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

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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

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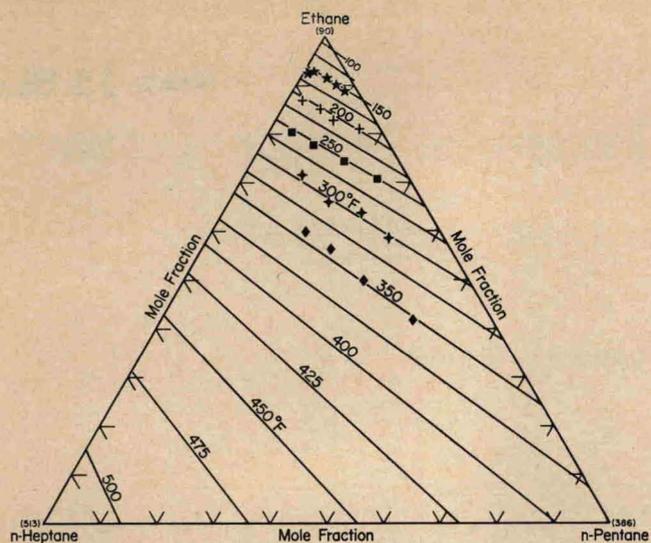


Figure 1—Critical temperatures for the ethane—n-pentane—n-heptane system.

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

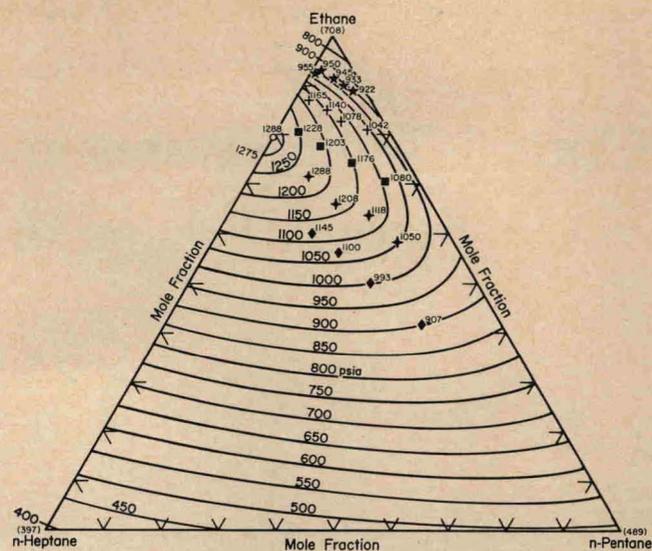


Figure 2—Critical pressures for the ethane—n-pentane—n-heptane system.

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

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References

- (1) Dastur, S. P., Ph.D. dissertation, Northwestern Univ., Evanston, Ill. (1964).
- (2) Rigas, T. J., D. F. Mason and George Thodos, Ind. Eng. Chem. 50, 1297 (1958).
- (3) Grieves, R. B. and George Thodos, Ind. Eng. Chem. (Fundamentals) 1, 45 (1962).

- (4) Reamer, H. H., B. H. Sage and W. N. Lacey, J. Chem. Eng. Data 5, 44 (1960).
- (5) Ekiner, Okan, Ph.D. dissertation (in process of compiling), Northwestern Univ., Evanston, Ill.
- (6) Kay, W. B., Ind. Eng. Chem. 30, 459 (1938).
- (7) Cummings, L. W. T., F. W. Stones and M. A. Volante, Ind. Eng. Chem. 25, 728 (1933).
- (8) Grieves, R. B. and George Thodos, A.I.Ch.E. Journal 6, 561 (1960).
- (9) Grieves, R. B. and George Thodos, A.I.Ch.E. Journal 8, 550 (1962).
- (10) Grieves, R. B. and George Thodos, A.I.Ch.E. Journal 9, 25 (1963).

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Hydrates in the Methane-Nitrogen System¹

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The gas hydrate equilibrium curves for systems containing methane and nitrogen have been obtained in the temperature interval 32°F. to 72°F. and between pressures of 350 and 5100 lb./sq.in.abs. The composition of the equilibrium gas and hydrate phases was determined experimentally at 32°F. and 44°F. This information was used to calculate vapor-solid equilibrium ratios for both nitrogen and methane. A comparison is made between the equilibrium ratios in this system which crystallizes in Structure I and the ratios in systems reported earlier which crystallize in Structure II.

Gas hydrates belong to a common class of substances known as clathrates. A clathrate compound is formed by the complete enclosure of one or more species of molecules in a suitable structure formed by another species. The binding forces between the two sets of molecules in clathrates are of a physical nature. When the host species is water, the clathrate is called a hydrate. It is generally believed that hydrates crystallize in two structures, referred to as Structure I and Structure II. Details concerning the crystal lattice of these structures have been described^(1,2,3) and a comprehensive survey of the thermodynamics of hydrate formation has been presented by van der Waals and Platteeuw⁽⁴⁾.

In view of the recent discovery of the hydrates of nitrogen and oxygen by Van Cleeff and Diepen⁽⁵⁾, it was decided to study the hydrate forming conditions in the ternary system containing nitrogen, methane and water. Apart from the scientific interest in this system, the information gained from the study would be of value in determining the hydrate forming conditions in methane rich natural gases containing nitrogen.

Theory

The solution theory of hydrate formation has been thoroughly summarized by Van der Waals and Platteeuw⁽⁴⁾. One of the important relationships correlating the properties of gas hydrates with the molecular properties is as follows:

$$Y_{K_i} = \frac{C_{K_i} P_K}{1 + \sum_{K=1}^n C_{K_i} P_K} \dots \dots \dots (1)$$

Les courbes d'équilibre de clathrates pour les systèmes contenant du méthane et de l'azote ont été obtenues entre les températures de 32° à 72°F. et les pressions de 350 à 5100 lbs/po². On a déterminé la composition à l'équilibre entre les phases gaz et clathrate à 32, 39.7 et 44°F. qui a été utilisée pour calculer le rapport vapeur-solide pour le méthane et l'azote. Ce rapport vapeur-solide est comparé avec un système antérieur qui cristallise différemment.

In this equation, Y_{K_i} represents the probability of finding a K -type molecule in an i -type cavity in the hydrate lattice, P_K is the partial pressure of a K -type gas in the equilibrium gas phase, and the C_{K_i} values represent constants characteristic of each k -type molecule in an i -type cavity. The summation is taken over the total number of components present, n .

If the number of i -type cavities per molecule of water in the hydrate lattice is defined by ν_i , then the number of molecules of any K species in all the cavities per molecule of water will be given by

$$\sum_{i=1}^m \nu_i Y_{K_i} \dots \dots \dots (2)$$

where m is the number of cavity types in the lattice. Thus, on a water free basis, the fraction of any particular K species in the hydrate will be

$$x_K = \frac{\sum_{i=1}^m \nu_i Y_{K_i}}{\sum_{K=1}^n \sum_{i=1}^m \nu_i Y_{K_i}} \dots \dots \dots (3)$$

This expression for the mole fraction of each species in the hydrate lattice can be directly related to the equilibrium ratios in gas-hydrate equilibrium as originally proposed by Carson and Katz⁽⁶⁾. These ratios were defined as the ratio between the mole fraction of a particular component in the gas phase to that in the co-existing hydrate phase on a water-free basis and they have been used to predict hydrate forming conditions in multicomponent systems. The equilibrium ratio for each component is given by

$$K_K = \frac{y_K}{x_K} \dots \dots \dots (4)$$

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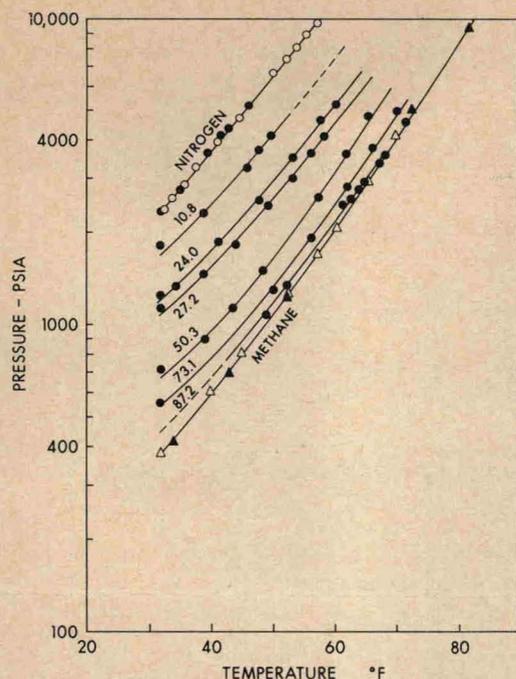


Figure 1—Initial hydrate forming conditions for the nitrogen-methane system.

● This work ○ Van Cleef and Diepen⁽⁵⁾ ▲ Deaton and Frost⁽¹⁰⁾ Kobayashi and Katz⁽¹²⁾ △ This work, methane. Numbers indicate mole % methane in the gas phase on a water free basis.

where y_K is the fraction of K in the equilibrium gas phase on a water free basis.

When equilibrium ratios are evaluated from experimental data for components in a system of two or more components, the ratios for the most volatile component are always greater than unity. The experimental values of the equilibrium ratios which have been reported for methane were all obtained for systems in which methane was the most volatile component and hence all the ratios are greater than unity. Furthermore, it is now known that all the systems which were studied formed hydrates in the Structure II crystal system.

One of the objects of this work was to experimentally determine equilibrium ratios for methane in a system where it was the less volatile of two components. In this way equilibrium ratios in the region less than unity would be obtained. Furthermore, with the system chosen, the hydrates would exist in the Structure I crystal system and the results would give an indication of the effect of structure on the equilibrium ratios.

It is apparent from Equations (1) and (3) that the Y_{K_i} values and hence the x_K values depend on the nature of the molecular constants and on the characteristics of the lattice cavities. Hence equilibrium ratios for Structure I systems would not be expected to agree with Structure II systems even for similar components.

Experimental Technique

The experimental equipment used in this investigation was similar to that used by earlier workers^(7,8). The equilibrium cell was a liquid level gauge capable of withstanding 6000 p.s.i.a. at 250°F. with a test pressure of 9000 p.s.i.a. The cell was constructed of type 316 stainless steel with sight glasses on both sides for visual observation. The cell was enclosed in a lucite jacket to hold the coolant which controlled the temperature of the cell and its contents. The temperature of the equilibrium mixture was measured with a calibrated iron constant thermocouple and a Leeds-Northrup Model K-2 potentiometer. The pressures were indicated on 0-1000 and 0-5000 p.s.i. Heise

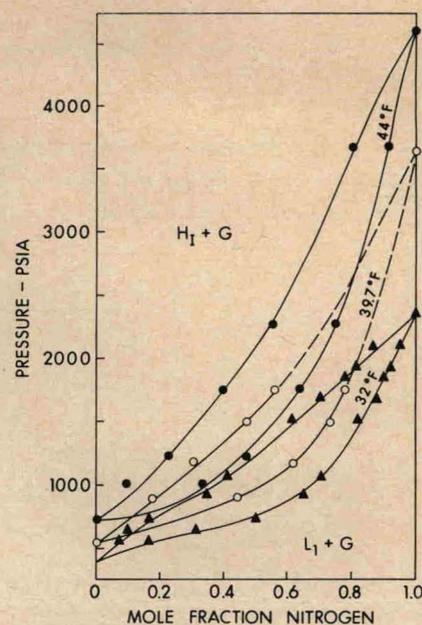


Figure 2—Pressure composition diagrams for the nitrogen-methane-water system.

bourdan tube gauges that had been calibrated in place with a Ruska dead weight tester. A rocker arm was provided for continuous agitation of the cell contents.

The experimental technique employed for the determination of the initial hydrate forming conditions was similar to that described by Otto⁽⁹⁾.

The determination of the pressure composition diagrams involves the analysis of the gas phase and the hydrate phase at a fixed pressure and the corresponding equilibrium temperature. A charge consisting of water and the desired gases was compressed to a pressure which was estimated to be about 25% greater than that needed for the initial hydrate forming conditions. The temperature was set at the desired value, and the cell was allowed to rock for four to six hours. During this period the pressure continued to fall due to the formation of hydrate. When the equilibrium between the phases was established no further drop in pressure was observed. It was recognized that this procedure involved the assumption that crystals of hydrate forming under transient conditions of pressure and gas phase composition would repeatedly decompose and reform gradually until they ultimately represented the equilibrium composition at the desired conditions. This assumption was thought to be reasonably valid in view of the time allowed and the fact that a liquid phase was always present.

The gas phase in equilibrium with the hydrate and water phase was analysed chromatographically. The gas from the equilibrium cell was isobarically transferred to an auxiliary cell, retaining the hydrate crystals at the top of the equilibrium cell. The pressure was then released and the hydrate crystals decomposed. The gas resulting from the decomposition of the hydrate was then analysed for nitrogen and methane.

Experimental Results*

The initial hydrate forming conditions of pure nitrogen and pure methane and of six mixtures of nitrogen and methane were investigated up to 5100 p.s.i.a. The pressure-temperature data of pure nitrogen and methane agreed very well with the data

*Tables 1, 2, 3 and 4 of this paper have been deposited with the National Depository of Unpublished Data, National Sciences Library, National Research Council, Ottawa 2, Ontario. Photo copies may be obtained on request.