Part I

Vapor-Liquid Equilibrium in the Ethane–*n*-Butane System

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The vapor-liquid phase behavior of the ethane–n-butane system has been experimentally investigated at 150°, 200°, and 250° F. for pressures ranging from 450 p.s.i.a. up to the critical region. The results of this study have been utilized to establish the corresponding critical pressures and compositions. The vapor-liquid equilibrium constants and critical values obtained from this study have been compared with the results presented by Kay for this system.

THE vapor-liquid equilibrium behavior of the ethane-*n*-butane system has been investigated for temperatures of 150°, 200°, and 250° F. and for pressures approaching the critical pressures of the mixtures. For this system, the only data reported in the literature are those obtained by Kay (*1*) in 1940. The results of the present investigation were not found to be in complete agreement with the data reported by Kay, particularly in the high pressure region.

EXPERIMENTAL EQUIPMENT

A bubble-point and dew-point method was employed by Kay to study the vapor-liquid equilibrium behavior of the ethane-*n*-butane system; whereas, in the present study, a variable volume vapor-liquid equilibrium cell was used for this purpose. The volume of the equilibrium cell was varied by a movable piston, which was actuated with mercury supplied from a positive displacement pump. The pressure of the system was measured with two Heise gages, which were connected to this mercury system. The gages were periodically calibrated with a dead weight gage tester and rechecked against the vapor pressure of a pure hydrocarbon for consistency. The indicated pressures were considered to be dependable and to be reproducible to within 3 p.s.i.a. for the pressure range encountered. The design of the equilibrium cell permitted the withdrawal of microsamples of the vapor and liquid phases at equilibrium. The complete details and construction of the equilibrium cell and auxiliary equipment have been described elsewhere (*3*). To obtain equilibrium conditions quickly, agitation was provided by a stirrer, which was magnetically coupled to a mechanical drive. The cell was surrounded by an air bath, which was capable of maintaining the over-all temperature of the cell to within 0.2° F. of the desired temperature. Under these conditions, the temperature gradient across the cell varied from 0.2° F. at 150° F. to 0.4° F. at 250° F.

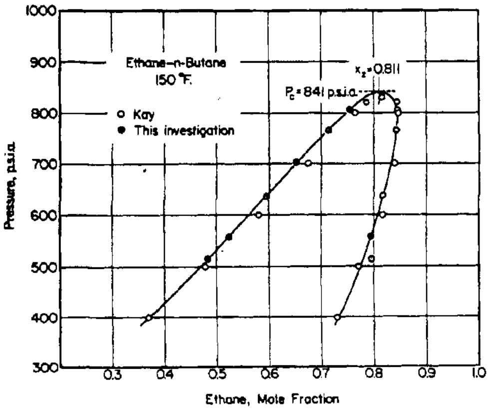

Figure 1. Vapor-liquid equilibrium behavior for the ethane–*n*-butane system at 150° F.

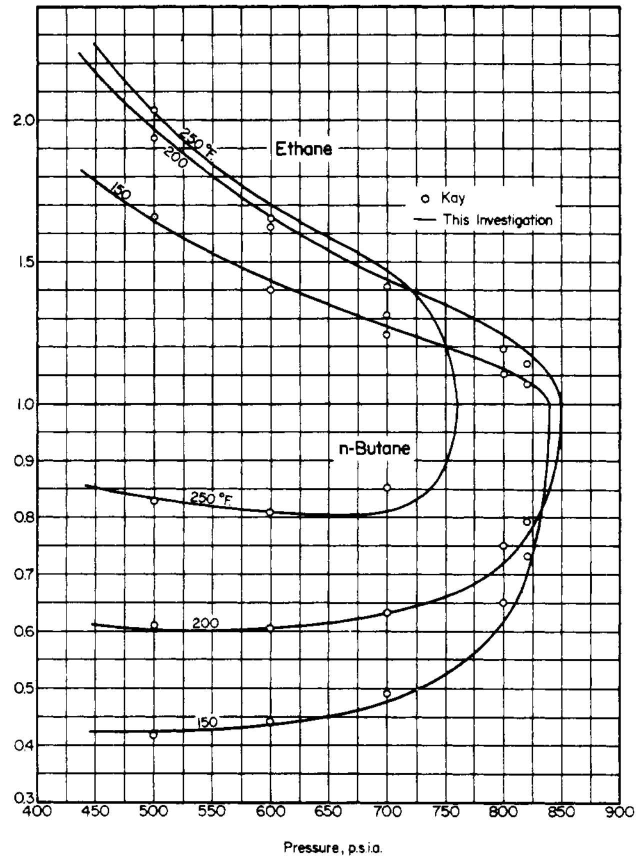

Figure 2. Relationships between *K* and pressure for the ethane–*n*-butane system at 150°, 200°, and 250° F.

Table I. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Butane System at 150°, 200°, and 250° F.

Pressure, P.S.I.A.	Vapor, Mole Fraction		Liquid, Mole Fraction		$K = y/x$	
	Ethane	*n*-Butane	Ethane	*n*-Butane	Ethane	*n*-Butane
			150° F.			
514	0.797	0.203	0.482	0.518	1.654	0.392
558	0.795	0.205	0.524	0.476	1.517	0.431
637	0.818	0.182	0.596	0.404	1.372	0.450
701	0.833	0.167	0.653	0.347	1.276	0.481
765	0.842	0.158	0.714	0.286	1.179	0.552
805	0.845	0.155	0.753	0.247	1.122	0.628
			200° F.			
509	0.575	0.425	0.299	0.701	1.923	0.606
547	0.599	0.401	0.322	0.678	1.860	0.591
594	0.614	0.386	0.364	0.636	1.687	0.607
613	0.618	0.382	0.381	0.619	1.622	0.617
666	0.639	0.361	0.424	0.576	1.507	0.627
691	0.650	0.350	0.437	0.563	1.487	0.622
769	0.662	0.338	0.506	0.494	1.308	0.684
795	0.665	0.335	0.529	0.471	1.257	0.711
			250° F.			
470	0.258	0.742	0.118	0.882	2.186	0.841
518	0.294	0.706	0.149	0.851	1.973	0.830
624	0.377	0.623	0.230	0.770	1.639	0.809
701	0.422	0.578	0.290	0.710	1.455	0.814
730	0.424	0.576	0.312	0.688	1.359	0.837

The vapor and liquid samples withdrawn from the equilibrium cell were analyzed on a gas-chromatography unit, standardized for this system with a mass spectrometer. Analyses carried out on the gas chromatograph were reproducible in a series of several measurements to within 1 mole % of a component based on the assumption that the mass spectrometer results represented the true composition.

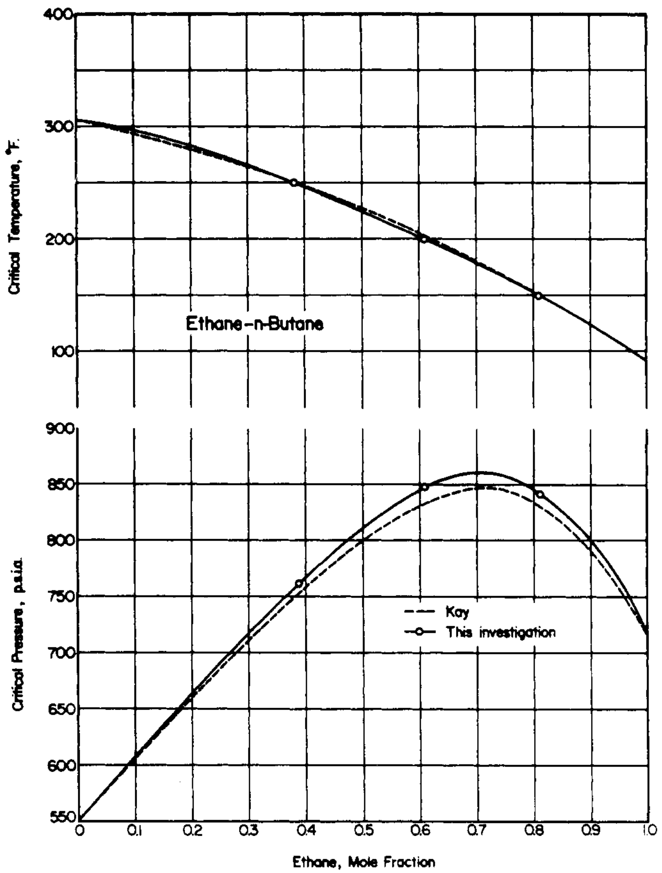

Figure 3. Relationships between critical temperature and composition and critical pressure and composition for the ethane–*n*-butane system

MATERIALS

The hydrocarbons used were reagent grade and were supplied by the Phillips Petroleum Co. The purity of ethane was certified by the supplier to be 99.91 mole % while that of *n*-butane was certified to be 99.94 mole %. Before charging the hydrocarbons to the equilibrium cell, these components were subjected to repeated freezings followed by high vacuum pumping to minimize the possibility of air contamination. This procedure is consistent with that recommended by Kay (*2*).

PROCEDURE AND RESULTS

Charges of binary mixtures of ethane and *n*-butane were introduced into the equilibrium cell for each of the three temperatures investigated. The composition of each charge was always adjusted so that the two-phase region could be realized for each temperature for pressures up to the critical region. Whenever necessary, the previous charges were removed, and new charges were introduced into the equilibrium cell in order to study the full range of pressures for a constant temperature. When plotted as pressure *vs.* composition at constant temperature, the data of Kay (*1*) provided an excellent guide for the proper compositions to be charged into the cell. If no such information were available, a trial-and-error procedure would have been necessary to establish the proper charge composition.

For each temperature, the pressure of the mixture was increased in steps, and the system was allowed to reach equilibrium. The system was found to reach a constant pressure in approximately two hours, except for conditions in the vicinity of the critical point. After equilibrium was attained, vapor and liquid samples were withdrawn and analyzed. The pressure of the system was steadily increased until the resulting compositions of the vapor and liquid

Table II. Final *K* Values for the Ethane–*n*-Butane System at 150°, 200°, and 250° F.

Pressure, P.S.I.A.	$K = y/x$ Ethane	$K = y/x$ *n*-Butane
	150° F.	
450	1.791	0.425
500	1.647	0.426
550	1.532	0.431
600	1.438	0.438
650	1.353	0.455
700	1.280	0.479
750	1.203	0.530
800	1.130	0.615
820	1.087	0.706
841[a]	1.000	1.000
	200° F.	
450	2.173	0.613
500	1.972	0.605
550	1.809	0.601
600	1.670	0.606
650	1.546	0.620
700	1.448	0.635
750	1.351	0.663
800	1.243	0.721
820	1.183	0.770
830	1.147	0.805
848[b]	1.000	1.000
	250° F.	
450	2.272	0.854
500	2.022	0.836
550	1.844	0.823
600	1.705	0.813
650	1.585	0.807
700	1.470	0.811
720	1.401	0.827
740	1.292	0.859
750	1.215	0.889
761[c]	1.000	1.000

Critical point: [a] $x_2 = 0.811$. [b] $x_2 = 0.610$. [c] $x_2 = 0.381$.

phases indicated that the estimated critical pressure was approached to within 30 p.s.i. To obtain data nearer the critical pressure becomes not only impractical due to the excessive time needed for the attainment of equilibrium, but in addition demands frequent adjustments in the over-all cell composition.

The equilibrium vapor-liquid phase boundaries of the system at 150° F. are presented in Figure 1. In this figure, the corresponding values reported by Kay (*1*) are also included. Similar curves were also established for 200° and 250° F. For each temperature some disagreement between the two sets of results is evident as shown in Figure 1 for the 150° F. isotherm. These differences are in excess of the 1 mole % tolerance maintained by the analytical equipment. The compositions of the equilibrium vapor and liquid phases obtained experimentally are presented in Table I.

Vapor-liquid equilibrium constants for 150° F. were calculated from the smoothed plot of Figure 1. The data at 200° and 250° F. were treated in a similar manner to obtain equilibrium constants for these temperatures. The resulting *K* values for the three temperatures are presented in Table II and have been plotted to obtain the *K vs.* pressure relationships shown in Figure 2. When these relationships were extended to $K = 1.00$, a pressure was established which when adjusted for consistency with the corresponding pressure-composition plot, as illustrated in Figure 1, served to define the critical pressure of the particular isotherm. The critical compositions corresponding to each temperature have been included in Table II and have been used to produce the critical temperature–composition and critical pressure–composition relationships presented in Figure 3. The critical values reported by Kay (*1*) for ethane and *n*-butane, have been used in this figure. Comparisons between the critical values of this study and those reported by Kay show some differences only for the critical pressures.

ACKNOWLEDGMENT

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Isothermal and Isobaric Vapor-Liquid Equilibrium Data System: Toluene–Isoamyl Alcohol

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Solutions of alcohols and aromatic hydrocarbons exhibit a high degree of nonideality as indicated by the heats of solution (*3*). Vapor-liquid equilibrium data under isobaric conditions for such systems (particularly those with wider boiling ranges) cannot be correlated by the conventional methods (*4*) which do not take into consideration the effect of temperature on the nonideality of the system. The present investigation studied the effect of temperature variation on the activity coefficients of the components of the system toluene–isoamyl alcohol under isobaric conditions. The vapor-liquid equilibrium data were taken at three different temperatures, 107°, 95°, and 80° C. and at a total pressure of 760 mm. of Hg. The activity coefficients under isothermal conditions are computed and correlated employing the Wohl's suffix Margules equations (*13*). The end values of the activity coefficient–composition curves, which are also the constants in the Margules equations, are related to the absolute temperature, and the relationship obtained is used to correlate the activity coefficients under isobaric conditions.