

VAPOUR-LIQUID EQUILIBRIA IN THE ETHANE-PROPANE SYSTEM AT HIGH PRESSURES*

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Vapour-liquid equilibria in the ethane-propane system were measured at 30.00, 50.00, 70.02, and 90.01°C in the whole concentration range. The detailed measurements were carried out in the neighbourhood of critical temperature of ethane (5 isotherms at 31.47, 32.23, 32.78, 33.35, and 34.40°C) and in the critical region of propane (2 isotherms at 94.07 and 96.03°C). Measurements in the critical region proved the assumption of critical exponent $\beta = 0.33$ to be correct also for two-component and two-phase fluid mixture within the entire concentration range.

The recent investigations¹⁻³ of the critical region of light hydrocarbons mixture containing almost pure component showed its practical importance for the separation processes. However, there is a very scarce experimental material which can be used for testing the proposed quantitative thermodynamic relations. Therefore, the data presented were determined enabling one the direct description of critical region. The measurements were carried out with transparent cell equipment described in previous paper⁴.

EXPERIMENTAL

Material used. Ethane, research grade, was supplied by Fluka, Switzerland, with 99.97% certified purity and with main admixture acetylene. Propane was research grade supplied by Fluka with 99.9% certified purity and isobutane as a main admixture. Both chemicals were not further purified.

Apparatus and procedure. The transparent cell equipment with forced circulation of vapour phase was described elsewhere⁴. The sampling technique was developed beforehand⁵. The analyses of mixture compositions were carried out by means of the gas chromatograph provided with the hydrogen flame ionization detector and nitrogen as a carrier gas. The column 950 mm long was filled by Porapak PS and operated at 60°C. The peak area factor was determined from the analyses of mixtures of known composition synthesized by differential consecutive weighings of a sample bomb after charging with pure components. The peak area factor was found equal $f = 1.49 \pm 0.02$ what is in an agreement with the theoretical value⁶ $f_{\text{theor}} = 1.48$. At least six analyses were made on each phase in such a way that the equilibrium in the system was not dis-

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TABLE I
Vapour-Liquid Equilibrium in the Ethane(1)-Propane(2) System

30.00°C			50.00°C			70.02°C		
x_1	y_1	P , atm	x_1	y_1	P , atm	x_1	y_1	P , atm
0.0000	0.0000	10.68 ^a	0.0000	0.0000	16.96 ^a	0.0000	0.0000	25.66 ^a
0.0245	0.0689	11.44	0.0271	0.0600	17.88	0.0475	0.0894	27.96
0.0538	0.1409	12.10	0.0665	0.1385	19.25	0.1319	0.2109	32.05
0.1244	0.2890	13.80	0.0778	0.1599	19.77	0.2224	0.3143	36.77
0.1748	0.3848	15.73	0.1097	0.2168	21.05	0.3269	0.4197	41.95
0.3217	0.5602	19.63	0.1466	0.2661	22.49	0.4039	0.4807	46.62
0.4392	0.6641	23.46	0.2287	0.3779	25.74	0.4208	0.4882	47.67
0.6180	0.7837	29.83	0.2363	0.3877	26.19	0.4335	0.4897	48.23
0.7085	0.8332	33.35	0.2660	0.4208	27.32	0.4450	0.4890	48.70
0.8074	0.8881	37.14	0.3217	0.4848	29.68	0.4475	0.4890	48.78
0.8813	0.9280	40.51	0.4278	0.5870	33.88	0.4486	0.4889	48.82
0.9124	0.9459	41.87	0.5015	0.6460	37.07	0.4542	0.4874	49.00
0.9374	0.9597	42.98	0.5653	0.6967	40.60	0.4567	0.4867	49.07
0.9527	0.9686	43.97	0.6666	0.7576	45.34	0.4589	0.4865	49.08
0.97590	0.98375	44.87	0.7035	0.7715	47.27	0.4783	0.4783	49.31 ^c
0.97632	0.98377	44.92	0.7332	0.7786	48.73	—	—	—
0.99080	0.99353	45.60	0.7504	0.7823	49.50	—	—	—
0.99473	0.99615	45.81	0.7586	0.7810	49.93	—	—	—
0.99476	0.99621	45.83	0.7621	0.7765	50.12	—	—	—
1.00000	1.00000	46.03 ^b	0.7755	0.7755	50.20 ^c	—	—	—

^a Saturated vapour pressure of propane; ^b saturated vapour pressure of ethane; ^c critical point.

TABLE II
Vapour-Liquid Equilibrium in the Ethane(1)-Propane(2) System Around the Critical Temperature of Ethane

31.47°C			32.25°C			32.78°C		
x_1	y_1	P , atm	x_1	y_1	P , atm	x_1	y_1	P , atm
0.94482	0.96193	44.81	0.94920	0.96451	45.54	0.94504	0.96075	45.95
0.95355	0.96747	45.29	0.96026	0.97101	46.18	0.96426	0.97287	47.00
0.96798	0.97648	46.12	0.97296	0.97922	46.91	0.97825	0.98262	47.75
0.97312	0.97991	46.34	0.98414	0.98714	47.47	0.98557	0.98792	48.15
0.98301	0.98675	46.84	0.99379	0.99462	47.98	0.98914	0.99021	48.35
0.99038	0.99218	47.12	0.99553	0.99592	48.09	0.99036	0.99116	48.42
1.00000	1.00000	47.42 ^a	0.99857	0.99857	48.17 ^b	0.99203	0.99203	48.47 ^b

TABLE II
(Continued)

33.35°C			34.40°C		
x_1	y_1	P , atm	x_1	y_1	P , atm
0.92324	0.94596	45.67	0.91260	0.93812	45.97
0.94703	0.96075	46.76	0.93511	0.95237	47.08
0.96367	0.97182	47.64	0.94682	0.95900	47.77
0.97382	0.97804	48.25	0.95873	0.96592	48.50
0.98131	0.98289	48.66	0.96668	0.97029	49.00
0.98387	0.98387	48.73 ^b	0.96967	0.96967	49.06 ^b

^a Saturated vapour pressure of ethane; ^b critical point.

TABLE III
Vapour-Liquid Equilibrium in the Ethane(1)-Propane(2) System Around the Critical Temperature of Propane

90.01°C			94.51°C			96.03°C		
x_1	y_1	P , atm	x_1	y_1	P , atm	x_1	y_1	P , atm
0.00000	0.00000	37.25 ^a	0.00000	0.00000	40.31 ^a	0.00000	0.00000	41.36 ^a
0.01161	0.01725	37.90	0.00555	0.00756	40.60	0.00473	0.00567	41.66
0.02137	0.03071	38.48	0.01785	0.02327	41.31	0.01504	0.01690	42.25
0.03954	0.05433	39.45	0.02790	0.03463	41.90	0.01793	0.01983	42.40
0.05657	0.07462	40.48	0.04130	0.04721	42.63	0.02111	0.02111	42.51 ^b
0.07161	0.09123	41.33	0.04924	0.05308	42.99	—	—	—
0.10173	0.12157	43.11	0.05521	0.05521	43.14 ^b	—	—	—
0.12241	0.13672	44.15	—	—	—	—	—	—
0.13333	0.14048	44.67	—	—	—	—	—	—
0.14017	0.14017	44.75 ^b	—	—	—	—	—	—

^a Saturated vapour pressure of propane; ^b critical point.

turbed and both liquid and vapour compositions were well reproduced. The time needed for the phase separation is dependent on the closeness of measured and critical conditions. For pressures up to $P \approx P_c - 4$ atm it was possible to sample during the circulation of vapour phase. It was necessary to wait for several minutes to attain reliable separation at higher pressures.

RESULTS AND DISCUSSION

The phase composition in mole fractions (x for liquid, y for vapour) and equilibrium pressure (P , atm) of the ethane-propane system at 30.00, 50.00, and 70.02°C are presented in Table I. The measurements in the neighbourhood of critical temperature of ethane, *i.e.* the isotherms 31.47, 32.25, 32.78, 33.35, and 34.40°C are summarized in Table II. The measurements in the vicinity of propane critical temperature – the isotherms 90.01, 94.51, and 96.03°C – are presented in Table III.

The behaviour of this system within the entire concentration range is shown in K -value *versus* pressure diagram in Fig. 1. The neighbourhoods of critical temperatures of both pure components are depicted in similar diagrams with expanded scale (Fig. 2 and 3). The critical exponent was evaluated graphically¹ as a slope of the curve in the plot of $(y_1/x_1 - 1.0)$ *versus* $(P_{cm} - P)$ in logarithmic scales for the least pressure difference (P_{cm} is the critical pressure of mixture). From this diagram,

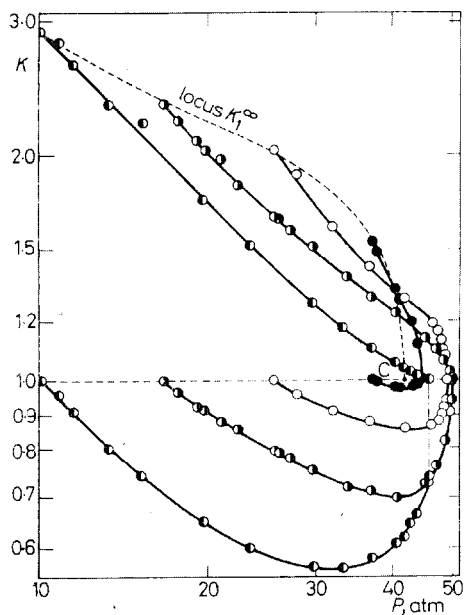


FIG. 1

K -Value *versus* Pressure Diagram for the Ethane-Propane System

- 30.00°C, ● 50.00°C, ○ 70.02°C,
- 90.01°C.

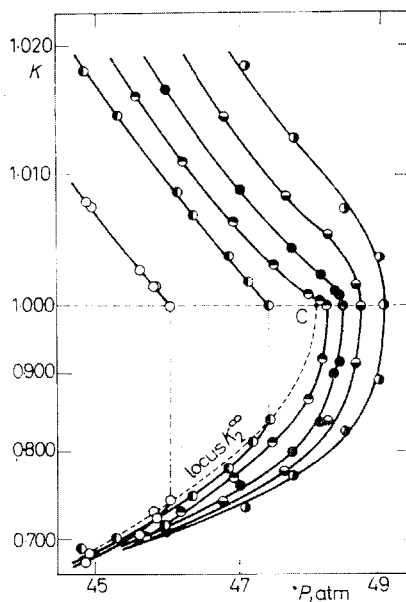


FIG. 2

K -Value *versus* Pressure Diagram for the Ethane-Propane System Around the Critical Temperature of Ethane

- 30.00°C, ○ 31.47°C, ● 32.25°C,
- 32.78°C, ● 33.35°C, ● 34.40°C.

presented in Fig. 4, it follows that $\beta = 0.33$ even for the isotherms in the neighbourhood of critical point of less volatile component.

The error analysis was carried out similarly as in the monograph⁷. The temperature was measured with an absolute accuracy of 0.01°C . The pressure was measured with an absolute accuracy of 0.05 atm, relative reading error was 0.01 atm. The predominant part of the total error was the error in composition determination. The statistic analysis of 50 incidentally selected experimental points by the Student's test showed 1.6% relative error due to the evaluation of chromatograms. The individual error contributions (temperature, pressure, and composition) become more pronounced during the calculation of total error in equilibrium ratio $K = y/x$. The total error is dependent on absolute values of x , T , and P and is equal to the sum of individual errors estimated as 0.1% in temperature, 0.5% in pressure, and 3.0% in composition determination, *i.e.* the total error is equal to 3.6% . However, the total error in K -value does not exceed 2% for the most of experimental points.

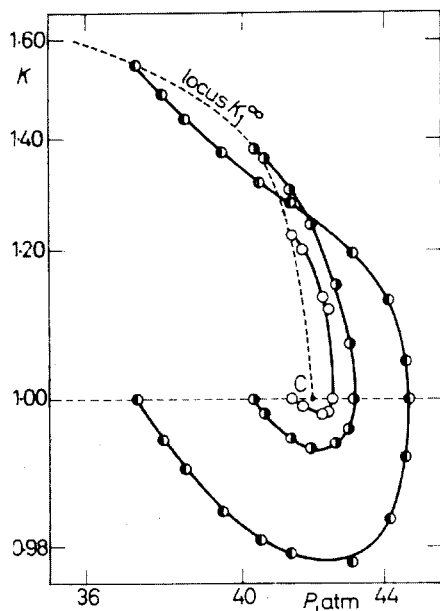


FIG. 3

K -Value versus Pressure Diagram for the Ethane-Propane System Around the Critical Temperature of Propane

○ 90.01°C , ● 94.51°C , ○ 96.03°C .

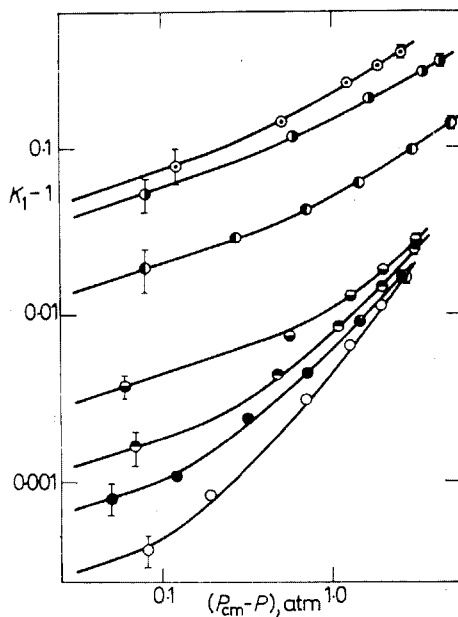


FIG. 4

Behaviour of the Ethane-Propane System Just Below Critical Locus

○ 32.25°C , ● 32.78°C , ● 33.35°C ,
● 34.40°C , ● 50.00°C , ● 90.01°C , ○ 94.51°C .

The comparison of our results was made with the data of Matschke and Thodos⁸ covering the corresponding high pressure range. The method of cross-plotting (diagram $\log K$ versus $1/T$) should be used because the data were not measured at the same temperature levels. The qualitative agreement was reached only and the greatest deviations were found on the critical locus: almost 1 atm for the composition $x = 0.75$. Wiese, Jacobs and Sage⁹ mentioned the similar discrepancies between their and Thodos' data. Another values on critical locus – but in very narrow composition range – were determined by Miniovich and Sorina¹⁰. The graphical comparison showed the values of our critical pressures lie between both sets^{8,10}. With respect to the fact that the measurements⁴ of vapour pressures of pure compounds entirely agree with published data only the error in composition determination could be assumed. Such error causes the shift of critical locus to the left or right; however, mere graphical comparison eliminates this error, too.

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