100° F. and found to be 0.11 B.t.u./Ft^{2}Hr.°F./Ft. The agreement is better than could be expected on the basis of the precision of the measured grease and oil conductivities. These are apparent soap conductivities and depend entirely on the validity of Equation 1. They are, however, consistent with values (*2*) for solids of this type.

Sodium Greases. The same general observations follow for sodium greases. The results for these greases are shown in Figure 3. Using Equation 1, the conductivity of the sodium soap was found to 0.16 B.t.u./Hr. Ft.^{2}° F./Ft. at 100° F. The remarks made concerning the accuracy and validity of the calcium soap calculations apply also to this case.

Clay Grease. The conductivity of the clay, calculated from Equation 1, was 1.10 B.t.u./Hr.Ft.^{2}° F./Ft. which could be compared to a value of 0.98 B.t.u./Hr.Ft.^{2}° F./Ft given by Forsythe (*2*).

Lithium Grease. These explanations apply as well to the results for the synthetic oil-lithium soap grease. The results for the hydrocarbon oil-lithium soap greases (7.5, 14.2, and 17.2% soap) did not follow as closely the simple behavior of the other greases. Figure 4 shows that the data for these greases scatter widely and that a higher conductivity was obtained for the 14.2% soap composition than for the 17.2% soap grease. This scatter and erratic behavior was observed during repeated determinations. Reproducibility would suddenly disappear even after a sequence of determinations had shown no effect on residence time, surrounding temperature, and reloading of the cell. The scattering is relatively small (about 7%), and the dash lines drawn in Figure 4 assume two soap compositions, 7.5 and 15%, and agree reasonably well with the prediction of Equation 1.

Effect of Grease Structure. A large variety of size, shape, and arrangement of the soap particles occurred among the greases studied. In some cases, greases of the same type would show quite different shapes—nearly spherical clumps in contrast to shardlike pieces. In all cases, the effect of the soap can be explained by Equation 1 as a simple composition effect. This implies that the character of the soap particles does not affect thermal conductivity. The thermal conductivity of the oils and soaps differs at most by a factor of 2; furthermore, most greases have a low soap content. Under these circumstances, the soap properties cannot be expected to affect the grease conductivity greatly. Measurements of thermal conductivity, therefore, would not characterize the structure of greases.

CONCLUSION

Thermal conductivity of greases is primarily determined by the thermal conductivity of the oils from which they are made. Thermal conductivity of a grease decreases with temperature at the same rate as its oil.

The effect of soap composition on the thermal conductivity of the greases can be determined by Equation 1 in terms of the conductivities of the pure soap and oil.

Thermal conductivity of greases is not sensitive to size or shape of the soap particles in the grease, and thermal conductivity measurements will not characterize the structure of greases.

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Critical Temperatures and Critical Pressures of Hydrocarbon Mixtures

Methane–Ethane–*n*-Butane System

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CONSIDERABLE experimental information on the critical temperatures and critical pressures of mixtures is presented in the literature. However, it is confined primarily to binary systems and complex mixtures of the natural gas type. Critical constants for systems lying between these two extremes are limited and for the most part have been obtained indirectly from vapor-liquid equilibrium studies. Rigas, Mason, and Thodos (*8*) present critical temperatures and critical pressures for four mixtures of the methane-propane-*n*-butane system. Price and Kobayashi (*5*) present vapor-liquid equilibrium data in the vicinity of the critical point for the methane-ethane-propane system, while Reamer, Sage, and Lacey are able to extract critical information from their vapor-liquid equilibrium data on the ternary systems, methane-*n*-butane-*n*-decane (*6*) and methane-propane-*n*-pentane (*7*) and Billman, Sage, and Lacey on the system methane-ethane-*n*-pentane (*1*).

To broaden the background involving these critical constants for ternary systems and to establish these values by a more direct approach, this investigation considered the three-component system, methane–ethane–*n*-butane.

ESTABLISHMENT OF CRITICAL TEMPERATURES AND CRITICAL PRESSURES

The experimental work of this investigation was conducted in a stainless steel visual *PVT* cell provided with a Herculite sight-glass which made possible the direct observation of the contents of the cell, confined in a cylindrical bore, 150 cc. in volume and 10 inches in length. External means were provided for manually rocking the *PVT* cell to aid in establishing equilibrium. Mercury under pressure was used to vary the free volume of the cell and the temperature of the system was maintained by placing the cell in a thermostated air bath. The details of equipment and mode of operation are described in detail (*3*); pressures should be accurate to within 3 p.s.i. and temperatures to 0.5° F.

The hydrocarbons used were research grade supplied by the Phillips Petroleum Co. The components were charged individually into the *PVT* cell in amounts necessary to approximate the desired composition. Briefly, the mixture was compressed at isothermal conditions with mercury until a single phase was visibly apparent. The pressure was then incrementally decreased and allowed to reach equilibrium. To hasten equilibrium, the *PVT* cell was repeatedly rocked until the pressure of the system no longer changed. At this point, the vapor-liquid interface was noted and used to establish the relative vapor and liquid volumes. This was continued until the full range of the equilibrium cell was traversed. The temperature of the system was then changed and the same procedure was repeated, to establish another pressure–liquid volume per cent isotherm. After several isotherms, covering both complete condensation and retrograde condensation, were established, the temperature of the system was raised sufficiently high to ensure the existence of a single phase during sampling. The composition of these samples was determined with the use of a mass spectrometer.

This approach allowed the establishment of pressure–liquid volume per cent isotherms. A typical set of isotherms is presented in Figure 1 for charge TB containing the following mole per cent composition: methane 19.3, ethane 47.0, and *n*-butane 33.7. For this charge, five isotherms ranging from 167.9° to 199.3° F. were determined. Complete liquefaction was noted for the 167.9° and 177.3° F. isotherms, while the remaining isotherms, 182.0°, 188.2°, and 199.3° F., exhibited retrograde condensation. These five isotherms were then used to generate the phase diagram shown in Figure 2. The point to which the lines of constant liquid volume per cent converge was taken as the critical point, which is t_c = 178° F. and p_c = 1108 p.s.i.a. for this mixture.

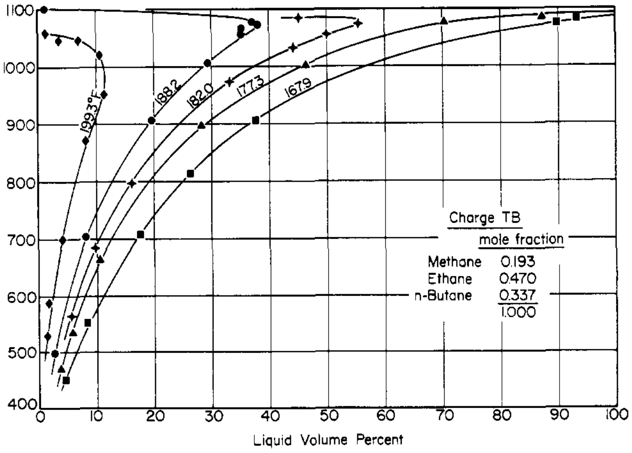

Figure 1. Liquid–volume per cent isotherms for typical three-component hydrocarbon system

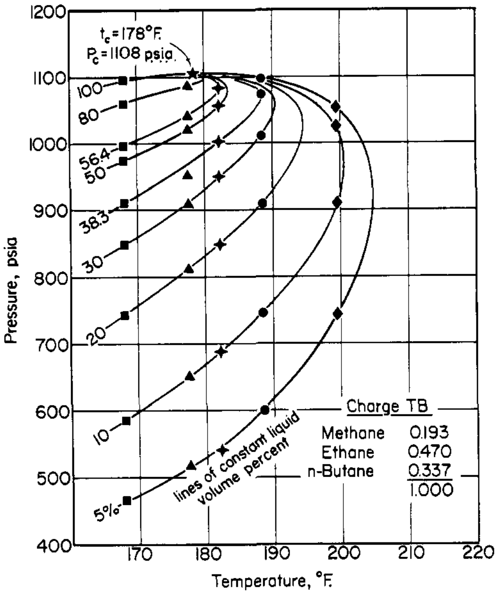

Figure 2. Phase diagram for typical three-component hydrocarbon system

In a similar manner, the critical temperatures and pressures of three additional ternary mixtures were obtained. The results of the work for this ternary system are:

	Mole Fraction				
Charge	Methane	Ethane	*n*-Butane	t_c, ° F.	p_c, P.S.I.A.
TB	0.193	0.470	0.337	178	1108
TC	0.391	0.354	0.255	137	1410
T1	0.007	0.879	0.114	124.5	795
T3	0.040	0.821	0.139	123	840

The dependability of these measurements was checked using two different binary compositions of the ethane–*n*-butane system. The resulting critical temperatures and critical pressures were in good agreement with the critical data reported by Kay (*4*) for this system. These comparisons are as follows:

	Mole Fraction		Critical Temp., ° F.		Critical Pressure, P.S.I.A.	
	Ethane	*n*-Butane	Kay (*4*)	This work	Kay (*4*)	This work
Charge B1	0.602	0.398	204	207	832	837
Charge B2	0.874	0.126	131	130	806	814

In addition, the vapor pressure of propane was measured in this equipment at 125.8°, 175.8°, and 198.3° F. These measured vapor pressures agreed well with values presented in the literature and differed at most by 6 p.s.i. at the highest temperature of 198.3° F., where the vapor pressure of propane is 564 p.s.i.a. and the experimental value was 570 p.s.i.a.

These critical temperatures and critical pressures represent the experimental part of this investigation. This information, although valuable, nevertheless is limited in its present form. However, it can be extended with the aid of information available on the critical temperatures and critical pressures of the respective binary systems to generate triangular plots able to define these critical values for the entire range of compositions of this ternary system.

DEVELOPMENT OF CRITICAL TEMPERATURE PLOT

The observed critical temperatures of the ternary mixtures and the critical temperatures reported in the literature for the binary systems ethane-*n*-butane (*4*), methane-ethane (*2*), and methane-*n*-butane (*9*) have been used to extend the data of this investigation to other compositions of the methane-ethane-*n*-butane system. This extension has been made possible by utilizing certain basic properties associated with triangular diagrams. Charges TB and TC proved valuable in this analysis because of their high methane content. These charges also possess the unique property of having an essentially constant ratio of ethane to *n*-butane. This ratio for charge TB is 0.470/0.337 = 1.395 and for charge TC is 0.354/0.255 = 1.388. This property permits a straight line to be drawn from pure methane through these two points which intersects the ethane-*n*-butane coordinates at $n_2 = 0.582$ and $n_4 = 0.418$. Since this line represents at all times a constant ethane-*n*-butane ratio, the mole fraction of methane completely defines all compositions on this line. Therefore a plot on rectilinear coordinates of the critical temperature *vs.* the mole fraction of methane produces from pure methane, from the two experimental values and from the corresponding methane-free binary system, a curve able to define the critical temperatures of other compositions having the same ethane-*n*-butane ratio. Thus with the aid of this rectilinear plot, critical temperatures can be established on the triangular composition diagram for all possible mole fractions of methane in ternary mixtures having the same ethane-*n*-butane ratio.

At this point it is convenient to introduce the composition parameter suggested by Reamer, Sage, and Lacey (*6*), defined by the following equations:

$$C_1 = \frac{n_2}{n_2 + n_4}$$

$$C_2 = \frac{n_1}{n_1 + n_4}$$

and

$$C_4 = \frac{n_1}{n_1 + n_2}$$

For the constant ethane-*n*-butane ratio considered above, the parameter becomes $C_1 = 0.470/(0.470 + 0.337) = 0.582$ for charge TB and $C_1 = 0.354/(0.354 + 0.255) = 0.581$ for charge TC. This corresponds to the ethane mole fraction of the methane-free binary system.

An extension of this approach, which involved each pure component and its corresponding binary system, has been applied to each experimental ternary composition. Thus each experimental value became an intersection of the three lines originating from each of the pure components and extending beyond this value to intersect the corresponding binary system. Considering lines passing through pure ethane and through the compositions of charges TB and TC, a rectilinear plot of critical temperature *vs.* ethane mole fraction may be constructed as shown in Figure 3. The curves shown in this figure have parametric values of $C_2 = n_1/(n_1 + n_4)$. The critical temperatures, $t_c = 248°$ F. and $t_c = 162°$ F. at $n_2 = 0$, represent the values for the corresponding ethane-free binary systems of charges TB and TC. The line $C_2 = 0.363$ has only a very slight curvature, while line $C_2 = 0.605$ is straight. It therefore can be assumed that the lines for values somewhat greater than $C_2 = 0.605$ will continue to be straight. Consequently, a straight horizontal line should exist that connects the critical temperature of pure ethane and that of a corresponding ethane-free mixture having the same critical temperature. Thus, for the critical temperature of ethane, $t_c = 90°$ F., there exists a binary mixture consisting of $n_1 = 0.738$ and $n_4 = 0.262$ that has the same critical temperature. This condition requires that the addition of ethane to this binary mixture will produce ternary compositions whose critical temperatures are all 90° F. A straight line connecting points $n_1 = 0.738$ and $n_4 = 0.262$ with $n_2 = 1.00$ represents the 90° F. isotherm for this ternary system on the triangular composition diagram. The information provided by this isotherm has been used with that already developed to account for the unknown critical temperatures of several ternary compositions.

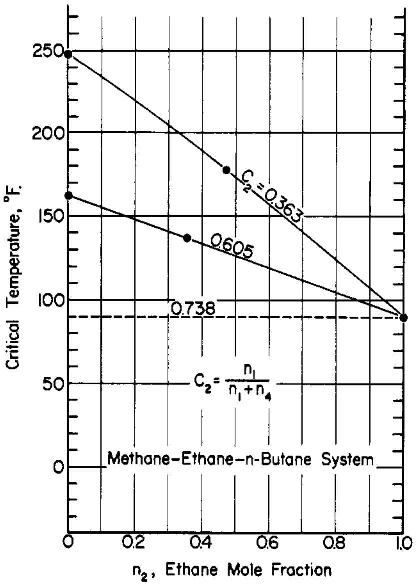

Figure 3. Parameters relating critical temperature to ethane composition

The results of this analysis are presented as open circles in Figure 4. The isotherms best represented by these points were linear and connected the compositions of binary systems having the same critical temperatures. These results suggest the possibility of interesting consequences that may be generally applicable to the prediction of the critical temperatures of ternary systems from information available for the corresponding binary systems.

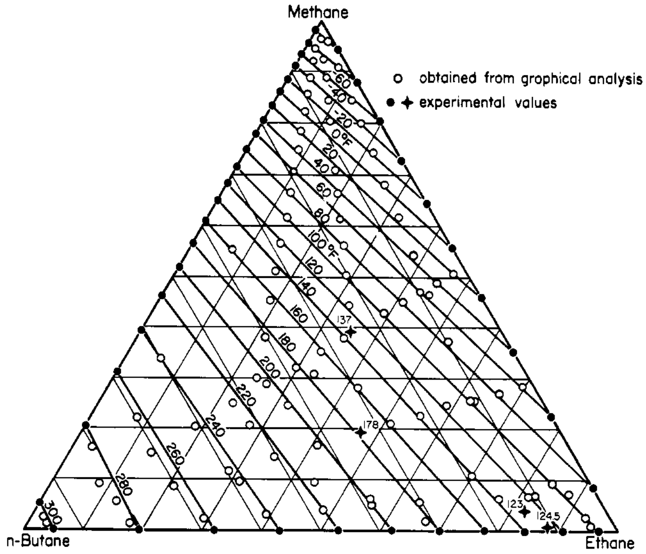

Figure 4. Critical temperatures for methane–ethane–*n*-butane system

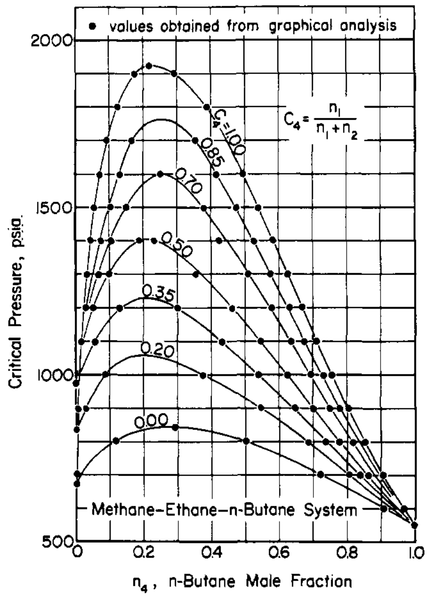

Figure 5. Parameters relating critical pressure to *n*-butane composition

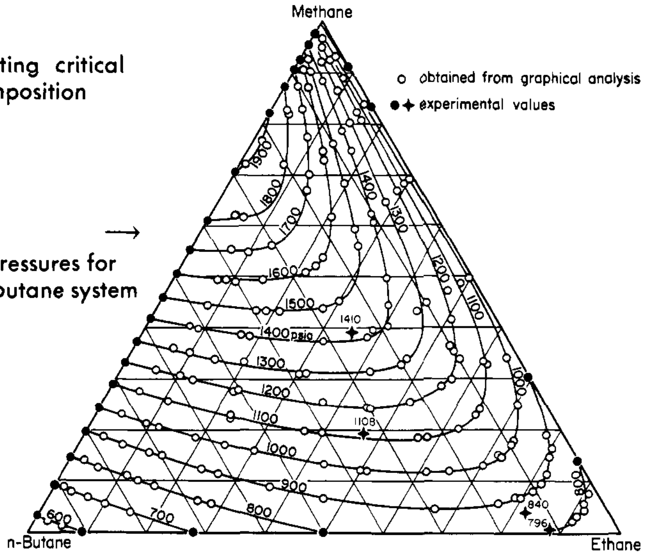

Figure 6. Critical pressures for methane–ethane–*n*-butane system

CRITICAL PRESSURE PLOT

The basic approach utilized for the development of Figure 4 has been applied to construct a corresponding plot for critical pressures. Since critical pressure curves exhibit maxima, it became necessary to develop supplementary graphical techniques. Thus, in addition to the straight lines connecting an experimental value with each of the pure components (lines of constant C_1, C_2, and C_4), three other lines corresponding to a constant composition of each pure component can be drawn through the same point, parallel to each of the three coordinate axes. The combined information obtained from these techniques enabled the construction of a preliminary critical pressure composition diagram. To test the resulting information and at the same time obtain better internal consistency, three cross plots were prepared. One of these, presented in Figure 5, relates the critical pressure to the composition of *n*-butane for constant C_4 parameters.

The final critical pressure plot obtained from the smoothed curves of these three cross plots is presented in Figure 6, where open circles represent values derived from the graphical treatment of the limited experimental data. These values proved adequate for the construction of the critical isobars of Figure 6. The experimental data are also presented in this figure.

COMPARISON WITH PREVIOUS WORK

The earlier experimental work of Forman (*3*), concerned with the determination of critical temperatures and critical pressures for six different compositions of the methane-ethane-*n*-butane system, has been compared with values resulting from the final critical temperature and critical pressure plots developed in this study. This comparison has been prompted by the fact that considerable experience has been gained and techniques have been improved since the original construction and operation of this equipment. Forman's experimental results for six compositions average 16.7° F. lower than the values obtained from Figure 4, while his results for critical pressures average 70 p.s.i. higher than values obtained from Figure 6.

CONCLUSIONS

The method used to develop triangular composition plots for the critical temperatures and critical pressures of ternary systems is generally applicable, not necessarily to this system, but to all ternary systems for which information for the respective binaries is known. By taking advantage of this approach, experimental data on a limited number of compositions may be used to produce the complete behavior of the ternary system. The functional relationships between critical temperatures and critical pressures on the one hand and composition on the other may be simple straight lines or curves.

NOMENCLATURE

C_1, C_2, C_4 = composition parameters for methane, ethane, and *n*-butane, respectively
n_1, n_2, n_4 = mole fraction of methane, ethane, and *n*-butane, respectively
p_c = critical pressure, p.s.i.a.
t_c = critical temperature, ° F.

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