corresponding to this constant temperature, which then automatically becomes the critical temperature of this mixture.

The experimental data of Price (*4*), which were limited to 0° and 50° F., are presented in Table III and are also included in Figures 1, 2, 3. Using the smoothing technique already outlined, the values presented in Table I were obtained and were used to produce the dashed curves of Figures 1 and 3. These curves do not necessarily pass through all the data points of Price. In Tables I and III, the vapor pressures of ethane were obtained from the work of Barkelew, Valentine, and Hurd (*1*); the vapor pressure data for propane were procured from the work of Stearns and George (*8*). The pure component critical temperatures and pressures presented in Table II were obtained from the compilation of Lydersen, Greenkorn, and Hougen (*2*).

For the total of approximately 70 sets of equilibrium data, the K values calculated from the experimental results showed an average deviation of 1.0% from the corresponding smoothed K's; 10% of these equilibrium constants exhibited deviations in excess of 3%, with a maximum of 9.8%. Similarly, the average deviation of the experimental equilibrium compositions was found to be 0.003

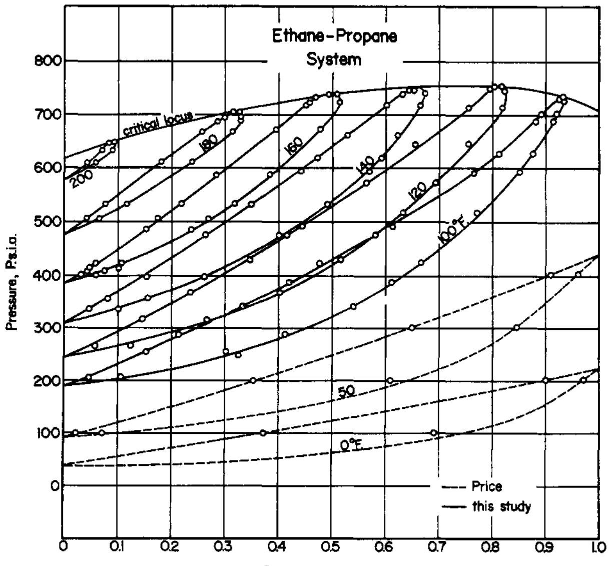

Figure 1. Pressure-composition diagram

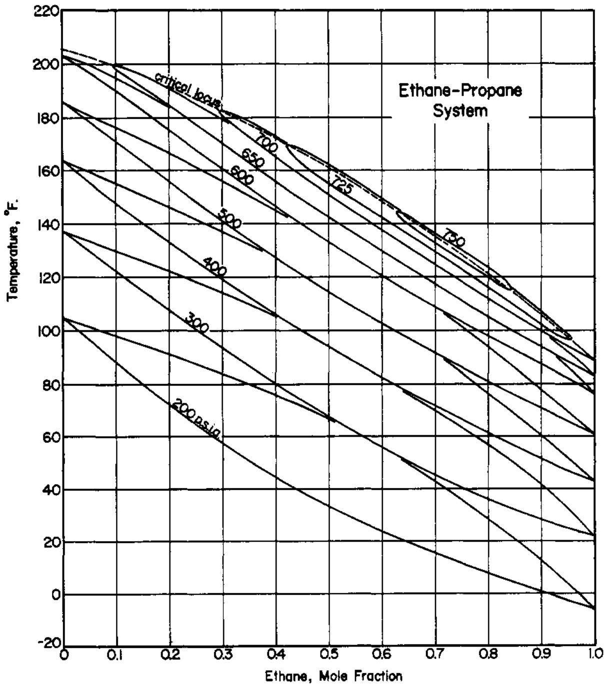

Figure 2. Temperature-composition diagram

Table I. Smoothed Equilibrium Compositions and Equilibrium Constants

Pressure, P.S.I.A.	Ethane, Mole Fraction		K	
	x_2	y_2	Ethane	Propane
		100° F.		
188.7[a]	0	0	2.66	1.00
200	0.0313	0.0789	2.52	0.951
250	0.149	0.310	2.08	0.811
300	0.255	0.455	1.79	0.732
350	0.353	0.558	1.58	0.683
400	0.447	0.638	1.43	0.655
450	0.535	0.704	1.32	0.636
500	0.622	0.764	1.23	0.625
550	0.705	0.816	1.16	0.624
600	0.781	0.861	1.10	0.635
650	0.843	0.894	1.06	0.672
700	0.895	0.922	1.03	0.739
725	0.919	0.935	1.02	0.825
731.5[b]	0.935	0.935	1.00	1.000
		120° F.		
243.4[a]	0	0	2.36	1.00
250	0.0130	0.0300	2.31	0.983
300	0.116	0.230	1.98	0.871
350	0.209	0.366	1.75	0.802
400	0.297	0.468	1.58	0.757
450	0.379	0.548	1.45	0.728
500	0.457	0.614	1.34	0.711
550	0.533	0.672	1.26	0.702
600	0.607	0.726	1.20	0.697
650	0.678	0.773	1.14	0.706
700	0.745	0.815	1.09	0.727
725	0.773	0.826	1.07	0.767
750	0.801	0.821	1.025	0.899
752.0[b]	0.810	0.810	1.00	1.000
		140° F.		
308.4[a]	0	0	2.21	1.00
350	0.0711	0.140	1.97	0.926
400	0.152	0.267	1.76	0.864
450	0.230	0.367	1.60	0.822
500	0.305	0.448	1.47	0.794
550	0.378	0.515	1.36	0.780
600	0.448	0.573	1.28	0.774
650	0.515	0.618	1.20	0.788
700	0.581	0.655	1.13	0.823
725	0.613	0.672	1.10	0.848
750	0.652	0.670	1.03	0.947
752.0[b]	0.6685	0.6685	1.00	1.000
		160° F.		
385.0[a]	0	0	1.97	1.00
400	0.0253	0.0480	1.90	0.977
450	0.104	0.176	1.70	0.920
500	0.174	0.270	1.55	0.884
550	0.241	0.343	1.42	0.866
600	0.305	0.403	1.32	0.859
650	0.369	0.457	1.24	0.861
700	0.432	0.502	1.16	0.877
725	0.463	0.516	1.11	0.901
738.0[b]	0.506	0.506	1.00	1.000
		180° F.		
473.2[a]	0	0	1.69	1.00
500	0.0356	0.0570	1.60	0.978
525	0.0693	0.106	1.53	0.961
550	0.102	0.149	1.46	0.948
575	0.135	0.188	1.39	0.939
600	0.168	0.225	1.34	0.931
625	0.201	0.262	1.30	0.924
650	0.235	0.294	1.25	0.923
675	0.270	0.324	1.20	0.926
700	0.309	0.331	1.07	0.968
705.0[b]	0.3215	0.3215	1.00	1.000
		200° F.		
575.0[a]	0	0	1.47	1.00
580	0.0065	0.0095	1.46	0.997
590	0.0193	0.0275	1.42	0.992
600	0.0320	0.0446	1.39	0.987
610	0.0445	0.0602	1.35	0.983
620	0.0566	0.0742	1.31	0.981
630	0.0682	0.0869	1.27	0.980
640	0.0791	0.0949	1.20	0.983
645	0.0846	0.0953	1.13	0.988
648.4[b]	0.0930	0.0930	1.00	1.000
		Data of Price (*4*)		
		0° F.		
37.8[a]	0	0	5.07	1.00
50	0.0785	0.304	3.87	0.755
100	0.373	0.743	1.99	0.410
150	0.646	0.891	1.38	0.308
200	0.901	0.972	1.08	0.287
219.7[c]	1.000	1.000	1.00	1.00
		50° F.		
91.5[a]	0	0	3.62	1.00
100	0.031	0.104	3.34	0.925
150	0.195	0.454	2.33	0.678
200	0.357	0.646	1.81	0.550
250	0.507	0.763	1.50	0.480
300	0.651	0.848	1.30	0.434
350	0.781	0.905	1.16	0.430
400	0.911	0.961	1.06	0.442
437.5[c]	1.000	1.000	1.00	1.000

[a] Vapor pressure of propane (*8*). [b] Critical point. [c] Vapor pressure of ethane (*1*).

mole fraction from the corresponding smoothed values. Again, 10% of these equilibrium compositions were found to deviate in excess of 0.010 mole fraction, with a maximum deviation of 0.027 mole fraction.

The majority of the deviations fall within the expected uncertainty of the mass spectrograph analyses. The larger deviations were primarily encountered at low pressures, where the uncertainty in their measurement contributes signficantly in producing these deviations. For pressures near the critical point, slow equilibrium responses contributed to an occasional deviation of significance.

Table II. Critical Temperatures and Critical Pressures

Ethane Mole Fraction	Critical Temp., ° R.	Critical Pressure, P.S.I.A.
0[a]	665.8	617.4
0.10	659.5	651
0.20	651.5	678
0.30	642.2	701
0.40	632.0	721
0.50	620.8	737
0.60	608.7	748
0.70	595.6	753
0.80	581.3	753
0.90	565.6	741
1.00[a]	549.7	708.5

[a] Critical points for ethane and propane (*2*).

Table III. Experimental Equilibrium Data of Price (*4*) for Ethane-Propane System at 0° and 50° F.

Pressure, P.S.I.A.	Ethane, Mole Fraction		K	
	x_2	y_2	Ethane	Propane
		0° F.		
37.8[a]	0	0	. . .	1.000
100	0.373	0.692	1.85	0.491
200	0.9013	0.9717	1.08	0.287
219.7[b]	1.00	1.000	1.00	1.000
		50° F.		
91.5[a]	0	0	. . .	1.000
100	0.0236	0.0720	3.05	0.951
200	0.357	0.612	1.72	0.603
300	0.651	0.848	1.30	0.434
400	0.9108	0.9606	1.05	0.442
437.5[b]	1.000	1.000	1.00	1.000

[a] Vapor pressure of propane (*8*). [b] Vapor pressure of ethane (*1*).

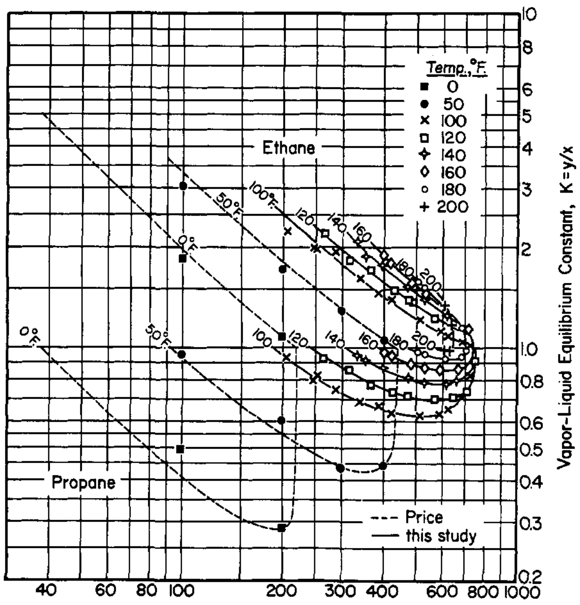

Figure 3. Vapor-liquid equilibrium constants

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for the support which made this study possible. Appreciation is also extended to T.W. Legatski of the Phillips Petroleum Co. for his interest and for the contribution of the hydrocarbons used.

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RECEIVED for review October 9, 1961. Accepted December 19, 1961.

Lennard-Jones Force Constants Predicted from Critical Properties

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EQUATIONS developed by Hirschfelder, Curtiss, and Bird (*4*) for the calculation of the transport properties of nonpolar gases at moderate pressures have found widespread application. These equations were developed using the Lennard-Jones force potential,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (1)$$

as the proper expression of the intermolecular forces between the molecules; and consequently, the equations require the Lennard-Jones force constants, ϵ/κ and σ, for the calculation of viscosity, thermal conductivity, and self-diffusivity. These equations can be expressed as follows:

$$\mu = 2.6693 \times 10^{-5}\,\frac{(MT)^{1/2}}{\sigma^2\Omega^{(2,2)*}[T_N]} \quad (2)$$

$$k = 19.891 \times 10^{-5}\,\frac{(T/M)^{1/2}}{\sigma^2\Omega^{(2,2)*}[T_N]} \quad (3)$$

$$\Delta = 262.80 \times 10^{-5}\,\frac{(T^3/M)^{1/2}}{\pi\sigma^2\Omega^{(1,1)*}[T_N]} \quad (4)$$

where $\Omega^{(1,1)*}[T_N]$ and $\Omega^{(2,2)*}[T_N]$ are tabulated functions of the normalized temperature, $T_N = T/(\epsilon/\kappa)$.

The Lennard-Jones force constants required in these equations can be obtained from either second virial coefficients or from viscosity data for gases. Hirschfelder, Bird, and Spotz (*3*) compare force constants obtained from both methods for a number of common substances. Equations 2, 3, and 4 can be applied only to those substances for which experimental *P-V-T* data and/or viscosities are available for the establishment of the force constants. Because of this limitation, several attempts have been made to relate the force constants of a substance to its critical properties. Bird, Stewart, and Lightfoot (*1*) present the following relationships between the Lennard-Jones force constants and the critical properties of a substance, which were developed from semitheoretical considerations:

$$\epsilon/\kappa = 0.77\,T_c \quad (5)$$

and

$$\sigma = 0.841\,v_c^{1/3} \quad (6)$$

Flynn (*2*) has calculated Lennard-Jones force constants from viscosity data for 16 hydrocarbons for which reliable experimental viscosities are available, including the normal paraffins up to nonane, olefins, acetylenes, naphthenes, and aromatics. These values and those determined from viscosity data by Hirschfelder, Curtiss, and Bird (*4*) for 11 nonhydrocarbon substances, including the inert and diatomic gases, carbon dioxide, and carbon tetrachloride, were used to compare the Lennard Jones force constants resulting from Equations 5 and 6. The data used in these calculations are presented in Table I. An average deviation of 20.4% resulted for the temperature force constant, ϵ/κ, and 4.6% for σ, the collision diameter.