

PREDICTION OF PRESSURE-TEMPERATURE PHASE  
ENVELOPES OF MULTICOMPONENT  
HYDROCARBON SYSTEMS

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## NOMENCLATURE

B	= Boiling point
C	= Constant
CP	= Critical point
F	= Number of independent phase rule variables
K	= Equilibrium constant, K-factor
M	= Molecular weight
n	= Number of components in a mixture
P	= System pressure
PT	= Operating pressure
PK	= Assumed convergence pressure
PKT	= Calculated convergence pressure
T	= System temperature
TC	= Critical temperature
V	= Volume
W	= Weight fraction
x	= Mole fraction of a component in liquid phase
y	= Mole fraction of a component in vapor phase
z	= Mole fraction of a component in a mixture

## Subscripts

av	= Average
C	= Component

i = Component identity index

l = light component index

h = heavy component index

## CHAPTER I

### INTRODUCTION

During the past two decades much effort has been devoted to the study of volumetric and phase behavior of pure paraffin hydrocarbons and their mixtures. Because of the practical importance in the petroleum, natural gas and related industries, most of the mixtures investigated consisted primarily of normal paraffin hydrocarbons with small quantities of nitrogen, carbon dioxide and/or some hydrogen sulfide present. Since the required experimental effort increases markedly with the number of components present, the vast majority of experimental data are for binary systems.

Industrial operations frequently involve mixtures containing more than two components. The operating temperature, pressure and composition are seldom the same as for those for which experimental data are available. For practical design, it is therefore necessary to develop correlations, by reducing, generalizing and extending the available data, to cover a wide range of conditions for both simple and complex mixtures.

Reservoir engineering problems involve the prediction of the properties of such complex mixtures. The study of these properties is encompassed in the science of phase behavior. This particular area is assuming greater importance in recent years, due to the fast depletion of available reserves which has prompted the need for deeper drilling operations. In turn, the need for better understanding of phase

relations, especially at high pressures where non-ideal behavior of mixtures is common, is apparent. An understanding of phase diagrams is fundamental to a thorough treatment of nearly all operations involved in volatile oil recovery, refining and transportation.

Very often, the phase envelopes which describe the fluid that exists in a reservoir are used for the classification of reservoirs. It is essential to know the type of reservoir in order to employ suitable production methods to recover a maximum amount of reserves economically. For example, if the reservoir pressure and temperature are sufficiently high relative to the phase envelope, as indicated by point A in Figure 1, it may be economically feasible to miscibly displace the fluid with a drier, less expensive gas.

Normally for a newly found reservoir, various production programs are considered to arrive at the most economical program, in the light of environmental conditions. The production method selected will depend mainly on the type of the reservoir. For instance, if reservoir conditions are represented by point d in Figure 1, the reservoir is classified as undersaturated. On the other hand, point A represents a condensate reservoir for which gas injection may be feasible.

In addition, there are several secondary benefits that can be derived from the phase envelope data. They include the development of correlations to predict the true critical pressure, true critical temperature of mixtures, and K-factor for the components in a given mixture.

The phase diagrams of reservoir fluids are normally generated by laboratory measurements involving expensive P-V-T equipment. Such methods are tedious and time consuming. Further, good experimental data

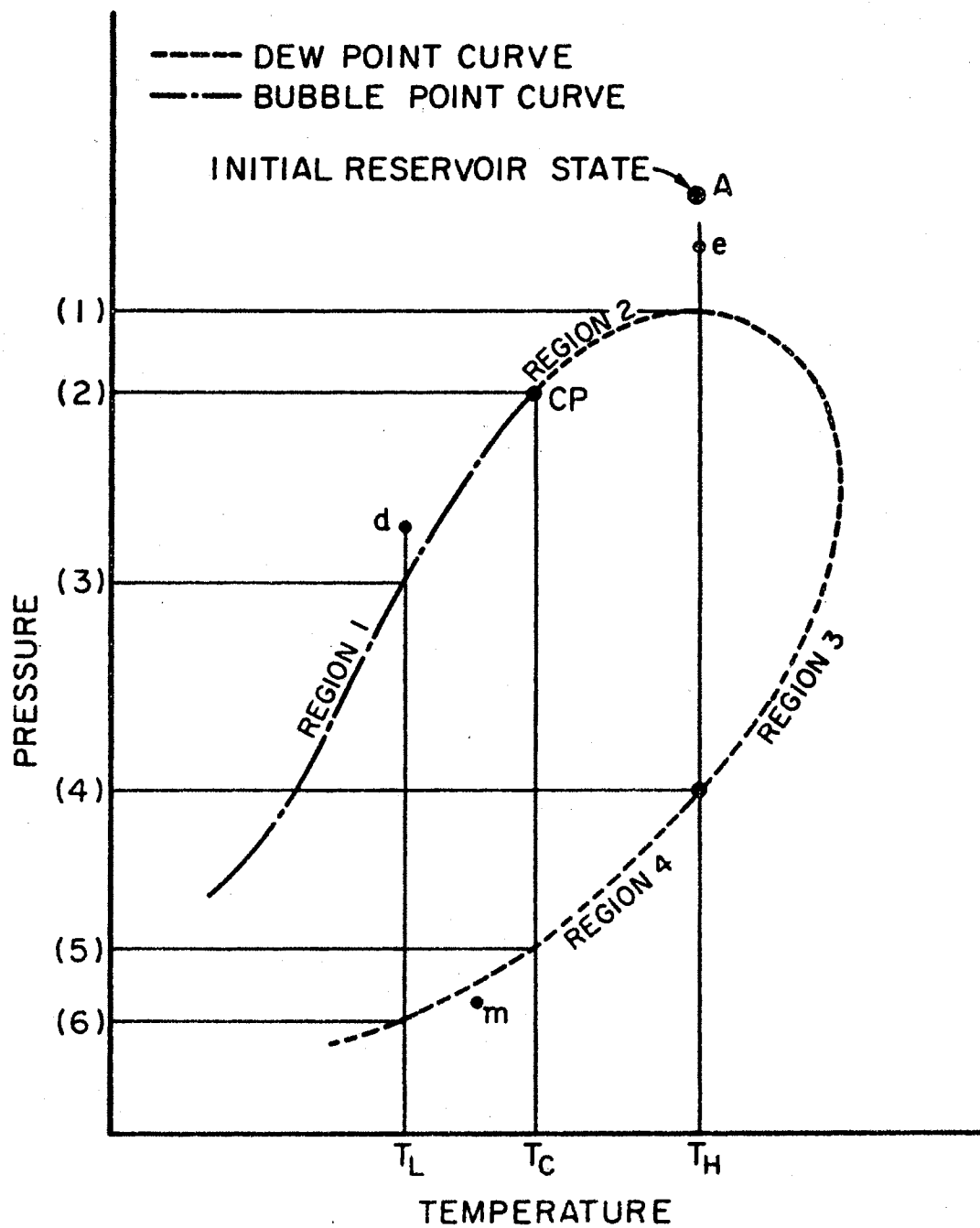


Figure 1. Pressure-Temperature Phase Envelope of a Multicomponent System

are not easily obtained, but require considerable experimental skill, experience and patience. It is therefore desirable to consider techniques for calculating the pressure-temperature phase envelopes for any reservoir fluid. Such techniques should be theoretically sound in order to be reliable for interpolation and extrapolation with respect to pressure, temperature, and composition.

It is the object of this work to develop a computer program to generate data necessary to plot phase diagrams describing reservoir fluids. The method developed in this study to generate the phase envelope is based on a recently published procedure for the calculation of convergence pressure known as the Critical Composition Method (59). There are several reasons for selecting the referenced method of approach. For one, it is a method which has been successfully used in phase envelope calculations at high pressures, especially in the neighborhood of critical region (58). At low pressures, where the assumption of ideal solution behavior is adequate, equations of state (3, 55) can be used with success. However, reservoir engineering phase calculations frequently involve high pressure process calculations and in such cases, only the Critical Composition Method has been used with accuracy (58).

As will be shown later, the accurate prediction of convergence pressure is mainly dependent on the accurate calculations of true critical temperature and critical pressure of mixtures. Further, an accurate phase envelope prediction is markedly influenced by the K-factors used, especially near the critical region. Hence, this study involves developments in these two major areas.



Presently no reliable method is available to predict the critical properties of mixtures. Many empirical correlations have been proposed for the calculation of critical temperatures and pressures (14, 19, 26, 28, 31, 41, 49, 68, 69, 74). However, none were adequate for predicting critical properties over a wide composition range. This led to the development of new correlations for calculating the critical states.

A number of correlations have been published for calculating K-factors. Some of them are empirical and others are semitheoretical (6, 24). But, no method is capable of accurately predicting the K-factors over a wide pressure and temperature range for multicomponent systems that include the critical state. The available data on K-factors (16, 17) are either restricted due to the lack of a suitable method for calculating convergence pressure and/or inaccuracy in the neighborhood of critical region. Techniques are developed in the present work to modify the existing Natural Gas Processors Suppliers Association K-factors in the region near critical state, so that the K-factors are in close agreement with the experimental values. Such improved K-factors can be of significant use to reservoir engineers faced with solving volatile oil and condensate problems.

## CHAPTER II

### PHASE DIAGRAMS

#### 2.1 Phase Diagrams

The designation "phase diagram" is used in this work in referring to the pressure-temperature phase envelope. In order to explain the method of phase envelope generation and to provide sufficient background for the application of convergence pressure theory, the following discussion is provided.

#### 2.2 One Component Systems

The analysis of one component system is relatively simple. For most pure components, the physical properties have been experimentally determined and are listed by Rossini et al. (57). According to Gibbs' phase rule for two phases coexisting in equilibrium,

$$F = c - p + 2 = 1 \quad \text{for } c = 1 \quad (2.1)$$

where

$F$  = degrees of freedom,

$c$  = number of components, and

$p$  = number of phases.

Thus, if the temperature of the system is specified that is below the critical temperature only one pressure exists when both liquid and gaseous phases are in equilibrium. This pressure corresponds to the

vapor pressure at the given temperature. For one component systems, the critical temperature can be defined as the temperature above which two phases cannot exist, regardless of the pressure of the system. Likewise, the critical pressure is that pressure above which vapor and liquid cannot coexist in equilibrium. The K-factor for a one component system at the vapor pressure is unity since only one component exists in each phase. A typical pressure-temperature phase diagram for a one component system is shown in Figure 2.

### 2.3 Two Component Systems

According to the phase rule, for a two-phase binary system at equilibrium, the number of intensive variables to be specified in order to completely specify the system is two. This results in a slightly more complex diagram than that of pure compounds. A typical phase diagram for a binary system is shown in Figure 3.

Two main differences are apparent when comparing a single component to two component system. The first one is that the pressure-temperature relationships can no longer be represented by a single vapor pressure curve; and secondly, a different definition of critical temperature and pressure must be used to describe the critical state.

The pressure-temperature diagram of a binary system takes the form of an envelope as shown in Figure 3. The area within the envelope defines the pressure-temperature range where a liquid coexists with vapor in equilibrium. Point C in Figure 3 represents the critical pressure and critical temperature of the mixture. The part of the phase boundary, DC, for temperatures less than the critical temperature is the bubble point locus. The rest of the portion of the envelope is the dew

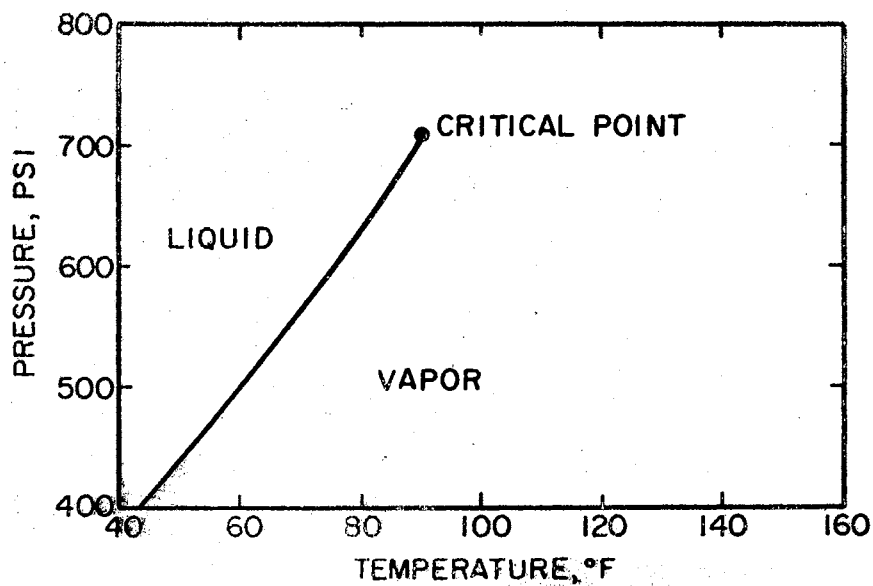


Figure 2. Pressure-Temperature Diagram for One Component System - Ethane

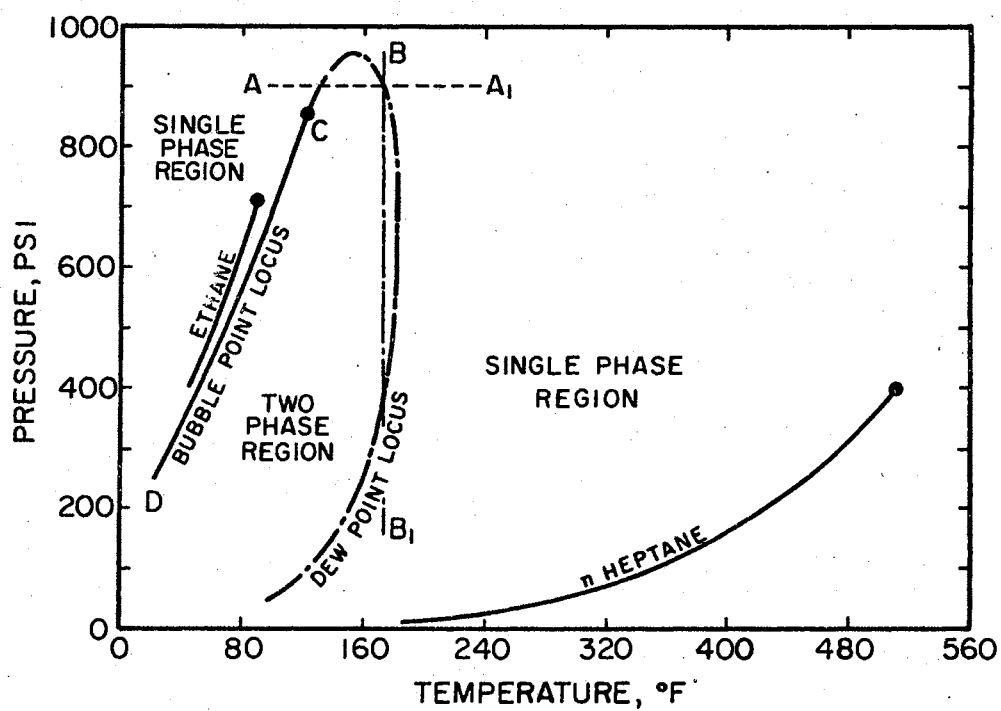


Figure 3. Pressure-Temperature Diagram for a Two Component System

point boundary. Pressures lower than that indicated by the dew point locus represent states where the mixture is entirely in the gas phase. At temperatures lower than the critical temperature, and pressures exceeding that indicated by bubble point locus, the mixture exists in a liquid state. No abrupt changes are observed in the values of properties measured in the single phase region outside the phase boundary. The fluid is considered to be liquid at the bubble point boundary and a vapor at the dew point boundary.

The salient features of this diagram are:

- (1) Two phases can coexist in equilibrium at a temperature above the critical temperature and a pressure above the critical pressure.
- (2) Along line  $B B_1$ , a temperature above the critical, an increase in pressure above the dew point first causes condensation as expected. However, with further increase in pressure, the condensed liquid will ultimately evaporate until the system is again all vapor, and enter into a single phase region. This phenomenon is known as isothermal retrograde vaporization.
- (3) Similarly, along the constant pressure line  $A A_1$ , an increase in temperature above the critical pressure causes condensation instead of vaporization. This phenomenon is referred to as isobaric retrograde condensation.

From inspection of Figure 3, it is apparent that the definition of the critical temperature and pressure used for a pure compound cannot be applied to a binary mixture, as multiple phases exist at pressures and temperatures greater than the critical values. Hence, the critical state is defined as that state at which all intensive properties of the

liquid and vapor phases become equal. This definition applies equally to pure compounds. The critical pressure, critical temperature, cricondetherm and cricondenbar are functions of the composition of the particular mixture.

The effect of the change in composition on the phase diagram is shown in Figure 4. When the concentration of the heavier component in the overall composition of the mixture is increased, a similar envelope is obtained having a critical state at  $C_1$ . A locus of such critical temperatures and pressures can be determined by varying the concentration of the lighter component in the overall mixture from 0 to 1. Such a critical locus is represented by DF in Figure 4. Every point on this locus is a critical pressure for the binary system composed of the given light and heavy components. Furthermore, for a given temperature, the convergence pressure is equal to the critical pressure at that temperature (60).

#### 2.4 Systems Containing Three or More Components

The phase diagram of a multicomponent mixture is similar in many respects to the phase diagram of a mixture of two components. A typical phase envelope for a natural hydrocarbon mixture is presented in Figure 5. Composition A represents a mixture of light hydrocarbons similar to the gas from an oil-gas separator at a producing well. In general, composition D represents a mixture of heavy hydrocarbons resembling the liquid phase recovered simultaneously at the separator. Compositions B and E represent hydrocarbon mixtures of intermediate composition, such as would be obtained by mixing fluids A and D in different proportions.

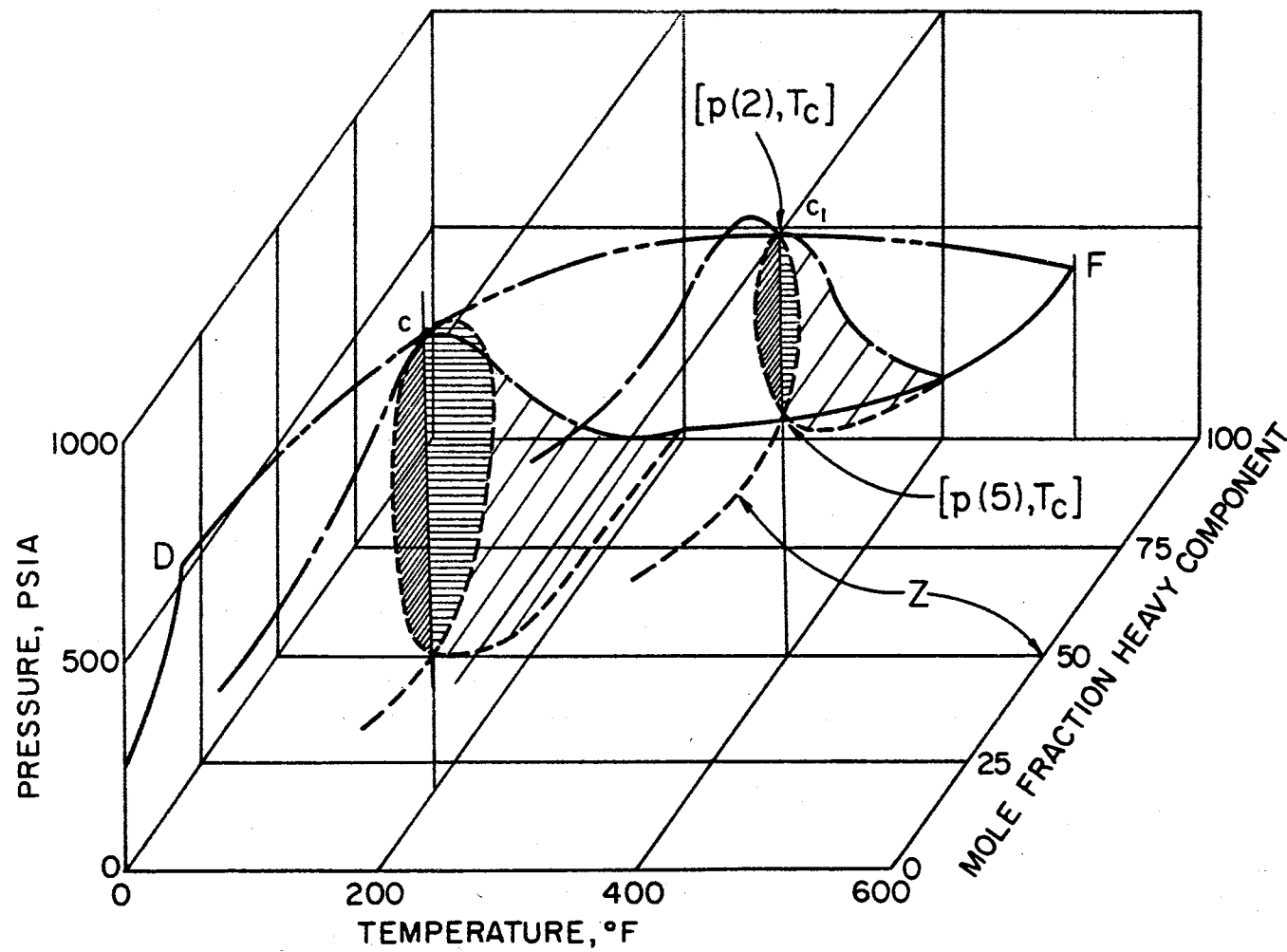


Figure 4. Pressure-Temperature-Composition Diagram of a Two Component System

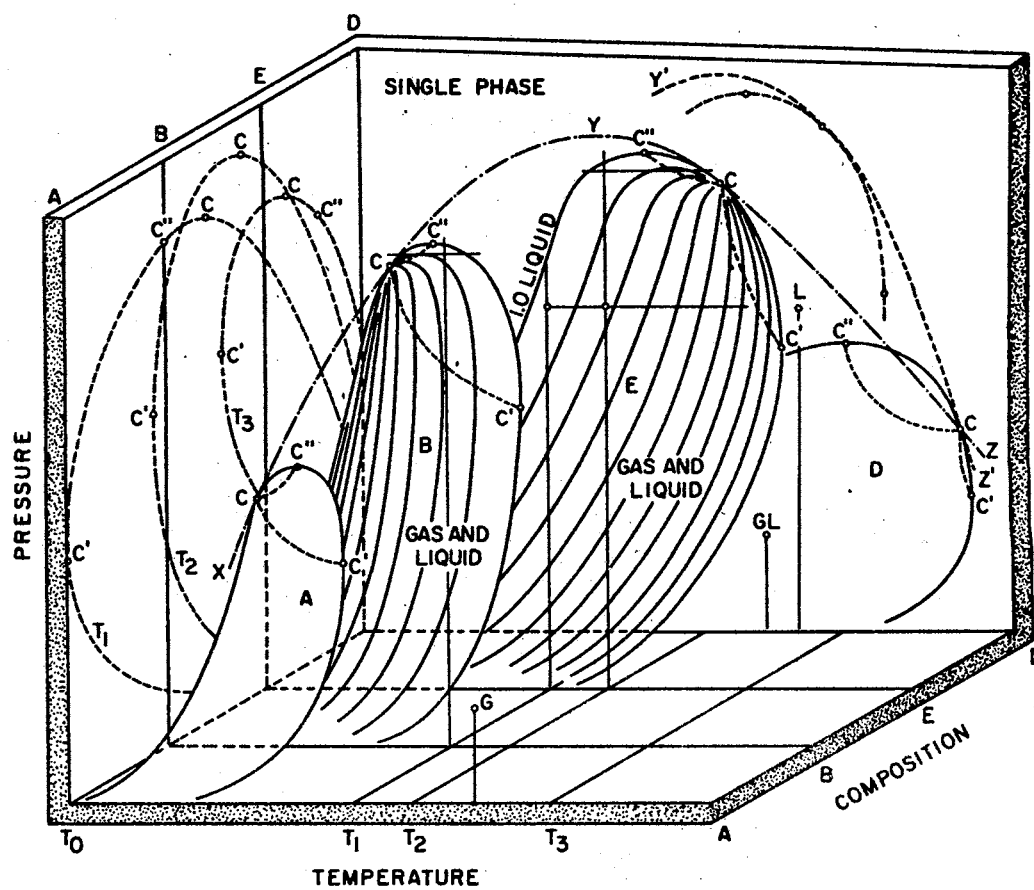


Figure 5. Phase Envelope for a Multicomponent System



Figure 5 shows four of the phase envelopes of innumerable number of envelopes that can be generated. The pressure-composition diagrams, at constant temperatures  $T_1$ ,  $T_2$ , and  $T_3$  are also shown by projecting the phase envelopes onto the pressure-composition plane. On each envelope the critical point is represented by C. A portion of the locus of critical points XYZ is projected on the pressure-temperature plane and is represented by Y'Z'. The curves within the two phase region of phase envelopes B and E represent the loci of constant liquid volume lines. The cricondenbar and cricondentherm are denoted by C" and C', respectively, for all the envelopes.

It is to be noted that the projection of point C onto the pressure-composition plane is not necessarily in the position of maximum pressure on projections of all pressure-composition sections at given temperatures.

At points within the phase envelope, the liquid and vapor coexist in equilibrium for a given mixture. At all other points outside the envelope, the mixture exists in a homogeneous single phase. The properties of single phase mixture vary with pressure, temperature and composition, but in a continuous manner. The single phase may be either liquid or gas. For instance, the phase relations for a reservoir fluid containing and producing only natural gas may be represented by point G. Similarly the phase relations at reservoir pressure and temperature of a homogeneous undersaturated crude oil in a reservoir having no gas cap may be denoted by point L with respect to envelope D. As the undersaturated crude oil is produced, dissolved gas is liberated when the pressure is lowered to the bubble point, and the mixture originally present in the reservoir as a single liquid phase flashes into two

phases. The state of an oil found coexisting with gas in a reservoir is represented by GL in Figure 5, in the pressure-temperature plane with respect to the envelope D.

The phenomenon of retrograde condensation and vaporization also occurs for multicomponent mixtures as explained for binary mixtures.

## CHAPTER III

### LITERATURE SURVEY

The literature contains many articles on the subject of phase behavior. Most of them deal with specific binary systems, while relatively few papers are available on ternary systems. Since the main interest of the present work concerns the phase behavior of reservoir fluids, a detailed review of literature is presented only for such systems. Table I presents the summary of experimental work carried out on binary and ternary systems.

In the past years, the phase envelopes of reservoir fluids were determined experimentally. Only recently has an attempt been made to determine them empirically (48).

Early work on the subject of phase behavior of gaseous mixtures can be dated to 1892 to the work of Kuenen (40). The first paper in the present era concerned with gas mixtures similar to natural gases is that of Sage, Lacey and Schaafsma (63), in which they presented the behavior of the methane-propane system. The nature of border curves between vapor and liquid phases and the critical temperature and pressure locus of this binary system were presented in this work.

In 1939, Katz, Vink and Davis (35) studied the phase envelopes of a mixture of natural gas and natural gasoline. A glass windowed cell was used in their experiment and the data were presented covering a pressure range of 1300 to 2600 psia in the temperature range of 85° to

TABLE I

SUMMARY OF EXPERIMENTAL WORK DONE ON PHASE BEHAVIOR  
OF BINARY AND TERNARY SYSTEMS

System	Year	Reference
Methane - Ethane	1953	4
	1959	51
Methane - Propane	1934	63
	1950	52
	1954	2
	1970	77
Methane - n Butane	1940	64
	1962	56
Methane - n Pentane	1942	66
Methane - n Heptane	1956	53
Ethane - Propane	1962	43
Ethane - n Butane	1940	37
Ethane - n Pentane	1960	54
Ethane - n Heptane	1938	36
Propane - n Butane	1940	47
	1970	39
Propane - n Pentane	1940	65
	1970	39
n Butane - n Heptane	1941	38
n Pentane - n Heptane	1933	8
Methane - Ethane - n Butane	1962	7
	1962	22
Ethane - Propane - n Pentane	1960	18
Ethane - n Pentane - n Heptane	1966	15
Propane - n Butane - n Pentane	1953	45
	1960	18
n Butane - n Pentane - n Hexane	1960	18

212<sup>o</sup>F. The critical point of the mixture studied was determined by visual observation. The approximate densities of the fluids in the single phase and two phase regions were also reported. However, the molecular weight of hexanes plus fraction was not presented.

Buckley (5), in 1941, presented the phase envelope of a natural gas system. The main object of his work was to obtain quantitative information on the limitations attending the recovery of distillate from natural gas by controlling the temperature and pressure of separation. The combined effects of pressure and temperature variation on the condensation phenomenon were discussed.

In 1942, Kurata and Katz (41) presented a method to calculate the critical temperatures and critical pressures of volatile hydrocarbon mixtures. Experiments were conducted on eleven mixtures covering a critical pressure range of 1706 to 2900 psia, and a critical temperature range of 54<sup>o</sup> to 189<sup>o</sup>F. For all the mixtures, the pressure-temperature envelopes were presented as a part of their study.

To meet the growing demand for equilibrium constants at high pressures, Standing and Katz (71) undertook the study of a crude oil and natural gas system in 1944. The reported data include the densities, equilibrium constants and the partial phase envelope for a mixture of 49.9<sup>o</sup> API crude oil and natural gas, having a gas-oil ratio of 3660 cubic feet per barrel. The variation of concentration and the molecular weight of heptane plus fraction on the phase diagrams were discussed qualitatively.

Two different mixtures containing five light paraffin hydrocarbons were studied in 1945 by Hanson and Brown (29). The experimental apparatus used was similar to the one used by Kurata and Katz. Phase

diagrams were determined for both the mixtures experimentally, including the critical states of the mixtures.

For the first time, a set of empirical correlations were reported in the literature by Standing (72) in 1947 for the calculation of bubble point pressures, formation volumes of bubble point liquids as a function of gas-oil ratio, oil gravity and the formation volume factor. The empirical correlations were based entirely on data collected for California oils and gases.

In 1948, experiments were conducted at low temperatures by Eilerts et al. (13). The phase behavior of four mixtures of natural gas and well condensate were studied in the temperature range of  $-65^{\circ}$  to  $100^{\circ}$  F by these investigators. The phase envelopes for the mixtures studied were reported along with the specific volumes and gas-oil ratios. The observation of a high critical temperature of the separator gas relative to the critical temperature of the gas condensate fluid flowing from the well was a significant aspect of this work.

The continued quest for adequate reserves has resulted in deeper drilling with high bottom hole pressures, with the result that the knowledge of phase relations at pressures above 10,000 psia became important. This led Rzasa and Katz (61) to study the phase behavior of methane-kensol 16 system, up to 25,000 psia and temperatures up to  $260^{\circ}$  F. The partial phase envelopes of six different mixtures with constant volume lines were presented. The studies at such high pressures are of considerable importance in producing and controlling oil reservoirs found at depths of the order of 12,000 to 15,000 feet.

In 1951, Weinaug and Bradley (75) presented the P-V-T data for a naturally occurring hydrocarbon system whose critical temperature was

near the reservoir temperature. The system investigated exhibited unusual behavior in the region below the critical temperature. When the pressure on the system was increased, normal condensation took place until a maximum percentage of liquid was formed. Further increase in pressure resulted in isothermal retrograde vaporization causing a decrease in liquid volume percentage. The liquid volume continued to decrease until it reached a minimum value. A further increase in pressure resulted in a larger increase in volume percentage, and the system finally passed into the single phase region through the bubble point. This behavior was called renascent vaporization or condensation by the authors.

Sage and Reamer (67) in 1952 reported experimental results on the volumetric behavior of gas condensate systems obtained from a Louisiana field. Though the paper did not directly present the phase envelopes, it was possible to draw them from the reported results for any gas-oil ratio between 6000 and 14,000 cubic feet per barrel. Additional work in the low temperature ranges were pursued by Gore, Davis and Kurata (9, 23). They studied the phase behavior of natural gases in the temperature range of  $-40^{\circ}$  to  $-200^{\circ}$  F. From the experimental data, pressure-volume curves were drawn at constant temperatures. A cross plot was made to construct the phase envelopes of the mixtures they studied. Empirical equations were developed by the authors to evaluate the critical pressure and critical temperature of the mixtures at low temperatures, by improving and extending the correlations proposed earlier by Kurata and Katz (41).

In the same period, Organick and Golding (48) presented a set of charts for the prediction of saturation pressures for condensate gas and

volatile oil mixtures. The saturation pressure was related directly to the composition of the mixture, with the aid of two generalized composition characteristics. They were the molal average boiling point and the modified molecular weight of the mixture calculated on the weight basis. A series of charts, each comprising a family of curves, were constructed to determine the saturation pressures.

In 1957, Eilerts et al. (14) published a complete set of phase diagrams for eight gas condensate fluids at various gas-oil ratios. The data were taken from the actual producing wells at the field by a mobile laboratory. The effects of the variation of gas-oil ratio on the phase diagrams were discussed in this monograph.

The data presented by Jacoby, Koeller and Berry (30), and Zaffarano, Cupps and Fry (78) were incomplete as far as the complete phase diagrams are concerned. Only a few points could be obtained from the data reported.

Experiments were conducted on a typical high pressure condensate system by Kilgren (42) in 1966. A partial phase envelope for the reservoir fluid was presented in his work. The envelope did not include the critical point. It was found during the experiment that the critical pressure was higher than the safe operating pressure of the P-V-T cell. Data were taken up to a maximum pressure of 14,000 psia.

Nemeth and Kennedy (44) in 1967 proposed an empirical equation based on experimental data for the calculation of upper dew point pressures of reservoir fluids. The equation suggested contained eleven constants. The dew point pressure was expressed as a function of composition of the reservoir fluid, pressure, temperature, and the density and molecular weight of heptane plus fraction. An average



deviation of 7.4% was noted between the experimental and calculated dew point pressures for the 480 systems tested.

In 1969, Farley, Weinaug and Wolfe (21) used the Benedict-Webb-Rubin equation of state to predict the dew point pressures of gas condensate systems. The heavy end of the component was arbitrarily split into ten pseudo components of increasing molecular weight, and the density and the molecular weight of these components were estimated by extrapolation. The coefficients of Benedict-Webb-Rubin equation were modified using the experimental data obtained from several gas condensate systems. The average deviation was reported to be 14.7% for the 19 systems tested.

In 1971, Kaliappan and Rowe (32) presented a systematic procedure to calculate the phase envelopes of multicomponent hydrocarbon systems, using the Critical Composition Method to calculate the convergence pressure (59).

## CHAPTER IV

### DEVELOPMENT OF CORRELATIONS

#### 4.1 Prerequisites for the Solution

The accuracy of a phase envelope prediction is dependent mainly on the correct selection of K-factors, for a given pressure, temperature and composition, for each component in a given mixture, including that for the heptane plus fraction. In turn, the effect of composition on the K-factors is evaluated through the convergence pressure parameter. This parameter can only be determined through accurate correlations to predict the true critical pressure and true critical temperature for a given mixture. Thus, the final results of this work are dependent on all these parameters. Hence, this chapter is devoted to a discussion of presently available methods to calculate these parameters, and to improvements and/or modifications made in evaluating them.

#### 4.2 K-factors

The K-factor or equilibrium ratio, is defined as the ratio of the mole fraction of a given component in the vapor phase  $y_i$ , to the mole fraction of the same component in the liquid phase  $x_i$ . Thus,

$$K_i = \frac{y_i}{x_i} \quad (4.1)$$

where

$K_i$  = equilibrium ratio of component  $i$ ,

$y_i$  = mole fraction of component  $i$  in the vapor phase, and

$x_i$  = mole fraction of component  $i$  in the liquid phase.

Several methods have been proposed and used in the literature for the determination of K-factors (6, 12, 24). However, the following two methods are most frequently used in industry.

- (1) K-factors are determined by using an equation of state to determine P-V-T-Z relationships of non-ideal solutions (3, 55). The calculation of K-factors through such equations of state are time consuming due to the iteration processes involved. To simplify such calculations, fugacity coefficients and activity coefficients have been introduced to account for the non-ideal behavior of solutions, and the results have been correlated as functions of pressure, temperature and molal average boiling points of the equilibrium phases (10).
- (2) K-factors have been directly correlated as a function of pressure, temperature and convergence pressure from experimental data. It has been observed that K-factors obtained experimentally as a function of pressure, for a mixture of fixed overall composition at constant temperature can be correlated as a function of a composition variable, called the convergence pressure (29, 33, 34).

In the present work, the second method was chosen for selecting K-factors.

#### 4.2.1 Modification of K-factors

K-factors obtained experimentally have been presented in the graphical form as a function of pressure, temperature and convergence

pressure by NGPSA (16, 17). K-factors are given for the components methane through decane for convergence pressures of 600, 800, 1000, 2000, 3000, 4000, 5000, 10000 and 20000 psi, covering a wide range of temperatures.

Analytical expressions were developed to fit these curves and the correlations were presented by NGPSA (46). A comparison of K-factors given by the NGPSA handbook to experimental values was made recently (32). This comparison indicated that the K-factors presented in the handbook are in error by as high as 50% in the vicinity of the critical state for the heavier components. A close examination of the methods employed by NGPSA to obtain the K-factor charts revealed some reasons for these errors. They are summarized as follows:

- (1) The experimental values of equilibrium constants are available for limited pressures and temperatures only. The other values were obtained by extrapolation and cross plotting available values.
- (2) Some of the published data are inconsistent with the other experimental data reported for the same component at the same pressure, temperature and convergence pressure.
- (3) The reduction of experimental data to discrete convergence pressures involves interpolation and extrapolation with its associated errors.
- (4) The critical pressure and temperature values, which were used to correlate the K-factors, differ considerably from recently reported values (7). This is due to improvements made in the experimental equipment and techniques.
- (5) The shape of the slope of K-factors with pressure for any

component at constant temperature differs considerably near the convergence pressure when binary and multicomponent mixtures are compared, especially those containing heavy components.

- (6) The revised NGPSA handbook contains K-factors generated through analytical expressions developed by Green and Hackmuth (24). Essentially, the expressions are developed only for binary mixtures and are of the form

$$K_i = \left(1 - \frac{PT}{PK}\right)^n f(PT) \quad (4.2)$$

where

$K_i$  = equilibrium constant for component  $i$ ,

$PT$  = operating pressure, psi,

$PK$  = convergence pressure, psi, and

$n$  = constant,

at constant temperature. Such correlations are not satisfactory at low temperatures for the less volatile component, and at high temperatures for the more volatile components in a binary mixture (24).

A complete modification of NGPSA K-factors at all pressures, temperatures and convergence pressures would involve an extensive collection of experimental values and would be quite time consuming. Further, for many components the experimental K-factors are not available over a considerable range of pressures and temperatures. The K-factors given in the handbook are the extrapolated values. However, it was decided to correct the existing K-factors in the neighborhood of critical region, since the K-factors of heavy components are extremely

sensitive to pressure in this region. The existing analytical correlations (46) do not converge to unity at the respective convergence pressures. Hence, a new method is developed in this study to force the K-factors of all the components to unity at the convergence pressure, in accordance with experimental observation as outlined below.

For pressures higher than 0.7 times the convergence pressure, the following expressions were considered to calculate the K-factors

$$K_i = C_1 \left(1 - \frac{PT}{PK}\right)^n + C_2 \left(\frac{PK}{PT} - 1\right) + 1 \quad (4.3)$$

$$K_i = C_1 \left(1 - \frac{PT}{PK}\right)^n + C_2 \left(1 - \frac{PT}{PK}\right)^n \frac{1}{PT} + 1 \quad (4.4)$$

$$K_i \sim C_1 \left(1 - \frac{PT}{PK}\right)^{n_1} + \frac{C_2}{n_2 PT} + C_3 \quad (4.5)$$

$$\ln K_i \sim C_1 \left(1 - \frac{\ln PT}{\ln PK}\right)^n - \ln PT + C_2 \quad (4.6)$$

where

$n, n_1, n_2, C_1, C_2, C_3 = \text{constants,}$

$PT = \text{operating pressure, and}$

$PK = \text{convergence pressure,}$

at constant temperature.

The salient features of these equations are that the K-factors become unity when the operating pressure is equal to the convergence pressure. Also, the slope of K-factor with pressure curve is infinite when the operating pressure is equal to the convergence pressure.

All the four equations (4.3) to (4.6) were tested extensively using available experimental values near the critical region. Equation

(4.3) was selected since it was simple to use and gave consistently good results.

It will now be shown that Equation (4.3) meets the requirements discussed earlier. At operating pressure  $P_T$  equal to the convergence pressure  $P_K$ , Equation (4.3) becomes,

$$K_i = 1 \quad . \quad (4.7)$$

Differentiating Equation (4.3) with respect to  $P_T$ ,

$$\frac{dK_i}{dP_T} = C_1 n \left(1 - \frac{P_T}{P_K}\right)^{n-1} \frac{(-1)}{P_K} - C_2 \left(\frac{P_K}{P_T^2}\right) \quad (4.8)$$

$$1 < n < 0 \quad (4.9)$$

for heavy components

$$C_1 < 0 \quad (4.10)$$

when

$$P_T = P_K, \quad \frac{dK_i}{dP_T} = +\infty \quad . \quad (4.11)$$

For the lightest component such as methane at higher temperatures, a slope of  $-\infty$  is required; then,

$$C_1 > 0 \quad . \quad (4.12)$$

The method of determining the values of  $C_1$ ,  $C_2$  and  $n$  at any temperature for a component  $i$  is explained in Appendix E.

#### 4.3 K-factors for the Heptane Plus Fraction

Usually in the analysis of reservoir fluid, the overall composition of the system will be reported for components carbon dioxide, nitrogen, and methane through hexane. The remaining heavy ends will be totalled

together and reported as heptane plus. The behavior of this heptane plus component is extremely difficult to predict, since the number and nature of components contained in this fraction varies widely from one reservoir fluid to another. Farley (21) proposed an empirical method to split this heptane plus into several pseudo components and to treat them individually. However, the suggested empirical K-factors involve the same order of uncertainty as treating it as one single component.

It is quite possible that two reservoir fluids with the same molecular weight for heptane plus may exhibit entirely different behaviors. Hence, the generalization of K-factors for heptane plus fraction is very difficult. However, if it is assumed that the heptane plus fraction contains only paraffin hydrocarbons, it is possible to predict the K-factors with reasonable accuracy (60).

The K-factors of the heptane plus is influenced by the molecular weight of heptane plus, the operating pressure PT, and the convergence pressure PK. In this work various combinations of these independent variables were tried; the relation finally chosen was of the form,

$$K_{C_{7+}} = K_{C_7} (K_{C_7}/K_{C_9})^m \quad (4.13)$$

where

$$m = \frac{W_{C_{7+}} - 100.198}{28.05} , \quad (4.14)$$

$$W_{C_{7+}} = M_{C_{7+}} - \frac{PT}{PK} (M_{C_{7+}} - 100.0) , \quad (4.15)$$

$$M_{C_{7+}} = \text{molecular weight of } C_{7+} ,$$

$$K_{C_{7+}} = \text{K-factor for } C_{7+} ,$$



$K_{C_7}$  = K-factor for heptane, and

$K_{C_9}$  = K-factor for n nonane.

#### 4.4 K-factors for Intermediate Convergence Pressures

The NGPSA K-factors are available only for 600, 800, 1000, 2000, 3000, 4000, 5000, 10000 and 20000 psi (16, 17). To calculate the K-factors for any other convergence pressure an interpolation procedure is developed in this study and is fully discussed in Appendix C.

#### 4.5 Critical Pressure and Critical Temperature Correlations

The accuracy of the phase envelope prediction technique is highly dependent on the ability to calculate the true critical temperature and true critical pressure of the mixture. It would be desirable to develop and employ methods for the calculation of critical temperatures and critical pressures of mixtures from molecular theory. But, this theory has not yet been developed to the point where, even the critical properties of binary mixtures containing components which differ considerably in their molecular weights can be accurately predicted. The evaluation of critical properties through an equation of state is quite complex even for ternary mixtures (70). The trend in the past has been to predict the critical properties through empirical correlations.

Various methods have been proposed to calculate the critical temperatures and pressures of mixtures (11, 14, 19, 25, 26, 28, 31, 41, 49, 50, 68, 69, 74). Most of the available correlations are for light

hydrocarbon mixtures, and every correlation suggested predicts the critical properties only for certain specified mixtures from which the correlations were derived. At present, no single correlation is available to cover all the mixtures available in the literature. Unfortunately much of the experimental critical property data are also questionable since it is extremely difficult to obtain such data in the laboratory.

The available experimental data on critical pressures and critical temperatures are abundant for binary mixtures. Hence, the correlations for predicting the critical properties for binary mixtures will be developed first, followed by the development of a new method to calculate these properties for more complex reservoir fluids.

#### 4.5.1 Binary Mixtures

The method selected for the calculation of critical pressure of binary systems is the same as the one proposed by Etter and Kay (19), with the exception that new coefficients were determined for their equation, using additional experimental data. The experimental critical pressures were plotted with the molecular weight of the mixture, calculated on a weight basis, instead of the conventional mole basis. Figure 6 illustrates such a plot for the methane-propane system. On the same graph, the critical pressures corresponding to methane weight fractions of 0.1 through 0.5, for intervals of 0.1 were calculated and marked. The slopes of the line joining the critical pressure of methane, point A, and the points of any weight fraction of methane were plotted as a function of the weight fraction of methane. The locus of these slopes was found to be a straight line on log-log paper as shown

in Figure 7. The equation for the critical pressure of the mixture can be developed from Figures 6 and 7.

From Figure 6, the equation for any line joining the point A and any arbitrary weight fraction of methane, point B, is

$$PC_{mix} = PC_{C_1} + m_i (M_{av} - M_{C_1}) \quad (4.16)$$

where

$PC_{mix}$  = critical pressure of mixture B,

$PC_{C_1}$  = critical pressure of methane,

$m_i$  = slope of the line AB,

$M_{av}$  = molecular weight of mixture B, calculated on weight basis, and

$M_{C_1}$  = molecular weight of methane.

From Figure 7, the value of  $m_i$  is evaluated as a function of composition:

$$m_i = m_o + a W_{C_i}^b \quad (4.17)$$

where

$m_o$  = slope of the line joining the point A and  $W_{C_1} = 0$ ,

$a$  = the intercept of line in Figure 7, at  $W_{C_i} = 1.0$ ,

$W_{C_i}$  = weight fraction of component i, and

$b$  = the slope of the line in Figure 7.

Combining Equations (4.16) and (4.17),

$$PC_{mix} = PC_{C_1} + (m_o + a W_{C_i}^b) (M_{av} - M_{C_1}) \quad (4.18)$$

Graphs similar to Figures 6 and 7 were drawn for all the binary mixtures of interest, and the values of the constants  $m_o$ ,  $a$  and  $b$  determined from them are given in Table II. For non-methane systems Equation (4.18) takes the form,

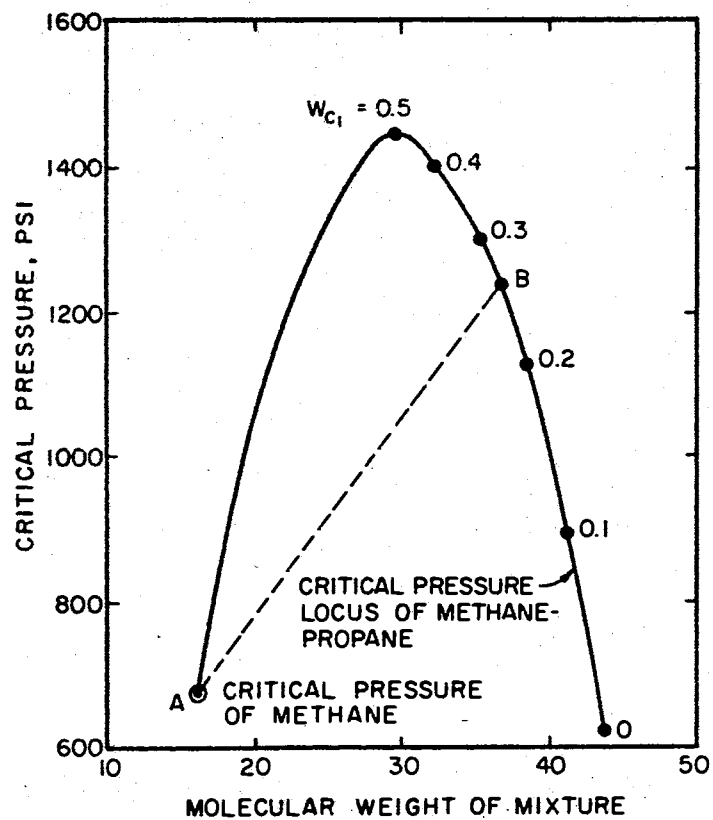


Figure 6. Critical Pressure Locus of Methane/Propane System

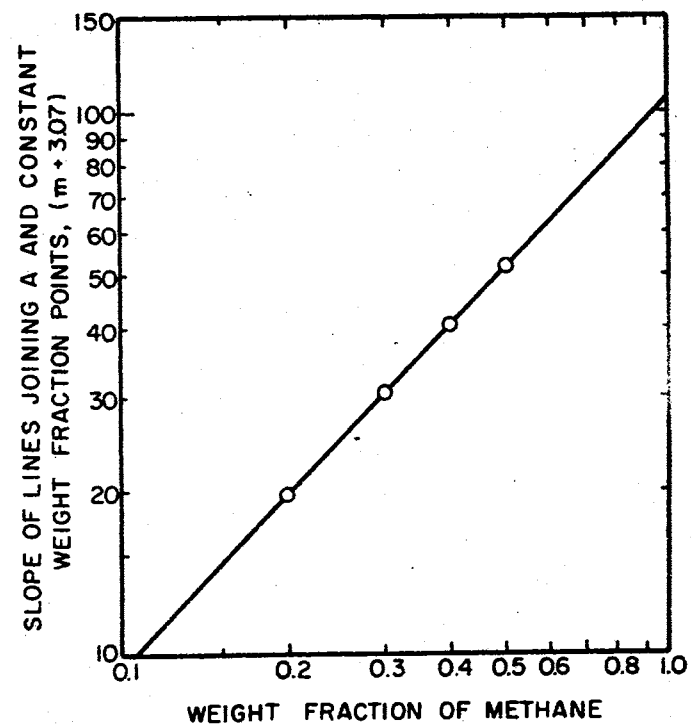


Figure 7. Locus of Slopes Joining A and Constant Weight Fraction Points

TABLE II  
CONSTANTS FOR CRITICAL PRESSURE CORRELATIONS

Mixture	$m_o$	a	b
Methane - Ethane	-3.07	72.1572	0.920056
Methane - Propane	-3.07	116.4855	1.046806
Methane - n Butane	-3.07	118.9940	0.930962
Methane - n Pentane	-3.07	143.2801	1.077983
Methane - n Hexane	-3.07	154.0000	1.130000
Methane - n Heptane	-3.07	161.4163	1.215067
Ethane binaries	-4.00	22.5412	1.188447
Propane binaries	-4.30	10.2732	1.159220
n Butane binaries	-3.50	8.5081	1.346540
n Pentane binaries	-3.00	5.1300	1.320000
n hexane $\emptyset$	-557	9400	2.006
$\emptyset$ binaries	$\frac{1.265}{M_1}$	$\frac{1.71}{M_1}$	$\frac{0.115}{M_1}$
n heptane $\emptyset$			

where  $M_1$  = Molecular weight of light component

$$PC_{mix} = PC_{C_1} + (m_o + a_i Z_1)^{b_i} (M_{av} - M_{C_1}) \quad (4.19)$$

where

$PC_{C_1}$  = critical pressure of lightest component in the mixture,

$Z_1$  = mole fraction of the lightest component, and

$M_{C_1}$  = molecular weight of the lightest component.

In order to calculate the critical temperature of binary mixtures, a different approach was adopted. Attempts to modify the relations proposed by Etter and Kay produced results which deviated from experimental values by more than 15%. But, the equations suggested by Grieves and Thodos (26) very closely predicted experimental critical temperatures; the maximum error for the binaries given in Table III was not more than 10%.

The empirical equation proposed by Grieves and Thodos for the calculation of critical temperature of a binary mixture is,

$$TC_{mix} = \frac{TC_1}{1 + A_{1h} \frac{Z_h}{Z_1}} + \frac{TC_h}{1 + A_{hl} \frac{Z_1}{Z_h}} \quad (4.20)$$

where

$TC_{mix}$  = critical temperature of the mixture, °R,

$TC_1$  = critical temperature of the light component in the mixture,

$TC_h$  = critical temperature of the heavy component in the mixture,

$Z_h$  = mole fraction of the heavy component,

$Z_1$  = mole fraction of the light component, and

$A_{hl}, A_{1h}$  = binary temperature coefficients.

The binary temperature coefficients are functions of the boiling points of the components in a given mixture. The coefficient  $A_{1h}$  refers to that of light component relative to the heavy component. Again in

TABLE III  
BINARY TEMPERATURE COEFFICIENTS FOR THE CRITICAL  
TEMPERATURE CORRELATIONS

Mixture	$A_{1h}$	$A_{h1}$
Methane - Ethane	1.450	0.650
Methane - Propane for $Z_1 < 0.7$	2.030	0.415
$Z_1 \geq 0.7$	2.300	0.420
Methane - n Butane	0.860	0.600
Methane - n Pentane	1.690	0.360
Methane - n Hexane	0.980	0.390
Methane - n Heptane	0.610	0.440
Ethane - Propane	0.966	0.986
Ethane - n Butane	0.849	0.960
Ethane - n Pentane	0.813	0.883
Ethane - n Hexane	0.840	0.800
Ethane - n Heptane	0.850	0.696
Propane - n Butane	1.017	0.973
Propane - n Pentane	0.914	0.986
Propane - n Hexane	0.840	0.960
Propane - n Heptane	0.810	0.910
n Butane - n Pentane	1.059	0.955
n Butane - n Hexane	0.950	0.990
n Butane - n Heptane	0.900	0.990
n Pentane - n Hexane	1.070	0.940
n Pentane - n Heptane	0.990	0.990
n Hexane - n Heptane	1.100	0.920

this study the available experimental data for the critical temperatures were used along with the Equation (4.20) to obtain optimum values of coefficients  $A_{1h}$  and  $A_{hl}$ . These coefficients are tabulated in Table III.

#### 4.5.2 Mixtures Containing Three or More

##### Components

The equation proposed, to calculate the critical pressure of mixtures containing three or more components, by Etter and Kay (19) is of the form,

$$PC_{mix} = \sum_{i=1}^n PC_{C_i} \cdot Z_i + \sum_{i=1}^{n-1} \Phi(Z_i) \quad (4.21)$$

where

$PC_{mix}$  = critical pressure of the mixture,

$PC_{C_i}$  = critical pressure of component i,

$Z_i$  = mole fraction of component i,

$\Phi(Z_i)$  = excess critical pressure for component i, and

$n$  = number of components in the mixture.

The term excess critical pressure is analogous to any excess thermodynamic function. Thus, the excess critical pressure of a mixture is "conceived as being made up of the contributions of each of the components, with the component of the lowest molecular weight producing the greatest effect in proportion to the amount present." The total excess critical pressure is "equal to the sum of the contributions of the excess critical pressure of the components, except the heaviest" (19).

The excess pressures for an n component system are calculated as follows:



For component 1:

$$\Phi(Z_1) = a_1 Z_1^{b_1} (M_{av} - M_{C_1}) \quad (4.22)$$

If component 1 is methane, then the mole fraction  $Z_1$  is replaced by weight fraction  $W_1$ . The value of  $a_1$  is 137 and  $b_1$  is 1.073 for methane.

For any other component  $i$ ,

$$\Phi(Z_i) = a_i \left[ \frac{Z_i}{1 - \sum_{j=1}^{i-1} Z_j} \right]^{b_i} \left[ \frac{M_{av} - \sum_{j=1}^{i-1} W_j M_j}{1 - \sum_{j=1}^{i-1} W_j} - M_i \right] \left[ 1 - \sum_{j=1}^{i-1} Z_j \right] \quad (4.23)$$

where

$M_j$  = molecular weight of component  $j$ ,

$M_{av}$  = average molecular weight of the mixture,

$W_j$  = weight fraction of component  $j$ , and

$a_i, b_i$  = constants, given in Table II.

For calculating the critical temperatures of mixtures containing three or more components, Equation (4.20) by Grieves and Thodos, was extended and expressed as,

$$TC_{mix} = \sum_{i=1}^n \frac{TC_i}{1 + \frac{1}{Z_i} \sum_{\substack{j=1 \\ j \neq i}}^n A_{ij} Z_j} \quad (4.24)$$

The binary temperature coefficients  $A_{ij}$  and  $A_{ji}$  are given in Table III.

Equations (4.21) and (4.24) predicted the critical properties of ternary mixtures within 10% of the experimental values. But, for

systems containing more than three components, the predicted critical pressures and temperatures deviated as much as 50% of the absolute experimental value. Hence, new correlations were derived in this study for the calculation of critical properties for systems containing four or more components and outlined below.

In order to correlate the critical pressures of mixtures, various parameters were considered. These included the boiling point, molecular weight, pure component critical properties, number of carbon atoms per molecule, and the molecular weight and the mole fraction of heptane plus fraction. After trying several combinations of the above parameters, two parameters were finally selected that closely predicted the experimental critical pressures. They are the molecular weight of the mixture and the molal average boiling point of the mixture.

The equation derived to predict the critical pressure of the mixture is of the form,

$$\log_e PC_{\text{mix}} = D - A \log_e \left( \frac{B}{M_{\text{av}}} \right) \quad (4.25)$$

where

$PC_{\text{mix}}$  = critical pressure of the mixture,

$D = 9.2103$ ,

$A, B$  = functions of molal average boiling points, and

$M_{\text{av}}$  = average molecular weight of the mixture.

The constants  $A$  and  $B$  are functions of molal average boiling point of the mixture, and are given in Table IV. The interpolated constants  $A$  and  $B$  are used for the intermediate values of molal average boiling points of the mixture.

The critical temperatures of the mixtures containing four or more components are correlated as a function of the critical temperature of

TABLE IV  
CONSTANTS FOR CALCULATING THE CRITICAL  
PRESSURE OF THE MIXTURES

Molal Average Boiling Point, °R	A	B
240	1.430	106
246	1.370	135
280	1.230	170
320	1.265	180
340	1.340	200
394	1.440	240
415	1.390	308
447	1.225	450
470	1.200	560

pure components of the mixture, the molecular weight of the mixture, and the boiling points of pure components.

The equation used to predict the critical temperature of the mixture is of the form,

$$\log_e TC_{\text{mix}} = V - U \log_e \left( \frac{K}{M_{\text{av}}} \right) \quad (4.26)$$

where

$TC_{\text{mix}}$  = critical temperature of the mixture, °R,

$V = 6.9078$ ,

$U, K$  = functions of  $R$ , and

$M_{\text{av}}$  = average molecular weight of the mixture.

The function  $R$  is correlated to the boiling points and the critical temperatures of pure components and is defined as,

$$R = \frac{\sum_{i=1}^n W_i \cdot TC_i \cdot B_i}{\sum_{i=1}^n W_i \cdot B_i} \quad (4.27)$$

where

$W_i$  = weight fraction of component  $i$ ,

$TC_i$  = critical temperature of component  $i$ , and

$B_i$  = boiling point of component  $i$ .

The values of  $U$  and  $K$  as a function of  $R$  are given in Table V.

TABLE V  
CONSTANTS FOR CALCULATING THE CRITICAL  
TEMPERATURE OF THE MIXTURES

Function R	U	K
485	1.770	39.5
505	1.910	43.9
700	1.520	61.5
720	1.420	66.0
735	0.825	68.1
755	1.250	70.2
765	1.168	73.0
900	1.109	117.4
1000	1.530	115.1
1050	1.610	131.1
1100	1.310	180.0
1200	1.110	240.0

## CHAPTER V

### GENERATION OF PHASE ENVELOPES

#### 5.1 General

The procedure for calculating a pressure-temperature phase envelope is divided into four regions: region 1 being the bubble point locus, regions 2 and 3 being upper and lower dew point loci, respectively, for temperatures greater than the critical temperature, while region 4 is the dew point locus for temperatures less than the critical temperature. All the four regions are shown in Figure 1.

The most difficult part in the generation of pressure-temperature phase envelope prediction is the portion of the envelope where the operating temperature is greater than the critical temperature. In this work the convergence pressure theory is successfully applied for the first time, to generate the entire phase envelope including the retrograde region. This is a significant contribution of the present study.

There are three different methods developed in this study to calculate the entire phase envelope, depending on whether the operating temperature is greater than, equal to, or less than the critical temperature of the system. Regions 1 and 4 are calculated using Method B, regions 2 and 3 are generated by Method C, while Method A is used to fix the critical point as well as the lower dew point pressure corresponding to the critical temperature.

In order to explain these three methods, first the technique for calculating the phase envelope of a binary system will be explained, followed by a description of the technique used for systems containing three or more components.

## 5.2 Two Component Systems

Figure 1 shows a typical pressure-temperature phase envelope of a binary mixture for fixed overall composition. In order to generate such an envelope, three methods are developed and are presented in the following sections. It is essential that these methods be followed in order in which they are given.

### 5.2.1 Method A - Steps for Calculating Two Phase

#### State Points at the Critical State

At the critical state, the calculational procedure is relatively simple, and involves no iteration procedure. From the known composition, the critical pressure, and critical temperature of the mixture are directly calculated. These calculations are made using the correlations developed in Section 4.5.1.

The steps to be followed in calculating the phase boundaries for the critical isotherm are as follows:

- (1) From the known overall composition of the system and pure component properties, the critical temperature of the mixture is calculated. This defines the critical isotherm  $T = T_C$  in Figure 1.
- (2) The critical pressure of the mixture is then calculated from the overall composition, using the relations developed in

Section 4.5.1. Steps 1 and 2 define the state  $[P(2), T_C]$ , the critical state of the phase diagram of Figure 1 or Figure 4.

- (3) Let the calculated critical pressure of step 2 be the convergence pressure of the system. Using this convergence pressure, various values of pressures are assumed so that the assumed pressures are less than the convergence pressure, and the values of  $\sum \frac{Z_i}{K_i}$  for each pressure are calculated. The pressure for which the sum  $\sum \frac{Z_i}{K_i}$  is equal to unity is the dew point. This is represented by the state  $[P(5), T_C]$  in Figures 1 and 4.

These three steps complete the calculations required to define the boundary state along the critical isotherm.

#### 5.2.2 Method B - Steps for Calculating the Boundary States for Temperatures Greater Than the Critical Isotherm

When the operating temperature is greater than the critical temperature of the system, the bubble point locus no longer exists. However, for every isotherm in this region two dew points exist for which  $\sum \frac{Z_i}{K_i}$  is equal to unity. These two points define the phase envelope boundary of the dew point curve in the retrograde region along a given isotherm. This method is used to generate regions 2 and 3 of the phase envelope.

The steps to be followed for the envelope calculations in the retrograde region are:



- (1) A value for the independent variable, temperature  $T$ , is assumed.
- (2) In general, for systems containing more than two components the convergence pressure for the two dew points are assumed.  
(For binary systems, the convergence pressures for the two dew points are the same and are directly calculated for the specified temperature. This is done by assuming various overall compositions of the system and calculating their critical temperatures until the critical mixture is found such that the critical temperature of the system is equal to the operating temperature. The critical pressure of this mixture is the convergence pressure of the binary mixture.)
- (3) For the now defined value of temperature  $T$  and convergence pressure, two different pressures are assumed corresponding to the two dew point pressures.
- (4) The  $K$ -factors for each component for the temperature  $T$ , assumed convergence pressures, and dew point pressures are then calculated.
- (5) The summation  $\sum \frac{Z_i}{K_i}$  are calculated for both the upper and lower dew points. If the calculated  $\sum \frac{Z_i}{K_i}$  is not equal to unity, the assumed dew point pressure values are changed and the steps 4 and 5 are repeated until the summation  $\sum \frac{Z_i}{K_i}$  is equal to unity for both the high pressure and low pressure cases.
- (6) For binary systems, the calculations are complete at this stage. For systems containing more than two components, the calculation proceeds to determine whether the assumed convergence pressure is equal to the actual convergence pressure for the system. The actual convergence pressure is

calculated for these cases using the Critical Composition Method outlined in Appendix G.

- (7) The assumed convergence pressures of step 2 are compared with the calculated convergence pressures of step 6. If the assumed and calculated values are equal, the two dew point pressures have been accurately defined. If not, new values for the convergence pressures are assumed and steps 3 through 7 are repeated.

### 5.2.3 Method C - Steps for Calculating the Bubble

#### Point and Dew Point Pressures for Operating

#### Temperatures Less Than the Critical

#### Temperature

The following steps establish the phase boundary envelopes for the case where the operating temperature  $T$  is less than the critical temperature  $T_C$ .

- (1) A value for the independent variable  $T$  is selected.
- (2) Two values of convergence pressures, one for the bubble point pressure and another for the dew point pressure, are assumed. For two component systems, the value of convergence pressure can be directly calculated as explained in Method B.
- (3) The bubble point pressure and the dew point pressure are assumed.
- (4) The  $K$ -factors for all the components of the mixture are computed for the bubble point and dew point pressures individually at the specified temperature, assumed operating pressure and the selected convergence pressure.

- (5) The summation  $\sum \frac{Z_i}{K_i}$  for the dew point and  $\sum Z_i \cdot K_i$  for the bubble point are calculated. If these values are different from unity, then new values of pressures are assumed and steps 4 and 5 are repeated until the summations are individually equal to unity.
- (6) This completes the calculation for the two component systems. For mixtures containing more than two constituents, the convergence pressures for the two states are calculated using the Critical Composition Method.
- (7) If the assumed values of convergence pressures of step 2 are equal to the calculated values of convergence pressures of step 6, the dew point and bubble point pressures have been accurately defined for the selected value of the independent variable  $T$ , and the calculations are complete for this isotherm. If not, steps 2 through 7 are repeated.

This procedure is repeated for other isotherms until the pressure-temperature phase envelope is adequately defined.

There is a particular problem in calculating the convergence pressure for the dew points in Method C. The tie lines that define the  $K$ -factors along the dew point curve do not always intersect the critical temperature locus at low temperatures, and a convergence pressure calculation cannot be made for these lower pressure cases. It was assumed that the convergence pressure used for the bubble point calculation may also be used to determine the dew point state. The implications of this assumption are discussed in the section describing the three component system calculations. Further, when the operating temperature for a binary system is lower than the critical temperature of the more

volatile component, again the convergence pressure for the system cannot be calculated. In such cases, the convergence pressure was assumed to be the same as the convergence pressure for the preceding temperature. The validity of such an assumption is justified in the next section.

### 5.3 Three Component Systems

The calculational procedure consisting of the three methods outlined above is general, and can be used to predict the phase envelopes of multicomponent systems containing three or more components. For ternary systems, the application of Gibbs' phase rule indicates that the degree of freedom is three, where convergence pressure is the third independent phase rule variable required to define the intensive properties at an equilibrium state. A rigorous mathematical proof is presented in Appendix H.

The pressure-temperature envelope for a ternary system, and its dependence on the convergence pressure calculation can be demonstrated with ternary diagrams coupled with the constant composition P-T phase envelope.

In Figure 1 three isotherms are represented, one passing through the critical point, called critical isotherm, the second represents a temperature  $T_H$  greater than the critical temperature and the third corresponding to a temperature  $T_L$  which is less than the critical. The intersection of these three isotherms with the P-T envelope define six states.

The convergence pressure used to define these six states are shown on the six accompanying ternary phase diagrams of Figures 8 and 9.

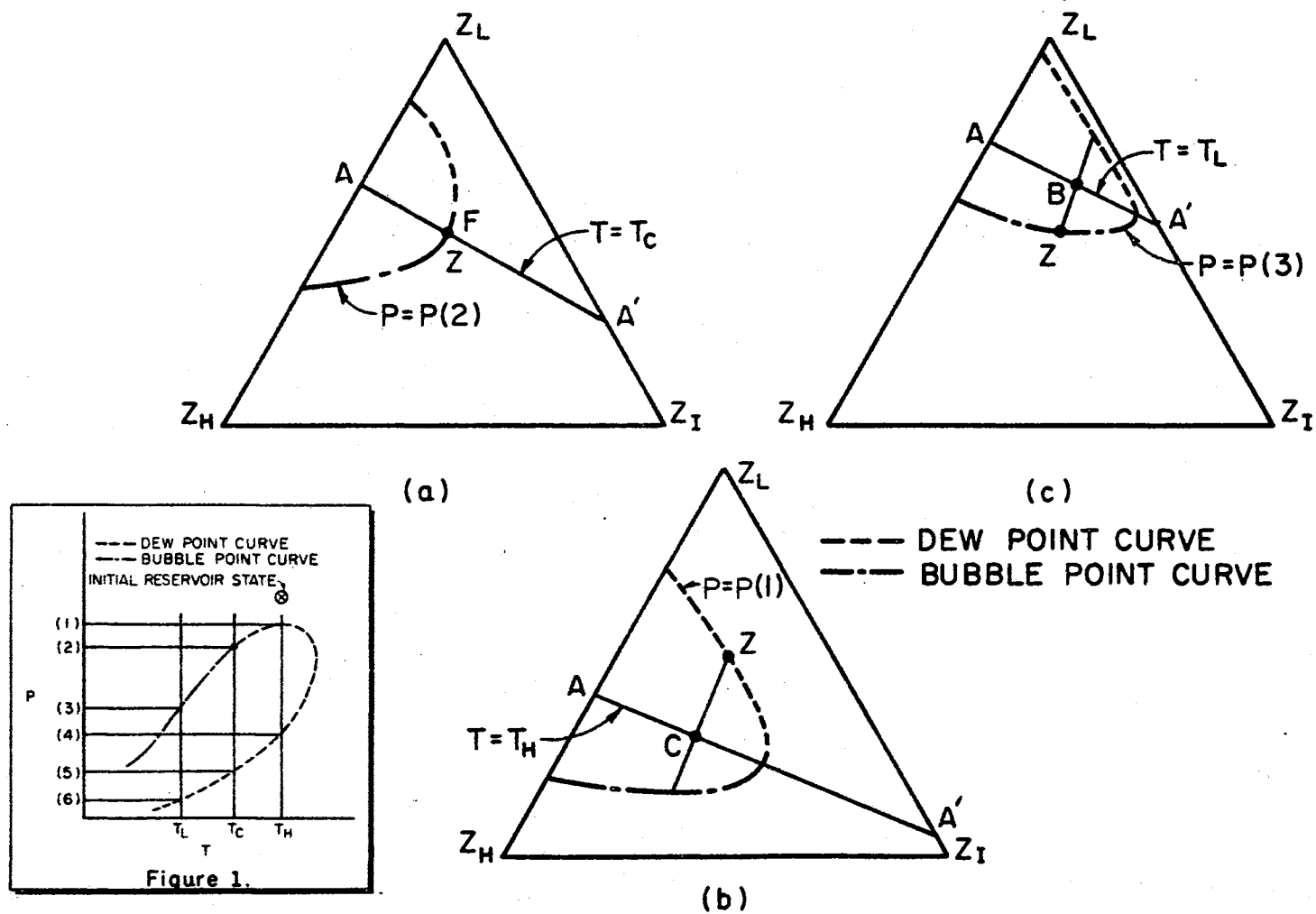


Figure 8. Compositions for Determining Convergence Pressures for High Pressure States

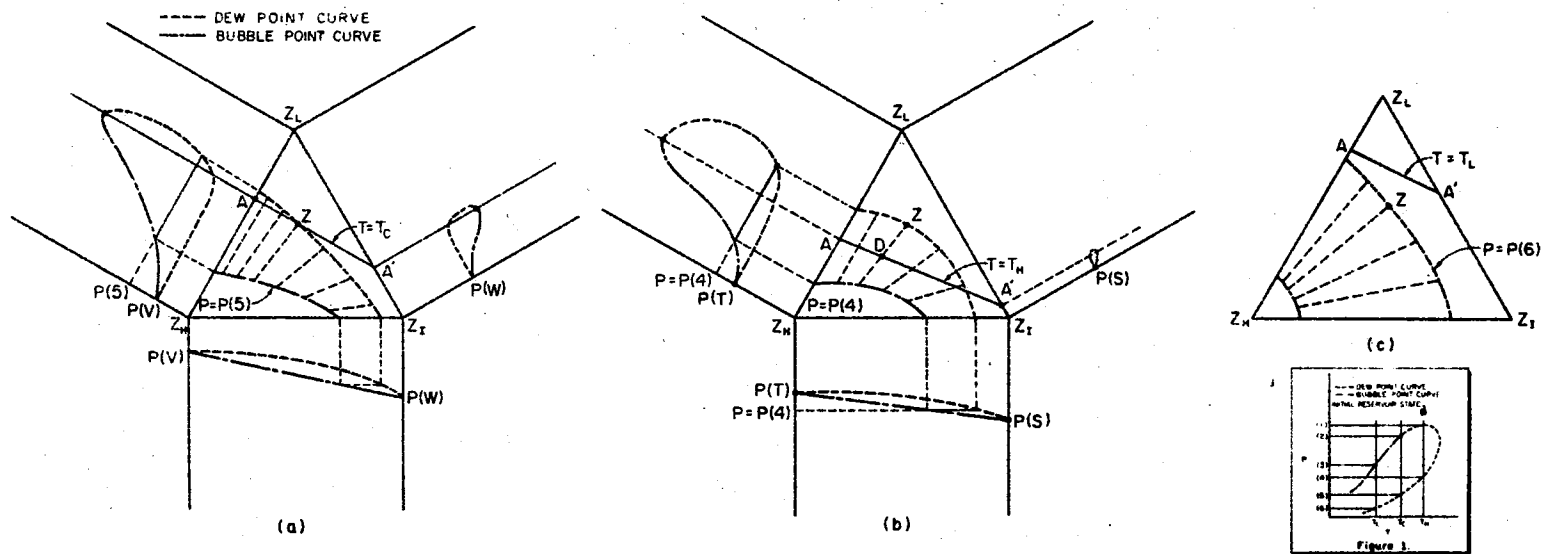


Figure 9. Compositions for Determining Convergence Pressures for Low Pressure States

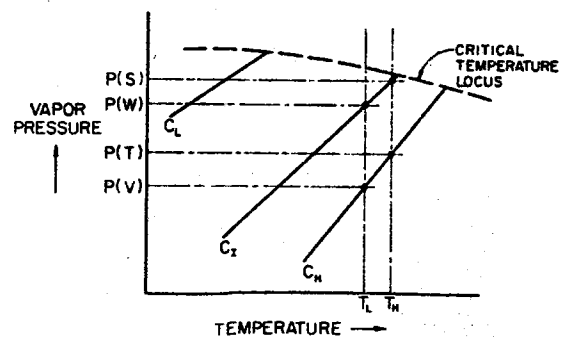


Figure 10. Vapor Pressure Chart

The overall composition of the mixture  $Z$  is a fixed common composition on all six of these diagrams. Each diagram has a temperature and pressure equivalent to one of these state points on the pressure-temperature envelope. Also, on each diagram are shown the bubble point and dew point lines that exist for compositions other than  $Z$ , but for the same temperature and pressure.  $Z$  is located on either the bubble point line or dew point line as indicated by the  $P$ - $T$  envelope. Figure 1 is redrawn on Figures 8 and 9 for convenience.

State  $[P(2), T_C]$  of Figure 1 represents the critical state and corresponds to point  $F$  in Figure 8a. The critical pressure of point  $F$  can be directly calculated from empirical correlations as outlined by Method A in Section 5.2.1. Pressure  $[P(2)]$  is the convergence pressure to be used in determining the dew point pressure state  $[P(5), T_C]$ . The composition envelope of Figure 9a also shows this state at this lower pressure. Shown in the same figure are pressure-composition envelopes for the two component systems that exists at  $T = T_C$ . At the apexes of this figure are shown the vapor pressures of the pure components.  $P(V)$  represents the vapor pressure of the heavy component and  $P(W)$ , the vapor pressure of the intermediate component. These two pressures are also shown on the vapor pressure chart of Figure 10. These envelopes cannot intersect the light component axis, since the operating temperature  $T_C$  is greater than the critical temperature of the light component. At low pressure the bubble point locus between  $P(V)$  and  $P(W)$  is nearly a straight line complying with Raoult's law.

Consider next the isotherm  $T_H$ . The intersection of this isotherm with the  $P$ - $T$  envelope defines states  $[P(1), T_H]$  and  $[P(4), T_H]$  on the dew point curve in the retrograde region. Method B, for calculating

these state points has been outlined in Section 5.2.2. The convergence pressure to be used to calculate state  $[P(1), T_H]$  is the critical pressure of mixture C of Figure 8b. The mixture Z necessarily lies on the dew point locus. Figure 9b shows the composition envelope at the lower pressure  $[P(4)]$ . Again the overall composition of mixture Z is located on the dew point locus. The critical pressure of mixture D is the convergence pressure associated with mixture Z at state  $[P(4), T_H]$ . In this case, the vapor pressures of heavy and intermediate components are  $P(T)$  and  $P(S)$ , respectively, and are also shown in Figure 10. The pressure  $P(S)$  is very close to the critical pressure of the intermediate component and, hence, the phase envelope for the light-intermediate binary is very small.

Finally, consider the isotherm  $T_L$  in Figure 1. The intersection of this isotherm with the phase envelope defines states  $[P(3), T_L]$  and  $[P(6), T_L]$ . The state  $[P(3), T_L]$  of fluid with composition Z is shown in Figure 8c. The convergence pressure used in determining the bubble point pressure  $[P(3)]$  is equal to the critical pressure of mixture B.

In general, the dew point pressure  $[P(6)]$  cannot be determined with a convergence pressure calculation since the tie line that terminates at state Z does not intersect the critical temperature locus as shown in Figure 9c. Hence, the convergence pressure used in determining the state  $[P(3), T_L]$  is also used to determine the state  $[P(6), T_L]$ . The rationale for this assumption is that the pressure  $[P(6)]$  is far removed from the convergence pressure where K-factors are still strongly dependent on temperature and pressure, but relatively independent of fluid composition. Thus, some error can be made in determining the convergence pressure without introducing much of an error in the K-factors



applicable to the state  $[P(6), T_L]$ . This assumption is justified graphically by Figure 11.

#### 5.4 Systems Containing More Than Three Components

To extend the convergence pressure predictions to systems containing four or more components violates Gibbs' phase rule, as explained in Appendix H, and, hence, empirical trends must be relied upon for any such extension. A trend has been noted in normalizing P-V-T data with respect to the critical state, and has been stated as the law of corresponding states. Similarly, a law has been stated based on experimental data that postulates convergence pressure as a correlating parameter for K-factors along with temperature and pressure for multi-component systems (62), (Appendix H).

The procedures discussed for the calculation of binary and ternary envelopes are extended to the calculation of phase envelopes for systems containing four or more components, by the use of the convergence pressure postulate (62). The accuracy of the calculation will depend upon the validity of convergence pressure theory, and how closely the system satisfies the criterion set forth by this theory. For instance, components of a given system must be of the same homologous series. If the system contains significant portions of aromatics, or non hydrocarbon species such as hydrogen sulfide, nitrogen or carbon dioxide, failure to predict the system behavior would be expected.

In the present work, the non hydrocarbons present in the systems studied are grouped as follows: the nitrogen present is grouped with ethane and the carbon dioxide is combined with propane. This decision

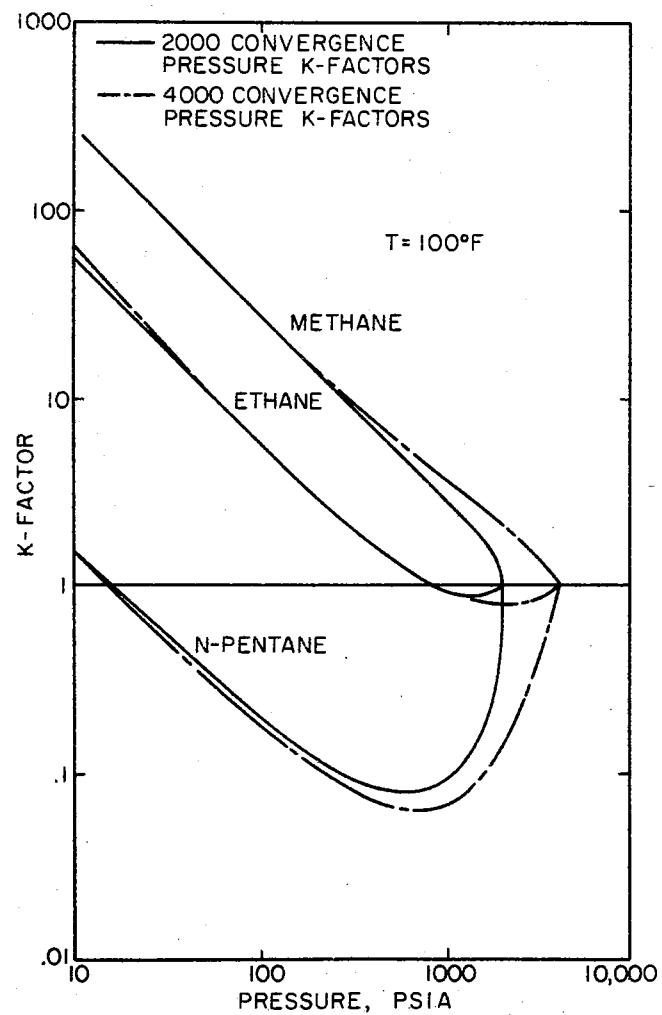


Figure 11. Effect of Convergence Pressure Error on Low Pressure K-factors

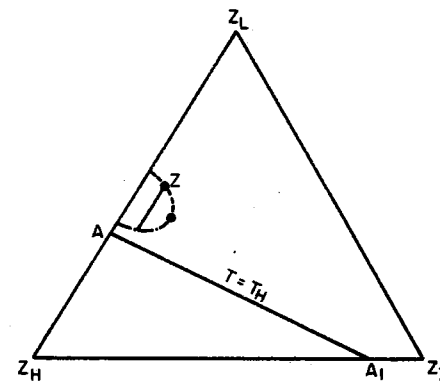


Figure 12. Probable Phase Diagram at Very High Pressure

was arbitrarily based on the molecular weights of the components. No other non hydrocarbon was present in the systems tested in this study.

One particular difficulty was encountered in the calculation of P-T envelope of reservoir fluids at very high pressures in the retrograde region. Consider the state  $[P(1), T_H]$  in Figure 1. It was noted that the tie line may not intersect the critical temperature locus at this high pressure, as indicated by Figure 12. In such cases, the K-factor for the heptane plus fraction was adjusted, so that an intersection occurred, and the convergence pressure was calculated as indicated earlier.

### 5.5 Computer Program

A generalized computer program was developed to generate the phase envelope of an n component system. The input data required are number of components in the mixture, the system overall composition, the critical temperatures, critical pressures, and molecular weights of pure components, the lower temperature limit to the phase envelope calculations  $T_{MIN}$ , and the spacing between adjacent isotherms  $\Delta T$ .

The flow chart of the computer program written is shown in Figure 13.

The program first calculates the critical temperature and critical pressure of the given system. Method A outlines this calculation. The state  $[P(5), T_C]$  is calculated next. For most of the reservoir fluids studied, the pressure  $[P(5)]$  was less than 50 psi. In such cases the program prints out "THE DEW POINT PRESSURE AT CRITICAL TEMPERATURE IS LESS THAN 50 PSI" and proceeds to calculate the dew point pressures in the retrograde region for temperatures greater than the critical

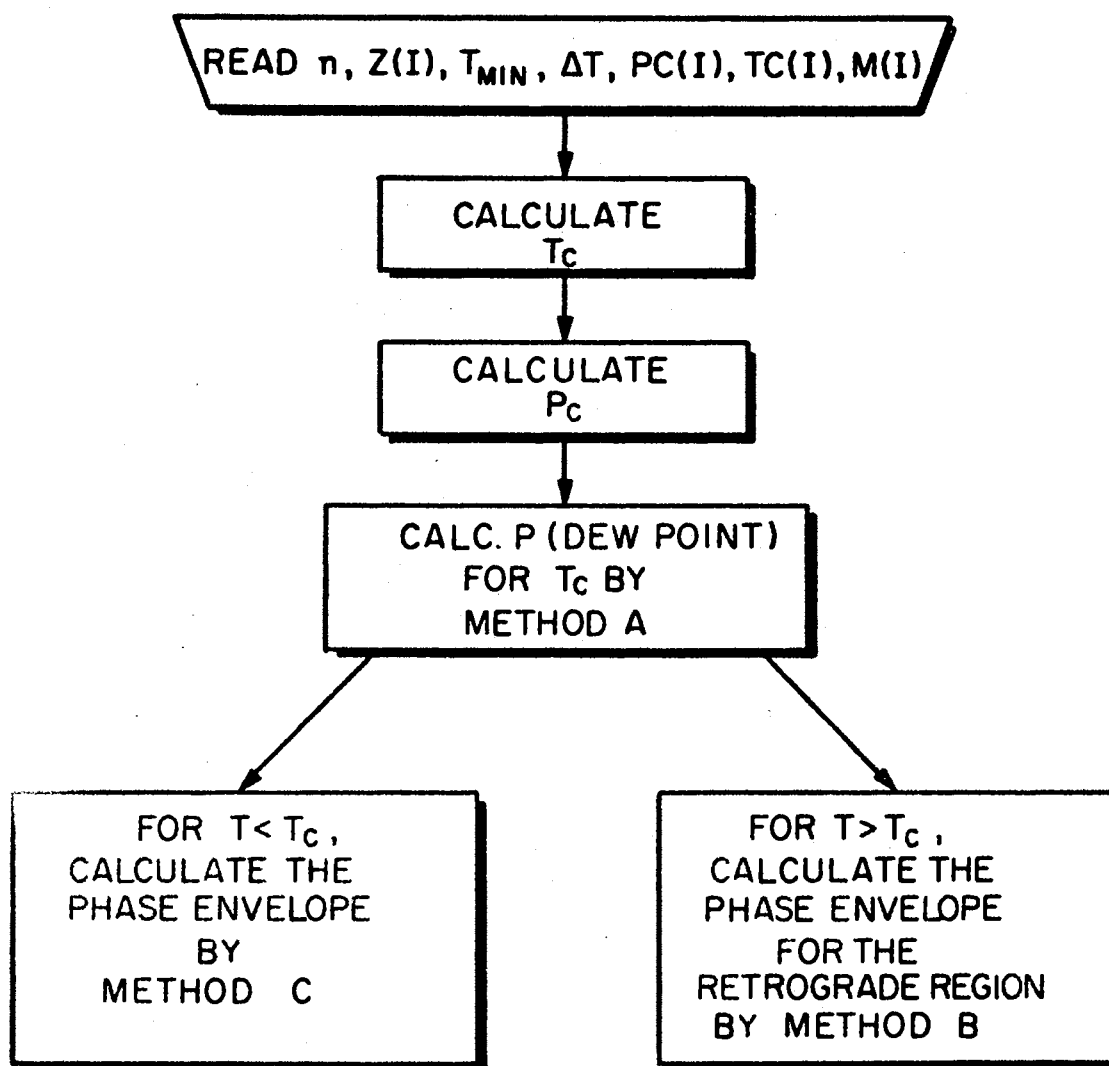


Figure 13. General Flow Diagram for the Calculation of Phase Envelopes

temperature. The procedure to be followed in this region is outlined under Method B. In all the systems tested, the value of  $\Delta T$  was set at 10 degrees and, hence, the cricondentherm calculated was estimated within 10 degrees. Method C was followed in generating the remainder of the envelope.

A flow diagram for the calculation of dew point pressure corresponding to critical temperature is presented in Figure 14 (Method A). Figures 15 and 16 are the flow charts for calculating the dew point locus (Method B) and the bubble point locus (Method C).

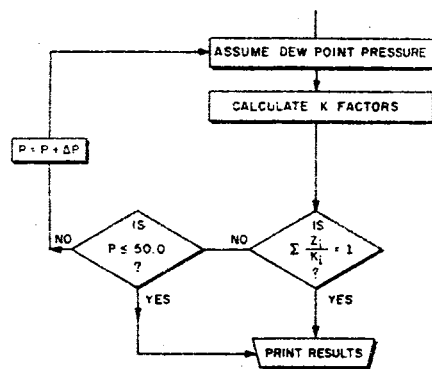


Figure 14. Flow Diagram for the Calculation of Dew Point Pressure Corresponding to Critical Point - Method A

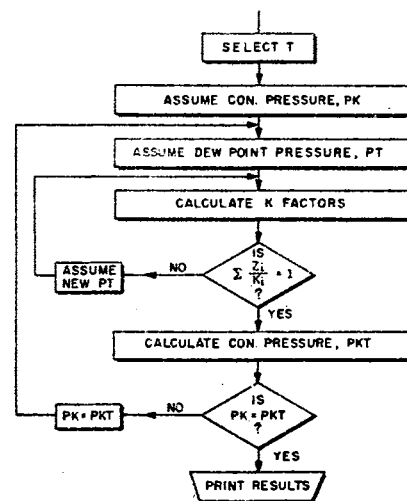


Figure 15. Flow Diagram for Calculating the Dew Point Locus

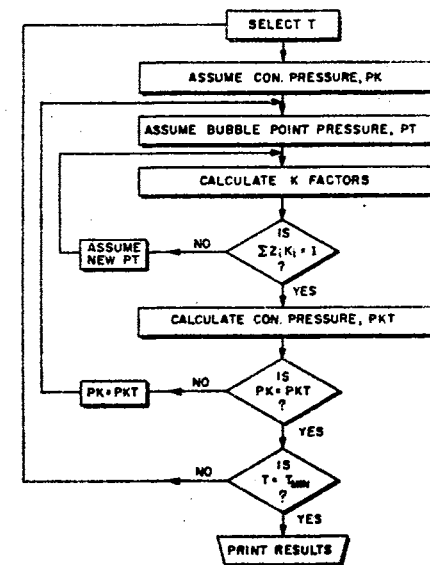


Figure 16. Flow Diagram for Calculating the Bubble Point Locus

## CHAPTER VI

### RESULTS

#### 6.1 Calculations Performed

Pressure-temperature phase envelopes were calculated for a total of sixty-three hydrocarbon systems. Forty-eight envelopes were generated for binary systems, and the rest include four ternary mixtures, two four component systems, two five component mixtures, one six component system and six actual reservoir fluids. Fourteen typical envelopes predicted are presented in this chapter in Figures 17 through 29 and the remaining are presented in Appendix I. The experimental data available in the literature for the calculated envelopes are also given in the figures. The K-factors calculated, the assumed and calculated convergence pressures, the critical compositions used for calculating the convergence pressures and the calculated phase envelope data for Figures 17 through 29 are given in Tables VI through XVIII.

#### 6.2 Binary Systems

Most of the published experimental data on the pressure-temperature envelopes were for binary systems. Hence, a major portion of the envelopes calculated are for two component systems. Figures 17, 18 and 19, and Figures 35 through 46 show the predicted phase envelopes for binary systems. The data used to plot the phase envelopes shown in Figures 17, 18 and 19 are presented in Tables VI through VIII.

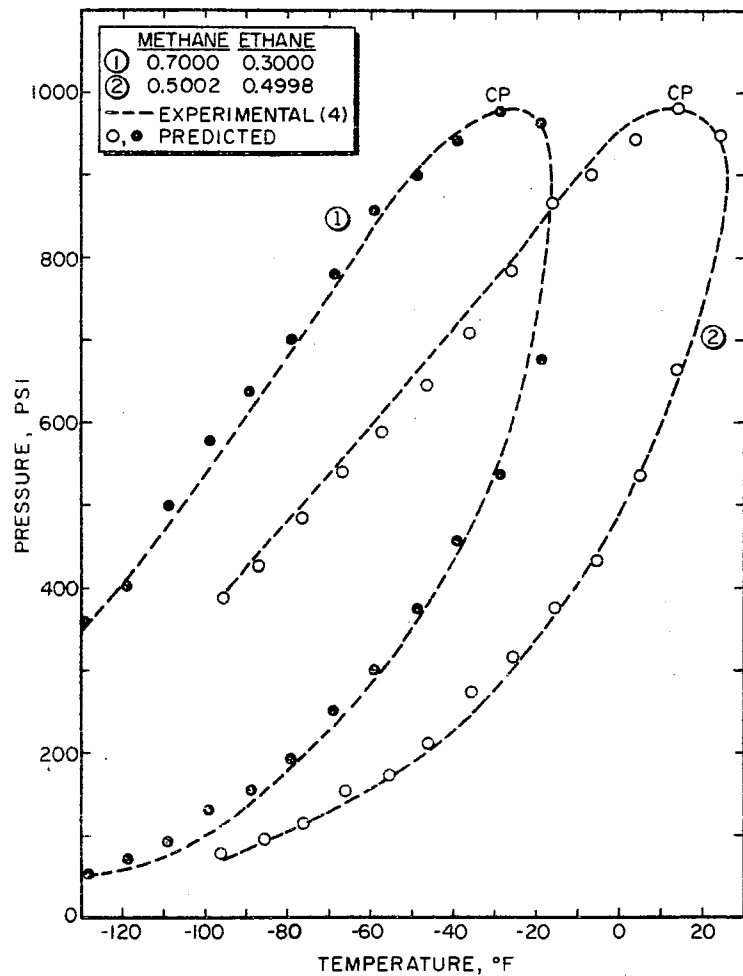


Figure 17. Pressure-Temperature Phase Envelopes for Methane/Ethane System  
(Concentration of Methane = 0.7000;  
Concentration of Methane = 0.5002)

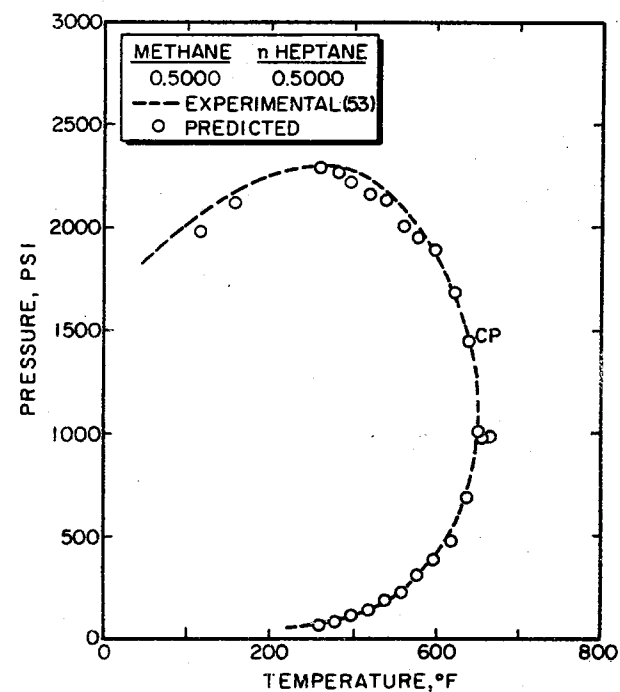


Figure 18. Pressure-Temperature Phase Envelope for Methane/n Heptane System



TABLE VI

## CALCULATED PHASE ENVELOPE DATA FOR METHANE/ETHANE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE: METHANE=0.7000; ETHANE=0.3000 CRITICAL PRESSURE OF THE MIXTURE = 975.00 PSI CRITICAL TEMPERATURE OF THE MIXTURE = -29.00 F				OVERALL COMPOSITION OF THE MIXTURE: METHANE=0.5002; ETHANE=0.4998 CRITICAL PRESSURE OF THE MIXTURE = 979.50 PSI CRITICAL TEMPERATURE OF THE MIXTURE = 14.00 F			
BP	PSI	TEMPERATURE F	CON.PRESSURE PSI	BP	PSI	TEMPERATURE F	CON.PRESSURE PSI
	964.0	-19.0	984.0	947.7		24.0	967.8
	675.0			660.8		14.0	979.5
	535.0	-29.0	975.0	940.0		4.0	986.8
940.8		-39.0	960.8	539.5			
900.5	455.0	-49.0	940.5	900.0		-6.0	989.1
860.5	374.9	-59.0	913.4	866.8	459.5	-16.0	986.8
780.5	300.4	-69.0	888.0	786.8	379.5	-26.0	977.7
700.5	254.9	-79.0	824.1	706.8	319.5	-36.0	964.8
640.5	194.9	-89.0	785.7	649.8	279.5	-46.0	946.2
580.5	154.9	-99.0	748.6	590.8	219.5	-56.0	926.5
500.5	134.9	-109.0	705.5	546.8	172.5	-66.0	897.0
400.5	94.9	-119.0	705.5	486.8	159.5	-76.0	865.1
360.5	74.9	-129.0	705.5	426.8	119.5	-86.0	796.8
	54.9			386.8	99.5	-96.0	761.6
					79.5		
K VALUE				K VALUE			
METHANE	ETHANE	METHANE	ETHANE	METHANE	ETHANE	METHANE	ETHANE
1.1460	0.7379	0.6600	0.3400	1.1670	0.8675	0.4500	0.5500
1.7670	0.4918			1.4810	0.7216	0.5002	0.4998
2.2130	0.4421	0.7000	0.3000	1.2700	0.7549	0.5500	0.4500
1.1310	0.6965	0.7400	0.2600	2.6200	0.6245		
2.4940	0.4086			1.1560	0.7701	0.6000	0.4000
1.1780	0.6172	0.7800	0.2200	3.0620	0.6053		
3.0440	0.3961			1.3890	0.6342	0.6400	0.3600
1.2070	0.5547	0.8200	0.1800	3.6570	0.6019		
3.4510	0.3775			1.5170	0.4838	0.6900	0.3100
1.2330	0.4873	0.8500	0.1500	4.2400	0.5944		
4.0920	0.3674			1.6080	0.4279	0.7300	0.2700
1.2780	0.3849	0.8830	0.1170	4.6830	0.5701		
5.1800	0.3752			1.6330	0.3819	0.7700	0.2300
1.2970	0.3258	0.9200	0.0800	5.8990	0.5896		
6.3240	0.3737			1.7120	0.3338	0.8020	0.1980
1.3170	0.2662	0.9500	0.0500	7.0940	0.5905		
6.8220	0.3503			1.7170	0.2946	0.8400	0.1600
1.3110	0.2893	0.9800	0.0200	7.6330	0.5505		
7.5530	0.3356			1.7890	0.2559	0.8730	0.1270
1.4110	0.1707			10.3500	0.5975		
12.6700	0.4046			1.8440	0.2278	0.9100	0.0900
1.4110	0.1346			12.1300	0.5992		
18.7500	0.4546			1.8380	0.2094	0.9400	0.0600
				15.2800	0.6347		

TABLE VII  
CALCULATED PHASE ENVELOPE DATA FOR  
METHANE/n HEPTANE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.5000; N HEPTANE=0.5000  
CRITICAL PRESSURE OF THE MIXTURE =1460.80 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 435.90 F

PRESSURE PSI BP	DP	TEMPERATURE F	CON. PRESSURE PSI
	988.7	465.9	1048.7
	983.2	455.9	1223.2
	996.5	445.9	1336.5
	681.5	435.9	1460.8
1675.2		415.9	1695.2
	480.8		
1890.2		395.9	1910.2
	380.8		
1970.2		375.9	2095.3
	300.8		
2064.1		355.9	2284.1
	220.8		
2124.7		335.9	2466.7
	180.8		
2164.1		315.9	2631.1
	140.8		
2224.2		295.9	2804.2
	120.8		
2264.5		275.9	2943.5
	90.7		
2284.8		255.9	3086.8
	60.7		
2124.1		155.9	3686.1
1984.4		115.9	3616.4

K VALUE		CRITICAL COMPOSITION	
METHANE	N HEPTANE	METHANE	N HEPTANE
1.4358	0.7119	0.4000	0.6000
1.9172	0.6490	0.4400	0.5600
2.3362	0.5970	0.4700	0.5300
1.2861	0.8904	0.5000	0.5000
1.4405	0.8180	0.5500	0.4500
6.0401	0.5397		
1.5020	0.7420	0.5900	0.4100
8.3552	0.5351		
1.9590	0.5057	0.6210	0.3790
11.2369	0.5244		
2.0717	0.3841	0.6500	0.3500
15.9747	0.5351		
2.2370	0.3156	0.6760	0.3240
19.9235	0.5102		
2.3740	0.2625	0.6980	0.3020
25.1654	0.5064		
2.5085	0.2159	0.7200	0.2800
28.5824	0.4644		
2.6109	0.1785	0.7370	0.2630
35.6648	0.5002		
2.6630	0.1480	0.7540	0.2460
43.9341	0.4778		
2.5509	0.0516	0.8230	0.1770
2.3711	0.0316	0.8460	0.1540

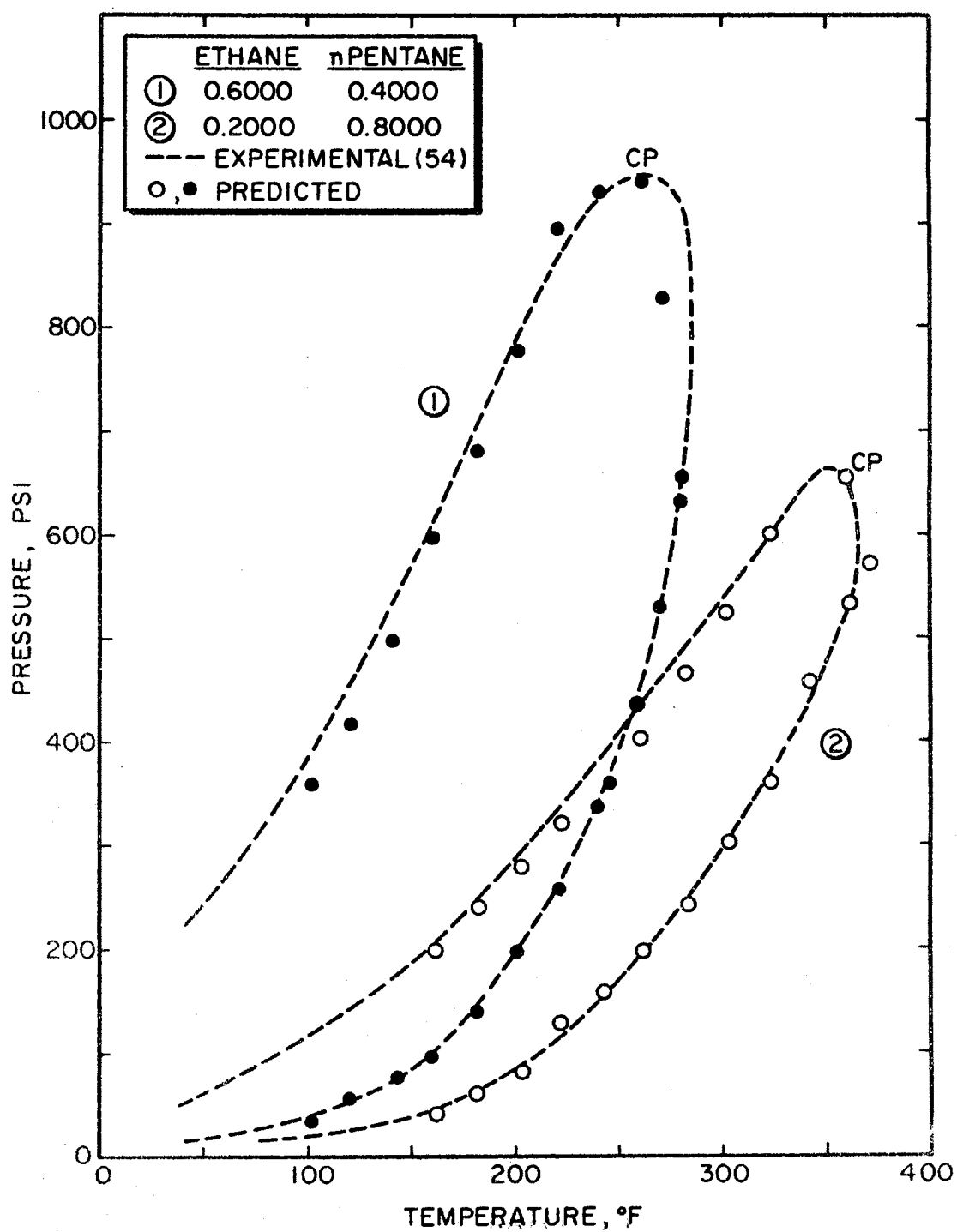


Figure 19. Pressure-Temperature Phase Envelopes for Ethane/n Pentane System

TABLE VIII

CALCULATED PHASE ENVELOPE DATA FOR ETHANE/*n* PENTANE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
 ETHANE=0.2000; N PENTANE=0.8000  
 CRITICAL PRESSURE OF THE MIXTURE = 660.40 PSI  
 CRITICAL TEMPERATURE OF THE MIXTURE = 362.00 F

PRESSURE BP	PSI DP	TEMPERATURE F	CON. PRESSURE PSI
	577.2	372.0	597.1
	534.7	362.0	660.4
	460.4	342.0	756.4
600.0		322.0	782.0
	360.4		
520.0		302.0	875.4
	300.4		
460.0		282.0	910.7
	240.4		
400.0		262.0	937.3
	200.4		
360.0		242.0	953.3
	160.4		
320.0		222.0	953.1
	130.4		
280.0		202.0	937.2
	80.4		
240.0		182.0	909.3
	60.4		
200.0		162.0	872.4
	40.4		

K VALUE		CRITICAL COMPOSITION	
ETHANE	N PENTANE	ETHANE	N PENTANE
1.2669	0.9348	0.1300	0.8700
1.8579	0.9512	0.2000	0.8000
2.5857	0.8623	0.3100	0.6900
1.4239	0.9052	0.3900	0.6100
3.4126	0.8666		
2.3979	0.6616	0.4700	0.5300
4.1218	0.8505		
2.6872	0.5957	0.5320	0.4680
5.0224	0.8544		
2.9931	0.5424	0.5930	0.4070
5.7891	0.8288		
3.1642	0.4852	0.6510	0.3490
6.8373	0.8204		
3.3244	0.4334	0.7550	0.2450
7.8725	0.8001		
3.4871	0.3868	0.8030	0.1970
10.4142	0.7723		
3.6700	0.3452	0.8500	0.1500
12.2117	0.7799		
3.8998	0.3083	0.8920	0.1080
15.9313	0.8604		

OVERALL COMPOSITION OF THE MIXTURE:  
 ETHANE=0.6000; N PENTANE=0.4000  
 CRITICAL PRESSURE OF THE MIXTURE = 939.70 PSI  
 CRITICAL TEMPERATURE OF THE MIXTURE = 260.60 F

PRESSURE BP	PSI DP	TEMPERATURE F	CON. PRESSURE PSI
	654.7	280.6	914.7
	639.7		
	828.3	270.6	928.3
	519.7		
	439.7	260.6	939.7
933.9		240.6	953.8
	339.7		
898.4		220.6	958.4
	259.7		
778.4		200.6	952.0
	199.7		
678.4		180.6	933.8
	139.7		
598.4		160.6	907.9
	99.7		
498.4		140.6	869.3
	79.7		
418.4		120.6	813.6
	59.7		
358.4		100.6	748.6
	39.7		

K VALUE		CRITICAL COMPOSITION	
ETHANE	N PENTANE	ETHANE	N PENTANE
2.0105	0.6089	0.5400	0.4600
1.9571	0.5757		
1.5352	0.6670	0.5700	0.4300
2.3701	0.5317		
2.7349	0.5157	0.6000	0.4000
1.2418	0.7253	0.6540	0.3460
3.3269	0.4944		
1.2642	0.6147	0.7100	0.2900
4.0206	0.4848		
1.4093	0.3716	0.7600	0.2400
4.7616	0.4727		
1.4713	0.2825	0.8100	0.1900
6.0683	0.4878		
1.4898	0.2190	0.8520	0.1480
7.4612	0.4944		
1.5417	0.1687	0.8950	0.1050
8.0779	0.4537		
1.5580	0.1345	0.9400	0.0600
9.1541	0.4337		
1.5658	0.1144	0.9800	0.0200
12.2225	0.4487		

A comparison between the experimental and calculated phase envelopes indicates that the predicted values are in good agreement with the experimental data. The maximum deviation between the experimental and calculated bubble point/dew point pressures is not more than 100 psi. The error in the predicted cricondenthem is within 25° F of the experimental value. Many inaccuracies are to be expected in the neighborhood of the critical region. This may be attributed in part to the inaccuracies in the correlations used to predict the critical temperature and critical pressure of the mixture and to uncertainties involved in the K-factors as the critical pressure is approached. The K-factors are extremely sensitive to pressure when the pressure is approximately equal to the convergence pressure. The success in predicting the envelopes so closely can be largely attributed to the accuracy of critical temperature and critical pressure correlations used, and the technique of evaluating K-factors at pressures higher than 0.7 times the convergence pressure.

### 6.3 Systems Containing Three or More Components

Figures 20, 47, 48 and 49 show the calculated phase envelopes for ternary systems. The maximum deviation between the experimental and calculated envelopes for either bubble point or dew point pressure is 125 psi. The maximum deviation of the cricondenthem from the experimental value is 15° F. The calculated phase envelope data for plotting Figure 20 is given in Table IX.

The main reason for the difference in the calculated and the experimental value of the cricondenthem may be attributed to the restriction imposed by the program. The difference between the two

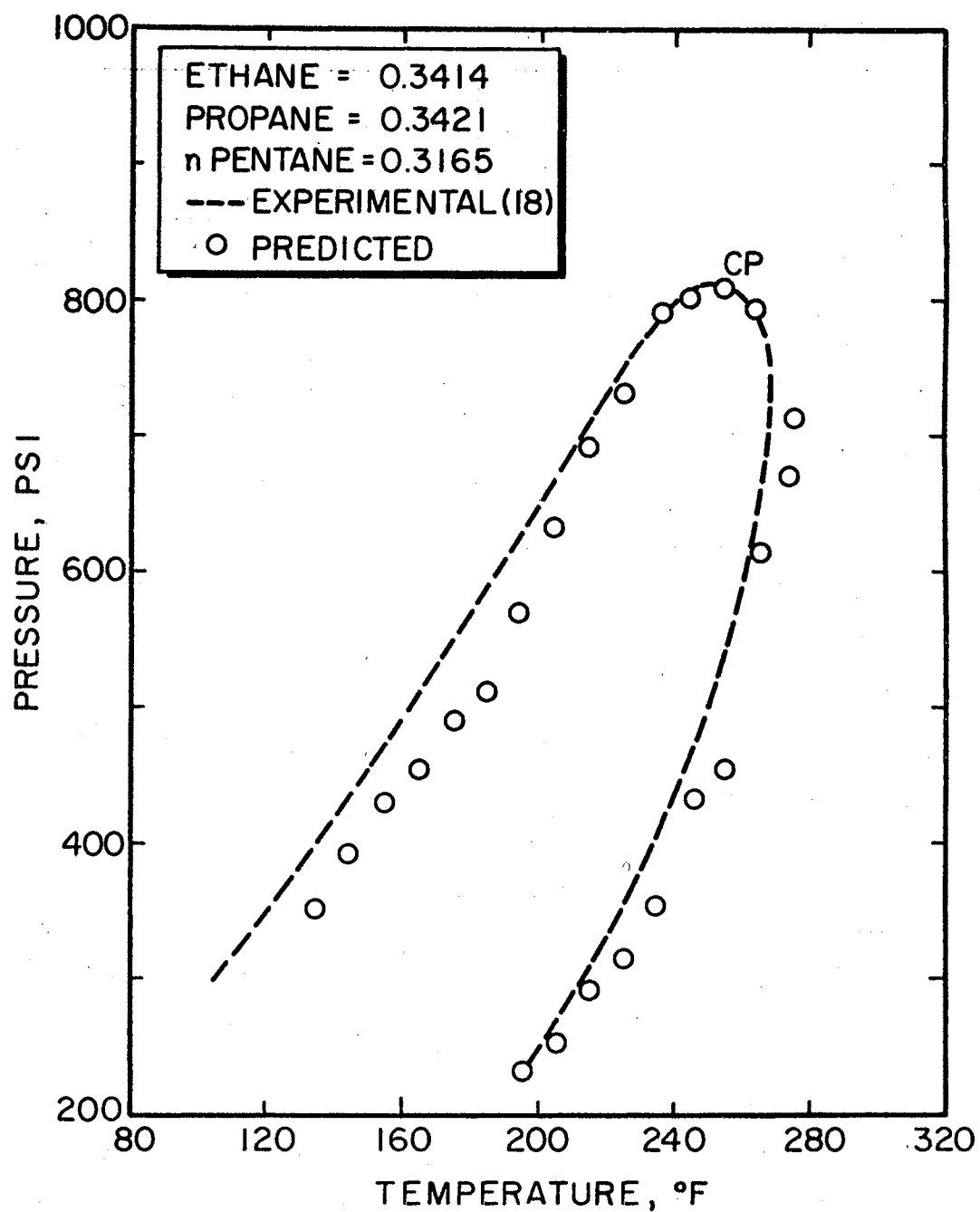


Figure 20. Pressure-Temperature Phase Envelope for Ethane/Propane/n Pentane System

TABLE IX

CALCULATED PHASE ENVELOPE DATA FOR  
ETHANE/PROPANE/n PENTANE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
ETHANE=0.3414; PROPANE=0.3421; N PENTANE=0.3165  
CRITICAL PRESSURE OF THE MIXTURE = 812.50 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 255.20 F

PRESSURE PSI		TEMPERATURE	CON. PRESSURE	
BP	DP	F	ASSUMED	CALCULATED
	712.5	275.2	812.5	786.5
	672.5		812.5	776.4
	792.5	265.2	812.5	791.5
	612.5		812.5	793.1
	452.5	255.2	812.5	812.5
800.6		245.2	820.6	819.8
	432.5		812.5	815.6
790.7		235.2	830.4	831.2
	352.5		812.5	821.7
730.4		225.2	830.4	841.5
	312.5		812.5	826.9
690.4		215.2	830.4	847.2
	292.5		812.5	828.0
630.4		205.2	830.4	850.9
	252.5		812.5	825.3
570.4		195.2	830.4	850.3
	232.5		812.5	820.3
510.4		185.2	830.4	851.9
490.4		175.2	830.4	846.7
450.4		165.2	830.4	836.3
430.4		155.2	830.4	827.1

K VALUE			CRITICAL COMPOSITION		
ETHANE	PROPANE	N PENTANE	ETHANE	PROPANE	N PENTANE
1.5613	1.1478	0.6583	0.2882	0.3221	0.3897
1.6503	1.1899	0.6255	0.2994	0.3251	0.3755
1.4264	1.0660	0.6971	0.3232	0.3385	0.3383
2.0331	1.3451	0.5369	0.3263	0.3345	0.3392
2.3289	1.4499	0.5074	0.3414	0.3421	0.3165
1.4926	1.0610	0.5607	0.3788	0.3474	0.2738
2.3730	1.4347	0.4756	0.3707	0.3579	0.2714
1.4678	1.0279	0.5281	0.4064	0.3462	0.2474
2.8133	1.5926	0.4754	0.3887	0.3695	0.2418
1.4418	1.0173	0.4969	0.4374	0.3452	0.2174
3.0669	1.6615	0.4644	0.4105	0.3805	0.2090
1.4769	0.9846	0.4335	0.4638	0.3467	0.1895
3.1641	1.6587	0.4402	0.4292	0.3925	0.1783
1.5521	0.9749	0.3668	0.4926	0.3455	0.1619
3.5197	1.7620	0.4368	0.4476	0.4060	0.1464
1.6392	0.9683	0.3155	0.5185	0.3460	0.1355
3.6688	1.7740	0.6552	0.4666	0.4160	0.1174
1.7430	0.9685	0.2770	0.5531	0.3328	0.1141
1.7420	0.9312	0.2496	0.5805	0.3274	0.0921
1.8027	0.9160	0.2244	0.6085	0.3228	0.0687
1.8734	0.9048	0.2032	0.6406	0.3085	0.0509

adjacent isotherms was set in the retrograde region as  $10^{\circ}\text{F}$  in most of the phase envelope calculations. Hence, it was possible to calculate the cricondenthem only to within  $10^{\circ}\text{F}$  accuracy.

The four component system phase envelopes presented in Figures 21 and 50, the five component systems shown in Figures 22 and 51, and the six component system given in Figure 23, show very close agreement between the calculated and the experimental values. The deviation of bubble point pressure or dew point pressure predicted does not vary more than 100 psi. The cricondenthems for all the mixtures are predicted within  $10^{\circ}\text{F}$  of the experimental values. The data contained in Tables X through XII were used in drawing Figures 21, 22 and 23.

Figures 24 through 29 show phase envelopes for various reservoir fluids. Tables XIII through XVIII present the calculated phase envelope data corresponding to these figures. In the literature only partial phase envelopes were presented for most of the fluids tested. Hence, it is difficult to assess the exact deviations in the bubble or dew point pressures calculated and the experimental values. But from the trend of the envelopes shown in Figures 24 through 29, it is estimated that the deviations are within 200 psi.

The composition of the systems tested contained carbon dioxide and nitrogen up to 5%. They were combined with propane and ethane, respectively, and treated as pure paraffin hydrocarbons. This may be one of the reasons for the deviations in the predicted and experimental values. However, the closeness between the calculated and experimental envelopes indicates that such a treatment is justified.

It is quite essential to know the molecular weight of heptane plus fraction for the phase envelope calculation. However, for some of the



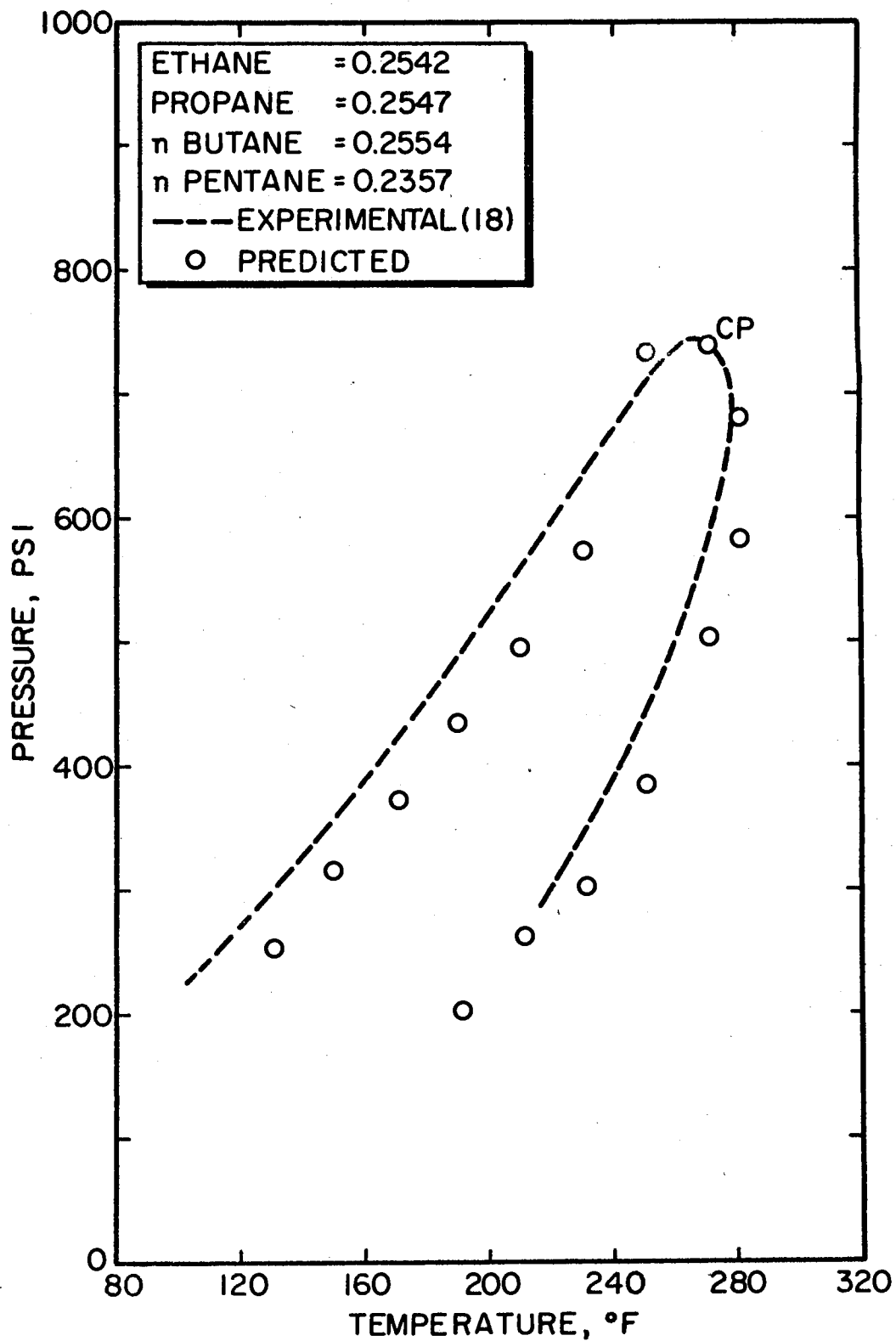


Figure 21. Pressure-Temperature Phase Envelope for Ethane/Propane/n Butane/n Pentane System

TABLE X  
CALCULATED PHASE ENVELOPE DATA FOR  
ETHANE/PROPANE/n BUTANE/n PENTANE  
SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
ETHANE=0.2542; PROPANE=0.2547; N BUTANE=0.2554;  
N PENTANE=0.2357;  
CRITICAL PRESSURE OF THE MIXTURE = 742.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 270.90 F

PRESSURE PSI BP	PRESSURE PSI DP	TEMPERATURE F	CON. PRESSURE	
			ASSUMED	CALCULATED
	681.6	280.9	741.6	722.5
	581.6		741.6	723.6
	501.6	270.9	742.0	742.0
732.1		250.9	772.1	775.4
	381.6		741.6	
572.1		230.9	772.1	804.4
	301.6		741.6	
492.1		210.9	772.1	818.9
	261.6		741.6	
432.1		190.9	772.1	
	201.6		741.6	
372.1		170.9	772.1	
312.1		150.9	772.1	
252.1		130.9	772.1	

K VALUE			
ETHANE	PROPANE	N BUTANE	N PENTANE
1.4555	1.1420	0.9379	0.7236
1.7051	1.2461	0.8975	0.6390
2.0310	1.3719	0.8718	0.5861
1.5040	1.0957	0.8237	0.5786
2.6585	1.5897	0.8755	0.5312
1.6709	1.1116	0.7114	0.4529
3.2017	1.7578	0.8951	0.5037
1.8564	1.1205	0.6342	0.3697
3.4479	1.7799	0.8481	0.4576
1.9813	1.0946	0.5689	0.3075
4.1145	1.9597	0.8772	0.4419
2.1191	1.0695	0.5143	0.2584
2.2875	1.0535	0.4695	0.2196
2.5176	1.0565	0.4331	0.1885

CRITICAL COMPOSITION			
ETHANE	PROPANE	N BUTANE	N PENTANE
0.2366	0.2468	0.2594	0.2572
0.2384	0.2472	0.2597	0.2547
0.2542	0.2547	0.2554	0.2357
0.3320	0.2699	0.2267	0.1714
0.4000	0.2837	0.1929	0.1234
0.4424	0.2816	0.1726	0.1034

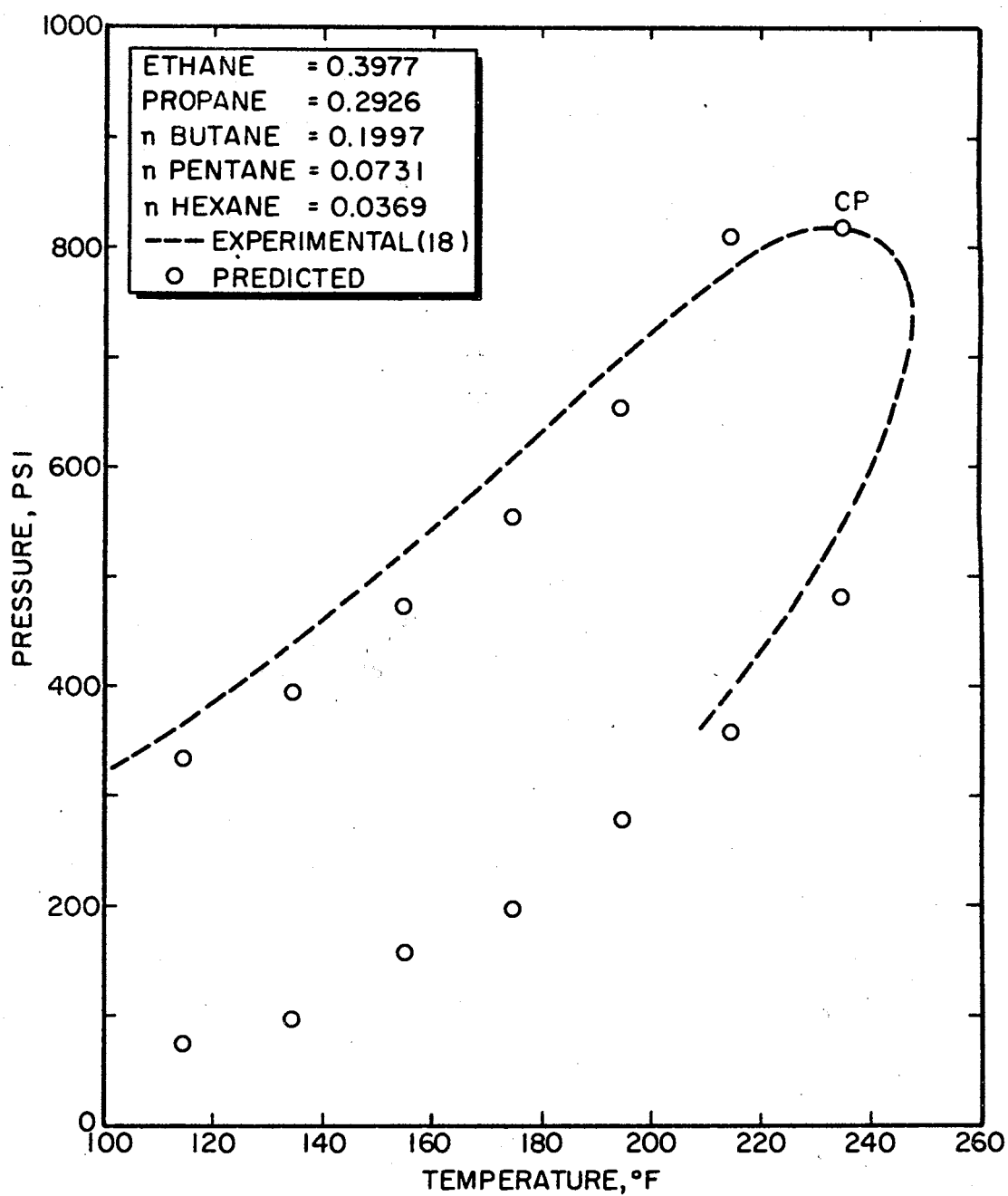


Figure 22. Pressure-Temperature Phase Envelope for Ethane/Propane/n Butane/n Pentane/n Hexane System

TABLE XI

CALCULATED PHASE ENVELOPE DATA FOR ETHANE/  
PROPANE/n BUTANE/n PENTANE/n HEXANE SYSTEM

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OVERALL COMPOSITION OF THE MIXTURE:

ETHANE=0.3977; PROPANE=0.2926; N BUTANE=0.1997;

N PENTANE=0.0731; N HEXANE=0.0369;

CRITICAL PRESSURE OF THE MIXTURE = 815.70 PSI

CRITICAL TEMPERATURE OF THE MIXTURE = 234.10 F

PRESSURE PSI		TEMPERATURE F	CON.PRESSURE	
BP	DP		ASSUMED	CALCULATED
	475.7	234.1	815.7	815.7
812.3		214.1	832.3	833.2
	355.7		815.7	
652.4		194.1	832.3	843.9
	275.7		815.7	
552.4		174.1	832.3	845.7
	195.7		815.7	
472.4		154.1	832.3	
	155.7		815.7	
392.4		134.1	832.3	
	95.7		815.7	
332.4		114.1	832.3	
	75.7		815.7	

K VALUE				
ETHANE	PROPANE	N BUTANE	N PENTANE	N HEXANE
2.1997	1.3176	0.7585	0.4296	0.2297
1.4117	0.9645	0.6901	0.4628	0.2957
2.6211	1.4215	0.7524	0.3927	0.1921
1.4720	0.9186	0.5813	0.3465	0.1966
3.1129	1.5396	0.7616	0.3704	0.1687
1.5786	0.8768	0.4867	0.2556	0.1271
3.9681	1.7820	0.8170	0.3674	0.1563
1.6616	0.8309	0.4184	0.1990	0.0892
4.4739	1.8625	0.7968	0.3331	0.1336
1.7721	0.7974	0.3672	0.1593	0.0651
6.3237	2.4169	0.9364	0.3565	0.1337
1.8379	0.7526	0.3204	0.1281	0.0485
6.9904	2.4964	0.8962	0.3162	0.1110

CRITICAL COMPOSITION				
ETHANE	PROPANE	N BUTANE	N PENTANE	N HEXANE
0.3977	0.2926	0.1997	0.0731	0.0369
0.4574	0.2885	0.1736	0.0557	0.0248
0.5251	0.2763	0.1421	0.0401	0.0164
0.5754	0.2644	0.1189	0.0300	0.0113

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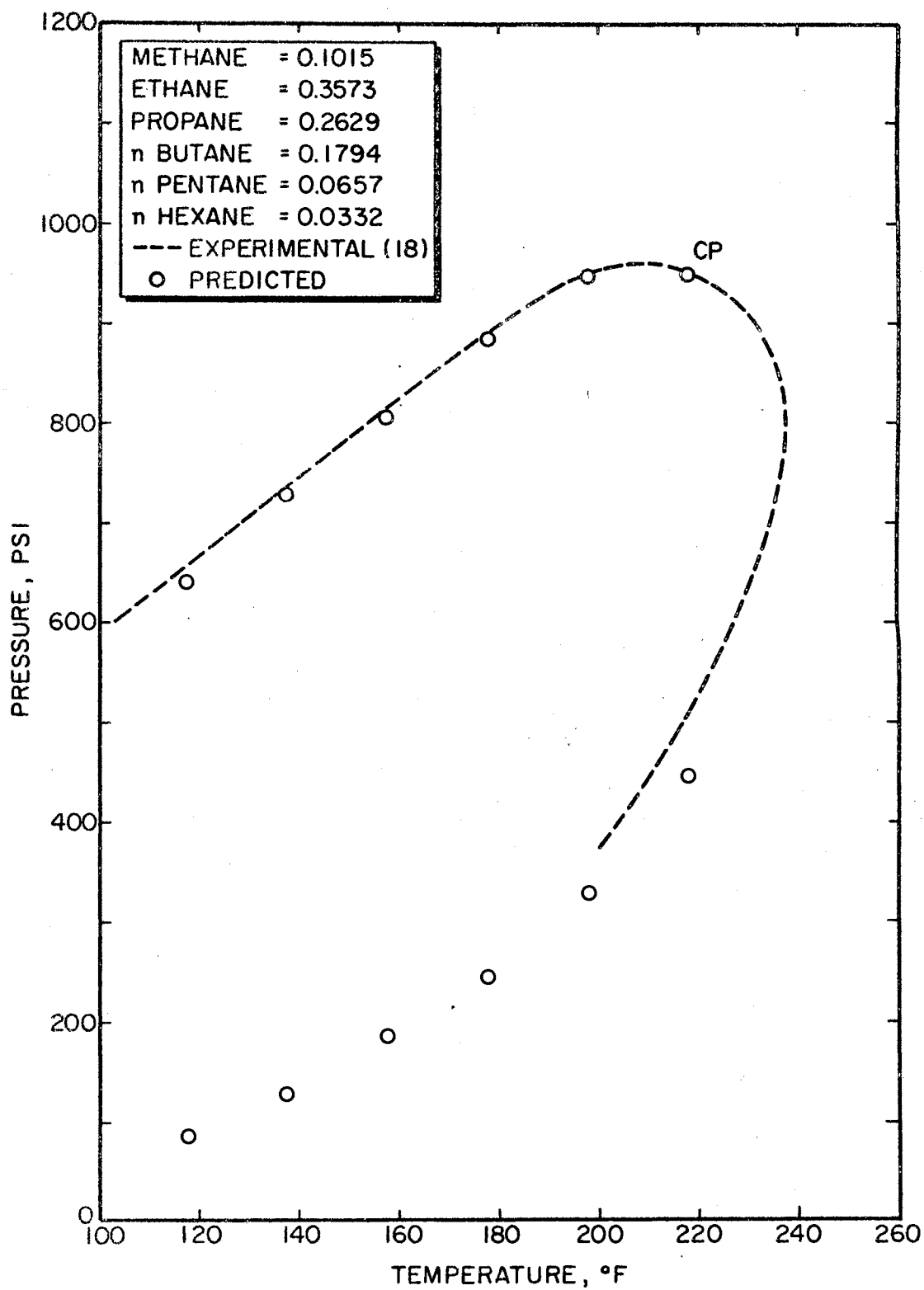


Figure 23. Pressure-Temperature Phase Envelope for Methane/  
Ethane/Propane/n Butane/n Pentane/n Hexane  
System

TABLE XII

CALCULATED PHASE ENVELOPE DATA FOR METHANE/  
ETHANE/PROPANE/n BUTANE/n PENTANE/  
n HEXANE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.1015; ETHANE=0.3573; PROPANE=0.2629;  
N BUTANE=0.1794; N PENTANE=0.0657; N HEXANE=0.0332;  
CRITICAL PRESSURE OF THE MIXTURE = 948.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 217.90 F

PRESSURE PSI		TEMPERATURE		CON. PRESSURE	
BP	DP	F	ASSUMED	CALCULATED	
	448.0	217.9	948.0	948.0	
948.0		197.9	1148.0	1142.5	
	328.0		948.0		
888.0		177.9	1148.0		
	248.0		948.0		
808.0		157.9	1148.0		
	188.0		948.0		
728.0		137.9	1148.0		
	128.0		948.0		
648.0		117.9	1148.0		
	88.0		948.0		

K VALUE					
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE	N HEXANE
4.1523	2.3912	1.2844	0.6744	0.3595	0.1824
1.5284	1.3008	0.8997	0.6130	0.4121	0.2629
6.1361	2.9557	1.4406	0.6928	0.3396	0.1579
1.8567	1.3643	0.8286	0.5043	0.3008	0.1723
8.5345	3.5192	1.5760	0.7062	0.3225	0.1401
2.2404	1.3891	0.7568	0.4147	0.2230	0.1153
11.7463	4.1376	1.7051	0.7123	0.3026	0.1233
2.5744	1.3729	0.6796	0.3417	0.1683	0.0800
18.2820	5.3114	1.9976	0.7688	0.3001	0.1143
3.1096	1.3802	0.6100	0.2780	0.1240	0.0534
27.7116	6.6726	2.3138	0.8216	0.2951	0.1051

CRITICAL COMPOSITION					
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE	N HEXANE
0.1015	0.3573	0.2629	0.1794	0.0657	0.0332
0.1164	0.4042	0.2585	0.1532	0.0479	0.0198

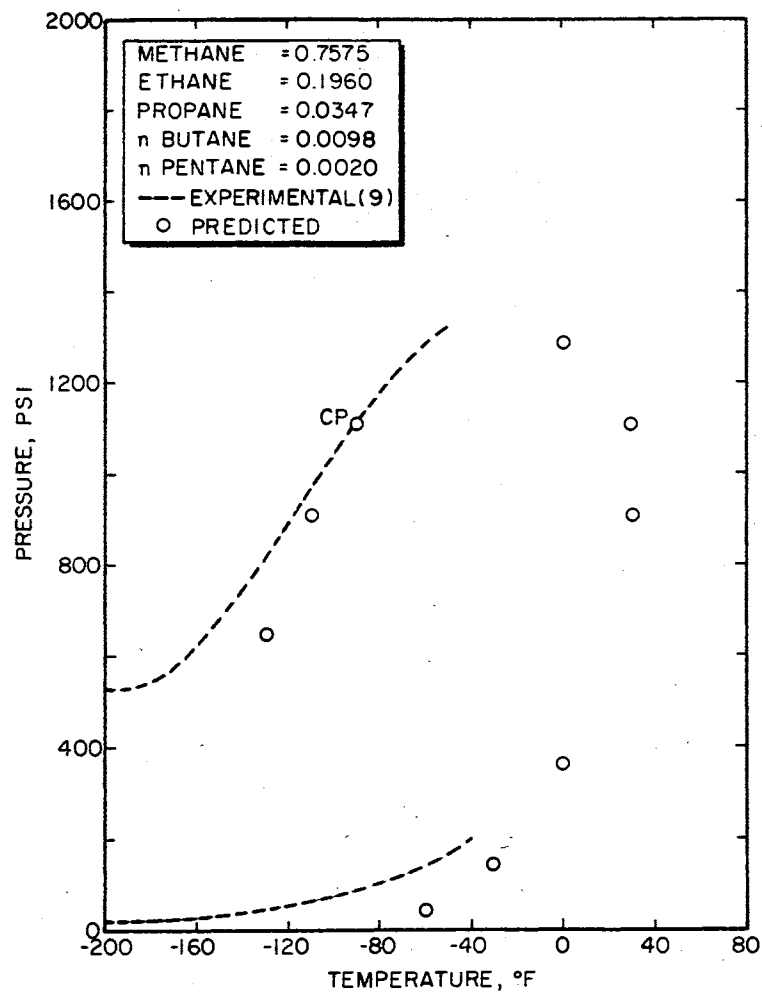


Figure 24. Pressure-Temperature Phase Envelope for a Natural Gas System

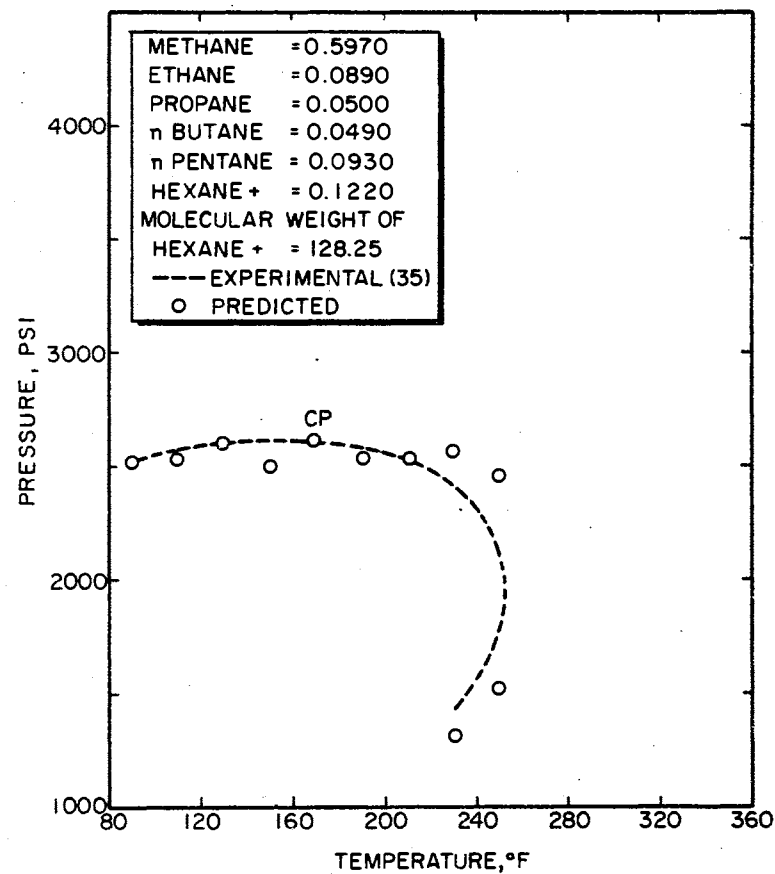


Figure 25. Pressure-Temperature Phase Envelope for a Mixture of Natural Gas and Natural Gasoline System

TABLE XIII

CALCULATED PHASE ENVELOPE DATA FOR A NATURAL GAS  
SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
 METHANE=0.7575; ETHANE=0.1960; PROPANE=0.0347;  
 N BUTANE=0.0098; N PENTANE=0.0020;  
 CRITICAL PRESSURE OF THE MIXTURE =1107.00 PSI  
 CRITICAL TEMPERATURE OF THE MIXTURE = -90.00 F

PRESSURE PSI		TEMPERATURE	CON. PRESSURE	
BP	DP	F	ASSUMED	CALCULATED
	1107.0	30.0	1207.0	1228.9
	907.0		1328.8	1323.5
	1287.0	0.0	1328.8	1359.7
	367.0		1276.9	1287.6
	147.0	-30.0	964.7	963.1
	47.0	-60.0	964.7	964.7
907.0		-110.0	1107.0	
643.0		-130.0	663.0	671.7

K VALUE				
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE
1.5202	0.4996	0.3227	0.0877	0.0497
1.6921	0.6439	0.2813	0.1141	0.0493
1.4448	0.3249	0.2405	0.0660	0.0376
4.1524	0.7025	0.1778	0.0485	0.0129
9.3426	0.9409	0.1822	0.0355	0.0067
28.5714	1.5653	0.2300	0.0323	0.0044
1.2984	0.1308	0.0258	0.0051	0.0014
1.2957	0.1626	0.0334	0.0018	0.0005

CRITICAL COMPOSITION				
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE
0.6356	0.2717	0.0592	0.0272	0.0063
0.6648	0.2284	0.0611	0.0324	0.0133
0.7217	0.2231	0.0405	0.0122	0.0025
0.7407	0.1984	0.0394	0.0153	0.0062
0.7583	0.1960	0.0345	0.0095	0.0017
0.7579	0.1960	0.0346	0.0097	0.0018
0.9653	0.0335	0.0012	0.0001	0.0000



TABLE XIV

CALCULATED PHASE ENVELOPE DATA FOR A MIXTURE OF  
NATURAL GAS AND NATURAL GASOLINE SYSTEM

OVERALL COMPOSITION OF THE MIXTURE:  
 METHANE=0.5970; ETHANE=0.0890; PROPANE=0.0500;  
 N BUTANE=0.0490; N PENTANE=0.0930; HEXANE +=0.1220;  
 MOLECULAR WEIGHT OF HEXANE + =128.25  
 CRITICAL PRESSURE OF THE MIXTURE =2615.00 PSI  
 CRITICAL TEMPERATURE OF THE MIXTURE = 169.00 F

PRESSURE PSI		TEMPERATURE	CON. PRESSURE	
BP	DP	F	ASSUMED	CALCULATED
	2455.0	249.0	2615.0	
	1510.0		2010.5	2040.9
	2575.0	229.0	2615.0	
	1310.0		2010.5	1984.5
	2535.0	209.0	2615.0	
	2535.0	189.0	2615.0	
2495.0		149.0	2615.0	
2596.0		129.0	2916.5	2913.4
2536.0		109.0	2916.5	2919.2
2514.0		89.0	2941.3	2934.5

K VALUE					
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE	HEXANE +
1.3017	1.0007	0.0878	0.8245	0.6800	0.3586
2.1821	1.3112	0.8426	0.5621	0.4123	0.4213
1.2465	1.1060	0.1002	0.8343	0.6922	0.3979
2.5137	1.4121	0.8012	0.4927	0.4527	0.3672
1.3187	0.9411	0.2262	0.7730	0.6156	0.2917
1.3051	0.9504	0.2692	0.7561	0.5953	0.2781
1.3346	0.9286	0.3479	0.6786	0.5074	0.1971
1.4315	0.8950	0.5018	0.5625	0.3895	0.0944
1.3813	0.8789	0.4943	0.5476	0.3757	0.0913
1.4323	0.8384	0.4499	0.4582	0.2941	0.0554

CRITICAL COMPOSITION					
METHANE	ETHANE	PROPANE	N BUTANE	N PENTANE	HEXANE +
0.4688	0.0707	0.0409	0.0421	0.0878	0.2897
0.4800	0.0723	0.0415	0.0425	0.0880	0.2757
0.6327	0.0876	0.0462	0.0457	0.0840	0.1038
0.6625	0.0859	0.0427	0.0426	0.0763	0.0900
0.7651	0.0798	0.0299	0.0314	0.0492	0.0446

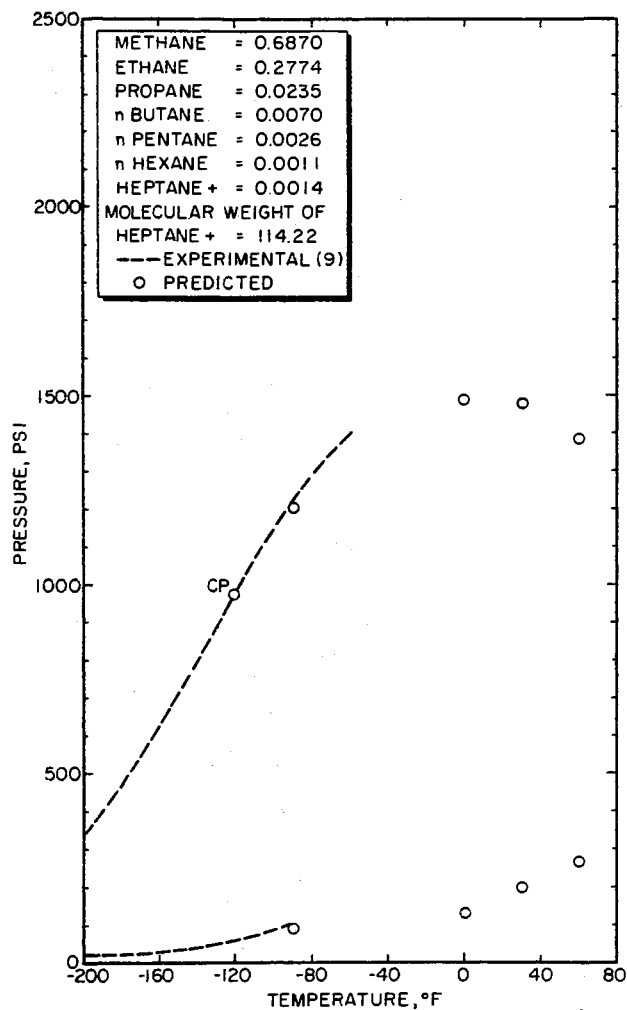


Figure 26. Pressure-Temperature Phase Envelope for a Natural Gas System (Molecular Weight of  $C_{7+}$  = 114.22)

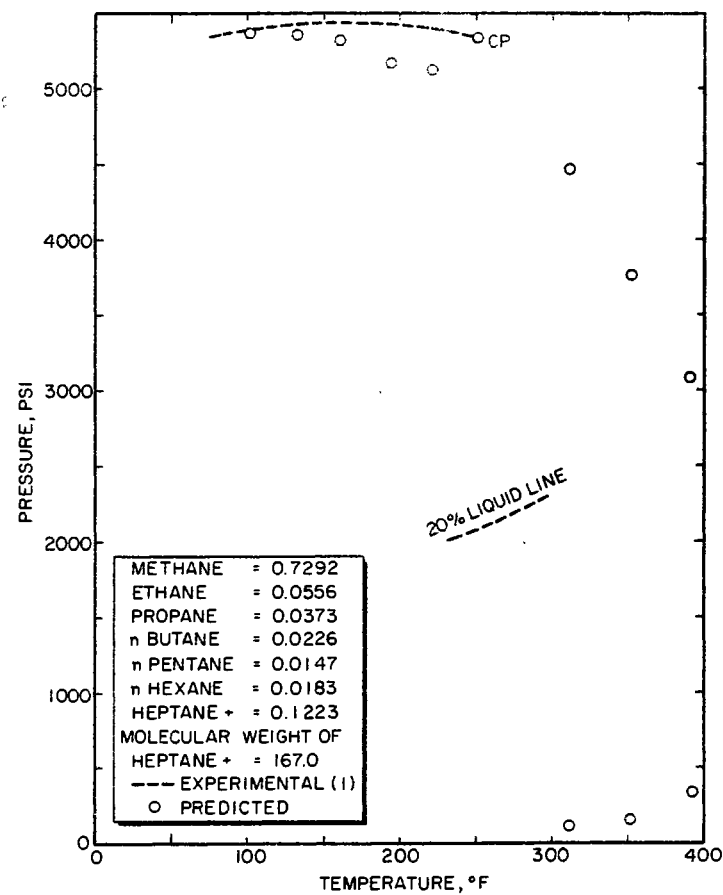


Figure 27. Pressure-Temperature Phase Envelope for a Gas Condensate Reservoir Fluid (Molecular Weight of  $C_{7+}$  = 167)

TABLE XV

CALCULATED PHASE ENVELOPE DATA FOR A  
NATURAL GAS SYSTEM

(Molecular Weight of  $C_7+$  = 114.22)

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.6870; ETHANE=0.2774; PROPANE=0.0235;  
N BUTANE=0.0070; N PENTANE=0.0026; N HEXANE=0.0011;  
HEPTANE +=0.0014;  
MOLECULAR WEIGHT OF HEPTANE + =114.22  
CRITICAL PRESSURE OF THE MIXTURE = 973.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE =-120.00 F

PRESSURE PSI BP	DP	TEMPERATURE F	CON. PRESSURE	
			ASSUMED	CALCULATED
	1385.6	60.0	1403.6	1429.4
	270.0		2000.6	1996.1
	1485.2	30.0	1585.2	1586.8
	200.0		1520.9	1518.6
	1492.2	0.0	1585.2	1589.7
	130.0		1172.7	1207.6
	1202.1	-90.0	1242.1	1215.4
	90.0		1115.2	1146.1

K VALUE			
METHANE	ETHANE	PROPANE	N BUTANE
1.4123	0.6949	0.4383	0.1758
13.2707	2.4855	0.6637	0.1955
1.2661	0.4897	0.4298	0.1237
12.7358	2.0008	0.4939	0.1286
1.1947	0.7212	0.4163	0.2051
12.7629	1.5705	0.4433	0.1293
1.3174	0.3346	0.1196	0.0179
13.2772	0.8598	0.1289	0.1905

K VALUE		
N PENTANE	N HEXANE	HEPTANE +
0.1062	0.0681	0.0946
0.0574	0.0170	0.0013
0.0913	0.0934	0.2244
0.0334	0.0085	0.0005
0.1205	0.0734	0.0470
0.0372	0.0092	0.0006
0.0057	0.0031	0.0070
0.0269	0.0033	0.0004

CRITICAL COMPOSITION			
METHANE	ETHANE	PROPANE	N BUTANE
0.5765	0.3417	0.0387	0.0209
0.6557	0.2692	0.0241	0.0084
0.6042	0.3126	0.0362	0.0177
0.6757	0.2749	0.0239	0.0078
0.6154	0.3025	0.0358	0.0167
0.6888	0.2777	0.0234	0.0068
0.7062	0.2636	0.0261	0.0057
0.6983	0.2766	0.0210	0.0037
N PENTANE	N HEXANE	HEPTANE +	
0.0105	0.0056	0.0061	
0.0047	0.0041	0.0338	
0.0101	0.0062	0.0130	
0.0039	0.0029	0.0029	
0.0079	0.0070	0.0147	
0.0023	0.0007	0.0003	
0.0020	0.0083	0.0011	
0.0003	0.0001	0.0000	

TABLE XVI

CALCULATED PHASE ENVELOPE DATA FOR A GAS  
CONDENSATE RESERVOIR FLUID  
(Molecular Weight of  $C_7^+$  = 167)

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.7292; ETHANE=0.0556; PROPANE=0.0373;  
N BUTANE=0.0226; N PENTANE=0.0147; N HEXANE=0.0183;  
HEPTANE + =0.1223;  
MOLECULAR WEIGHT OF HEPTANE + =167.00  
CRITICAL PRESSURE OF THE MIXTURE =5350.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 251.00 F

PRESSURE PSI BP	DP	TEMPERATURE F	CON. PRESSURE	
			ASSUMED	CALCULATED
	3096.3	391.0	3256.3	
	330.0		1237.8	
	3756.3	351.0	3956.3	
	150.0		1237.8	
	4451.1	311.0	4851.1	
	110.0		1237.8	
5114.4		221.0	5134.4	5130.3
5153.3		191.0	5253.3	5249.8
5323.0		161.0	5343.0	5344.3
5361.4		131.0	5381.4	5383.3
5363.3		101.0	5383.3	5381.9

K VALUE			
METHANE	ETHANE	PROPANE	N BUTANE
1.1146	1.0086	0.6165	0.9215
7.4733	4.1200	2.3365	2.0640
1.2131	1.0091	0.9983	0.9247
18.3934	10.3587	6.0430	3.4081
1.1811	1.0532	0.9823	0.8873
26.0960	13.0618	6.9731	3.6580
1.4733	0.9709	0.8053	0.6552
1.4537	0.9464	0.7860	0.6445
1.4346	0.9212	0.7641	0.6280
1.4164	0.8934	0.7364	0.6008
1.3937	0.8612	0.7021	0.5617

K VALUE		
N PENTANE	N HEXANE	HEPTANE +
0.9125	0.5171	0.5650
1.3088	0.8584	0.1474
0.8275	0.6924	0.5128
1.9546	0.9937	0.1347
0.7936	0.7532	0.5462
1.9530	1.0641	0.0925
0.4814	0.4143	0.2442
0.4647	0.4060	0.2376
0.4439	0.3925	0.2274
0.4162	0.3692	0.2100
0.3821	0.3363	0.1862

## CRITICAL COMPOSITION

METHANE	ETHANE	PROPANE	N BUTANE
0.7452	0.0555	0.0368	0.0220
0.7637	0.0552	0.0362	0.0211
0.7743	0.0548	0.0354	0.0258
0.7793	0.0543	0.0349	0.0201
0.7915	0.0534	0.0339	0.0193

## CRITICAL COMPOSITION

N PENTANE	N HEXANE	HEPTANE +
0.0139	0.0171	0.1095
0.0129	0.0158	0.0951
0.0124	0.0149	0.0874
0.0120	0.0145	0.0849
0.0112	0.0135	0.0772

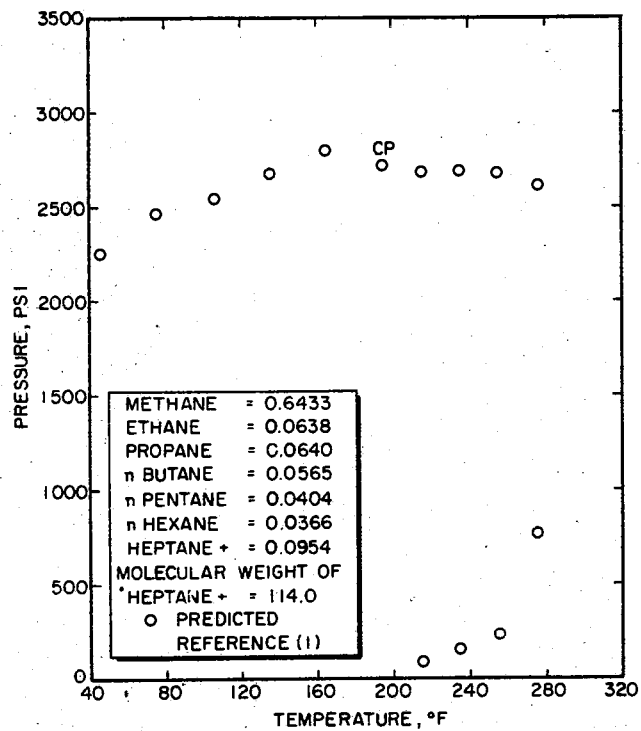


Figure 28. Pressure-Temperature Phase Envelope for a Gas Condensate Reservoir Fluid (Molecular Weight of  $C_{7+} = 114$ )

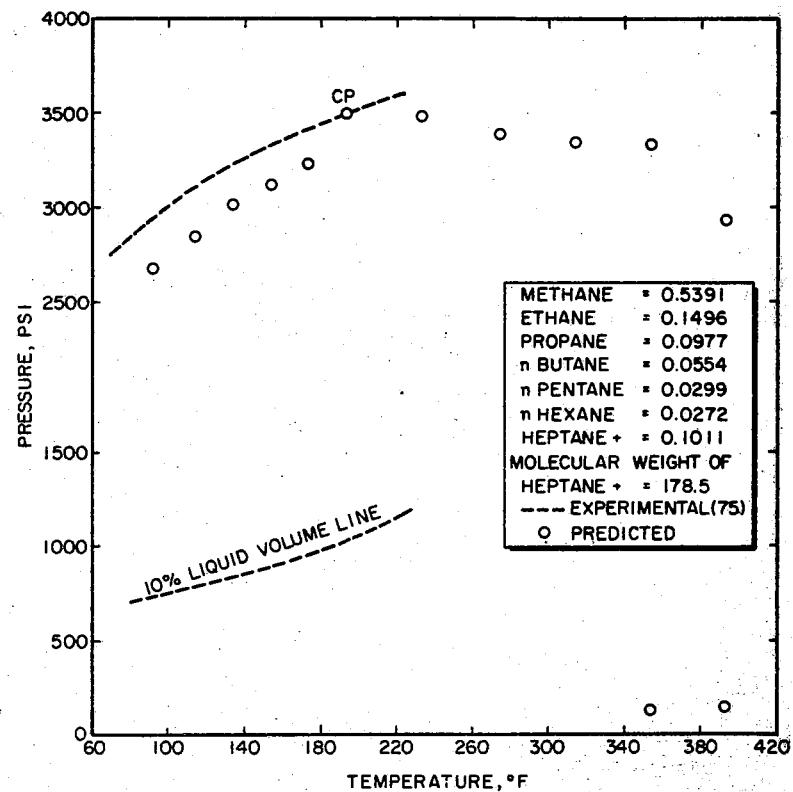


Figure 29. Pressure-Temperature Phase Envelope for a Naturally Occurring Hydrocarbon Mixture

TABLE XVII  
CALCULATED PHASE ENVELOPE DATA FOR A  
GAS CONDENSATE RESERVOIR FLUID  
(Molecular Weight of  $C_7+$  = 114)

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.6433; ETHANE=0.0638; PROPANE=0.0640;  
N BUTANE=0.0565; N PENTANE=0.0404; N HEXANE=0.0366;  
HEPTANE +=0.0954;  
MOLECULAR WEIGHT OF HEPTANE + =114.00  
CRITICAL PRESSURE OF THE MIXTURE =2720.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 195.00 F

BP	PRESSURE PSI	TEMPERATURE F	CON. PRESSURE ASSUMED	CON. PRESSURE CALCULATED
	OP			
	2620.0	275.0	2720.0	
	770.0		779.8	
	2680.0	255.0	2720.0	
	230.0		920.6	942.6
	2680.0	235.0	2720.0	
	150.0		1080.9	1053.8
	2680.0	215.0	2720.0	
	90.0		1276.5	1275.8
2800.0		165.0	2820.0	
2680.0		135.0	2820.0	
2556.9		105.0	2716.9	2748.5
2436.9		75.0	2617.2	2654.0
2258.9		45.0	2498.9	2509.9

K VALUE			
METHANE	ETHANE	PROPANE	N BUTANE
1.2071	1.0010	0.1109	0.8798
1.1407	1.3183	1.0623	0.9602
1.2007	1.0098	0.1882	0.8703
9.5247	4.9097	2.6115	1.3413
1.1938	1.0696	0.2558	0.8603
17.1031	7.5006	3.5482	1.6578
1.1862	0.9279	0.3115	0.8500
31.8494	11.9083	5.0843	2.2417
1.2108	0.9479	0.5395	0.7773
1.2353	0.9305	0.5284	0.7173
1.2769	0.9024	0.4470	0.6347
1.3091	0.8651	0.3836	0.5431
1.3700	0.7997	0.3101	0.4070

K VALUE		
N PENTANE	N HEXANE	HEPTANE +
0.7559	0.7361	0.5952
0.8122	0.6503	0.6755
0.7410	0.7356	0.5887
0.7130	0.3702	0.1336
0.7263	0.7354	0.5832
0.8037	0.3930	0.1148
0.7117	0.7345	0.5778
1.0070	0.4666	0.1110
0.6179	0.6243	0.4524
0.5493	0.5417	0.3782
0.4611	0.4434	0.3024
0.3682	0.3297	0.2196
0.2421	0.1831	0.1148

CRITICAL COMPOSITION			
METHANE	ETHANE	PROPANE	N BUTANE
0.2988	0.0334	0.0404	0.0479
0.3444	0.0365	0.0414	0.0455
0.3964	0.0407	0.0437	0.0441
0.7403	0.0604	0.0439	0.0449
0.7819	0.0578	0.0364	0.0385
0.8235	0.0541	0.0302	0.0309

CRITICAL COMPOSITION		
N PENTANE	N HEXANE	HEPTANE +
0.0501	0.0735	0.4559
0.0452	0.0637	0.4233
0.0403	0.0530	0.3818
0.0281	0.0251	0.0573
0.0226	0.0195	0.0433
0.0170	0.0137	0.0306

TABLE XVIII

CALCULATED PHASE ENVELOPE DATA FOR A  
NATURALLY OCCURRING HYDROCARBON  
MIXTURE

OVERALL COMPOSITION OF THE MIXTURE:  
METHANE=0.5391; ETHANE=0.1496; PROPANE=0.0977;  
N BUTANE=0.0554; N PENTANE=0.0299; N HEXANE=0.0272;  
HEPTANE +=0.1011;  
MOLECULAR WEIGHT OF HEPTANE + =178.50  
CRITICAL PRESSURE OF THE MIXTURE =3495.00 PSI  
CRITICAL TEMPERATURE OF THE MIXTURE = 193.40 F

BP	PRESSURE PSI	TEMPERATURE		CON. PRESSURE	
	DP	F	ASSUMED	CALCULATED	
	2735.0	393.4	3595.0		
	150.0		1893.8		
	3335.0	353.4	3595.0		
	130.0		1893.8		
	3355.0	313.4	3595.0		
	3395.0	273.4	3595.0		
	3495.0	233.4	3595.0		3624.9
3229.3		173.4	3729.3		3707.3
3109.3		153.4	3729.3		3745.8
3009.8		133.4	3829.8		3821.9
2829.7		113.4	3829.7		3861.3
2669.8		93.4	3889.8		3917.5

K VALUE			
METHANE	ETHANE	PROPANE	N BUTANE
1.1362	1.0159	0.9529	0.9161
21.0101	12.9165	7.1985	4.3231
1.1414	1.0094	0.9931	0.8960
24.8849	13.9673	7.1936	4.0650
1.1326	1.0036	0.9966	0.8915
1.1749	1.0010	0.9709	0.8573
1.2131	1.0044	0.9247	0.8184
1.2206	1.0146	0.8512	0.7666
1.2681	1.0475	0.7973	0.6999
1.3846	0.8992	0.7087	0.5749
1.4052	0.8688	0.6541	0.5129
1.4489	0.8255	0.5816	0.4271

K VALUE		
N PENTANE	N HEXANE	HEPTANE +
0.8862	0.5739	0.5191
2.5600	1.5367	0.1044
0.8593	0.5484	0.4767
2.2897	1.3039	0.0595
0.8447	0.5530	0.4618
0.7832	0.5275	0.3899
0.7148	0.4927	0.3195
0.6324	0.4466	0.2456
0.5500	0.3732	0.1791
0.4118	0.2776	0.0960
0.3522	0.2250	0.0696
0.2751	0.1610	0.0413

CRITICAL COMPOSITION			
METHANE	ETHANE	PROPANE	N BUTANE
0.5411	0.1496	0.0976	0.0552
0.5667	0.1500	0.0945	0.0525
0.5761	0.1514	0.0926	0.0511
0.5949	0.1454	0.0898	0.0488
0.6096	0.1432	0.0867	0.0466
0.6267	0.1401	0.0828	0.0438

CRITICAL COMPOSITION		
N PENTANE	N HEXANE	HEPTANE +
0.0298	0.0269	0.0998
0.0275	0.0240	0.0848
0.0264	0.0228	0.0796
0.0249	0.0216	0.0746
0.0235	0.0203	0.0711
0.0220	0.0189	0.0657

envelopes reported in the literature, this value was not given. In such cases, various values for the molecular weights were assumed, and corresponding critical pressures of the mixtures calculated, until the reported critical pressure equaled the calculated critical pressure. This value of the molecular weight was used to complete the phase envelope prediction.

In all 63 envelopes predicted, the increment in the pressure step in calculating the phase envelopes for Methods A, B and C, explained in Chapter V, was set as 20 psi. The tolerance set for the calculated and the assumed convergence pressure was 50 psi in order to reduce the number of iterations. The maximum number of iterations is not more than five throughout this study. Since the K-factors are very sensitive to the convergence pressures in the critical region, a small error in pressure would result in a considerable difference between the calculated and the experimental values in this region. It is quite probable that the experimental P-T envelope itself might be inaccurate due to the sampling procedures adopted for obtaining data for the construction of these envelopes.



## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

A generalized procedure was developed to generate the pressure-temperature phase envelopes of reservoir fluids. The most difficult part of the problem was the prediction of the phase envelope in the region where the operating temperature of the system is greater than the critical temperature. Through the application of the convergence pressure theory, the entire phase envelope was predicted in this work for all mixtures studied. This was the major contribution of this work.

Other significant aspects of the present study are summarized as follows:

- (1) Reliable correlations were developed for predicting the critical pressures and critical temperatures of complex hydrocarbon mixtures.
- (2) K-factors in the neighborhood of the critical region were modified for components methane through hexane, so that the calculated K-factors were in agreement with experimental values.
- (3) A technique was developed to predict the K-factors of the heptane plus fraction, such that the predicted K-factors were in agreement with experimental values.

- (4) An interpolation routine was developed to calculate the K-factors for any intermediate convergence pressure value of the NGPSA K-factor correlations.
- (5) A method was developed to calculate the critical composition, without iteration, for ternary systems. This method is presented in Appendix F.

## 7.2 Recommendations for Further Work

Based on the discussions in the preceding chapters the following recommendations for further work are suggested:

- (1) Even though the proposed correlations for the prediction of critical pressures and critical temperatures are quite accurate, they are still empirical in nature. Hence, suitable correlations need to be developed, based on molecular theory, for complex hydrocarbon systems.
- (2) Applicability of convergence pressure theory to systems containing significant amounts of nitrogen, hydrogen sulfide and carbon dioxide needs to be investigated.
- (3) Experimental investigation of K-factors, especially for heavier components in the neighborhood of critical region, need to be carried out. The existing K-factor charts need to be thoroughly modified in this region in light of the experimental data.
- (4) Better techniques need to be developed to determine the K-factor for the heptane plus fraction.
- (5) Experimental studies need to be conducted to verify the

convergence pressure postulate for systems containing more than three components.

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## APPENDIX A

### SUBROUTINE FLASH

Subroutine FLASH is called by the main program in order to calculate the equilibrium phase compositions of a given mixture. The overall composition of the system and the K-factors for the various constituents are transmitted to this subroutine from the main program.

Let

$F$  = moles of feed,

$V$  = moles of equilibrium vapor,

$L$  = moles of equilibrium liquid,

$Z_i$  = mole fraction of constituent  $i$  in the feed,

$x_i$  = mole fraction of constituent  $i$  in liquid,

$y_i$  = mole fraction of constituent  $i$  in vapor, and

$i$  = component identify index.

By definition, at equilibrium,

$$K_i \equiv \frac{y_i}{x_i} \quad . \quad (A.1)$$

By material balance, the total moles of feed

$$F = L + V \quad . \quad (A.2)$$

For constituent  $i$ , by material balance,

$$Z_i F = x_i L + y_i V \quad . \quad (A.3)$$

Substituting Equation (A.1) in (A.3),

$$Z_i F = \frac{y_i}{K_i} \cdot L + y_i V \quad . \quad (A.4)$$

Solving for  $y_i$ ,

$$y_i = \frac{F}{V} \cdot \frac{K_i Z_i}{K_i + \frac{L}{V}} \quad . \quad (A.5)$$

The sum of the mole fractions of all the constituents in the liquid phase, and the sum of the mole fractions of all the components in the vapor phase are equal to one.

$$\sum_{i=1}^n x_i = \sum_{i=1}^n y_i = 1.0 \quad . \quad (\text{A.6})$$

From Equations (A.5) and (A.6),

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \frac{F}{V} \left( \frac{K_i Z_i}{K_i + \frac{L}{V}} \right) = 1.0 \quad . \quad (\text{A.7})$$

Letting  $F = 1.0$ ,

$$L + V = 1.0 \quad (\text{A.8})$$

$$\sum_{i=1}^n y_i = \sum_{i=1}^n \frac{K_i Z_i}{V(K_i + \frac{1-V}{V})} = \sum_{i=1}^n \frac{K_i Z_i}{1 + V(K_i - 1)} = 1.0 \quad . \quad (\text{A.9})$$

From Equations (A.1), (A.5), (A.6), and (A.8),

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{1}{V} \frac{Z_i}{K_i + \frac{1-V}{V}} = \sum_{i=1}^n \frac{Z_i}{1 + V(K_i - 1)} = 1.0 \quad . \quad (\text{A.10})$$

Thus, by Equations (A.9) and (A.10),

$$f(V) \equiv \sum_{i=1}^n y_i - \sum_{i=1}^n x_i = \sum_{i=1}^n \frac{Z_i (K_i - 1)}{1 + V(K_i - 1)} = 0 \quad . \quad (\text{A.11})$$

The procedure to calculate the values of  $x_i$  and  $y_i$  is as follows:

- (1) Assume a value for  $V$  between 0 and 1.
- (2) Use Equation (A.11) to calculate the function  $f(V)$ .

- (3) If  $f(V) = 0$ , the assumed value is correct, otherwise, repeat steps 1 and 2 such that  $f(V) = 0$ .
- (4) Setting  $F = 1$ , calculate the value of  $y_i$  using Equations (A.5) and (A.8).
- (5) Calculate the value of  $x_i$  using Equation (A.1).

The nature of the function  $f(V)$  is illustrated in Figure 31. The function  $f(V)$  is monotonically decreasing and is single valued between  $V = 0$  and  $V = 1.0$ . This can be proved by taking the partial derivative of  $f(V)$  with respect to  $V$ .

$$\frac{\partial f(V)}{\partial V} = \frac{\partial}{\partial V} \left[ \sum_{i=1}^n \frac{Z_i (K_i - 1)}{1 + V(K_i - 1)} \right] = - \sum_{i=1}^n \frac{Z_i (K_i - 1)^2}{[1 + V(K_i - 1)]^2} \quad (\text{A.12})$$

The slope of the function  $f(V)$  is always negative, since  $Z_i$  is always positive.

The overall composition of mixture B shown in Figure 30 can be flashed into two equilibrium phases. The behavior of function  $f(V)$  for this case is shown in Figure 31. On the other hand, if the overall composition were to be represented either by the point D, a single phase gas region, or by the point A, a single phase liquid region, a meaningful solution for the function  $f(V)$  would not result. That is,  $V$  will be either negative or greater than unity.

Hence, it is imperative to test the given overall composition of the mixture with its associated  $K$ -factors to determine whether the fluid exists in single phase region or two phase region before flash calculations are performed.

The following equations are used to test the above conditions in the program. At the dew point, the amount of liquid phase present is

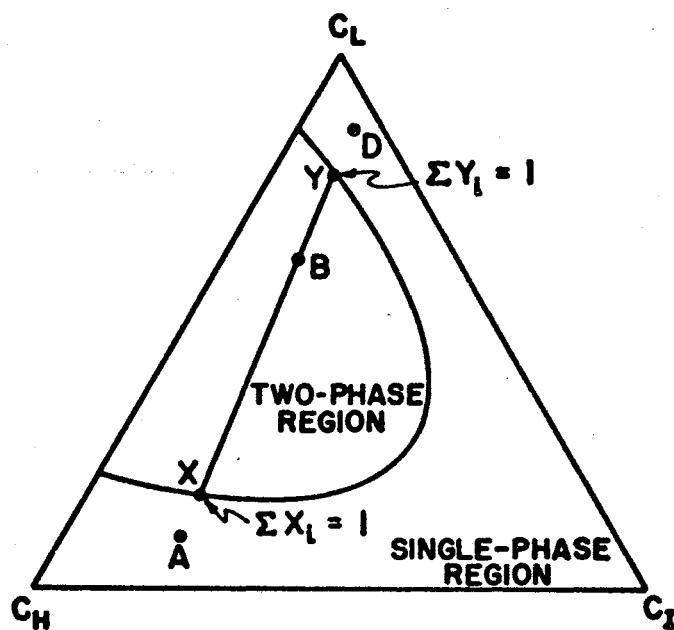


Figure 30. Composition Diagram Illustrating the Regions of Applicability of Flash Calculation

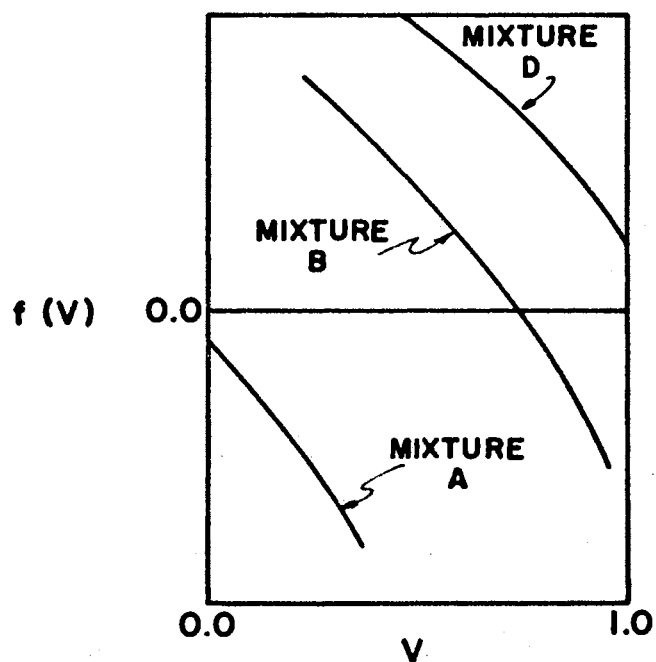


Figure 31. The Nature of the Function  $f(V)$

infinitesimal.

$L \rightarrow 0$  and  $V \rightarrow 1.0$ ; so,

$$\sum_{i=1}^n x_i = \lim_{V \rightarrow 1.0} \sum_{i=1}^n \frac{Z_i}{1 + V(K_i - 1)} = \sum_{i=1}^n \frac{Z_i}{K_i} = 1.0 \quad . \quad (\text{A.13})$$

At the bubble point,  $L \rightarrow 1.0$ , and  $V \rightarrow 0$ , and

$$\sum_{i=1}^n y_i = \lim_{V \rightarrow 0} \sum_{i=1}^n \frac{K_i Z_i}{1 + V(K_i - 1)} = \sum_{i=1}^n K_i Z_i = 1.0 \quad . \quad (\text{A.14})$$

As a first step, the bubble point test is carried out in the program by calculating,

$$B = \sum_{i=1}^n K_i Z_i - 1.0 \quad . \quad (\text{A.15})$$

A negative value of  $B$  indicates that the fluid is in a single phase liquid region, and no attempt is made to calculate the equilibrium phase compositions. The program prints out the message, THE MIXTURE IS IN SINGLE PHASE- LIQUID REGION and returns to the main program. If  $B$  is zero or positive, the dew point test is made.

$$D = \sum_{i=1}^n \frac{Z_i}{K_i} - 1.0 \quad . \quad (\text{A.16})$$

If  $D$  is negative, the mixture exists as a single phase vapor and the program prints out, THE MIXTURE IS IN SINGLE PHASE- VAPOR REGION. If  $B$  and  $D$  are non negative, then the mixture is in two phase region and the flash calculation is performed.

Once these tests are passed, the value of  $V$  for the function  $f(V)$  is calculated as follows. The value of the function  $f(V)$  is calculated by incrementing the value of  $V$  by 0.1, until the function becomes negative. The interval in which the function becomes negative is divided into ten parts, and the process is repeated. This is carried out until  $V$  is determined to the accuracy of the fifth decimal place. This value of  $V$  is then used to calculate the equilibrium phase compositions.



## APPENDIX B

### SUBROUTINE AVALK

The object of subroutine AVALK is to calculate the K-factors for all the components in a mixture for a given value of pressure temperature and convergence pressure. The K-factors for components methane through decane have been given in graphical form in NGPSA data book (16, 17). Empirical equations have been derived to fit these graphs (46) with good accuracy. It was found that the equations recommended predict the K-factors within 5% error of the graphical values in most regions. Equations are given for various components, for convergence pressures of 600, 800, 1000, 2000, 3000, 4000, 5000, 10000 and 20000 psi.

From the main program, the pressure, temperature, and convergence pressure are transmitted to this subroutine. As a first step, the program checks to determine whether the K-factors can be calculated with the available range of convergence pressures. If the K-factors are desired for convergence pressures less than 600 psi, or greater than 20000 psi, the program sets the convergence pressure as 600 psi or 20000 psi and proceeds with the calculation of the K-factors. In these cases, it prints out a message, THE CONVERGENCE PRESSURE IS LESS THAN 600 PSI or THE CONVERGENCE PRESSURE IS GREATER THAN 20000 PSI. None of the calculations in this work involved convergence pressures greater than 10000 psi.

If the convergence pressure for which the K-factors are desired is exactly equal to the one of the nine convergence pressures, the program directly uses the appropriate equations and constants and calculates the K-factors. On the other hand, if the convergence pressure is not the same as the nine convergence pressures listed, then interpolation or extrapolation procedures were used to determine the K-factors for each component.

The procedure for interpolation or extrapolation techniques will now be explained with the aid of an example. Let the operating pressure for a given system be 750 psia and the operating temperature be 100°F, and suppose the K-factors are desired for a convergence pressure of 2500 psia. The subroutine, then selects two successive convergence pressures, bracketting the convergence pressure of interest, 2000 and 3000 psia for which the K-factors are directly calculable. The K-factors for each component are then calculated for the operating temperature of 100°F and at a pressure of 750 psia, and for convergence pressures of 2000 and 3000 psia separately. The subroutine EXTRAP is then called to find the K-factors at a convergence pressure of 2500 psia.

An extrapolation technique is needed in certain cases. For example, if the operating pressure were to be 2200 psi instead of 750 psi, and the operating temperature and the convergence pressure of the system are unchanged, the program would select the two convergence pressures 2000 and 3000 psi as explained. In such a case, the K-factors calculated for the convergence pressure of 2000 psi would have no meaning, since the operating pressure of the system 2200 psia, is greater than the convergence pressure of 2000 psia. In these cases an extrapolation procedure is required.

After selecting the upper convergence pressure of 3000 psia the program checks to determine whether an interpolation or extrapolation scheme to be employed, by comparing the operating pressure with the lower convergence pressure. If the lower convergence pressure is greater than the operating pressure, the program proceeds to use the interpolation technique. If not, the subroutine selects the next higher convergence pressure of 4000 psia, and calculates the K-factors for the

operating pressure of 2200 psia and temperature of 100° F, with convergence pressures of 3000 and 4000 psia. Then, subroutine EXTRAP is called to calculate the K-factors at a convergence pressure of 2500 psia.

In this program, for convergence pressures 600, 3000, 5000 and 20000 psi, the constants given by NGAA in 1957 were used and for the other convergence pressures the coefficients given in 1966 were used.

## APPENDIX C

### SUBROUTINE EXTRAP

The function of subroutine EXTRAP is to determine the K-factors of all the components in a given mixture for the values of convergence pressures other than 600, 800, 1000, 2000, 3000, 4000, 5000, 10000 and 20000 psi. The input parameters for this subroutine are the K-factors for all the components at any two successive convergence pressures and the operating pressure of the system. The K-factors for any intermediate convergence pressure are calculated by an interpolation formula that passes through the K-factor data transmitted from subroutine AVALK. In order to explain the nature of the interpolating formula that was chosen, a plot of convergence pressure with K-factors are shown in Figure 32, for a methane, ethane, pentane system, at a temperature of 100°F and for various operating pressures.

Figure 32 suggests that the nature of the function to be selected should have the following characteristics:

- (1) The K-factors for all the components should be equal to unity, when the operating pressure is equal to the convergence pressure. This represents the critical state of the mixture.
- (2) The function should not have a maxima or minima or any point of inflection.
- (3) The K-factors must approach the critical pressure asymptotically as shown. This trend has been observed for most of the paraffin hydrocarbon systems.

The function chosen to satisfy these criteria was,

$$Y = 10^A X^B \quad (C.1)$$

where

$$Y = PK - PT,$$

$$X = \log C(i),$$

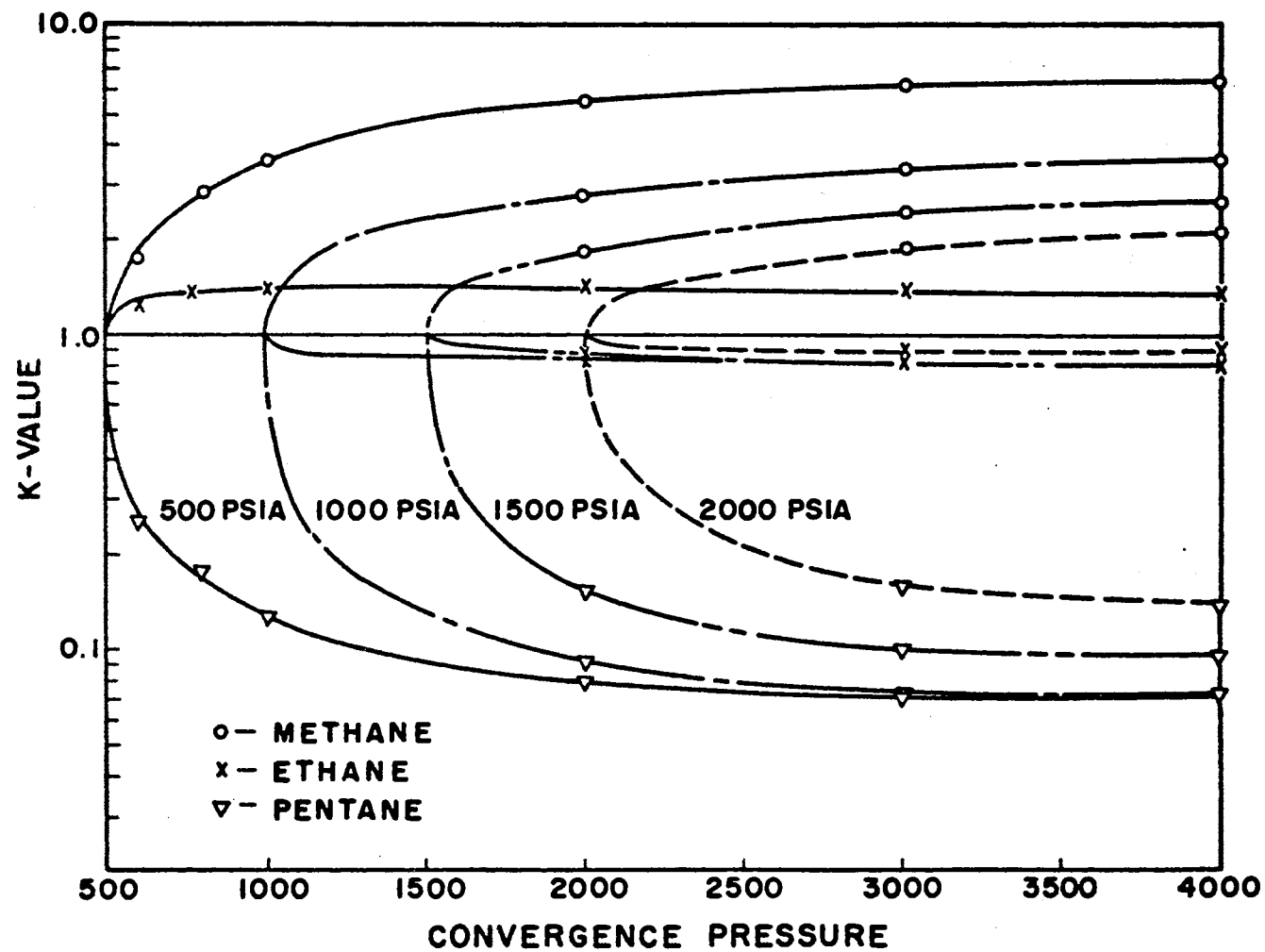


Figure 32. K-factor Data for Methane/Ethane/n Pentane at 100°F

PK = convergence pressure,

PT = operating pressure, and

C(i) = K-factor for component i.

When the operating pressure PT equals the convergence pressure PK, Y = 0. The parameter X = 0, if B is always positive. In other words, the K-factor of component i is equal to one. This condition represents the critical state.

The function  $Y = 10^A X^B$  has no maxima or minima or point of inflection.

The slope of the function  $Y = 10^A X^B$  is,

$$\frac{dY}{dX} = B \cdot 10^A X^{B-1} . \quad (C.2)$$

When X = 0, Y = 0, the slope is always 0.

Thus, all three required conditions are satisfied by the selected function.

Using two sets of K-factors for two convergence pressures, the constants A and B are first evaluated in the program. The calculation of A and B is simplified if the Equation (C.1) is expressed in a different form. Taking logarithms on both sides of Equation (C.1),

$$\log Y = A + B \log X . \quad (C.3)$$

The linear equation is solved for A and B, using two sets of Y and X.

By the same procedure, the constants A(i) and B(i) are calculated for all the n components. Once these constants are known, the K-factor for any component i can be calculated for the desired convergence pressure by the relations,



$$X(i) = 10^{\frac{\log Y(i) - A(i)}{B(i)}} \quad (C.4)$$

$$K(i) \equiv C(i) = 10^{X(i)} \quad (C.5)$$

There are two restrictions to using Equation (C.1). They are:

- (1) Equation (C.1) will not work in the neighborhood of critical mixture if  $B \leq 0$ . Such a case can be avoided by selecting the preceding value of convergence pressure and its K-factors. For this case, the program prints out, THE PRECEDING VALUE OF CONVERGENCE PRESSURE IS SELECTED, SINCE THE VALUE OF B IS ZERO OR NEGATIVE. Throughout the present work, such a situation has arisen only once.
- (2) The values of A and B calculated with the two sets of convergence pressures and K-factors are:

$$B = \log \frac{[PK(2) - PT]}{[PK(1) - PT]} \bigg/ \log \frac{[\log C(2,i)]}{[\log C(1,i)]} \quad (C.6)$$

$$A = \log [PK(2) - PT] - B \log [\log C(2,i)] \quad (C.7)$$

where

$C(1,i)$  = K-factor of component  $i$  at the lower convergence pressure, determined by subroutine AVALK,PK(1),

$C(2,i)$  = K-factor of component  $i$  at the upper convergence pressure, determined by subroutine AVALK,PK(2),

and

PT = system operating pressure.

The Equations (C.6) and (C.7) are to be used for interpolating K-factors which are greater than unity. For components whose K-factors

are less than unity, the values of A and B are,

$$B = \log \frac{[PK(2)-PT]}{[PK(1)-PT]} \bigg/ \log \frac{[-\log C(2,i)]}{[-\log C(1,i)]} \quad (C.8)$$

$$A = \log [PK(2)-PT] - B \log [-\log C(2,i)] \quad . \quad (C.9)$$

The Equations (C.8) and (C.9) avoid logarithms of negative numbers. However, there is one particular problem in the use of the above equations. Suppose for the component ethane, the K-factor is desired for an operating pressure of 900 psi, and an operating temperature of 100° F for a 1500 psi convergence pressure. Subroutine AVALK would select the lower and upper convergence pressures as 1000 and 2000 psi, respectively, and the corresponding K-factors are 0.94 and 1.07. In this case, neither of the sets of Equations (C.6) and (C.7) or (C.8) and (C.9) can be used to calculate A and B. Under such circumstances the K-factor is set as 1.001 for the convergence pressure of 1000 psi, and the program proceeds, and a message is printed out: A VALUE OF 1.001 IS ASSUMED INSTEAD OF 0.94 FOR THE CONVERGENCE PRESSURE OF 1000 PSI. The validity of this assumption is finally checked in the light of the deviation of the result.

## APPENDIX D

### SUBROUTINE CVPR

The object of subroutine CVPR is to calculate the convergence pressure associated with a given tie line. In Figure 33, the line AA' represents the locus of compositions whose critical temperature is equal to the operating temperature. The convergence pressure is equal to the critical pressure of the mixture defined by the intersection of the tie line with the critical temperature locus. This critical mixture is represented by the point G.

The subroutine first seeks a mixture along the tie line MN such that the critical temperature of the mixture is equal to the operating temperature. This is performed by adding small increments of liquid of composition M to the vapor of composition N. For every overall composition, the subroutine VECTEM is called to test whether the overall composition has a critical temperature less than, equal to, or greater than the operating temperature. This process is repeated until a mixture of overall composition whose critical temperature is equal to or within three degrees of operating temperature is defined. Then the critical pressure of this critical mixture is calculated using suitable correlations derived in Chapter IV. This critical pressure is the calculated convergence pressure [PKT].

This type of iteration procedure to calculate the critical composition is necessary for systems containing four or more components. For ternary systems, a direct solution was derived in Appendix F. At very low pressures, or at low temperatures, an intersection of the tie line with the critical temperature locus may not be possible as explained in Chapter V. Therefore, before attempting to calculate the critical composition, the program first evaluates the critical temperatures corresponding to the points M and N. If an intersection of the tie line

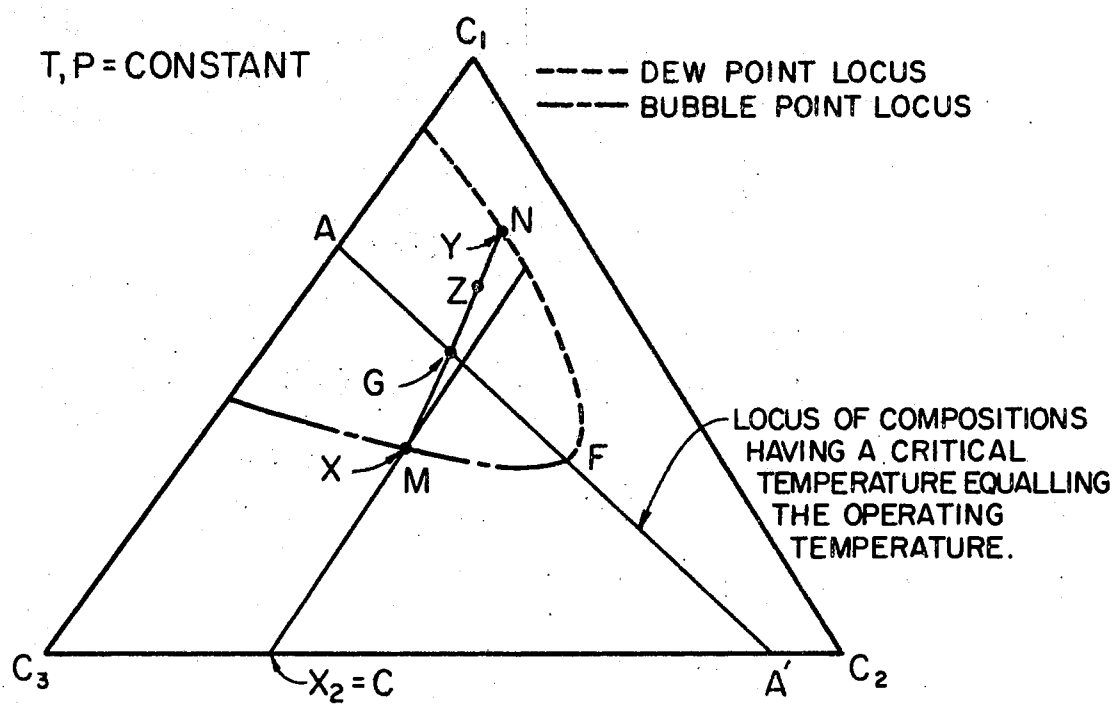


Figure 33. Ternary Phase Diagram of a Three Component System

with the critical temperature locus is not possible, the program prints out: AN INTERSECTION OF THE TIELINE WITH THE CRITICAL TEMPERATURE LOCUS IS NOT POSSIBLE.

In essence, the above procedure results in the definition of a critical composition composed of a mixture of equilibrium gas and liquid which has a critical temperature equalling the operating temperature. The critical pressure of this mixture is the convergence pressure.

## APPENDIX E

### SUBROUTINE FRAN

The object of this subroutine is to calculate the K-factors for all the components in a given mixture when the operating pressure is greater than 0.7 times the convergence pressure. The equation used to calculate the K-factors in the neighborhood of the critical region is of the form,

$$K_i = C_{1i} \left(1 - \frac{PT}{PK}\right)^n + C_{2i} \left(\frac{PK}{PT} - 1\right) + 1.0 \quad (E.1)$$

where

$K_i$  = K-factor of component  $i$ ,

$C_{1i}$ ,  $C_{2i}$  = constants for component  $i$ ,

$PK$  = convergence pressure, and

$PT$  = operating pressure.

The properties of Equation (E.1) have already been discussed in Chapter IV.

The program first selects three values of pressures  $PT_1$ ,  $PT_2$  and  $PT_3$  at the specified operating temperature,  $T$ , such that  $\frac{PT_i}{PK}$ ,  $i = 1, 2, 3$ , is less than 0.7, for each component in the given mixture. By calling the subroutine AVALK, three K-factors  $K_{1i}$ ,  $K_{2i}$  and  $K_{3i}$  for component  $i$  are computed at pressures  $PT_1$ ,  $PT_2$  and  $PT_3$ , respectively, for the convergence pressure  $PK$  and the operating temperature  $T$ .

Next, a value for the index  $n$  is assumed such that  $n > 0$ , and the constants  $C_{1i}$  and  $C_{2i}$  are evaluated using the calculated values of  $K_{1i}$  and  $K_{2i}$  at the operating pressures  $PT_1$  and  $PT_2$  for the component  $i$ . The K-factor at the pressure  $PT_3$  is then calculated using Equation (E.1) and the constants  $C_{1i}$  and  $C_{2i}$ . If the calculated K-factor is equal to the previously computed value  $K_{3i}$ , the assumed value of the index  $n$  is correct. Otherwise, a new value for  $n$  is assumed and the procedure is repeated until a correct value of index  $n$  is calculated.



The constants  $C_{1i}$ ,  $C_{2i}$  and the index  $n$  are then used to calculate the K-factor of component  $i$  at any other operating pressure  $[PT]$ .

## APPENDIX F

### SUBROUTINE VECTEM

The object of subroutine VECTEM is to determine whether a particular mixture has a critical temperature equal to the operating temperature for which the K-factors are desired. The accuracy of the convergence pressure calculation depends in part on the ability to calculate the true critical temperature of the mixture.

Two different equations are used in this subroutine for calculating the critical temperature of mixtures. Equation (4.20) was used for the calculation of critical temperatures of binary mixtures, while Equation (4.26) was programmed for mixtures containing four or more components. The constants for these equations are given in Tables IV and V, respectively. Since Equations (4.20) and (4.26) are simple to program, no further discussion is required concerning these equations.

For calculating the critical temperatures of ternary systems, a different procedure is adopted. It is possible to calculate the critical mixture and hence the critical temperature of ternary systems through the use of Equation (4.20).

Grieves and Thodos have observed experimentally that the locus of compositions having the same critical temperature is linear for ternary systems containing normal paraffin hydrocarbons (27). Based on the above statement, a method was devised for ternary systems to determine the composition of the mixture whose critical temperature is equal to the operating temperature.

In Figure 34, line AA' represents the locus of compositions whose critical temperature is equal to the operating temperature. Depending upon the value of the operating temperature with respect to the critical temperature of the intermediate component the end A' will lie on  $C_L - C_I$  as shown in Figure 34a or on  $C_H - C_I$  as represented in Figure 34b. The

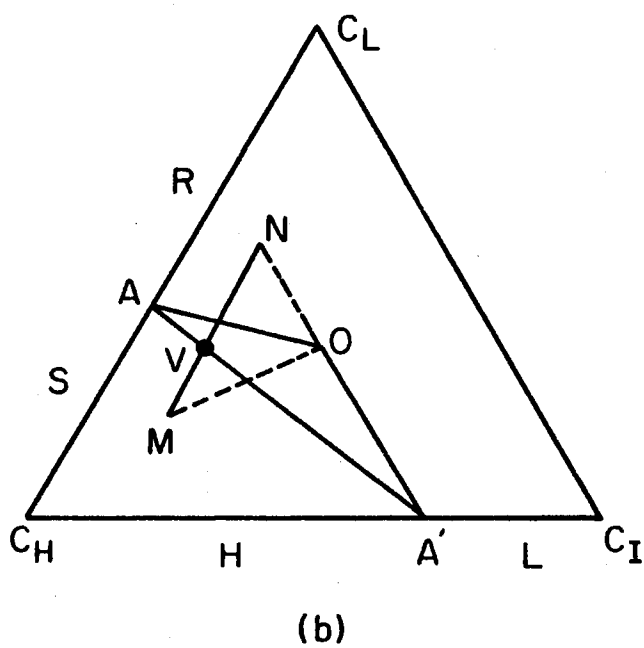
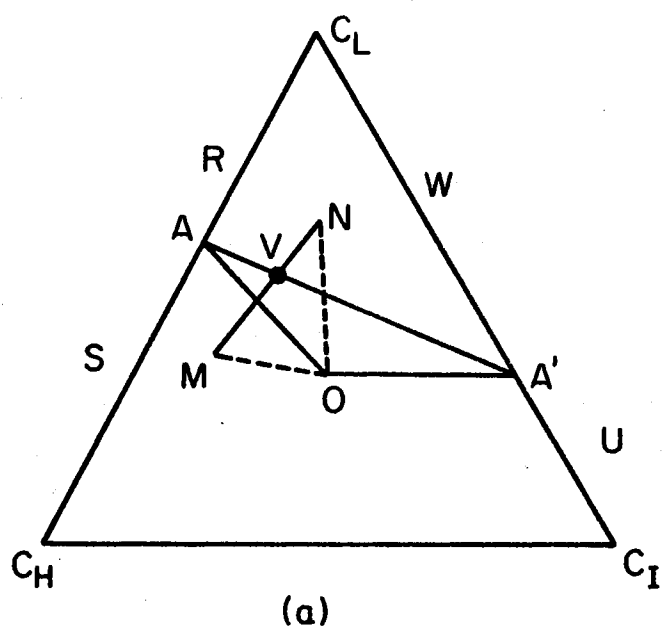


Figure 34. Compositions Used by  
Subroutine VECTEM

tie line MN, obtained by flashing a given mixture  $Z_1$  is also shown in Figure 34. Now, the desired compositions of the critical mixture  $V(i)$ ,  $i = 1, 2, 3$  are calculated as follows.

The general equation for a three dimensional plane is represented as,

$$X + C_1 Y + C_2 Z + C_3 = 0 \quad (F.1)$$

where  $C_1$ ,  $C_2$  and  $C_3$  are constants.

The ternary diagram represents compositions, for which the following relation holds,

$$X + Y + Z = 1 \quad (F.2)$$

Equation (F.2) is also derivable from (F.1) by substituting the coordinates of the plane (1,0,0), (0,1,0) and (0,0,1), and eliminating the constants  $C_1$ ,  $C_2$  and  $C_3$ .

The equation for the plane OMN is,

$$X + C_4 Y + C_5 Z + C_6 = 0 \quad (F.3)$$

The coordinates of the plane OMN are (0,0,0),  $(y_1, y_2, y_3)$  and  $(x_1, x_2, x_3)$ . The values of equilibrium phase compositions  $x_i$  and  $y_i$  are known through the flash calculations. Eliminating the constants  $C_4$ ,  $C_5$  and  $C_6$  using the coordinates of the plane OMN, the Equation (F.3) assumes the form,

$$X - \left[ \frac{y_1}{y_2} + \frac{y_3}{y_2} \left( \frac{x_1 y_2 - y_1 x_2}{x_2 y_3 - y_2 x_3} \right) \right] Y + \left( \frac{x_1 y_2 - y_1 x_2}{x_2 y_3 - y_2 x_3} \right) Z = 0 \quad (F.4)$$

The coordinates of the plane OAA' shown in Figure 34a, are (0,0,0), (S,0,R) and (W,U,0). Using Equation (F.1), and the coordinates of the

plane OAA', the equation for the plane OAA' is written as,

$$X - \left(\frac{W}{U}\right)Y - \left(\frac{S}{R}\right)Z = 0 \quad . \quad (F.5)$$

The compositions V(i) are now calculated by solving the three simultaneous Equations (F.2), (F.4) and (F.5).

$$V(3) = Z = \frac{\left(1 + \frac{W}{U}\right) - \left(1 + y_{12} + y_{32}\bar{Y}\right)}{\left(1 - \bar{Y}\right)\left(1 + \frac{W}{U}\right) - \left(1 + \frac{S}{R}\right)\left(1 + y_{12} + y_{32}\bar{Y}\right)} \quad (F.6)$$

$$V(2) = Y = \frac{1 - V(3)\left(1 + \frac{S}{R}\right)}{\left(1 + \frac{W}{U}\right)} \quad (F.7)$$

$$V(1) = X = 1 - V(2) - V(3) \quad (F.8)$$

where

$$y_{12} = \frac{y_1}{y_2} \quad , \quad (F.9)$$

$$y_{32} = \frac{y_3}{y_2} \quad , \text{ and} \quad (F.10)$$

$$\bar{Y} = \frac{(x_1 y_2 - y_1 x_2)}{(x_2 y_3 - y_2 x_3)} \quad . \quad (F.11)$$

When the end of the critical locus point A' lies on  $C_I - C_H$  as shown in Figure 34b, the compositions V(i) becomes,

$$V(3) = \frac{\left(\frac{1 - S \cdot L}{R \cdot H}\right) - \left(1 + y_{12} + y_{32}\bar{Y}\right)}{\left(1 - \bar{Y}\right)\left(1 - \frac{S \cdot L}{R \cdot H}\right) - \left(1 + \frac{S}{R}\right)\left(1 + y_{12} + y_{32}\bar{Y}\right)} \quad (F.12)$$

$$V(2) = \frac{1 - V(3)\left(1 + \frac{S}{R}\right)}{\left(1 - \frac{S \cdot L}{R \cdot H}\right)} \quad (F.13)$$

$$V(1) = 1 - V(3) - V(2) \quad . \quad (F.14)$$

The values of R and W, or R and H can be calculated by using the Equation (4.20).

## APPENDIX G

### STEPS FOR THE CALCULATION OF CONVERGENCE PRESSURE BY CRITICAL COMPOSITION METHOD



Convergence pressure was recently defined as the critical pressure of a mixture in the critical state that when flashed to the operating pressure, results in a tie line that passes through the mixture of fixed overall composition that is being flashed. The critical temperature of the critical mixture is equal to the operating temperature (60). Based on this definition, the following method was developed to determine the convergence pressure of a mixture Z, as shown in Figure 33, that exists in a two phase region.

- (1) A value for the convergence pressure,  $P_K$ , is assumed for the mixture Z.
- (2) For this assumed convergence pressure and known equilibrium pressure and temperature, the K-factors for all the components in the mixture Z are calculated from suitable correlations (46).
- (3) A flash calculation is performed to determine the compositions of the coexisting phases into which mixture Z will separate at equilibrium. This establishes the tie line MN.
- (4) Then, the composition of the mixture G, defined by the intersection of the tie line MN with the true critical temperature locus AA', is calculated. This is done by calculating the critical temperatures along the tie line MN until a value is calculated that equals the operating temperature.
- (5) The true critical pressure of the mixture G is calculated using suitable empirical correlations. This is the calculated convergence pressure,  $P_{KT}$ .

- (6) If the assumed convergence pressure,  $P_K$ , of step 1 equals the calculated convergence pressure of step 5, the calculations are complete.
- (7) If the assumed and calculated values are different, a new value of convergence pressure,  $P_K$ , is assumed and steps 2 through 6 are repeated.

Experience has shown that a solution is quickly reached if the new assumed convergence pressure is set equal to the one just calculated.

Recent work has shown that this method can be used to predict composition phase envelopes such as that shown in Figure 33, up to and through the critical state (58).

## APPENDIX H

MATHEMATICAL PROOF SHOWING CONVERGENCE PRESSURE  
IS A PHASE RULE VARIABLE

It will be demonstrated in this appendix that convergence pressure is strictly a phase rule variable for a ternary system. The extension of the convergence pressure concept to systems containing four or more components requires a postulate which is stated in this appendix.

The Gibbs' phase rule fixes the number of intensive variables such as pressure, temperature and the concentration of the components that must be arbitrarily specified in order to completely define the intensive state of a system at equilibrium. The phase rule does not give any insight into the relation between these variables.

Consider a system consisting of three components. Referring to Figure 33, the convergence pressure to be applied to mixture Z is the critical pressure of mixture G defined by the intersection of tie line MN and the critical temperature locus AA'. Thus the calculated convergence pressure, PKT, is a function of the concentration of the three components existing in the critical mixture.

$$PKT = PKT(G) . \quad (H.1)$$

In turn, the composition of mixture G is determined from the equilibrium temperature T and compositions of liquid and vapor phases established through the flash calculation involving the equilibrium constants. Hence,

$$G = G(T, x_i, y_i), i = 1,2,3 \quad (H.2)$$

where

$y_i$  = concentration of component i in vapor phase, and

$x_i$  = concentration of component i in the liquid phase.

Also, the sum of the mole fractions of components in the vapor phase and the sum of the mole fractions of the components in the liquid phase

are equal to one.

$$\sum_{i=1}^3 x_i = \sum_{i=1}^3 y_i = 1.0 \quad . \quad (\text{H.3})$$

This reduces the number of independent variables to five. Thus,

$$G = G(T, y_1, y_2, x_1, x_2) \quad . \quad (\text{H.4})$$

Now, the conventional application of the phase rule shows that the degrees of freedom for a ternary system coexisting in two phases at equilibrium is three. Specification of pressure and temperature defines a specific phase envelope such as that shown in Figure 33. If a third intensive variable  $x_2$  is specified, then the intensive states of the system is completely defined including  $x_1$ ,  $x_2$ ,  $x_3$  and  $y_1$ ,  $y_2$ ,  $y_3$ . Thus, the K-factors are also uniquely determined by specifying three of the phase rule variables. Hence, for a system of three degrees of freedom,  $K_1$ ,  $K_2$  and  $K_3$  can be determined as

$$K_1 = K_1(T, P, x_2) = \frac{y_1}{x_1} \quad (\text{H.5})$$

$$K_2 = K_2(T, P, x_2) = \frac{y_2}{x_2} \quad (\text{H.6})$$

$$K_3 = K_3(T, P, x_2) = \frac{y_3}{x_3} \quad (\text{H.7})$$

Substituting Equations (H.5) and (H.6) into (H.4),

$$G = G[T, K_1(T, P, x_2)x_1, K_2(T, P, x_2)x_2, x_1, x_2] \quad (\text{H.8})$$

or simply

$$G = G(T, P, x_1, x_2) \quad . \quad (\text{H.9})$$

As stated earlier, when  $x_2$  is specified in addition to the temperature and pressure, all the intensive variables of the system are completely determined including  $x_1$ . Thus,  $x_1$  can no longer be considered as an independent variable, and the Equation (H.9) takes the form,

$$G = G(T, P, x_2) \quad . \quad (H.10)$$

Substitution of Equation (H.10) into (H.1) yields,

$$PKT = PKT(T, P, x_2) \quad . \quad (H.11)$$

Thus, the convergence pressure is a variable that, in itself, is a function of commonly used phase rule variables.

This implies that if the K-factors are correlated as a function of pressure, temperature, and convergence pressure for a ternary system, then in fact the K-factors are correlated as follows:

$$K_i = K_i(T, P, x_2) \quad (H.12)$$

which is a thermodynamically rigorous correlation for a three component system.

The extension of convergence pressure concept to systems containing four or more components violates Gibbs' phase rule. For example, for a four component system, it can be similarly shown that,

$$K_i = K_i(T, P, x_1, x_2) \quad (H.13)$$

$$PKT = PKT(T, P, x_1, x_2) \quad . \quad (H.14)$$

Hence, a postulate is required to replace a function of four independent variables by a function of three independent variables

pressure, temperature, and convergence pressure only. This postulate was proposed and stated by Rzasa and others (62) as,

The equilibrium vaporization constant for one component in a complex system is the same as the equilibrium constant at the same temperature and pressure for the same component in another system, whether or not composed of the same number or kind of components provided only the convergence pressures of the two systems are exactly the same at the same temperature and that the components are of the same homologous series.

If this postulate is valid, then the K-factors can be correlated as a function of pressure, temperature, and convergence pressure. The results of the calculations made in this work offers a posterior proof that this postulate is valid.

## APPENDIX I

### CALCULATED PRESSURE-TEMPERATURE PHASE ENVELOPES



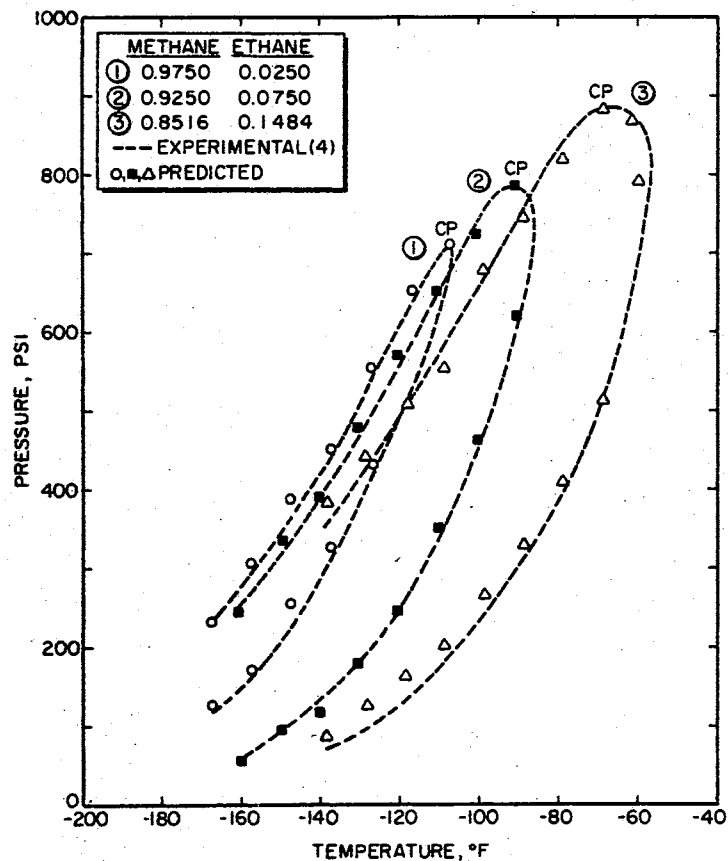


Figure 35. Pressure-Temperature Phase Envelopes for Methane/Ethane System (Concentration of Methane = 0.9750; Concentration of Methane = 0.9250; Concentration of Methane = 0.8516)

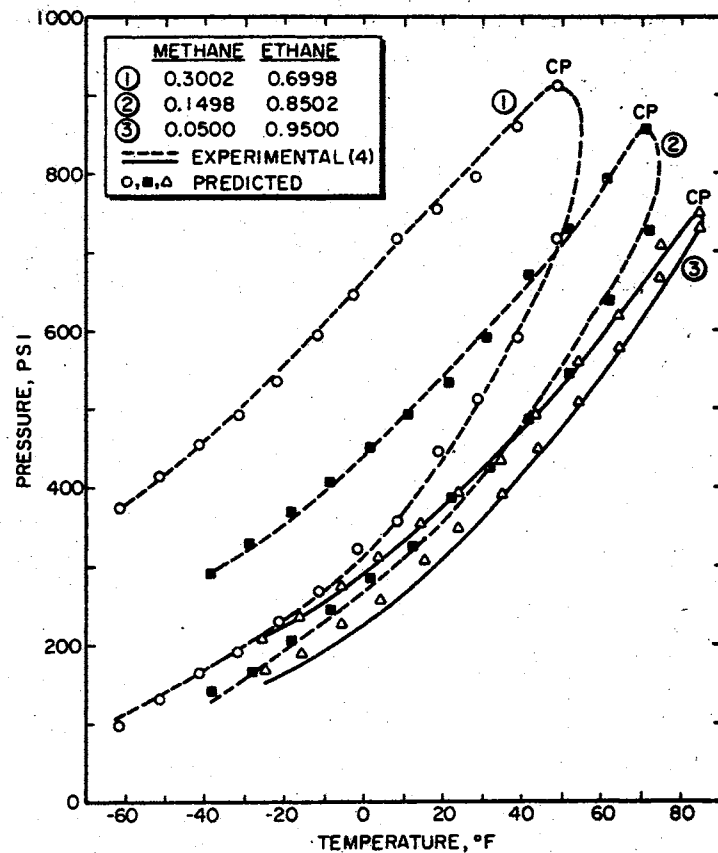


Figure 36. Pressure-Temperature Phase Envelopes for Methane/Ethane System (Concentration of Methane = 0.3002; Concentration of Methane = 0.1498; Concentration of Methane = 0.0500)

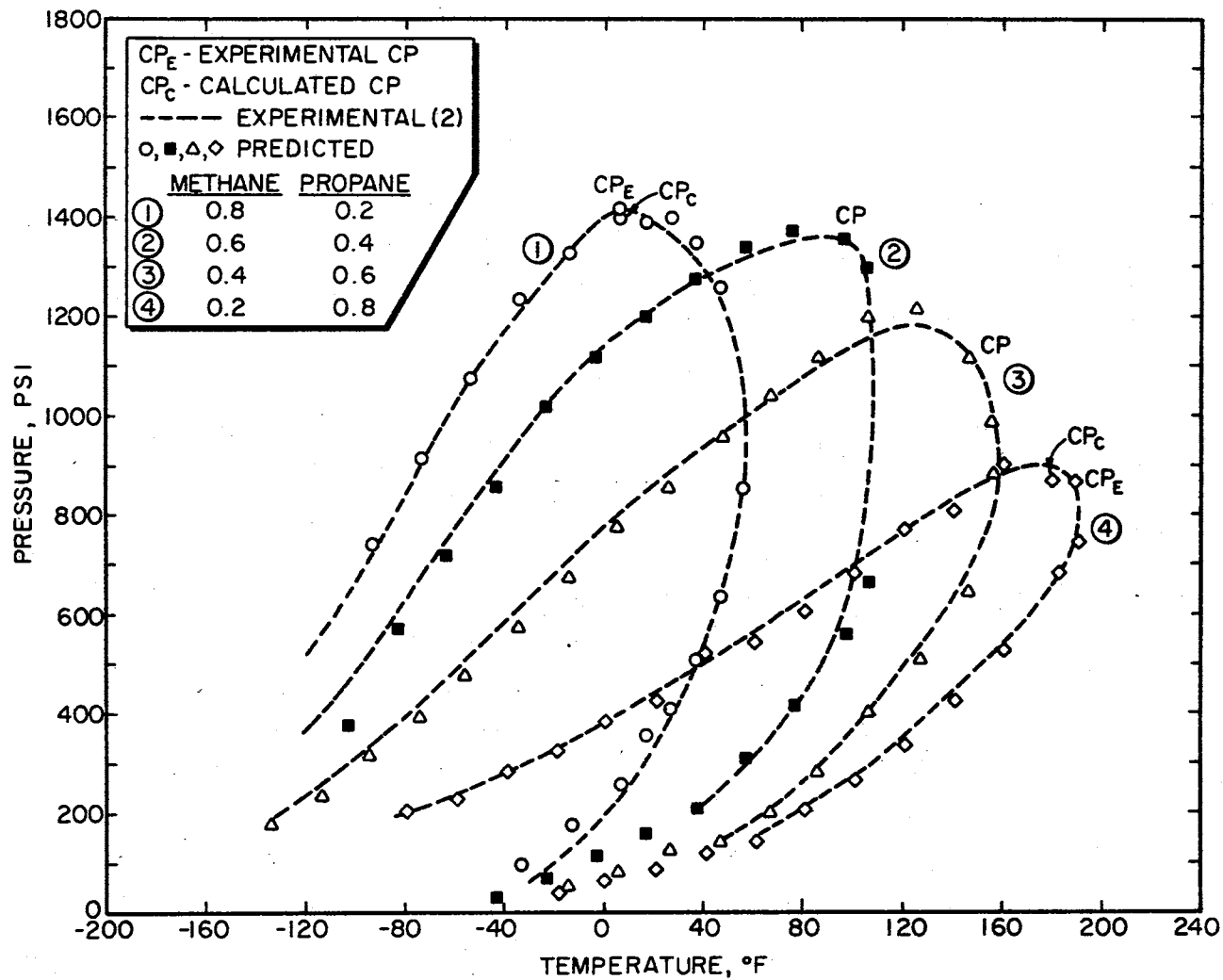


Figure 37. Pressure-Temperature Phase Envelopes for Methane/Propane System

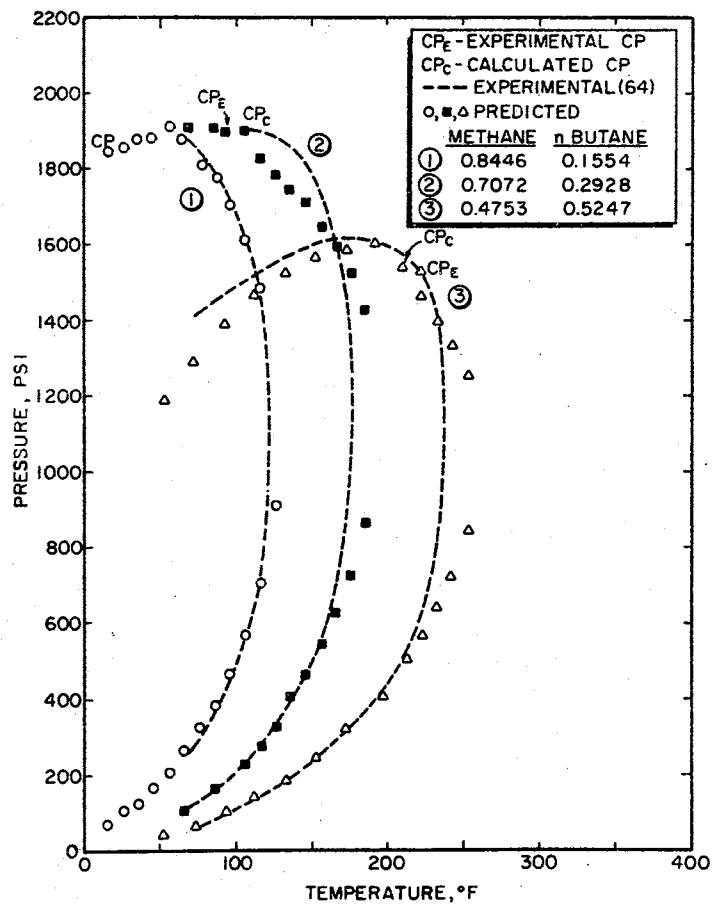


Figure 38. Pressure-Temperature Phase Envelopes for Methane/  
n Butane System

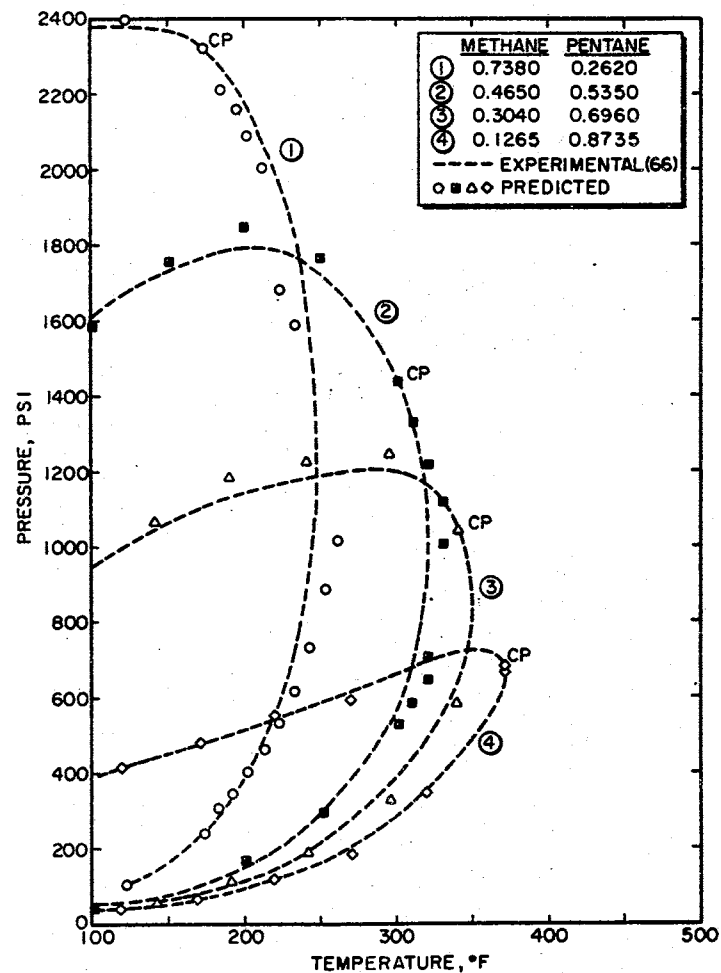


Figure 39. Pressure-Temperature Phase Envelopes for Methane/  
n Pentane System

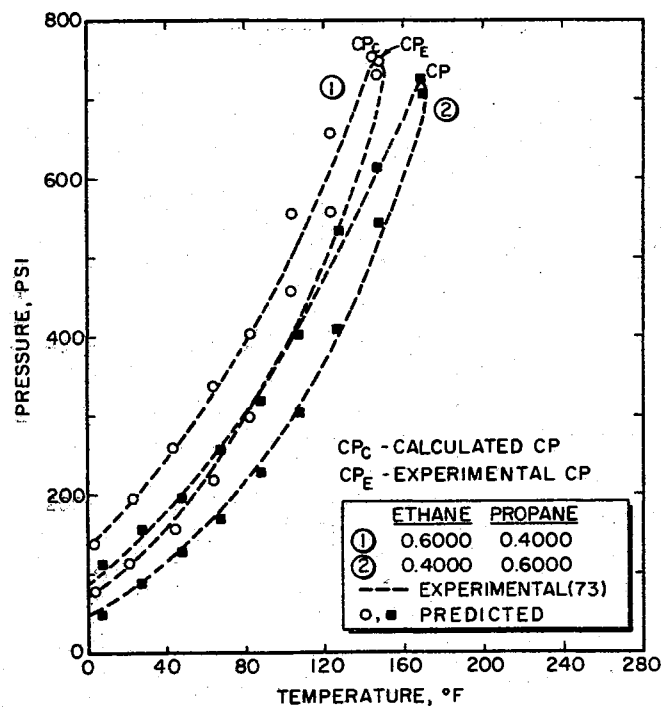


Figure 40. Pressure-Temperature Phase Envelopes for Ethane/Propane System

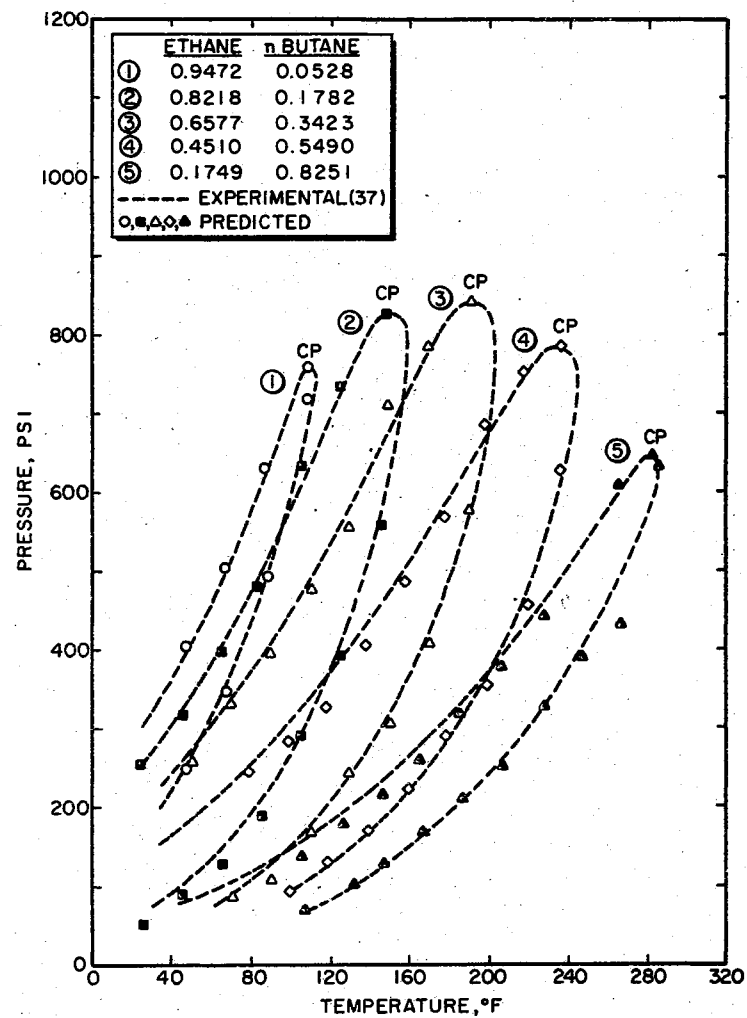


Figure 41. Pressure-Temperature Phase Envelopes for Ethane/n Butane System

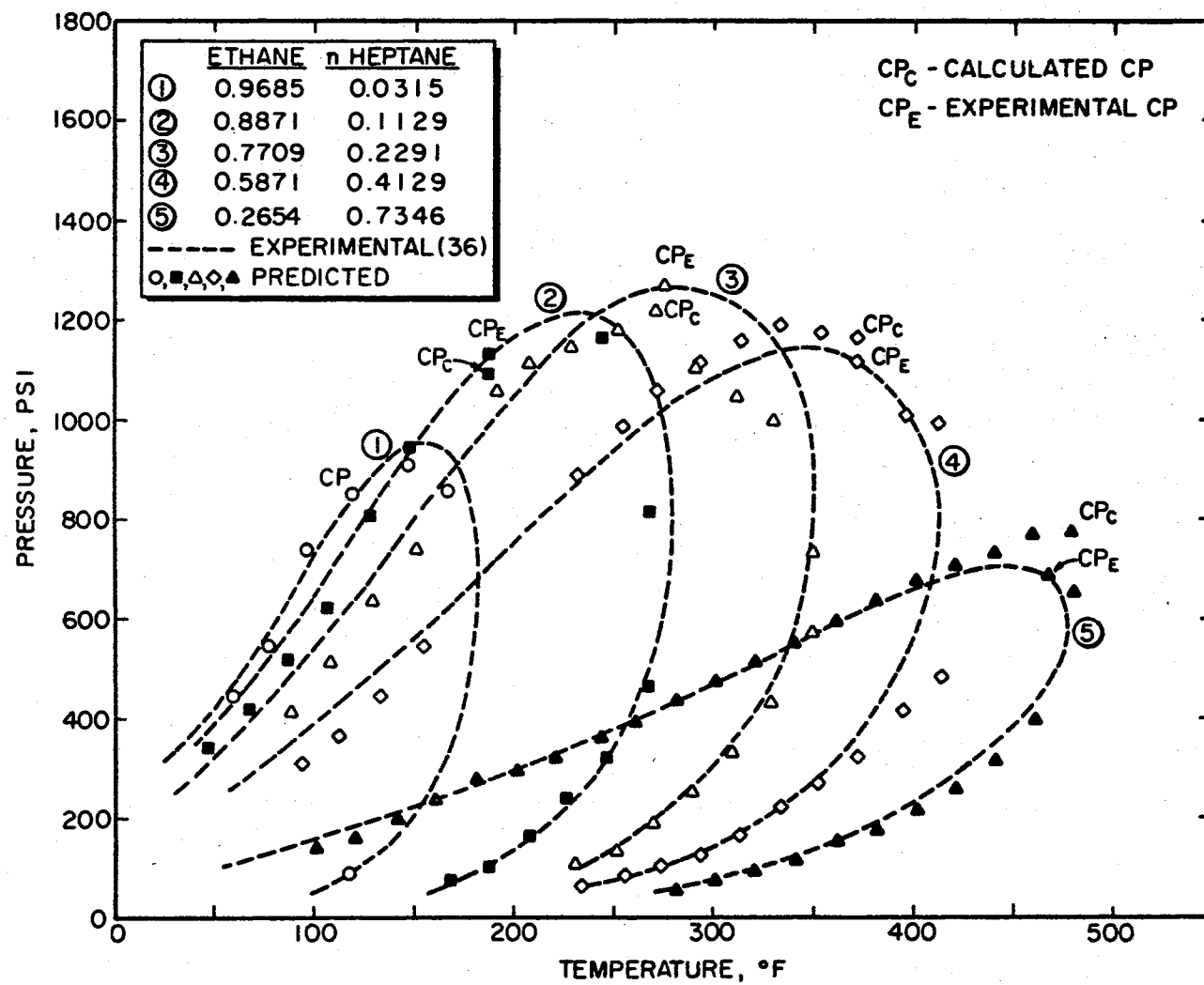


Figure 42. Pressure-Temperature Phase Envelopes for Ethane/n Heptane System

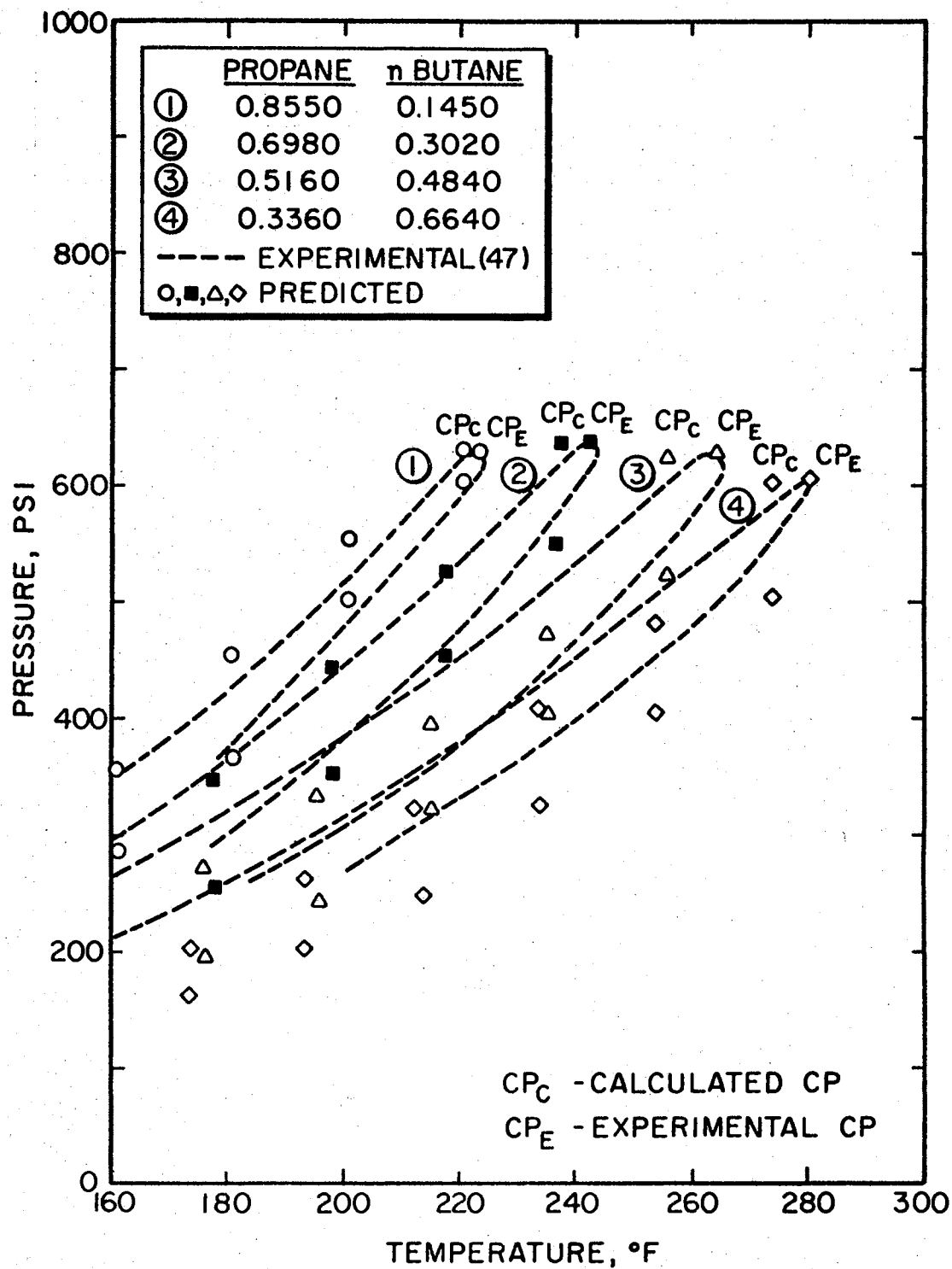


Figure 43. Pressure-Temperature Phase Envelopes for Propane/n Butane System

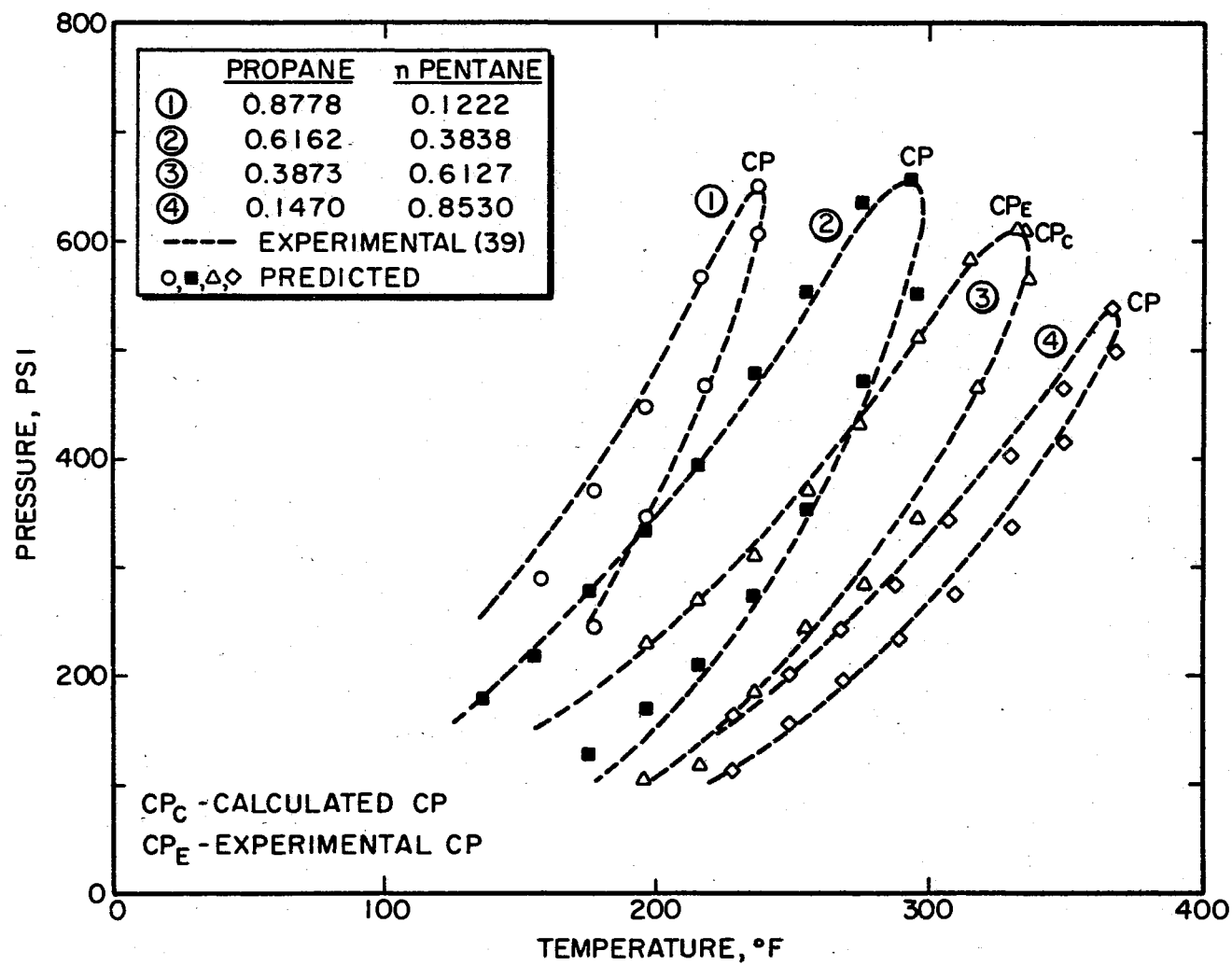


Figure 44. Pressure-Temperature Phase Envelopes for Propane/n Pentane System

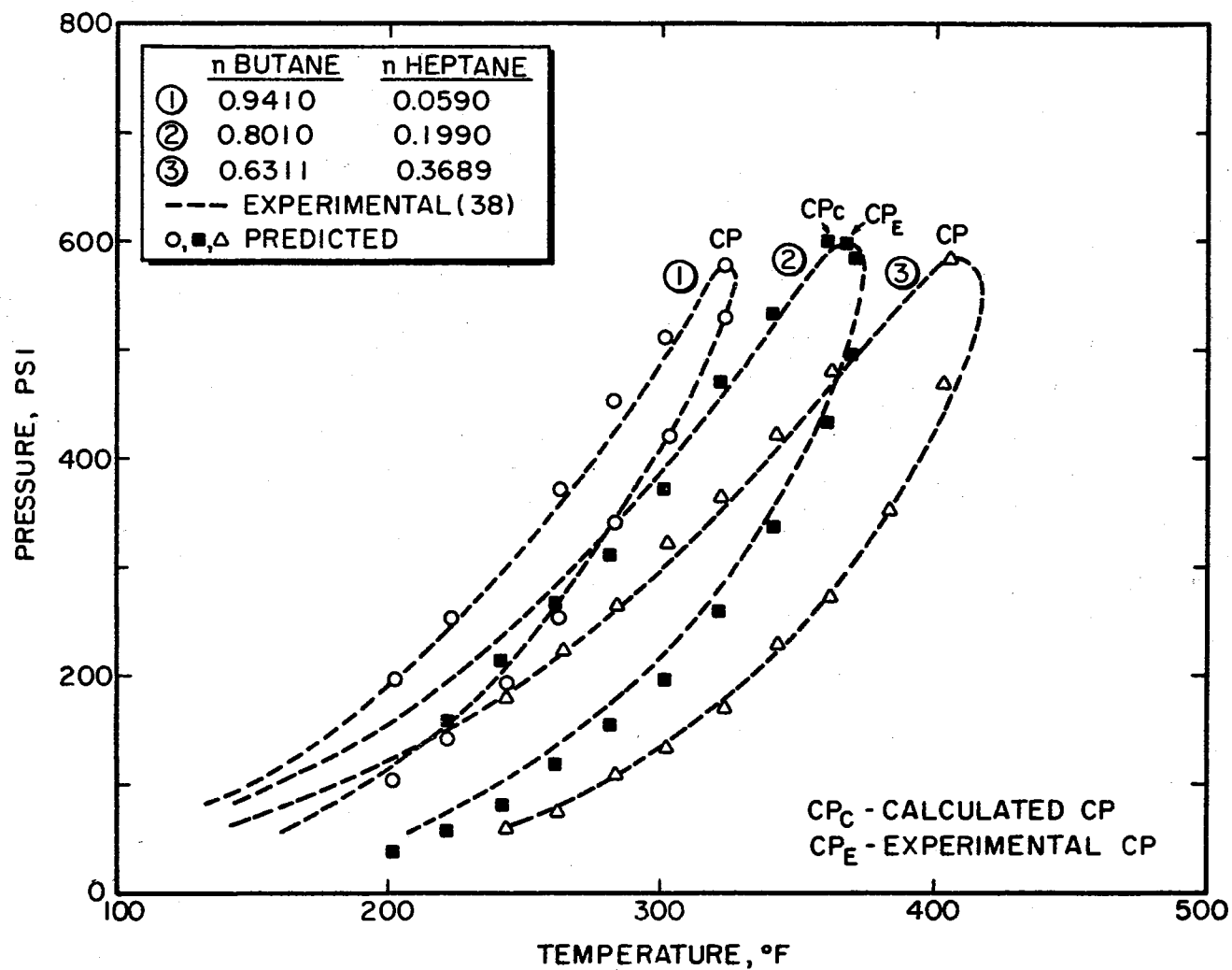


Figure 45. Pressure-Temperature Phase Envelopes for n Butane/n Heptane System



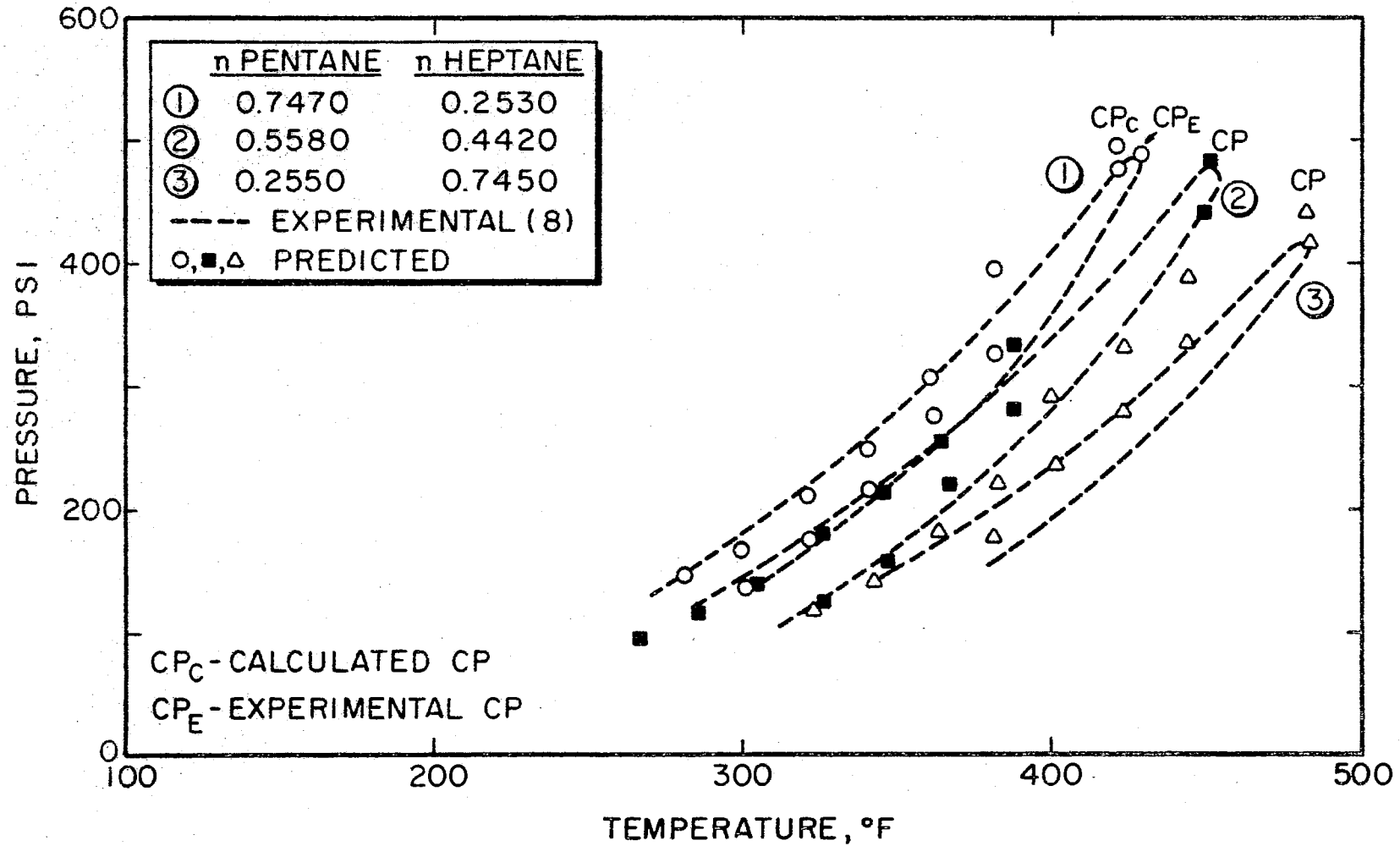


Figure 46. Pressure-Temperature Phase Envelopes for n Pentane/n Heptane System

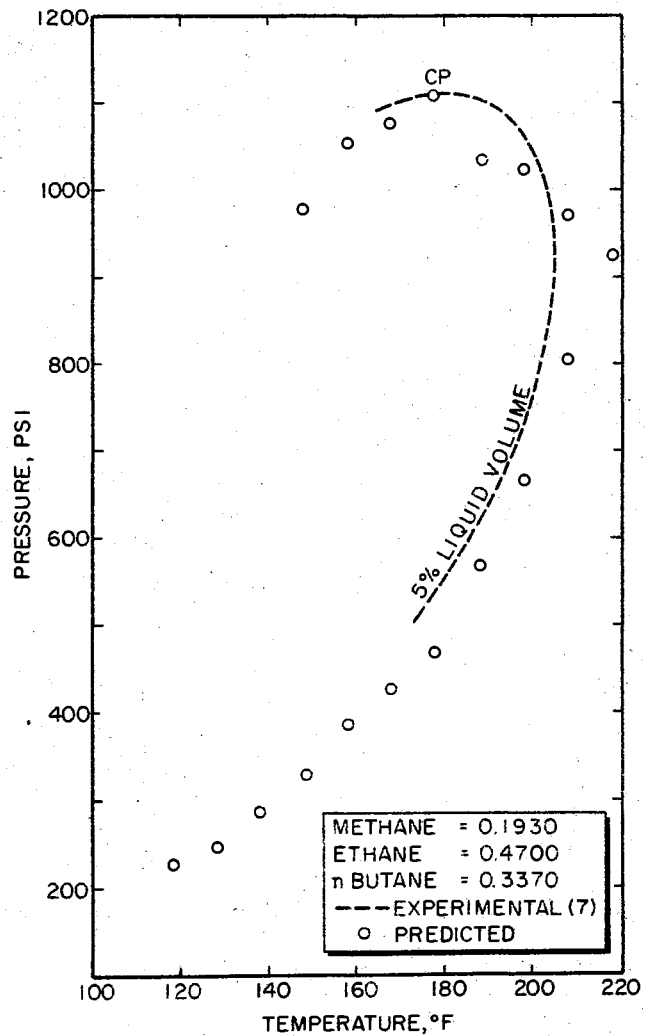


Figure 47. Pressure-Temperature Phase Envelope for Methane/Ethane/n Butane System

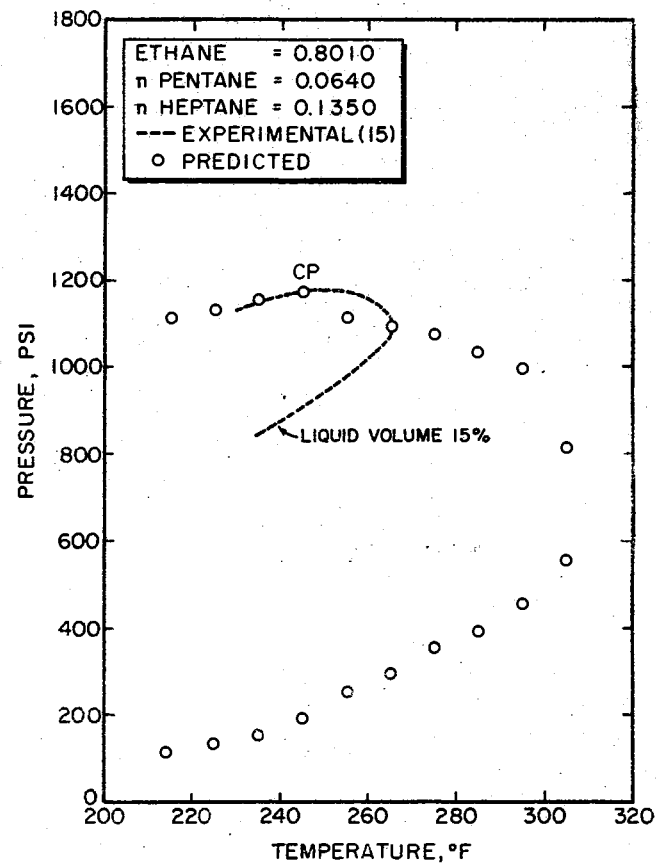


Figure 48. Pressure-Temperature Phase Envelope for Ethane/n Pentane/n Heptane System

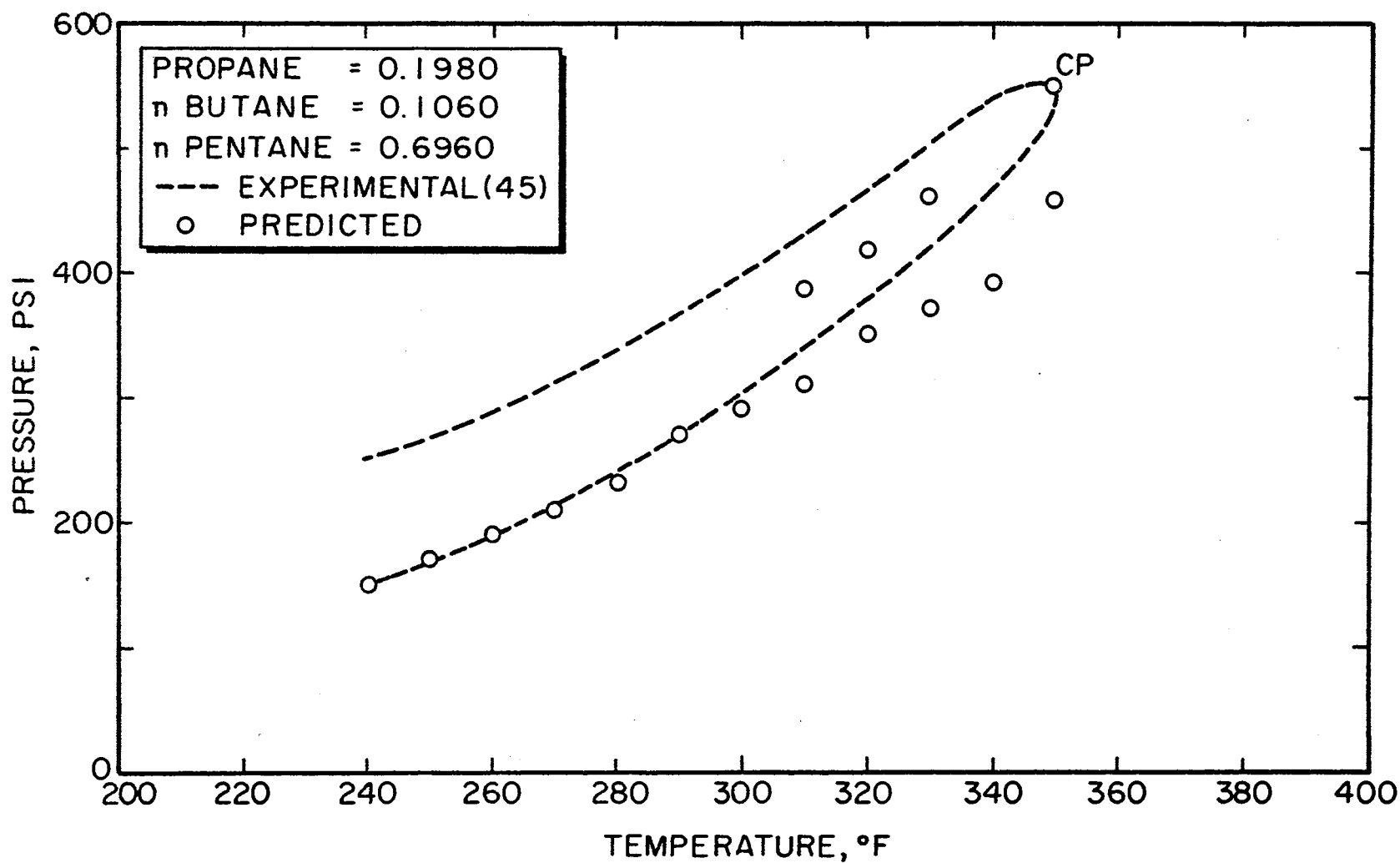


Figure 49. Pressure-Temperature Phase Envelope for Propane/n Butane/n Pentane System

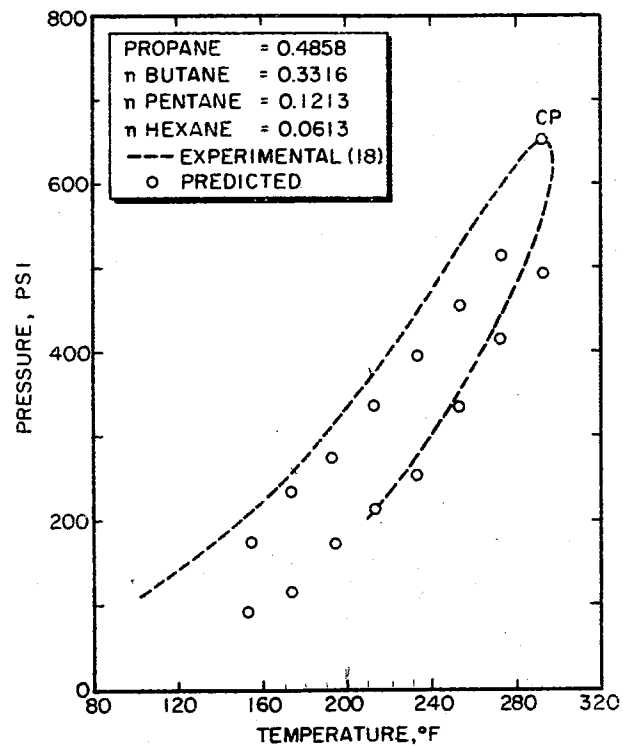


Figure 50. Pressure-Temperature Phase Envelope for Propane/n Butane/n Pentane/n Hexane System

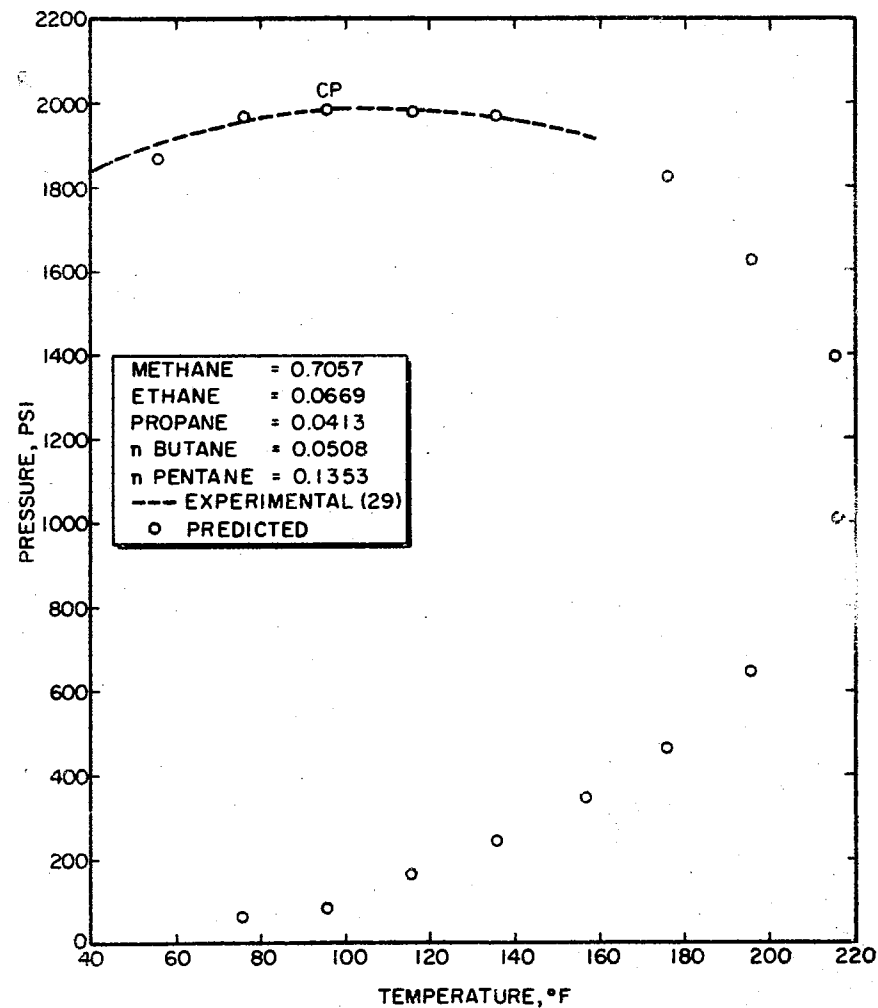


Figure 51. Pressure-Temperature Phase Envelope for Methane/Ethane/Propane/n Butane/n Pentane System

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