

1/ Critical Temperature
 2/ " pressure
 3 ethane

4. pentane
 5. heptane

05-0150

15 1965

Critical Temperatures and Pressures of the Ternary System, Ethane—n-Pentane—n-Heptane¹

SOLI P. DASTUR² and GEORGE THODOS²

The critical temperatures and critical pressures established in the vapor-liquid equilibrium studies of the ethane—n-pentane—n-heptane system, in conjunction with the critical behavior of the three corresponding binary systems, were used to develop the critical behavior of this ternary system. The results of this development are presented in the form of triangular plots for critical temperature and critical pressure and cover the complete range of composition for this system.

The critical state of multicomponent systems is of importance in establishing the limiting conditions of temperature and pressure to which the coexisting liquid and vapor phase border curves converge. For binary systems this behavior is represented by critical temperature-composition and critical pressure-composition loci. On the other hand, for a ternary system this behavior of the critical temperature and critical pressure manifests itself in the form of surfaces bounded by the corresponding binaries on the faces of a triangular prism.

Experimental Equipment and Procedure

In the course of an experimental vapor-liquid equilibrium study on the ethane—n-pentane—n-heptane system⁽¹⁾, an equilibrium cell was used with a movable piston actuated with mercury acting as the pressure transmitting fluid, thus varying the volume of the cell available to the system. In order to expedite the attainment of equilibrium, the coexisting vapor and liquid phases were agitated with a stirrer which was magnetically coupled to a mechanically rotating chain drive. The cell was surrounded by an air bath whose temperature was recorded and controlled with a Brown Elektronik instrument provided with an automatic reset. Electric strip heaters provided the heat necessary to maintain the desired temperature. Four calibrated iron constantan thermocouples imbedded in different wells located in the body of the cell measured the temperature of the cell within 0.2°F. The maximum temperature gradient encountered from the top, to the bottom of the cell was found to be 0.6°F. The pressure of the system was measured by means of a Heise gauge having a span of 0—2500 p.s.i. graduated in divisions of 2 p.s.i. This gauge, capable of reproducing pressures to 1 p.s.i. was calibrated periodically against a standard dead weight gauge.

The critical state was approached for cell charges of different overall compositions by varying the pressure of the system at constant temperature. Using this approach, coexisting vapor and liquid phase microsamples⁽²⁾ were withdrawn and were analyzed in a gas chromatograph. This unit was capable of reproducing compositions within one mole percent of a component. This procedure was continued until the vapor and liquid compositions of each component approached each other on a

Les températures et pressions critiques établies lors d'études de l'équilibre vapeur-liquide du système éthane-n-pentane-n-heptane sont utilisées, de concert avec le comportement critique des trois systèmes binaires correspondants, pour développer le comportement critique du système ternaire. Les résultats couvrent la gamme complète de composition et sont présentés à l'aide de diagrammes triangulaires.

pressure-composition diagram, thus permitting the extension of the liquid and vapor lines to the critical pressure. In order to insure that this pressure represented the critical pressure of the system, the overall composition of each charge was prepared to correspond to the critical composition of the system at the temperature under investigation⁽³⁾.

Critical Temperatures.

To establish the critical temperatures of ternary mixtures over the complete range of compositions, the critical temperature-composition relationships of the corresponding binaries were used as the end points of the linear relationships on a triangular plot to represent the critical temperatures in the three component region⁽³⁾. The critical constants presented for these systems by Reamer, Sage, and Lacey⁽⁴⁾ for ethane—n-pentane, by Ekiner⁽⁵⁾ for ethane—n-heptane, and by Cummings, Stones, and Volante⁽⁷⁾ for n-pentane—n-heptane, were used to establish the linear critical temperature relationships presented in Figure 1. Recent experimental critical temperature and critical pressure determinations on the ethane—n-heptane system by Ekiner⁽⁵⁾ produced values that are slightly different from those reported by Kay⁽⁶⁾. The values of Ekiner were used in this study because the experimental equipment used by him was specifically constructed for the establishment of the critical temperature and critical pressure of the system. For the n-pentane—n-heptane system, Cummings, Stones, and Volante⁽⁷⁾ report bubble-point and dew-point values for only three binary mixtures. Since the critical point is not clearly defined by them, it became necessary to establish these values as the extrapolations of their bubble-point and dew-point lines. In order to check the validity of these extrapolations, the complete critical temperature and critical pressure loci for this system were calculated using the method of Grieves and Thodos^(8,9,10). These two sets of critical values were found to be in good agreement.

In Figure 1 are also included the critical composition points resulting from the experimental vapor-liquid equilibrium measurements of Dastur⁽¹⁾ at 150, 200, 250, 300 and 350°F. To arrive at these critical compositions for each temperature, it became necessary to extrapolate on a pressure-composition diagram the equilibrium vapor and liquid compositions of the ternary mixtures to a pressure where these two lines merged. As pointed out, this pressure becomes the critical pressure of the mixture, since the overall composition of each cell charge

¹Manuscript received March 18; accepted July 2, 1964.

²Northwestern University, Evanston, Ill., U.S.A.

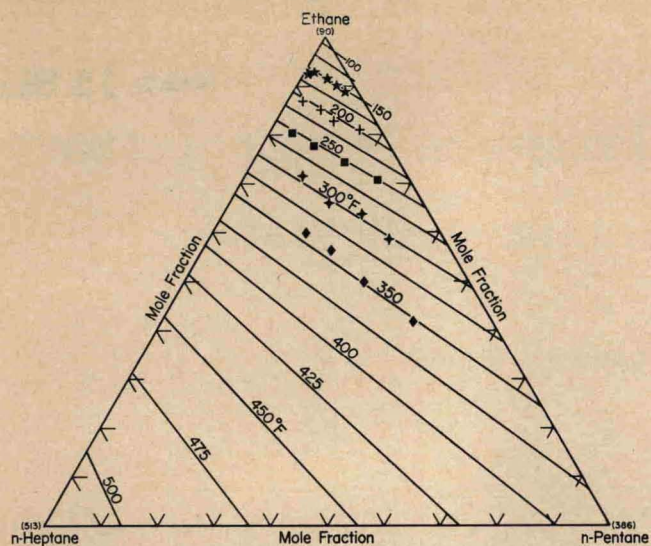


Figure 1—Critical temperatures for the ethane—n-pentane—n-heptane system.

was prepared specifically in accordance with the linear relationships of critical temperature presented in Figure 1. The values reported by Dastur⁽¹⁾ are in general in good agreement with the linear critical temperature lines of Figure 1, except for two mixtures at 350°F. which exhibit a small deviation.

Critical Pressures.

The critical pressure-composition relationship of binary systems is characterized by a maximum critical pressure which is higher than the critical pressure of each constituent of the binary system⁽⁸⁾. Furthermore, the greater the diversity of the two constituents of the binary system, the greater becomes the maximum pressure for the system. The composition corresponding to this maximum pressure also tends to shift in the direction of the lighter component.

TABLE 1
CRITICAL TEMPERATURES, PRESSURES, AND COMPOSITIONS
FOR THE ETHANE — n-PENTANE — n-HEPTANE SYSTEM

Critical Temperature °F.	Critical Pressure, p.s.i.a.	Critical Composition, mole fraction		
		Ethane	n-Pentane	n-Heptane
150	955	0.924	0.009	0.067
150	950	0.929	0.018	0.053
150	945	0.914	0.046	0.040
150	933	0.900	0.070	0.030
150	922	0.888	0.092	0.020
200	1165	0.869	0.025	0.106
200	1140	0.848	0.069	0.083
200	1078	0.826	0.101	0.073
200	1042	0.809	0.157	0.034
250	1228	0.802	0.040	0.158
250	1203	0.776	0.092	0.132
250	1176	0.741	0.162	0.097
250	1080	0.706	0.238	0.056
300	1288	0.715	0.102	0.183
300	1208	0.660	0.177	0.163
300	1118	0.637	0.245	0.118
300	1050	0.585	0.320	0.095
350	1145	0.599	0.165	0.236
350	1100	0.562	0.230	0.208
350	993	0.499	0.318	0.183
350	907	0.417	0.446	0.137

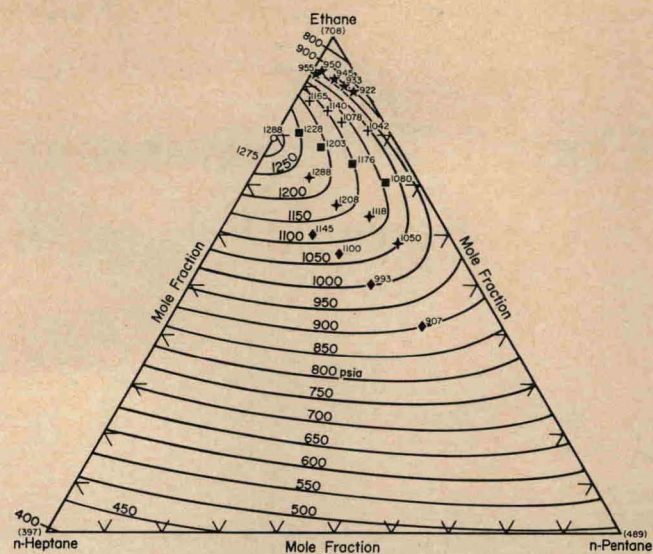


Figure 2—Critical pressures for the ethane—n-pentane—n-heptane system.

The critical pressure-composition relationships for the binary systems, ethane—n-pentane⁽⁴⁾, ethane—n-heptane⁽⁵⁾, and n-pentane—n-heptane⁽⁷⁾ constitute the basis for representing the critical pressure surface of the ternary system on a triangular prism. A useful representation of this surface can be made by projecting constant critical pressure contours on a triangular composition diagram.

To produce these projections, straight lines representing constant composition parameters, $C = x_6/(x_6 + x_7)$, are used. These lines originate from the pure ethane apex and terminate on the n-pentane—n-heptane binary coordinate line. The critical pressures corresponding to the intersections of each of these lines with the 150, 200, 250, 300 and 350°F. critical isotherms permitted the construction of a critical pressure-composition relationship whose end points represent the critical pressure of the n-pentane—n-heptane system on the one hand and that of pure ethane on the other. Each of these relationships corresponding to a constant composition parameter represents the intersection of the critical pressure surface and a vertical plane passing through the ethane apex. This procedure was continued using several constant composition parameter lines and thus covered the entire composition range of this ternary system.

The results of this development are presented in Figure 2 which represents on a triangular composition plot critical pressure contours at regular pressure intervals. For the ethane—n-pentane—n-heptane system, the highest critical pressure of 1288 p.s.i.a. is encountered on the ethane—n-heptane binary system for $x_2 = 0.795$. Since the maximum critical pressure of the ethane—n-pentane binary system is 990 p.s.i.a. and occurs at $x_2 = 0.707$, the critical pressure isobars above 990 p.s.i.a. do not intersect the ethane—n-pentane coordinate line, but terminate on the ethane—n-heptane coordinate line. Below critical pressures of 990 p.s.i.a., all these isobars originate from the ethane—n-heptane coordinate line and terminate either on the ethane—n-pentane or the n-pentane—n-heptane coordinate line.

Figure 2 also includes the critical pressures resulting from the vapor-liquid equilibrium studies of Dastur⁽¹⁾. Considering the extrapolations and interpolations involved, the agreement between these values and those obtained from Figure 2 is good. The critical values obtained from the vapor-liquid equilibrium studies of the ethane—n-pentane—n-heptane system⁽¹⁾ used in this development and appearing in Figures 1 and 2, are presented in Table 1.

Nomenclature

C = composition parameter, $x_6/(x_6 + x_7)$
 x = mole fraction in liquid phase