

The Methane-Propane-*n*-Pentane System

Critical Temperatures and Pressures of Ternary Systems from Limited Data

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INCREASED INTEREST in critical temperatures and pressures of multicomponent mixtures requires the establishment of these properties for various systems. Considerable information is available for the critical temperatures and pressures of binary systems, which could be used to establish the critical temperatures and pressures for systems containing more than two components. Cota and Thodos (1) and Grieves and Thodos (4) have developed methods for the determination of the complete critical temperature and pressure loci of ternary systems. These methods require meager experimental critical pressures for the ternary system to establish completely its critical pressure behavior.

Experimental critical pressures are available for only the following four systems:

System	No. of Points
Methane-ethane- <i>n</i> -butane (1)	4
Ethane-propane- <i>n</i> -pentane (2)	1
Propane- <i>n</i> -butane- <i>n</i> -pentane (2)	1
<i>n</i> -Butane- <i>n</i> -pentane- <i>n</i> -hexane (2)	1

However, data resulting from experimental vapor-liquid equilibrium investigations for ternary systems are frequently available for the region near the critical point. Therefore, this information could be used to establish the critical pressure behavior of ternary systems for which no experimental critical values are available. In the present study, the conclusions of the previous investigators (1, 4) concerning critical temperatures have been verified by establishing the behavior of this property over a complete range of compositions for the ternary system, methane-propane-*n*-pentane; and experimental vapor-liquid equilibrium data available for this system have been used to establish completely its critical pressure behavior.

From vapor-liquid equilibrium data for the investigated ternary system (3) and for the methane-*n*-pentane system (7), the critical compositions at the experimental conditions for the ternary system were established to be as follows:

	Mole Fraction	
	160° F. 1500 P.s.i.a.	220° F. 1500 P.s.i.a.
Methane	0.520	0.473
Propane	0.356	0.266
<i>n</i> -Pentane	0.124	0.261

These values are considered more accurate than similar critical compositions reported previously (4).

CRITICAL TEMPERATURES

From the experimental critical temperatures reported for the related binaries of the ternary system (5, 6, 7), the critical compositions for convenient temperature intervals were plotted along the coordinates of a triangular plot, as shown in Figure 1. The critical compositions of the ternary system at 1500 p.s.i.a. and 160 and 220° F. were also included in this figure.

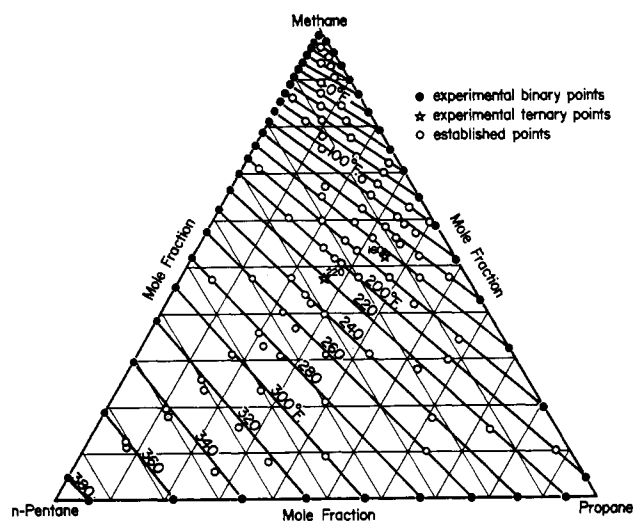


Figure 1. Critical temperature-composition diagram for the methane-propane-*n*-pentane system

To establish the complete critical temperature loci, a procedure, previously outlined (1), was used to produce critical temperature values, which are included as open circles in Figure 1. The points obtained in this manner for each temperature were found to lie on a straight line joining the binary compositions having the same critical temperature. This behavior confirms the conclusion of Grieves and Thodos (4) that the critical temperatures of a normally behaving ternary system can be completely established from only the corresponding binary systems.

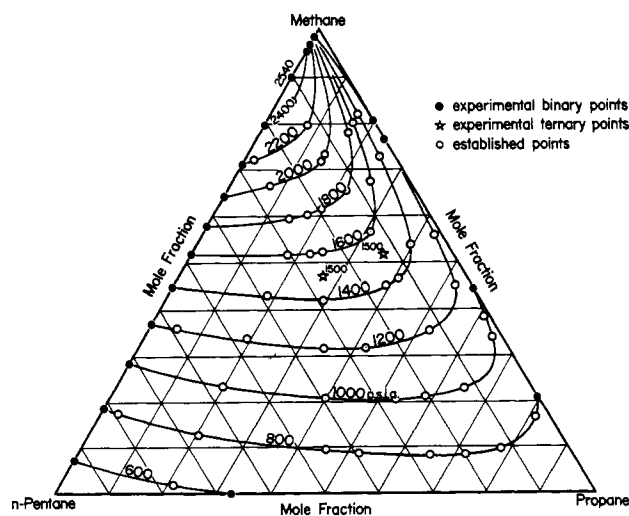


Figure 2. Critical pressure-composition diagram for the methane-propane-*n*-pentane system

CRITICAL PRESSURES

Similarly, critical pressures reported by the investigators of each binary system (5, 6, 7) were plotted along the coordinates of a triangular plot in which the established critical compositions for the ternary system were included (Figure 2). Critical pressures at convenient intervals were determined as before (1) and were also included in the triangular plot.

When the compositions having the same critical pressure in the triangular plot were connected, curves were obtained which possessed a point of maximum propane composition for each critical pressure (Figure 2). Since the binary compositions having the same critical pressure could not be joined with a straight line, the results of this study indicate that, unlike the critical temperature, at least one experimental ternary point located near the center of the

triangular plot is necessary to determine the complete critical pressure diagram for a ternary system.

LITERATURE CITED

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Solubility of Methyl, Ethyl, and Vinyl Acetylene in Several Solvents

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DURING A STUDY of the removal of acetylene impurities from various hydrocarbon streams, it was necessary to determine the solubilities of three acetylene compounds in several solvents, such as water, methanol, and aqueous solutions of ammonium hydroxide, sodium hydroxide, and sodium chloride. The acetylene compounds were the methyl, ethyl, and vinyl homologs of the series. Each solubility, expressed as the Bunsen coefficient, was measured as a function of temperature in the range 0 to 60°C. for partial pressures of the order of 1 atm. These coefficients were also correlated with temperature. It was necessary to measure the solubilities of the acetylenes in the above solvents, since a literature search revealed no such information.

EXPERIMENTAL

Apparatus. The apparatus (Figure 1) consisted mainly of a glass manifold CFHK attached by vents to either a vacuum pump or the atmosphere; a gas buret and a mercury-filled manometer, both equipped with mercury leveling bulbs; a source of gas supply and a vessel I, for holding the solvent in a thermostat. The apparatus consists entirely of glass connections except for a flexible connector between the manifold and the sample holder. This connector consisted of two pieces of glass tubing joined by three very short pieces of rubber vacuum tubing. Although the bulk of the surface was glass, there still was sufficient flexibility for shaking. The above hydrocarbons are readily soluble in rubber, and for this reason a minimum of rubber tubing was used. Since the results obtained for both increasing and decreasing temperature show no hysteresis effect, it was concluded that the apparatus gave reproducibly accurate results.

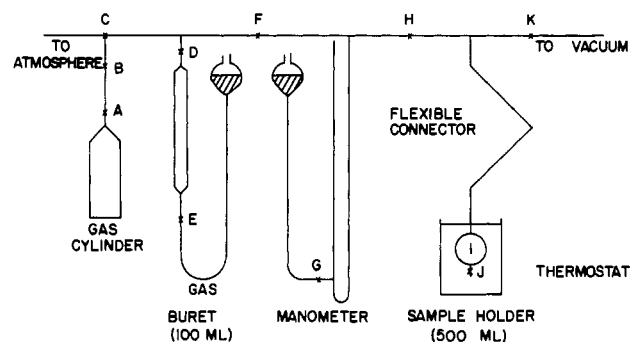


Figure 1. Apparatus for measuring acetylene solubilities

Procedure. Before each run, the whole system was flushed at least twice with nitrogen. The sample holder was disconnected from the manifold, filled with a known volume of solvent, reattached, and placed in the thermostat. These operations were carried out under an atmosphere of nitrogen. The temperature of the thermostat was set at 0°C., and the system was pumped out for approximately 15 minutes by attaching a vacuum pump at K. After this period, K was closed, and the system under vacuum was allowed to equilibrate. When equilibrium was reached, the pressure was read from the manometer. The difference between this and atmospheric pressure gives the vapor pressure of the solvent at 0°C. By changing the temperature of the thermostat, the vapor pressures were then measured at 30°, 45°, and 60°C. A knowledge of the vapor pressures at these temperatures, made it possible to check the apparatus—by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperatures. Such a plot should be linear, should extrapolate through the normal boiling point of the solvent in question, and should provide a value for the heat of vaporization of this solvent. In each of these experiments, all three criteria have been fulfilled.