

Vapor-Liquid Equilibrium Data for Ethane-Propane System at Low Temperatures

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Vapor-liquid equilibrium data were obtained experimentally at 0°, -50°, -100°, -150°, -200°, and -230° F., using a specially designed apparatus suitable for low-temperature phase-equilibrium studies. At -230° F., the system exhibits behavior undistinguishable from the ideal solution, and for all practical purposes it may be considered as ideal, even at -200° F.

AN EXPERIMENTAL study of vapor-liquid equilibrium of the ethane-propane system at low temperatures was conducted as part of an over-all effort to study thermophysical properties of natural gas and its components, needed for design of liquefaction systems and storage facilities for liquefied natural gas. The vapor-liquid equilibrium data for the ethane-propane system at temperatures above 0° F. have been reported by Matschke (2) and Price (3).

EXPERIMENTAL

Research grade ethane and propane purchased from the Matheson Co., Inc., were used, with the guaranteed purity of 99.9 mole % ethane and 99.99 mole % propane.

Two different types of apparatus were used in obtaining experimental data. The results from the two sources proved to be entirely compatible.

The first apparatus was of the circulation type, especially designed for low temperature and both high-pressure and high-vacuum applications. The liquid phase was run over a rotating disk in the vapor space of the equilibrium cell, thus creating a large contact area between the phases. At the same time, both liquid and vapor phases were circulated through respective sampling loops provided with suitable valves offering the possibility of trapping vapor and liquid samples inside the loops without disturbing equilibrium. Each phase was provided with two such loops. This makes it possible to take two consecutive samples of each phase under exactly the same conditions, and thus double-check the results. The apparatus was suitable in the temperature range from -320° to 450° F., and in the pressure range from 10⁻⁴ torr to 1000 p.s.i.a.

The second apparatus was of the continuous flow type, also designed for use at low temperatures. A prepared mixture of gases was forced to flow through a bundle of capillary tubes at constant pressure and temperature into the equilibrium cell, where liquid and vapor phases were separated and directed to a chromatograph for analysis of the composition. This apparatus was suitable for operation in the pressure range from atmospheric to 3000 p.s.i.a., and temperature range from -320° to 500° F.

Temperatures in both apparatus were measured with calibrated copper-constantan thermocouples and Type K-3 Leeds and Northrup potentiometer, with an accuracy of at least 0.1° F. Pressures above 100 p.s.i.a.

were measured with a calibrated and certified high-precision Heise gage with a maximum error of ±1.0 p.s.i. Pressures from atmospheric to 100 p.s.i.a. were measured with another certified Heise gage with a maximum error of ±0.1 p.s.i. For pressures between atmospheric and 20.0 mm. of Hg, a manometer having a precision of 0.5 mm. of Hg was used, while absolute pressures below 20.0 mm. of Hg were measured with a MKS Baratron, coupled with a Stokes gage, with a compound error of 4.0% of the reading at most, mainly due to the Stokes gage.

The samples were analyzed on a Beckman GC-5 chromatograph with a precision claimed by the manufacturer of at least 0.5% of full scale and a sensitivity of 50 p.p.b. when using a flame ionization detector, or at least 12,000 Dimbat-Porter-Strauss number when using a thermal conductivity detector. When the pressure was below atmospheric, the samples were pressurized with helium in order to feed the chromatograph. This dilution had the effect of magnifying the errors of gas analysis. The accuracy of the analysis was ±1.5 mole % for

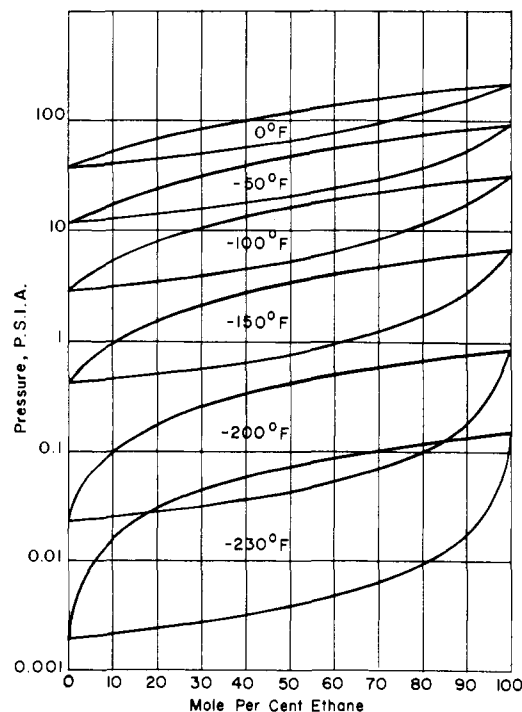


Figure 1. Condensed pressure vs. composition diagram for the ethane-propane system at low temperatures

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Table I. Smoothed Experimental Data

Pressure, P.S.I.A.	Ethane, Mole %		K_2	K_3	Remarks
	Liquid	Vapor			
				0° F.	
37.6	0.00	0.00		1.00	Vapor pressure of pure propane
45.3	5.10	19.66	3.85	0.85	
75.6	24.95	58.54	2.35	0.55	
90.0	34.35	68.15	1.98	0.48	
120.5	53.00	81.16	1.53	0.40	
121.0	53.70	81.23	1.51	0.40	
126.1	57.50	83.57	1.45	0.39	
131.2	60.00	84.32	1.40	0.39	
159.0	74.60	89.70	1.20	0.40	
204.8	94.60	98.18	1.04	0.34	
218.0	100.00	100.00	1.00		Vapor pressure of pure ethane
				-50° F.	
11.02	0.00	0.00		1.00	Vapor pressure of pure propane
15.03	6.45	30.20	4.68	0.75	
28.00	25.15	67.66	2.69	0.43	
41.00	44.24	84.80	1.92	0.27	
54.90	59.35	89.77	1.51	0.25	
66.50	72.45	94.09	1.30	0.21	
75.00	81.44	96.31	1.18	0.20	
92.90	100.00	100.00	1.00		Vapor pressure of pure ethane
				-100° F.	
2.96	0.00	0.00		1.00	Vapor pressure of pure propane
4.75	7.05	41.72	5.92	0.63	
8.00	19.18	69.23	3.61	0.38	
15.15	45.80	88.52	1.93	0.21	
19.90	63.31	93.80	1.48	0.17	
20.00	63.65	93.84	1.47	0.17	
23.00	74.15	95.96	1.29	0.16	
28.15	91.34	98.67	1.08	0.15	
31.34	100.00	100.00	1.00		Vapor pressure of pure ethane
Pressure, Mm. Hg	Ethane, Mole %		K_2	K_3	Remarks
	Liquid	Vapor			
				-150° F.	
21.5	0.00	0.00		1.00	Vapor pressure of pure propane
30.0	2.80	29.97	10.70	0.72	
51.0	9.75	61.35	6.29	0.43	
80.0	18.73	77.54	4.14	0.28	
165.0	44.45	92.46	2.08	0.14	
234.0	64.61	96.33	1.49	0.10	
291.0	80.95	98.51	1.22	0.08	
341.0	94.70	99.67	1.05	0.06	
363.2	100.00	100.00	1.00		Vapor pressure of pure ethane
				-200° F.	
1.158	0.00	0.00		1.00	Vapor pressure of pure propane
5.066	9.18	79.48	8.66	0.22	
8.468	17.12	88.63	5.18	0.14	
21.000	44.35	94.44	2.13	0.10	
25.500	56.90	97.91	1.72	0.05	
29.500	66.29	98.62	1.49	0.04	
37.000	83.84	99.48	1.19	0.03	
43.928	100.00	100.00	1.00		Vapor pressure of pure ethane
				-230° F.	
0.094	0.00	0.00		1.00	Vapor pressure of pure propane
0.136	0.61	33.10	54.26	0.67	
0.500	5.20	78.75	15.14	0.22	
1.000	11.80	89.80	7.61	0.12	
1.703	21.44	95.69	4.46	0.06	
2.250	28.40	97.25	3.42	0.04	
3.000	38.40	98.20	2.56	0.03	
3.595	46.64	98.60	2.11	0.03	
4.077	53.00	98.90	1.87	0.02	
5.402	70.60	99.40	1.41	0.02	
6.000	78.50	99.50	1.27	0.02	
6.591	86.50	99.68	1.15	0.02	
7.000	91.75	99.80	1.09	0.02	
7.600	100.00	100.00	1.00		Vapor pressure of pure ethane

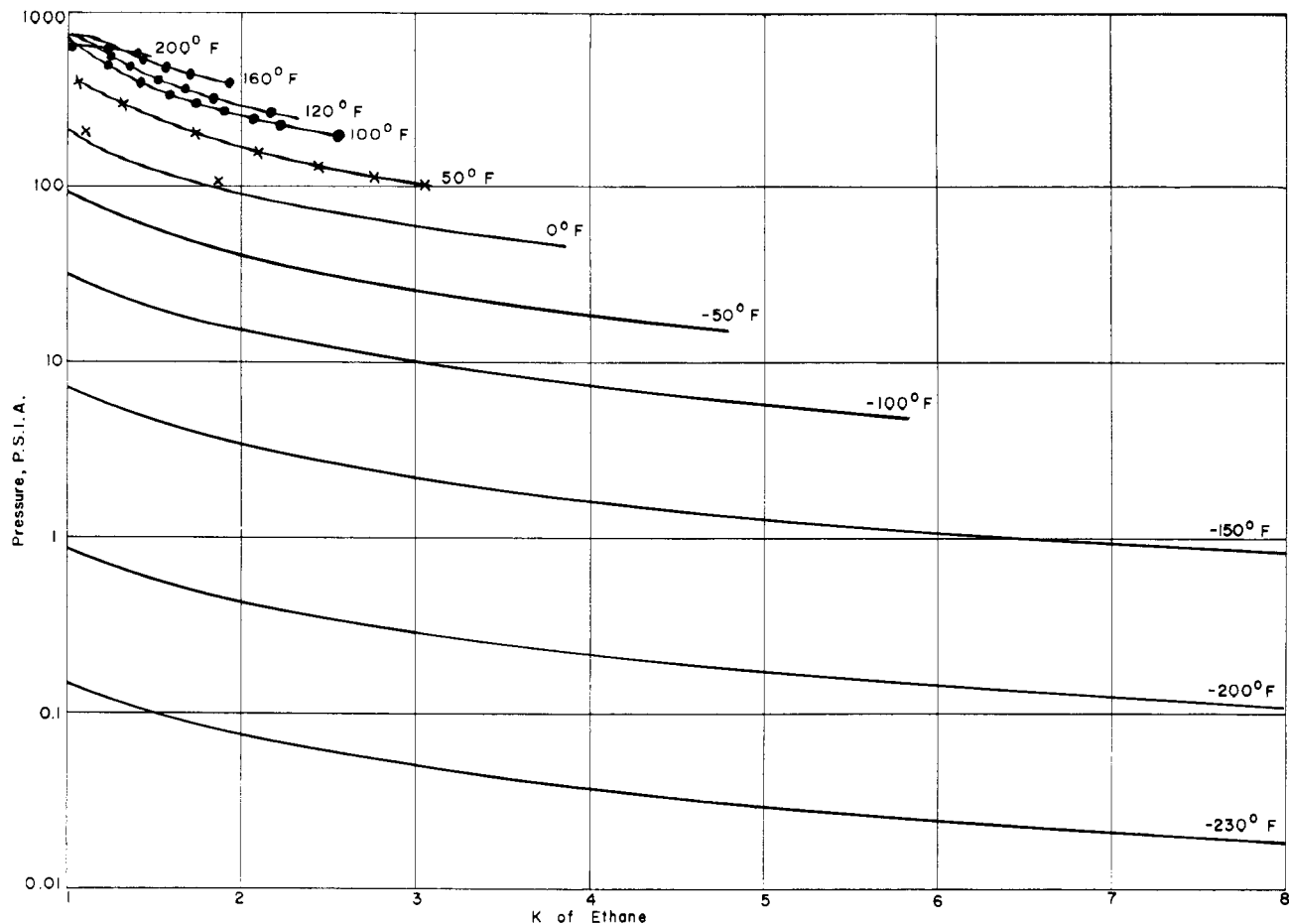


Figure 2. Equilibrium constant of ethane vs. pressure diagrams for the ethane-propane system

●—●—●—●—Matschke × × × × Price ————— Djordjevich

isotherms above -200°F . and ± 3.0 mole % for -200° and -230°F . isotherms.

RESULTS

The experiments were conducted at 0° , -50° , -100° , -150° , -200° , and -230°F . isotherms. The over-all pressure range was from 0.094 mm. of Hg abs. to 218 p.s.i.a.

The smoothed experimental results are presented in Table I, together with the calculated values of equilibrium constants K_2 and K_3 of ethane and propane, respectively. The average absolute deviation of the experimental data from the smoothed values is 1.43 mole %, while the over-all standard deviation is 2.20 mole %. The scattering of the experimental data around the smoothed data increased with lowering of pressure below atmospheric, because of higher relative influence of errors in sample analysis under such conditions. The standard deviation is 1.71 mole % at 0°F ., 1.73 mole % at -50°F ., 1.88 mole % at -100°F ., 2.62 mole % at -150°F ., 2.67 mole % at -200°F ., and 2.39 mole % at -230°F .

Figure 1 represents a semi-log plot of pressure vs. composition of the system at constant temperatures. Figure 2 contains the plot of equilibrium constants of ethane vs. pressure at constant temperature. K -values calculated with Matschke's and Price's data are also included. Price obtained only two pairs of data at 0°F ., with K -values of ethane somewhat higher than those in the present work. Matschke's data, taken in the vicinity of the critical locus, result in the markedly different shape of the K -value curves.

CONCLUSIONS

A comparison between the experimental data and results calculated on the basis of ideal solution laws (1) shows that the lower the temperature, the more closely the behavior of the mixture approaches that of an ideal solution. At temperatures below -200°F ., deviations from ideality begin to fall below the limits of experimental error. On this basis, -200°F . may be considered as roughly the dividing temperature between ideal and nonideal behavior.

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