value obtained for the left hand side of Equation 7 indicates that the data are consistent.

Constants were determined for several correlation equations including the Wilson equation (*13*). However, it was not possible to obtain a satisfactory correlation of the experimental activity coefficients. In particular, the behavior of the *p*-cresol activity coefficient at high cresol concentrations could not be reproduced by any of the equations.

This behavior has been observed in other systems where association is known to occur, and Meehan and Murphy (*8*) have proposed correlating equations for systems involving an associating component. Future work will be concerned with the application of these equations and the measuring of vapor densities and heats of mixing for *p*-cresol with selected hydrocarbons. These measurements will make possible a more rigorous thermodynamic analysis of this system.

NOMENCLATURE

f_i = fugacity of pure component i at the temperature and pressure of the solution
$\hat{f}_i$ = fugacity of component i in mixture
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor
z = compressibility factor
B_{ii} = second virial coefficient of component i, cc./g.-mole
P = total pressure, atm.
P_i^s = vapor pressure of pure component i, atm.
R = gas constant, 82.06 cc.-atm./g.-mole °K.
T = temperature, °K.
V = molar volume of vapor phase
V_i^L = molar volume of pure component i in liquid phase
γ_i = liquid phase activity coefficient of component i
ϕ_i = fugacity coefficient for pure component i
$\hat{\phi}_i$ = fugacity coefficient of component i in solution
ΔH = molar enthalpy change upon mixing

Subscripts

1 = component 1, *n*-octane
2 = component 2, *p*-cresol

Superscripts

v = vapor phase
L = liquid phase

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

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Experimental critical temperatures and pressures have been established for three different mixtures of the ethane–*n*-butane–*n*-heptane system. These critical values, in conjunction with the critical behavior of the corresponding binaries of this ternary system, have been utilized to generate critical temperature and critical pressure relationships which cover the entire composition range of this ternary system. These relationships are presented graphically on triangular plots from which the critical temperature and critical pressure can be readily obtained for any composition of this ternary system.

CONTINUED interest in the experimental determination of the critical properties of hydrocarbon systems having more than two components, has brought to focus the need of investigating a ternary hydrocarbon system. Therefore, this study was limited to the experimental investigation of the critical temperatures and critical pressures of three different mixtures of the ethane–*n*-butane–*n*-heptane system.

The details of the experimental equipment and procedure are described at length eleswhere (*1*). In this study, a visual *PVT* cell using mercury as the pressurizing medium was used to obtain, at isothermal conditions, the relative amounts of the coexisting vapor and liquid phases in equilibrium with each other. The hydrocarbons used were obtained from the Phillips Petroleum Co., were research grade, and were claimed by the manufacturer to have the following purities: ethane, 99.96; *n*-butane, 99.94; and *n*-heptane, 99.78 mole %.

The experimental determination of the critical temperature and critical pressure of a ternary mixture involved the establishment of several pressure-liquid volume per cent isotherms in the vicinity of the critical point. In the course of investigating a mixture, small samples were removed for analysis after increasing the temperature and pressure of the system sufficiently to ensure the existence of a single homogeneous phase. The composition of these samples was determined with a mass spectrometer. Duplicate samples were always taken, and the composition of each mixture was not considered final unless each component agreed within 1 mole %.

EXPERIMENTAL RESULTS

The results of the experimental procedure yielded for charge I the pressure-liquid volume per cent isotherms presented in Figure 1. A cross plot of these isotherms produced constant quality relationships of pressure *vs.* temperature as shown in Figure 2. These constant quality relationships were interpolated to a point of convergence, which represents the critical temperature and pressure. For this mixture, the critical temperature and critical pressure were $t_c = 329°$ F. and $p_c = 959$ p.s.i.a., respectively. The established critical values and corresponding compositions of the three ternary mixtures investigated are summarized as follows:

	Mole Fraction			Critical Values	
Charge	Ethane	*n*-Butane	*n*-Heptane	t_c, ° F.	p_c, p.s.i.a.
I	0.429	0.373	0.198	329	959
II	0.726	0.171	0.103	235	1103
III	0.514	0.412	0.074	261	929

The results of these three mixtures constitute the only experimental information available for this ternary system. To extend this background, these experimental critical values have been used along with the critical temperature and critical pressure behavior of the corresponding binaries to generate relationships which are applicable over the entire composition range of this ternary system.

CRITICAL TEMPERATURES

The critical temperatures established for the three ternary mixtures of this system are presented in the triangular composition diagram of Figure 3. This figure also shows critical isotherms which are linear and which were developed from information obtained from the binary systems of the ternary system, ethane–*n*-butane–*n*-heptane. Grieves and Thodos (*2*) have indicated that the critical temperature isotherms of ternary hydrocarbon systems are linear and terminate at the binary systems at compositions corresponding to their critical temperatures. In this connection, they point out from a study of 29 ternary hydrocarbon mixtures that the average deviation from this linearity is 0.93%.

To establish the isotherms, the critical temperature behavior of the binary systems, ethane–*n*-butane (*3*), *n*-butane–*n*-heptane (*4*), and ethane–*n*-heptane (*1*) were used. Binary compositions having the same critical temperature were connected with straight lines to produce the critical isotherms (Figure 3). The critical temperatures determined experimentally in this study for the three ternary compositions are consistent with the over-all pattern of the critical temperature behavior established with these linear critical isotherms for this system.

The linear relationships of Figure 3 can be treated analytically to express the dependence of composition for any critical temperature isotherm. For this ternary system, all critical isotherms originate from the ethane–*n*-heptane binary system, which contains the lightest and the heaviest components of this ternary system. The critical isotherm passing through the points $(n_{27})_2 = 0.750$, $(n_{27})_7 = 0.250$ and pure *n*-butane divides the composition diagram into two regions. If the inequality;

$$(n_{247})_2 > 0.750\,[1 - (n_{247})_4] \tag{1}$$

is satisfied, then the ternary mixture of composition $(n_{247})_2$, $(n_{247})_4$, $(n_{247})_7$ lies in the ethane-rich region. For this case, the critical isotherm can be expressed as;

$$(n_{247})_2 = \frac{(n_{27})_2 - (n_{24})_2}{(n_{27})_4 - (n_{24})_4}\,(n_{247})_4 + (n_{27})_2 \tag{2}$$

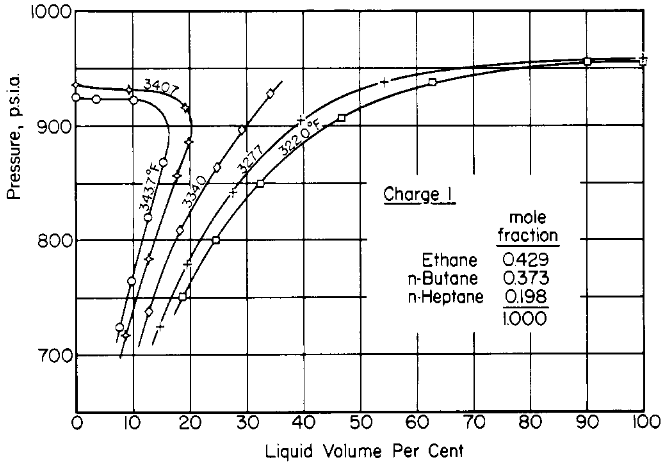

Figure 1. Isothermal relationships between pressure and liquid volume per cent for a fixed charge of ethane–*n*-butane–*n*-heptane

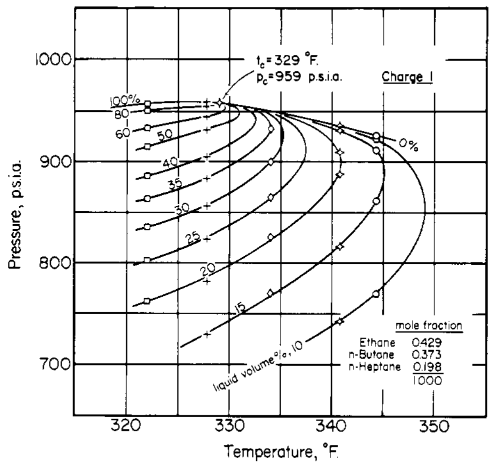

Figure 2. Constant quality relationships of pressure *vs.* temperature for the establishment of the critical temperature and pressure of charge I

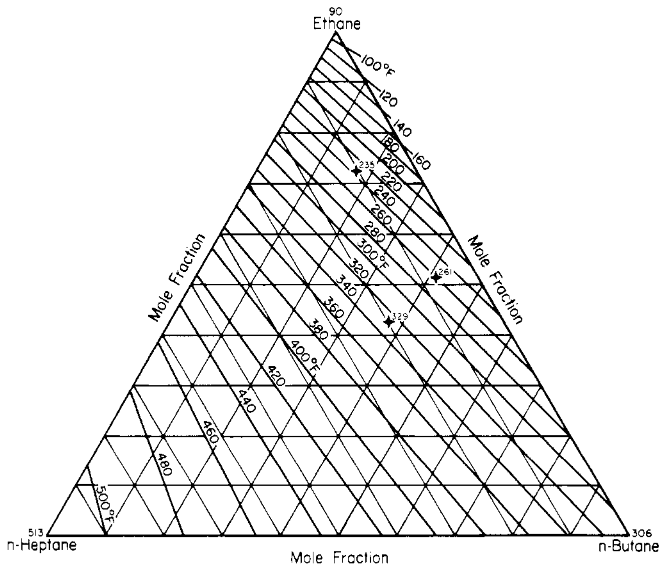

Figure 3. Critical temperature isotherms for the ethane–*n*-butane–*n*-heptane system

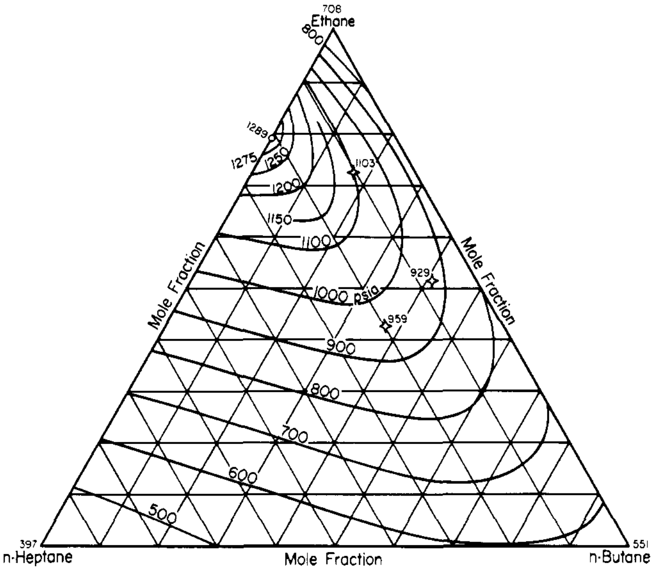

Figure 4. Critical pressure isobars for the ternary system ethane–*n*-butane–*n*-heptane

where $(n_{27})_4 = 0$. On the other hand, if the inequality is not satisfied, the ternary mixture lies in the ethane-lean region, for which the critical temperature isotherm can be expressed as;

$$(n_{247})_2 = \frac{(n_{27})_2 - (n_{27})_4}{(n_{27})_4 - (n_{47})_4} (n_{247})_4 + (n_{27})_2 \tag{3}$$

where $(n_{27})_4 = 0$. The calculation of the critical temperature of a ternary mixture, will involve the use of either Equation 2 or Equation 3 and requires a trial-and-error procedure.

CRITICAL PRESSURES

The three critical pressure measurements were utilized in conjunction with the critical pressure behavior of the corresponding binary systems to generate the critical pressure relationships presented in Figure 4. For a ternary system, the highest critical pressure always occurs on the maximum critical pressure of any one of its corresponding binary systems. For this ternary system, the maximum critical pressure is 1289 p.s.i.a., which corresponds to the maximum critical pressure of the ethane-*n*-heptane system, occurring at $n_2 = 0.795$. A straight line connecting this maximum point on a triangular diagram and passing through an experimental value terminates on either of the other two binary systems. This approach produces from this straight line three compositions whose critical pressures are accessible. For these three values, a plot of P_c *vs.* $(n_{247})_4$ produced a smooth relationship. The same approach was applied to the other two experimental points using always this maximum pressure as a focal point.

A straight line originating from pure ethane on the triangular plot intersects each of the already established straight lines which pass through the experimental points, and terminates on the *n*-butane-*n*-heptane system. Each of these intersections represents a composition and a critical pressure which was obtained from the P_c *vs.* $(n_{247})_4$ plots. These three ternary compositions and their corresponding critical pressures with the critical pressure of pure ethane and the critical pressure of the termination point on the *n*-butane-*n*-heptane system permit the establishment of the relationships of P_c *vs.*$(n_{247})_2$ corresponding to the straight line originating from pure ethane. This procedure was repeated for a pencil of straight lines radiating from pure ethane and all terminating on the *n*-butane-*n*-heptane binary system. A cross plot of these P_c *vs.* $(n_{247})_2$ relationships permitted the construction of the critical isobars of Figure 4.

Because of the temperature limitations imposed on the experimental unit, it was not possible to operate at elevated temperatures in the *n*-heptane-rich region. This limitation confined this study to temperatures below 350° F. to maintain functional the Buna-N rubber O-ring seal around the sight glass. At this temperature level, the possibility of springing leaks around the Teflon gaskets situated at the end closures of the visual *PVT* cell was minimized.

NOMENCLATURE

n = mole fraction
t_c = critical temperature, ° F.
P_c = critical pressure, p.s.i.a.

Subscripts

2 = ethane
4 = *n*-butane
7 = *n*-heptane

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