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Critical Temperatures and Critical Pressures
of the Ethane–n-Pentane–n-Heptane System

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Critical temperatures and critical pressures were established experimentally for three mixtures consisting of ethane, n-pentane, and n-heptane. These determinations were carried out in a visual liquid piston type PVT cell which utilized mercury as the pressurizing medium. These critical measurements served as the basis necessary for the development of the critical temperature and critical pressure behavior over the entire composition range of this ternary system. The final relationships are presented on triangular plots and permit the establishment of the critical temperature and critical pressure of any composition for this ternary system. Based on the linear behavior of the critical temperature, analytical relationships are developed that permit the direct calculation of this critical property from a knowledge of the critical behavior of the corresponding binaries.

EXPERIMENTAL critical temperature and critical pressure measurements available in the literature mostly are restricted to binary hydrocarbon systems. For systems containing more than two components, critical temperature and pressure measurements are rather scarce, and consequently present an inconvenience to the development of a method capable of predicting these critical properties for systems containing more than two components. Furthermore, attempts to utilize such experimental measurements, of necessity, require that such information become available for three- and four-component systems. Such information will assist in the general understanding of the critical state behavior of multicomponent hydrocarbon systems.

In this study the system ethane–n-pentane–n-heptane was investigated. This ternary system was selected particularly because the critical temperature and critical pressure behavior of the corresponding binary systems are presented in the literature. This information, coupled with measurements on this ternary system, was utilized for the development of relationships for the critical temperature and critical pressure of this ternary system over its complete range of composition.

EXPERIMENTAL PROCEDURE

The experimental procedure used in this investigation is identical to that described elsewhere for the ethane–n-heptane system (3). The basic feature of the experimental unit was represented by a visual PVT cell of the liquid piston type which utilized mercury as the displacing fluid.

Visual observations of the vapor-liquid meniscus at constant temperature conditions and varying pressures permitted the establishment of the phase behavior of the ternary mixture confined in the PVT cell. This approach was utilized for three different ethane–n-pentane–n-heptane mixtures, which yielded relationships comparable to those presented in Figure 1. The hydrocarbons used in this

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investigation were research grade and were claimed to have the following purities:

	Mole %
Ethane	99.96
n-Pentane	99.84
n-Heptane	99.78

The components first were introduced into a charging cell preceding the visual PVT cell where they were solidified with liquid nitrogen and then were exposed to vacuum. To ensure complete removal of any noncondensables, the charging cell and its contents were warmed to room temperature, then resolidified with liquid nitrogen, and evacuated. This procedure was repeated at least three times.

In Figure 1 are presented the isothermal relationships of liquid volume per cent vs. pressure for temperatures ranging from 237.9° to 266.1° F. for a mole fraction composition consisting of the following: ethane = 0.801, n-pentane = 0.064, and n-heptane = 0.135. Compositions were established with a mass spectrometer. In Figure 1, the isotherms 237.9° and 241.8° F. indicate conventional behavior and exhibit complete liquefaction at the highest pressures. On the other hand, the isotherms 248.6°, 251.6°, and 266.1° F. exhibit a retrograde behavior and are characterized with complete vaporization at their highest pressure. The experimental information presented in Figure 1 was crossplotted for constant values of liquid volume per cent to produce the pressure vs. temperature relationships presented in Figure 2. The point of convergence of these relationships represents the critical point of this mixture, which, for charge A, was t_c = 245° F. and P_c = 1175 p.s.i.a. A similar procedure was adopted for two additional ternary mixtures for which critical temperatures and critical pressures were established. The experimental values used to obtain the relationships for the ternary mixture of Figures 1 and 2 and for the other two mixtures of this study are available elsewhere (2). The uncertainty in these measurements is 2 p.s.i.a. for pressure and 1° F. for temperature. The mass spectroscopy analyses should be reliable to
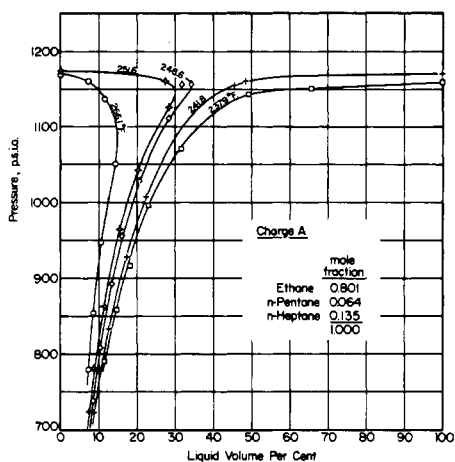
Figure 1. Isothermal relationships between pressure and liquid volume % for a fixed charge of ethane-n-pentane-n-heptane (charge A)
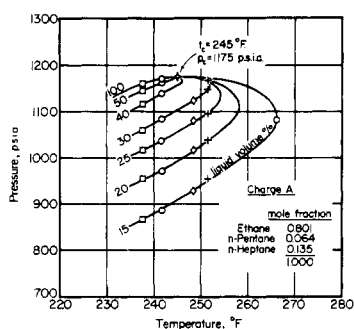

Figure 2. Constant liquid volume % relationships between pressure and temperature for establishment of the critical temperature and pressure (charge A)

within 1% of the absolute value of a component. The results for the three mixtures investigated are as follows:

Charge	Composition, Mole Fraction			Critical Temp., °F.	Critical Press., P.S.I.A.
	Ethane	n-Pentane	n-Heptane		
A	0.801	0.064	0.135	245	1175
B	0.612	0.271	0.117	299	1038
C	0.615	0.296	0.089	289	1024

Because of the temperature limitations imposed on the equipment by the presence of the O-ring seal around the sight glass, operating cell temperatures much above 300° F. were avoided. This experimental limitation permitted the establishment of critical values only for ternary mixtures rich in ethane. In order to obtain a complete coverage of the critical temperature and critical pressure behavior over the complete composition range, this information was coupled with the behavior of the corresponding binary systems to obtain critical temperature and critical pressure relationships applicable over the entire range of compositions. For the binary systems, the experimental critical temperatures and critical pressures presented by Ekiner and Thodos for the ethane-n-pentane (4) and ethane-n-heptane (3) systems and by Cummings, Stones, and Volante (1) for the n-pentane-n-heptane system were used.

DEVELOPMENT OF CRITICAL STATE RELATIONSHIPS

Critical Temperature. The critical temperatures established for the three ternary mixtures of this study were used to test the validity of the linear isothermal critical temperature

relationships proposed by Grieves and Thodos (5) for ternary systems. In their study, Grieves and Thodos point out that a straight line connecting the compositions of two binary systems having the same critical temperature establishes the critical temperature locus of all ternary mixtures which lie on this critical isotherm. Following this approach, the linear critical temperature isotherms presented in Figure 3 were established. The critical temperatures for the three ternary mixtures of this study are found to be consistent with the over-all pattern presented in Figure 3.

The linear relationships of Figure 3 can be expressed analytically after considering the properties of triangular plots. The coordinate lines of this triangular plot represent binary compositions of the respective systems, while a point within the triangle represents the composition of a ternary mixture. The linear critical temperature isotherm passing through a ternary mixture of composition $(n_{257})_2$, $(n_{257})_5$, and $(n_{257})_7$ and terminating on the ethane-n-heptane and the ethane-n-pentane systems can be expressed analytically in the point-slope form. By using the properties of similar triangles, it follows that the slope of the line is $[(n_{27})_2 - (n_{25})_2]/[(n_{27})_5 - (n_{25})_5]$ and the intercept is $(n_{27})_2$. Therefore,

$$(n_{257})_2 = \frac{(n_{27})_2 - (n_{25})_2}{(n_{27})_5 - (n_{25})_5} (n_{257})_5 + (n_{27})_2 \tag{1}$$

Similarly, the equation of the linear critical temperature isotherm terminating on ethane-n-heptane and the n-pentane-n-heptane binary systems becomes

$$(n_{257})_2 = \frac{(n_{27})_2 - (n_{57})_2}{(n_{27})_5 - (n_{57})_5} (n_{257})_5 + (n_{27})_2 \tag{2}$$

where n_{27}, n_{25}, and n_{57} represent the binary compositions of the respective components. The variables associated with Equations 1 and 2 are indicated in Figure 4.

The application of Equation 1 is valid for this ternary system if the following inequality is satisfied:

$$(n_{257})_2 \geqq 0.603 \left[1 - (n_{257})_5\right] \tag{3}$$

Conversely, if Equation 3 is not satisfied, then Equation 2 becomes applicable. When this inequality becomes

$$(n_{257})_2 = 0.603 \left[1 - (n_{257})_5\right] \tag{4}$$

it represents the critical temperature isotherm which starts at the intermediate component, n-pentane, and terminates on an ethane-n-heptane composition which has the same critical temperature as pure n-pentane. This composition is $(n_{27})_2 = 0.603$ and $(n_{27})_7 = 0.388$.

Since for the ethane-n-heptane system, $(n_{27})_5 = 0$, and similarly for the n-pentane-n-heptane system, $(n_{57})_2 = 0$, Equations 1 and 2 reduce, respectively, to the following:

$$(n_{257})_2 = -\frac{(n_{27})_2 - (n_{25})_2}{(n_{25})_5} (n_{257})_5 + (n_{27})_2 \tag{5}$$

and

$$(n_{257})_2 = -\frac{(n_{27})_2}{(n_{57})_5} (n_{257})_5 + (n_{27})_2 \tag{6}$$

Equations 5 and 6 represent the final forms to be used for the establishment of the critical temperature of this ternary system. The following example considers the steps necessary for the estimation of the critical temperature of an ethane-n-pentane-n-heptane mixture.

Example. Calculate the critical temperature of an ethane-n-pentane-n-heptane mixture consisting of the following: $(n_{257})_2 = 0.801$, $(n_{257})_5 = 0.064$, and $(n_{257})_7 = 0.135$. For this
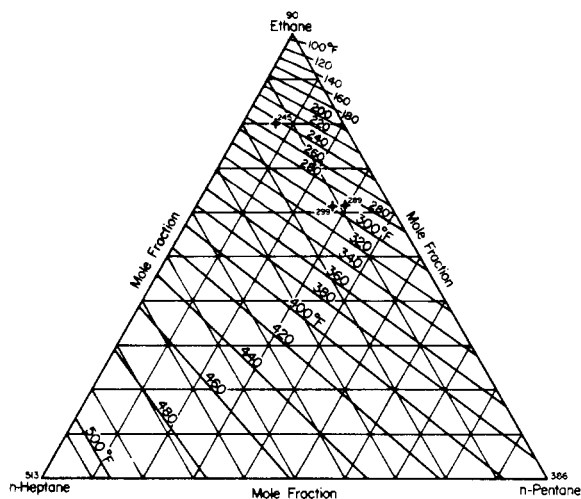
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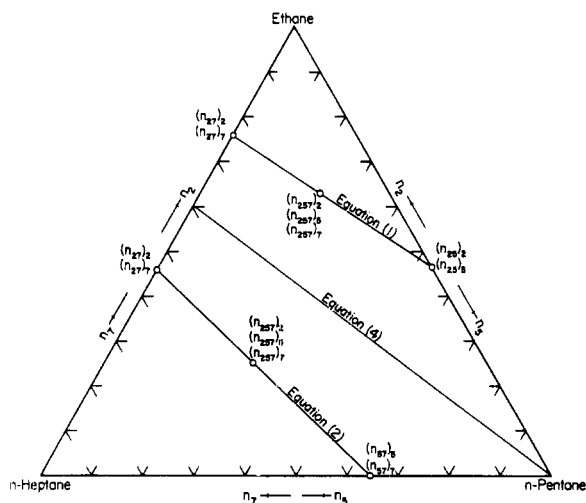Figure 3. Critical temperature isotherms for the ethane–n-pentane–n-heptane system

Figure 4. Diagrammatic representation of the ethane–n-pentane–n-heptane system and corresponding binary compositions of critical temperature isotherms
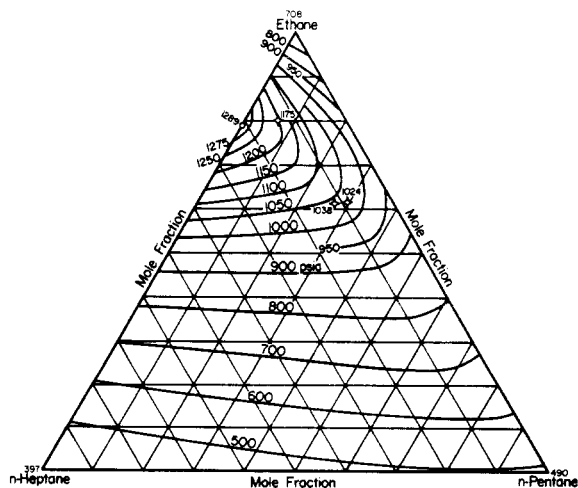

Figure 5. Critical pressure isobars for the ethane–n-pentane–n-heptane system

estimation, the critical temperature loci of the corresponding three binary systems are to be used.

To decide whether Equation 5 or Equation 6 is applicable to this composition, Equation 3 is used to obtain

$$(n_{257})_2 = 0.801 > 0.603 \ (1 - 0.064) = 0.564$$

Therefore, Equation 5 is applicable. To obtain a proximity to the actual critical value, the pseudocritical temperature corresponding to this mixture is first obtained and is then adjusted by suitably increasing it to satisfy Equation 5. Thus,

$$T'_c = 549.8 \ (0.801) + 845.6 \ (0.064) + 972.3 \ (0.135) = 625.8° \text{ R.}$$

Assuming the critical temperature of this ternary mixture to be 700° R., the corresponding binary compositions having this critical temperature are found from the experimental studies of Ekiner and Thodos (3, 4) to be, $(n_{27})_2 = 0.842$ and $(n_{25})_2 = 0.644$. Substituting these values into Equation 5 yields

$$(n_{257})_2 = 0.801 \neq -\frac{0.842 - 0.644}{1 - 0.644} (0.064) + 0.842 = 0.786$$

The difference of $0.801 - 0.786 = 0.015$ indicates that the assumed critical temperature is close to the actual value. For this case, if the calculated composition value, $(n_{257})_2 = 0.786$, is less than the actual value, $(n_{257})_2 = 0.801$, then a higher critical temperature should be assumed. Conversely, if Equation 3 indicates that Equation 6 be used, then under the same conditions a lower critical temperature should be assumed. By assuming a critical temperature of 707° R., the following binary compositions apply: $(n_{27})_2 = 0.833$ and $(n_{25})_2 = 0.653$. When these values are substituted into Equation 5, the following is obtained:

$$(n_{257})_2 = 0.801 = -\frac{0.833 - 0.653}{1 - 0.653} (0.064) + 0.833 = 0.800$$

Thus, since Equation 5 is satisfied, the assumed critical temperature of 707° R. (247° F.) properly represents the critical temperature calculated with the use of this method. The experimental critical temperature established for this ternary mixture (charge A) was 245° F.

Critical Pressure. To obtain the complete critical pressure behavior of this ternary system, the three critical pressure measurements were used along with the complete critical pressure behavior of the three binary systems. A plot of critical pressure *vs.* composition for the binary systems, ethane–n-heptane and ethane–n-pentane, produced relationships, each of which exhibited a maximum. These two relationships served as border curves and assisted in the establishment of comparable curves which had a parameter of constant mole ratio of n-pentane to n-heptane and which passed through the experimental critical pressures. All of these relationships have a starting point on the n-pentane–n-heptane binary system (ethane = 0.00 mole fraction) and terminate on pure ethane. This information, coupled with the properties associated with triangular plots, produced the final relationships presented in Figure 5 for the critical pressure behavior of this ternary system. The highest critical pressure of 1289 p.s.i.a. is exhibited on the ethane–n-heptane binary system at the composition, $(n_{27})_2 = 0.792$, $(n_{27})_7 = 0.208$, around which constant continuous pressure contours are generated which begin and end on this binary system. For a critical pressure of 966 p.s.i.a., the corresponding contour becomes tangent to the ethane–n-pentane binary coordinate at $(n_{25})_2 = 0.750$ and $(n_{25})_5 = 0.250$. For pressures below 966 p.s.i.a., these contours become discontinuous over the range of the ethane–n-pentane binary system. Figure 5 presents the results of this treatment and permits the establishment of the critical pressure of any ternary composition of this ternary system.

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High Temperature Properties of Potassium

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A virial equation of state for potassium with coefficients through the fourth virial is derived from PVT data covering a temperature range from 1600° to 2525° F. The equation is used thermodynamically to obtain superheat and saturation properties of the vapor. Values of the enthalpy, entropy, specific volume, and specific heat for some 200 selected states are tabulated in the temperature range from 1400° to 2500° F., and in the pressure range from 2.9 to 499.3 p.s.i.a.

THE ALKALI METALS are being considered as thermodynamic working fluids in advanced power converters, and reliable values of their properties are required. The existing thermodynamic properties for alkali metal vapors have been calculated in most cases from spectroscopic data, vapor-pressure data, and published thermodynamic functions. The agreement among the calculated properties for a given metal is poor and not acceptable. The principal objective at NRL was to determine experimentally for a wide temperature range the important thermodynamic properties of three metal vapors—sodium, potassium, and cesium. This was to be achieved by a thermodynamic reduction of pressure-volume-temperature data. The *PVT* measurements for each metal to 2500° F. have now been published. This article, the fourth in the series, describes the thermodynamic treatment of the potassium *PVT* data and presents the first thermodynamic properties of this metal derived directly from measured compressibilities.

TREATMENT OF *PVT* DATA

Methods. Spectroscopic studies (4) have shown that the vapor of an alkali metal contains molecular species with two or more atoms. For a strongly associating vapor, such as that of potassium, the important properties—enthalpy, entropy, and specific heat—may be reduced from *PVT* data by either of two methods. In the first, the gas is treated as a monatomic assembly with all apparent imperfections given by a virial equation of state, and the thermodynamic quantities are obtained as corrections to those of the monatomic gas in terms of the virial coefficients. In the second method, equilibrium constants are derived for the molecular reactions by treating the gas as a mixture of molecular species, and the thermodynamic quantities are derived from the enthalpy changes associated with changes in the molecular composition of the vapor. The latter method, commonly called the quasichemical, generally assumes that all species behave as perfect gases.

While the two methods should be effectively equivalent from the standpoint of obtaining the three properties—enthalpy, entropy, and specific heat—a higher degree of confidence was placed in the well-established thermodynamic relationships of the virial method. The virial equation of state for potassium with coefficients through the fourth virial was obtained from the raw *PVT* data and used to compute enthalpy, entropy, specific volume, and specific heat of potassium vapor.

Derivation of Virial Coefficients. The virial equation of state in the volume expansion form,

$$\frac{p\bar{V}}{RT} = A + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \ldots \qquad (1)$$

was chosen for this analysis, and the four coefficients are commonly called the first, second, third, and fourth virial. With this form of the equation, the first virial coefficient theoretically should be unity.

The virial coefficients are temperature-dependent and were derived graphically by plotting functions along constant temperature lines. Compressibility data at 50° temperature intervals were obtained from large-scale plots of the observed data for the nine experiments reported by Stone *et al.* (9). Virial coefficients were obtained from these data by a procedure similar to that devised by Hirschfelder, McClure, and Weeks (7). The second virial coefficient at each temperature was obtained as the lim $[(z - 1) \bar{V}]_{(1/\bar{V} \to 0)}$, the third virial as the lim $Q_{(1/\bar{V} \to 0)}$ where Q is defined as $[(z - 1) \bar{V} - B] \bar{V}$, and the fourth virial as $dQ/d(1/\bar{V})$.

It was noted from preliminary plots of z vs. $1/\bar{V}$ for isotherms covering the temperature range that the deviations of observed compressibility factors from fitted curves