# AN EQUATION OF STATE APPROACH TO THE PREDICTION OF CRITICAL STATES OF MIXTURES

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# AN EQUATION OF STATE APPROACH TO THE PREDICTION OF CRITICAL STATES OF MIXTURES

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# PREFACE

An exploratory investigation was made in attempt to integrate the thermodynamic criteria of the critical states of mixtures with suitable equations of state describing the volumetric and phase behavior of mixtures to predict the critical properties of binary and ternary mixtures. The fundamental thermodynamic criteria of the critical state was investigated in detail. Computer programs were developed and used for binary and ternary mixture critical state calculations using the Redlich-Kwong and the Benedict-Webb-Rubin equations of state. The results of a wide variety of binary and ternary systems were analyzed and compared with experimental data and empirical correlation results.

I wish to express my sincere thanks for the advice and guidance given by Professors K. C. Chao and R. L. Robinson, Jr. during this investigation. I would also like to thank the Oklahoma State University Computing Center for the use of their facilities and the National Aeronautic and Space Administration for providing financial support during the course of my doctoral studies.

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# CHAPTER I

# INTRODUCTION

Critical states of pure substances and mixtures are of interest for a number of reasons. From a theoretical point of view, vapor-liquid critical states define the regions of homogeneous and heterogeneous phases. In addition, the critical region is intricately connected with retrograde phenomena and related to both gas-gas equilibrium and liquid-liquid critical solution phenomena. From an engineering point of view, dependable values of the critical properties are essential in the proper design of processes and equipment in the petroleum and natural gas industries. In spite of the interest and importance of critical states, particularly for mixtures, methods for predicting critical properties based on the thermodynamic criteria of the critical state are almost nonexistent. At the present time empirical methods must be used to obtain values of the critical properties of mixtures for typical engineering applications.

The purpose of this study is to integrate the thermodynamic criteria defining the critical states of mixtures with suitable equations of state describing the volumetric and phase behavior of the mixture to predict the critical properties of binary and ternary mixtures.

The importance of this equation of state approach to predict the critical state is a result of the inter-relationship of the equation of state and critical state investigations. Improvements in equations of state can be applied directly to obtain improvements in the prediction of critical states. Conversely, equation of state studies can be enriched by information from the study of critical states. In addition, the equation of state approach is not restricted to mixtures of a few classes of chemical substances as is the case for empirical prediction methods.

Four primary objectives were associated with this investigation. They are:

1) To review and investigate the thermodynamic criteria of the critical state and, if necessary, transform these criteria into equivalent conditions better suited for engineering calculations,
2) To select suitable equations of state and perform numerical calculations using the critical state criteria to predict the critical properties of binary and ternary mixtures,
3) To determine the need and methods required for optimizing the binary interaction parameters in the mixing rules of the selected equations of state to increase the accuracy of the critical state predictions,
4) To investigate the use of the optimized binary interaction parameters in ternary mixture critical state calculations and in vapor-liquid equilibrium calculations in the retrograde region.

In order to achieve these objectives, computer programs using the critical state criteria and associated numerical search procedures were written and applied to a variety of binary and ternary mixtures of interest. The results of these calculations were analyzed and compared with empirical calculations. Comments and recommendations were made on the equation of state approach to critical state predictions, the general level of accuracy and applicability, and the implications for future work in this area of thermodynamic research.

# CHAPTER II

# BACKGROUND

## A. The Critical State

The concept of a critical state in vapor-liquid equilibrium phenomena dates back to 1783 when James Watt speculated that the density of water and steam might become equal at a sufficiently high temperature. Nearly forty years later the first experimental observation of the disappearance of the vapor-liquid interface was made by Cagnaird de la Tour. In 1863 Thomas Andrews became the first to use the term "critical point" in his work. (3) Later Andrews' classical work and considerations of the van der Waals equation of state were used to define the critical state as that unique point where the vapor-liquid meniscus disappeared and the two phases became a single, homogeneous phase.

The acceptance of the concept of a unique critical point associated with the disappearance of the vapor-liquid meniscus has not been complete. A critical region has been postulated by some observers (11, 15,89) because of the observation of small differences and fluctuations in the physical properties of the two phases near the critical point. However, any critical region, if it does exist, is very small. (48) Thus, the classical concept of a unique critical point on a continuous P-V-T-x surface is still important in engineering applications.

## B. Critical State Theory for Pure Components

An examination of the basic thermodynamic theory of the critical state is best begun by discussing pure substances since composition effects need not be considered. The classical definition of the critical point requires the liquid and vapor phases to be in equilibrium and to have the same density. The equilibrium requirement can be expressed in thermodynamic terms by

$$T_l = T_g \tag{1}$$

$$P_l = P_g \tag{2}$$

$$\mu_l = \mu_g \tag{3}$$

and the density requirement by

$$V_l = V_g \ . \tag{4}$$

Equivalently, the three independent variables of temperature, volume, and molar Helmholtz free energy can be used to define the critical point. (77)

$$T_l = T_g \tag{5}$$

$$\left(\frac{\partial A}{\partial V}\right)_{T\ l} = \left(\frac{\partial A}{\partial V}\right)_{T\ g} \tag{6}$$

$$A_l - V_l\left(\frac{\partial A}{\partial V}\right)_{T\ l} = A_g - V_g\left(\frac{\partial A}{\partial V}\right)_{T\ g} \tag{7}$$

$$V_l = V_g \ . \tag{8}$$

The free energy of real systems is not a continuous differential function of volume in the two-phase region as a consequence of the vapor-liquid equilibrium phenomenon. However, if the free energy is assumed to be a continuous differentiable function of volume in the two-phase region, then classical thermodynamics can be applied to the study of the critical state. This is not a particularly limiting assumption since it leads to results which agree qualitatively with experimental results, approximate statistical theories, and empirical equations of state. (77)

The importance of the assumption of a continuous free energy function to critical state theory can best be shown in terms of the isotherms in a plot of pressure versus volume for a pure component. An isotherm in the single-phase region, designated $T_1$ in Figure 1, at a temperature greater than the critical temperature is a continuous differentiable curve as is the critical isotherm, $T_c$. However, an isotherm at a temperature less than the critical temperature, $T_2$ along the curve ALVB in Figure 1, is not a continuous differentiable curve in the two-phase region. By assuming that the free energy is a continuous differentiable function of volume as discussed previously, the isotherm $T_2$ can be considered to follow curve LMNV in the two-phase region. (77)

The locus of points corresponding to L, M, N, and V generated by the isotherms having a temperature less than the critical temperature approach each other and eventually coincide at the critical point as a point of inflexion on the critical isotherm as shown in Figure 1. Thus, the critical point can be represented by the equations

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \qquad \left(\frac{\partial^3 P}{\partial V^3}\right)_{T_c} < 0 \quad (9)$$

or equivalently in terms of the molar Helmholtz free energy by

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T_c} = 0 \qquad \left(\frac{\partial^3 A}{\partial V^3}\right)_{T_c} = 0 \qquad \left(\frac{\partial^4 A}{\partial V^4}\right)_{T_c} > 0 . \quad (10)$$

The critical temperature, pressure, and volume are defined as the temperature, pressure, and volume existing at the critical point. An examination of Figure 1 and equation 9 shows that the critical temperature is the highest temperature at which the vapor and liquid can coexist in equilibrium.

The locus of points corresponding to M and N, curves CM and CN in Figure 1, are of particular interest in relation of the criteria of mechanical stability of a single component system. To be mechanically stable with respect to adjacent phases, a phase must satisfy certain conditions, i.e. the production of entropy must be negative when the phase is perturbed by the formation of a phase infinitesmally different from it. In general, three mechanical stability conditions must be considered: 1) the initial phase is stable with respect to all other adjacent phases, 2) the initial phase is stable with respect to all adjacent phases except for at least one phase with respect to which it is not stable, and 3) the initial phase is unstable with respect to all adjacent phases. (66) Phases satisfying conditions 1, 2 and 3 are classified as stable, metastable, and unstable phases respectively. Rowlinson (77) shows that the criteria for mechanical stability in terms of negative entropy production in a single component system can also be expressed as

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0 \tag{11}$$

or equivalently in terms of the slopes of the isotherms in Figure 1 as

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \tag{12}$$

Therefore, the curves MC, NC and the two-phase equilibrium boundary divide a single component system into stable, metastable, and unstable states. In the single phase region of the system, the isotherm slopes are continuously negative and the phase is mechanically stable. In the

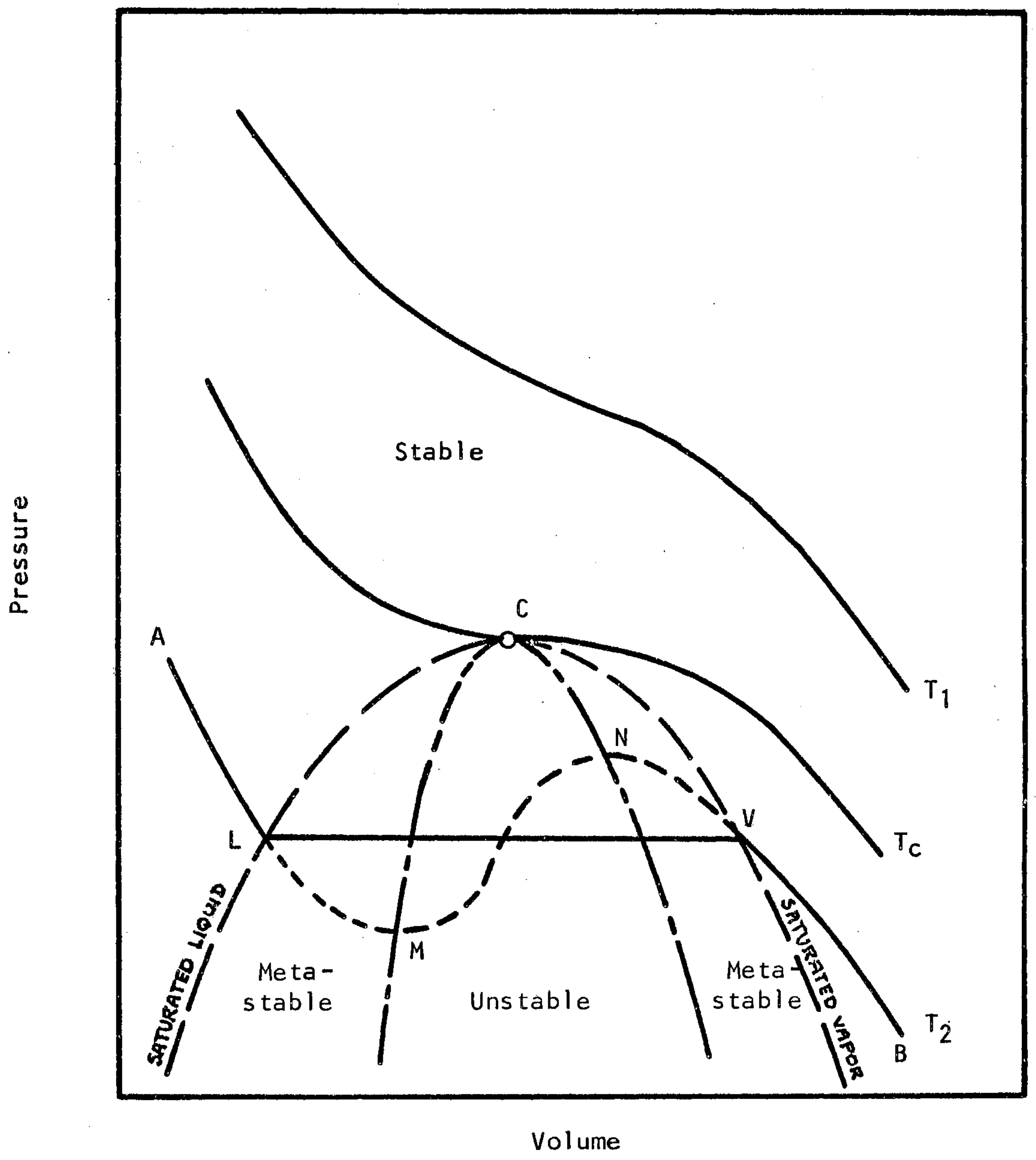

Figure 1. Pressure-Volume Diagram for a Pure Substance

regions bounded by the curves LCM and VCN a phase is metastable. That is, equation 12 is satisfied but the phase will eventually decompose into stable vapor and liquid phases. These metastable states should correspond to subcooled liquid and superheated vapor states. The region bounded by the curve MCN in Figure 1 is completely unstable since equation 12 is not satisfied. In this region a stable phase cannot exist and will spontaneously decompose into two stable or metastable phases. Thus, the critical point of a single component system is at the limit of mechanical stability and can be considered as a point common to the mechanical stability boundary and the two-phase equilibrium boundary. (66)

## C. Critical Property Measurements

Experimental measurements of critical properties can be difficult even for a pure substance because of the unusual mechanical, thermal, and optical properties at the critical point. The compressibility is infinite so that the gravitational field of the earth can produce density gradients in a fluid only a few centimeters high. This makes accurate measurements of the critical density very difficult to obtain. The heat capacity at constant pressure is infinite and the heat capacity at constant volume is very large so that thermal equilibrium is difficult to obtain. A phenomenon known as critical opalescence, strong scattering of light, can cause complete opacity at the critical point which limits direct visual observation of the disappearance of the vapor-liquid meniscus. (77) Thus, the experimental measurement of the critical properties with a high degree of precision and accuracy often proves to be very difficult.

There are a variety of experimental methods and apparatuses used in measuring physical properties at the critical point. Experimental units are divided into two basic classes: 1) nonvisual and 2) visual equipment. The nonvisual equipment is designed for volumetric and phase equilibria studies. Sampling facilities are required for the analysis of the vapor and liquid phases in equilibrium. The critical properties are determined indirectly by extrapolation of the vapor-liquid equilibrium data. Examples of this nonvisual type of equipment are used by Sage and Lacey. (78, 79, 80) The visual type of equipment allows direct observation of the disappearance of the vapor-liquid meniscus at the critical point. No sampling facilities are required. Examples of this visual type of equipment are used by Kay (42), Katz and co-workers (39,40,65), and Thodos and co-workers. (26) Descriptions of the various experimental procedures and equipment for measuring the critical properties are presented by Kobe and Lynn (48) and Tamplin. (87) Tabulations of the critical temperature, pressure, and volume for inert gases, hydrocarbons, non-hydrocarbons, and miscellaneous compounds are presented by Kobe and Lynn (48) and Michael and Thodos. (56) Often significant variations in the critical properties of a given pure substance appear in the literature as a result of the difficulties encountered in the experimental measurement of the critical properties.

The tabulation of critical properties for binary and multicomponent mixtures is much less extensive than for pure substances. The most complete reference summaries for critical properties of binary mixtures are presented by Sutton (86) and Rowlinson. (77) Only a very few ternary and higher mixture critical properties have been investigated. Most of these systems have been summarized by Sutton. (86)

## D. Critical State Correlations

The need for values of critical properties in engineering calculations and the difficulties encountered in experimental work near the critical point have made critical property correlations very important. A history and discussion of available correlations, both empirical and theoretical, appear in the following section.

At the present time tabulations of experimental critical property data, $T_c$, $P_c$, and $V_c$ in particular, exist for the pure components commonly encountered in most engineering calculations. As a result, pure component critical state correlations are now more of a convenience than an absolute necessity for common substances. However, many empirical correlations of varying complexity and accuracy do exist for predicting the critical temperature, pressure and volume for pure components. These correlations have been summarized in detail by Kobe and Lynn (48), Michael and Thodos (56), and Gambill (27,28).

The critical properties of mixtures have not been extensively tabulated, particularly for mixtures containing more than two components. Thus, critical state correlations for mixtures are much more important than is the case for pure components. A wide variety of empirical correlations, usually with an average boiling temperature and composition of the mixture as parameters, have been proposed. These correlations are divided into two classes: 1) correlations which apply to simple mixtures of known composition and 2) correlations which apply to complex petroleum fractions. In general, the correlations for both classes of mixtures are limited to hydrocarbons and often only to aliphatic and simple aromatic hydrocarbons.

Several empirical correlations for the critical temperature and pressure of simple hydrocarbon mixtures have been proposed. The correlations suggested by Pawlewski (64) and Kay (41) are the most important from a historical point of view. More accurate correlations have been proposed by Joffe (36), Grieves and Thodos (32,34), Organick (62,63), and Etter and Kay (25). Edmister (21) summarized the critical state correlations available for hydrocarbon mixtures up to 1949. The best of these correlations are accurate within approximately 1% for the critical temperature and 3-5% for the critical pressure. Grieves and Thodos (34) present one of the few correlations for critical volumes of mixtures.

Correlations to predict the critical state of complex petroleum fractions have also been presented. The most significant correlations have been suggested by Smith and Watson(85), Kurata and Katz (50), Roess (76), Eilerts (23), and Edmister and Pollock. (22) Organick (63) also contributed a correlation and presented a comparison of his method with the Kurata-Katz, Smith-Watson, and Edmister-Pollock correlations.

Equations of state were introduced into critical state correlations in an attempt to integrate vapor-liquid equilibrium behavior with the critical point. The following correlations may be considered as the first steps toward the work carried out in this investigation, i.e. the prediction of the critical point on the basis of the thermodynamic criteria of the critical point and a suitable equation of state.

Michael and Thodos (56) rearranged the equations defining the constants a and b of the van der Waals equation of state to obtain expressions for the critical temperature and pressure. The resulting expressions were

$$T_c = \frac{8a}{27bR} \tag{13}$$

$$P_c = \frac{a}{27\ b^2} \quad . \tag{14}$$

The values of the constants a and b were obtained from the empirical relations

$$a = (\alpha \bar{P} + \beta)^{1.523} \tag{15}$$

$$b = (\alpha' \bar{P} + \beta')^{1.299} \tag{16}$$

where the constants $\alpha$, $\alpha'$, $\beta$, and $\beta'$ and the parachor $\bar{P}$ were determined for the given hydrocarbon. The average deviation of the predicted critical constants from the experimental critical values was 1.8% for pure substances. No attempt was made to apply this procedure to mixtures.

Chueh and Prausnitz (14) noted that Rowlinson (77) had shown that the critical temperature of binary mixtures was a simple quadratic function of the mole fraction as described by

$$T_{c_m} = x_1^2 T_{c_1} + x_2^2 T_{c_2} + 2x_1 x_2 \Delta T_{12} \tag{17}$$

where $\Delta T_{12}$ depends on the energy characteristic of the 1-2 molecular interaction. Rowlinson's expression for the critical temperature was limited to simple, spherically-symmetric molecules of nearly equal size. To eliminate this restriction, Chueh and Prausnitz correlated the critical temperature as a quadratic function of the surface fraction $\theta_i$:

$$T_{c_m} = \theta_1^2 T_{c_1} + \theta_2^2 T_{c_2} + 2\theta_1 \theta_2 \tau_{12} \tag{18}$$

where $\tau_{12}$ is a parameter characteristic of the 1-2 molecular interaction. The surface fraction is calculated from

$$\theta_i = \frac{x_i V_{c_i}^{2/3}}{\sum_{i=1}^{n} x_i V_{c_i}^{2/3}} \quad . \tag{19}$$

The critical volume was also correlated as a quadratic function of the surface fraction:

$$V_{c_m} = \theta_1^2 V_{c_1} + \theta_2^2 V_{c_2} + 2\,\theta_1\theta_2\,\mathcal{V}_{12} \qquad (20)$$

where $\mathcal{V}_{12}$ is characteristic of the 1-2 molecular interaction.

A similar quadratic correlation of the critical pressure with the surface fraction was tried and failed since the dependence of the critical pressure on composition is much more strongly nonlinear than that for the critical temperature or volume. A successful alternative proved to be using the predicted critical temperature and volume in a modified Redlich-Kwong equation of state to obtain the critical pressure. The average deviation for the critical temperature was 0.4% and that for the critical pressure was 4.3% for binary through quinary multicomponent mixtures.

Redlich and Kister (73) were the first to attempt to predict the critical locus of binary mixtures using the thermodynamic criteria of the critical point. The fugacity coefficients of the pure components defined by

$$\ln \phi_i = \int_0^P (\bar{V}_i/RT - 1/P)\, dP \qquad (21)$$

where $\bar{V}_i$ is the partial molal volume of component i were used to define the identity of the two phases in equilibrium with each other at the critical state:

$$\left(\frac{\partial \ln \phi_1}{\partial x_1}\right)_{T,P} = -\frac{1}{x_1} \qquad (22)$$

$$\left(\frac{\partial^2 \ln \phi_1}{\partial x_1^2}\right)_{T,P} = \frac{1}{x_1^2} \qquad (23)$$

These critical state equations were transformed using the definition of the fugacity coefficient in terms of the partial molal volumes and the Gibbs-Duhem equation to give two equivalent equations in terms of P-V-T-x derivatives which could be evaluated using an equation of state.

$$\int_{\infty}^{V} \left(\frac{\partial^2 P}{\partial x_1^2}\right)_{T,V} dV - \left(\frac{\partial P}{\partial x_1}\right)_{T,V} \left(\frac{\partial V}{\partial P}\right)_{T,x_1} = \frac{RT}{x_1 \; x_2} \qquad (24)$$

$$\int_{\infty}^{V} \left(\frac{\partial^3 P}{\partial x_1^3}\right)_{T,V} dV + 2 \left(\frac{\partial^2 P}{\partial x_1^2}\right)_{T,V} \left(\frac{\partial V}{\partial x_1}\right)_{T,P} + \left(\frac{\partial^2 P}{\partial x_1 \, \partial V}\right)_{T} \left(\frac{\partial V}{\partial x_1}\right)^2_{T,P}$$

$$+ \left(\frac{\partial P}{\partial x_1}\right)_{T,V} \left(\frac{\partial^2 V}{\partial x_1^2}\right)_{T,P} = \frac{RT \; (x_1 - x_2)}{x_1^2 \;\; x_2^2} \qquad (25)$$

The appearance of the second and third derivatives of the pressure in these complicated critical relations places a serious strain on an equation of state. Thus, they predicted, an equation of state must be very accurate in the critical region to furnish "satisfactory" results in predicting the critical locus.

Redlich and Kister indicated that numerical results could be obtained without serious difficulties but they did not carry out these calculations. Instead, they proposed a simpler method for predicting the critical locus of binary mixtures. Using equations 24 and 25, the limiting slopes of the critical locus as the mixture approached its two pure component limits ($x_1$ = 1.0 and $x_2$ = 1.0) were derived. The equations for the limiting slopes of the critical temperature and critical pressure are

$$\left(\frac{\partial T}{\partial x_1}\right)_c = \frac{\dfrac{(x_1 - x_2)}{RT} \left(\dfrac{\partial P}{\partial x_1}\right)^2_{T,V} - \left(\dfrac{\partial^2 P}{\partial V \, \partial x_1}\right)_{x_1}}{\left(\dfrac{\partial^2 P}{\partial T \, \partial V}\right)_{x_1}} \qquad (26)$$

$$\left(\frac{\partial P}{\partial x_1}\right)_c = \left(\frac{\partial P}{\partial x_1}\right)_{T,V} + \left(\frac{\partial P}{\partial T}\right)_{V,x_1} \left(\frac{\partial T}{\partial x_1}\right)_c \qquad (27)$$

Hyperbolic interpolation was used to extend the prediction of the critical locus over the entire composition range of the mixture. The resulting interpolation equations for the critical temperature and critical pressure are

$$T_{c_m} = x_1 T_{c_1} + x_2 T_{c_2} + \frac{\Delta t_2 \; \Delta t_1 \; x_1 \; x_2}{\Delta t_2 \, x_1 - \Delta t_1 \, x_2} \qquad (28)$$

$$P_{c_m} = x_1 P_{c_1} + x_2 P_{c_2} + \frac{\Delta P_2 \; \Delta P_1 \; x_1 \; x_2}{\Delta P_2 \, x_1 - \Delta P_1 \, x_2} \qquad (29)$$

where $\Delta t_i = T_{c_1} - T_{c_2} - T_{i_{lim}}$ and $\Delta P_i = P_{c_1} - P_{c_2} - P_{i_{lim}}$.

The limiting slopes $T_{i_{lim}}$ and $P_{i_{lim}}$ are defined by

$$T_{i_{lim}} = \lim_{x_i \to 1} \left(\frac{\partial T}{\partial x_i}\right)_c \qquad (30)$$

$$P_{i_{lim}} = \lim_{x_i \to 1} \left(\frac{\partial P}{\partial x_i}\right)_c \qquad (31)$$

The Redlich-Kwong equation of state (74) was substituted into the interpolation equations for the critical temperature and pressure and the results were compared graphically with experimental data. In general, there was qualitative agreement for both critical temperature and pressure over the entire composition range of the binary mixtures.

In an extension of the work carried out by Redlich and Kister, the Benedict-Webb-Rubin equation of state was substituted into the limiting slope and interpolation equations by Ackerman and Redlich (1) to predict the critical locus of binary mixtures. The agreement between the critical locus predicted by the B-W-R equation of state and the experimental data was also qualitative. However, the more elaborate B-W-R equation did not prove to be consistently better in predicting the critical locus than the simpler Redlich-Kwong equation of state. Ackerman and Redlich concluded that the coefficients of the B-W-R equation must be chosen specifically to fit data in the critical region before more quantitative results could be obtained.

Concurrently with this investigation, Joffe and Zudkevitch (38) continued the equation of state approach to the prediction of the critical state of mixtures begun by Redlich and Kister. The rigorous critical state conditions developed by Redlich and Kister, equations 24 and 25, were evaluated using a slightly modified Redlich-Kwong equation of state. The modification of the Redlich-Kwong equation was a result of earlier work by Joffe and Zudkevitch. (37) They found that substantial improvement in the representation of the fugacity of gas mixtures was obtained by using the mixing rules

$$a = a_1x_1^2 + 2a_{12}x_1x_2 + a_2x_2^2 \tag{32}$$

$$b = b_1x_1^2 + 2b_{12}x_1x_2 + b_2x_2^2 \tag{33}$$

and treating the interaction parameters $\theta$ and $\phi$ in the interaction relations

$$a_{12} = \theta \sqrt{a_1a_2} \tag{34}$$

$$b_{12} = \phi \sqrt{b_1b_2} \tag{35}$$

as empirical parameters. Substitution of the appropriate derivatives evaluated in terms of the Redlich-Kwong equation and the modified mixing rules into the critical state equations resulted in two highly complicated expressions. The simultaneous solution of these two critical state equations to obtain the critical temperature and pressure was performed graphically for the ethane-carbon dioxide and n-butane-carbon dioxide binary mixtures. Critical temperatures calculated in this manner agreed very well with experimental data. However, only fair agreement was obtained for the critical pressure or volume.

In analyzing the extension of this equation of state approach to multicomponent mixtures, Joffe and Zudkevitch concluded that the critical conditions lead to such involved relations that a practical calculational procedure would be very complex even for binary mixtures. As a result, an extension of the limiting slopes method developed by Redlich and Kister was presented to provide a means for determining the critical constants for multicomponent mixtures.

The thermodynamics of the critical state of pure substances, binary mixtures, and multicomponent mixtures were reviewed and discussed by Opfell and Sage. (60) The thermodynamic equations defining the critical state of binary mixtures were derived in terms of the molar Helmholtz free energy. The conclusion of the theoretical investigation of the critical state was that an equation of state could be used in conjunction with the critical state criteria to determine the critical point of mixtures. However, the critical state relations would be relatively complicated even for binary mixtures. The general form of the thermodynamic equations defining the critical state of multicomponent mixtures in terms of the molar Gibbs free energy was also presented and discussed.

# CHAPTER III

## CRITICAL STATE THERMODYNAMIC THEORY

### A. Binary Mixture Theory

The addition of a second chemical species to a one-component system often greatly complicates the system from a thermodynamic point of view. Unfortunately, the vapor-liquid critical phenomenon behaves in this manner. Consider the plots of pressure versus temperature for a pure substance and a binary mixture. Line AK in Figure 2a represents the vapor-liquid equilibrium curve of a pure substance. The critical point K is the highest temperature and pressure at which vapor-liquid equilibrium can occur. This is not the case for binary mixtures. Consider the vapor-liquid equilibrium boundary ABLKMD of the binary mixture in Figure 2b. In general, the critical point K, the point at which the two phases are identical, is not the highest temperature or pressure on the two-phase equilibrium boundary. The highest pressure, point L, and the highest temperature, point M, on the two-phase equilibrium boundary are known as the cricondenbar and cricondentherm, respectively. The high-pressure and high-temperature region near the critical point which has been shaded in Figure 2b is known as the retrograde region. An isobar in the high-pressure region, area BLKB, has two bubble point temperatures rather than a bubble point and a dew point temperature which occurs at pressures below the critical pressure.

Similarly, an isotherm in the high-temperature region, area KMDK, has two dew point pressures. From the differences in the characteristics of the critical point on the P-T plots, the fact that the thermodynamic criteria of the critical state of pure substances and binary mixtures differ considerably is not surprising.

The identity of the vapor and liquid phases in equilibrium at the critical point must be satisfied by mixtures as well as pure substances. The differences in the critical state criteria of pure substances and mixtures arises from the introduction of additional chemical species. Therefore, the role of diffusion equilibrium and stability in defining the critical point must be investigated for multicomponent mixtures.

Prigogine and Defay (66) used the general conditions for equilibrium at constant temperature and pressure in an unperturbed binary system to derive the necessary and sufficient conditions for diffusion stability in a binary system:

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,P} > 0 \tag{36}$$

$$\left(\frac{\partial \mu_2}{\partial n_2}\right)_{T,P} > 0 \tag{37}$$

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,P}\left(\frac{\partial \mu_2}{\partial n_2}\right)_{T,P} - \left(\frac{\partial \mu_1}{\partial n_2}\right)^2_{T,P} \geq 0 \ . \tag{38}$$

In addition, equilibrium in a binary system also requires that

$$\left(\frac{\partial \mu_2}{\partial n_2}\right)_{T,P} = \left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,P} \tag{39}$$

and

$$\left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,P} = \left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,P} \tag{40}$$

A comparison of equations 38, 39, and 40 then suggests the basic condition for diffusion stability for a binary system:

$$\left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,P} = \left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,P} < 0 \tag{41}$$

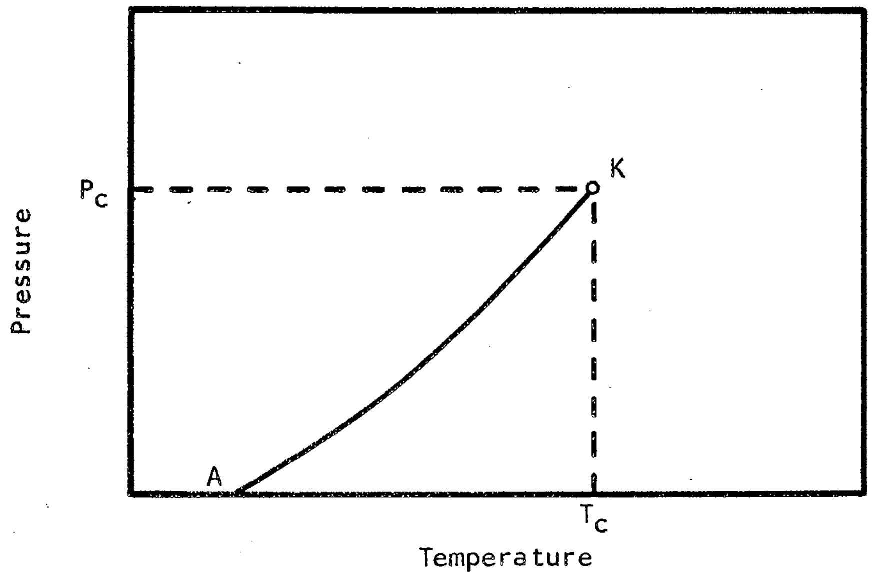

Figure 2a. Pressure-Temperature Diagram for a Pure Substance

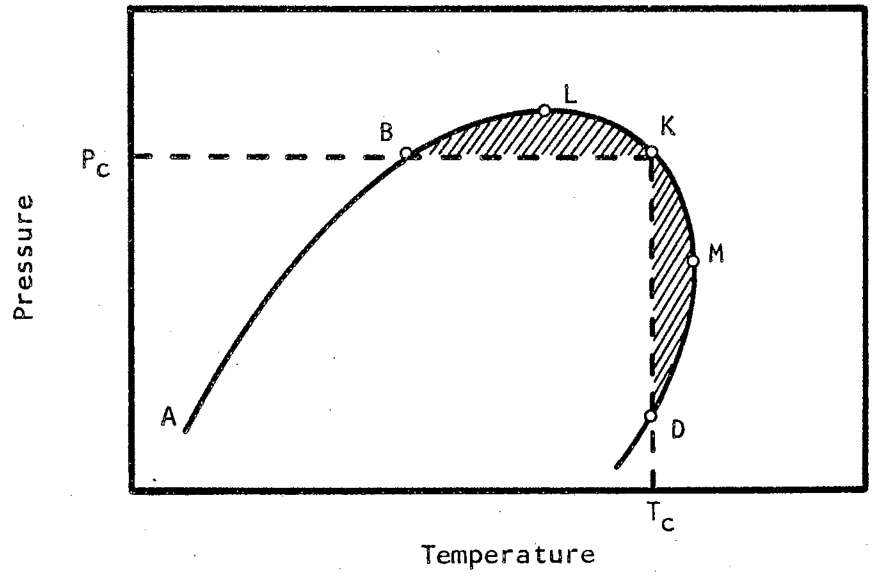

Figure 2b. Pressure-Temperature Diagram for a Binary Mixture

In general, there are three diffusion stability conditions that can exist: 1) the initial phase is stable with respect to all other adjacent phases, 2) the initial phase is stable with respect to all adjacent phases except for at least one phase with respect to which it is not stable, and 3) the initial phase is unstable with respect to all adjacent phases. Phases satisfying conditions 1, 2, and 3 are classified as stable, metastable, and unstable phases with respect to diffusion.

The relationship of the diffusion stability and critical state criteria for binary mixtures can best be shown in terms of the isotherms in a plot of chemical potential of component 1 versus the mole fraction of component 2 in the mixture. An isotherm in the single phase region, designated $T_1$ in Figure 3, has a negative slope and therefore, is stable with respect to diffusion. However, an isotherm in the two-phase region, designated $T_2$ along the curve ALMNVB, has positive, zero, and negative sloped portions indicating the existence of unstable and metastable states as well as stable states. The curves KM, KN, and the two-phase equilibrium boundary divide the binary system into stable, metastable, and unstable states. In the single phase region the isotherm slopes are continuously negative and the phase is stable with respect to diffusion. In the regions bounded by curves LKM and NKV a phase is metastable and will eventually decompose into stable vapor and liquid phases. The region bounded by the curve MKN is completely unstable and any phase in this region will spontaneously decompose into two stable or metastable phases. The locus of points corresponding to L, M, N, and V generated by the isotherms having a temperature less than critical temperature approach each other and eventually coincide

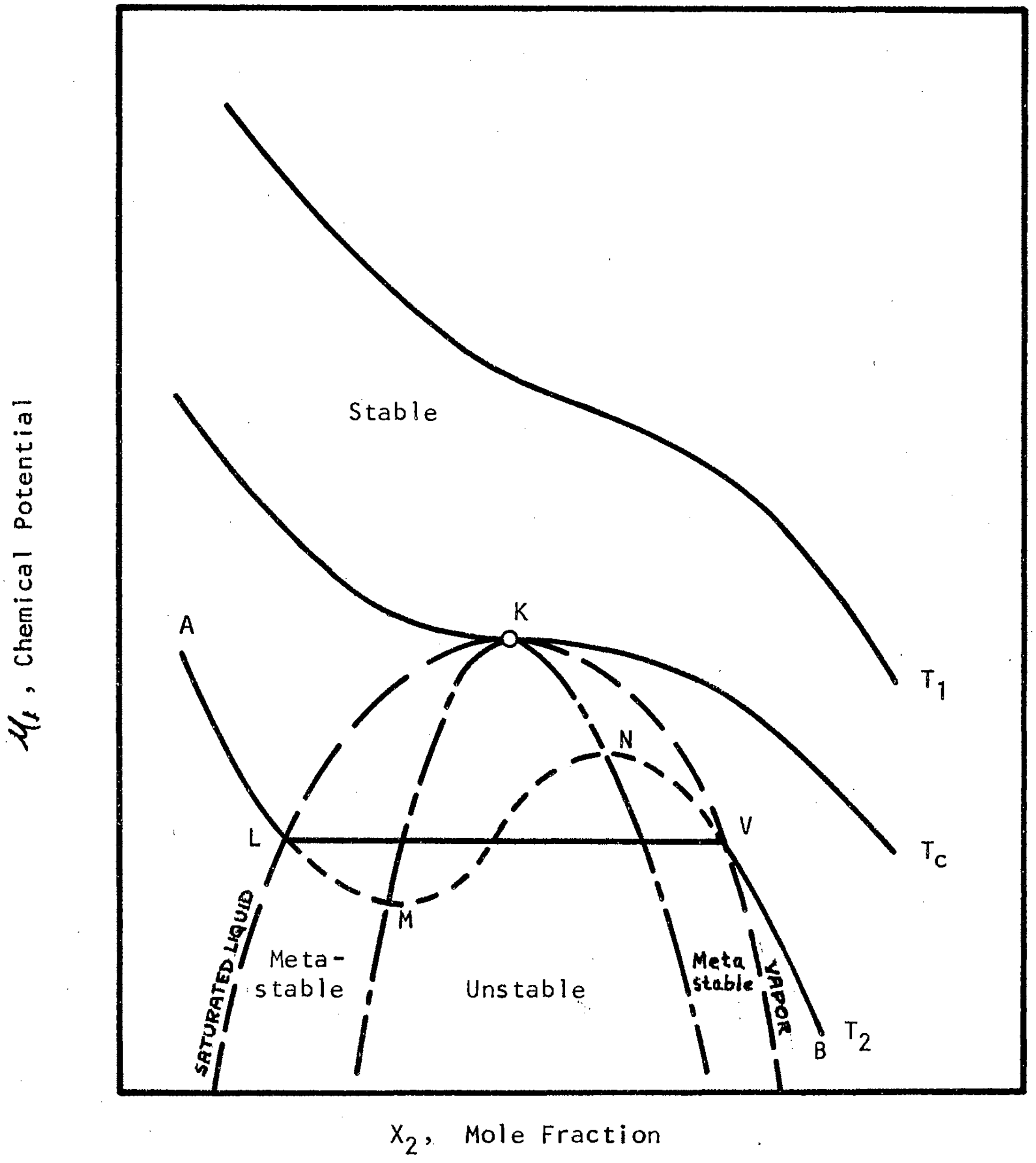

Figure 3. A Plot of the Chemical Potential of Component 1 Versus the Mole Fraction of Component 2 for a Binary Mixture

at the critical point as a point of inflection on the critical isotherm. Thus, the criteria for the critical point of binary mixtures can be represented by (66)

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = 0 \tag{42}$$

$$\left(\frac{\partial^2 \mu_1}{\partial x_2^2}\right)_{T,P} = 0 \tag{43}$$

$$\left(\frac{\partial^3 \mu_1}{\partial x_2^3}\right)_{T,P} < 0 . \tag{44}$$

The critical state relations for binary mixtures can be expressed more conveniently in terms of molal Gibbs free energy. The fundamental relationship between the chemical potential and molal Gibbs free energy is (66)

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = - x_2 \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} . \tag{45}$$

Therefore, the critical state relations can be rewritten as (77)

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = 0 \tag{46}$$

$$\left(\frac{\partial^3 G}{\partial x_2^3}\right)_{T,P} = 0 \tag{47}$$

$$\left(\frac{\partial^4 G}{\partial x_2^4}\right)_{T,P} > 0 . \tag{48}$$

The critical relations for binary mixtures were derived from considerations of diffusion stability and not in terms of mechanical stability as was used to define the critical state of pure substances. Nevertheless, the condition of mechanical stability,

$$\left(\frac{\partial P}{\partial V}\right)_{T,x_2} < 0 \tag{49}$$

must be satisfied for binary mixtures as it was for pure components.

The relationship between the conditions of mechanical and diffusion stability is best derived by considering the first critical state relation, equation 46, in terms of the molar Helmholtz free energy. The details of the derivation are presented in the following section.

The definitions of the molar Gibbs and Helmholtz free energy,

$$G = U - TS + PV \tag{50}$$

$$A = U - TS \tag{51}$$

were combined to give the basic relation between the two free energies:

$$A = G - PV \ . \tag{52}$$

Differentiating this relation with respect to $x_2$ at constant T and V resulted in

$$\left(\frac{\partial A}{\partial x_2}\right)_{T,V} = \left(\frac{\partial G}{\partial x_2}\right)_{T,V} - V\left(\frac{\partial P}{\partial x_2}\right)_{T,V} . \tag{53}$$

The partial derivative $\left(\frac{\partial G}{\partial x_2}\right)_{T,V}$ can be expressed in terms of $\left(\frac{\partial G}{\partial x_2}\right)_{T,P}$ by considering the molar Gibbs free energy as a function of both T, P, and $x_2$ and T, V, and $x_2$. If $G = G(T, V, x_2)$, the total differential dG can be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{V,x_2} dT + \left(\frac{\partial G}{\partial V}\right)_{T,x_2} dV + \left(\frac{\partial G}{\partial x_2}\right)_{T,V} dx_2 \ . \tag{54}$$

Similarly, if $G = G(T, P, x_2)$, the total differential dG can be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,x_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,x_2} dP + \left(\frac{\partial G}{\partial x_2}\right)_{T,P} dx_2 . \tag{55}$$

Likewise, the total differential dP for an equation of state of the form $P = P(T, V, x_2)$ can be written as

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,x_2} dT + \left(\frac{\partial P}{\partial V}\right)_{T,x_2} dV + \left(\frac{\partial P}{\partial x_2}\right)_{T,V} dx_2 \ . \tag{56}$$

Combining equations 55 and 56 resulted in

$$dG = \left[\left(\frac{\partial G}{\partial T}\right)_{P,x_2} + \left(\frac{\partial G}{\partial P}\right)_{T,x_2}\left(\frac{\partial P}{\partial T}\right)_{V,x_2}\right] dT + \left[\left(\frac{\partial G}{\partial x_2}\right)_{T,P} + \left(\frac{\partial G}{\partial P}\right)_{T,x_2}\left(\frac{\partial P}{\partial x_2}\right)_{T,V}\right] dx_2 + \left[\left(\frac{\partial G}{\partial P}\right)_{T,x_2}\left(\frac{\partial P}{\partial V}\right)_{T,x_2}\right] dV. \quad (57)$$

A comparison of the coefficients of $dx_2$ in equations 54 and 57 lead to the relation

$$\left(\frac{\partial G}{\partial x_2}\right)_{T,V} = \left(\frac{\partial G}{\partial x_2}\right)_{T,P} + \left(\frac{\partial G}{\partial P}\right)_{T,x_2}\left(\frac{\partial P}{\partial x_2}\right)_{T,V} . \quad (58)$$

Therefore, equation 53 could be written as

$$\left(\frac{\partial A}{\partial x_2}\right)_{T,V} = \left(\frac{\partial G}{\partial x_2}\right)_{T,P} + \left(\frac{\partial G}{\partial P}\right)_{T,x_2}\left(\frac{\partial P}{\partial x_2}\right)_{T,V} - V\left(\frac{\partial P}{\partial x_2}\right)_{T,V} . \quad (59)$$

However,

$$\left(\frac{\partial G}{\partial P}\right)_{T,x_2} = V \quad (60)$$

for a binary mixture. (66) Substituting this relation into equation 59 resulted in the desired relationship between the derivatives of the molar Gibbs and Helmholtz free energy with respect to $x_2$:

$$\left(\frac{\partial G}{\partial x_2}\right)_{T,P} = \left(\frac{\partial A}{\partial x_2}\right)_{T,V} \quad (61)$$

The second derivative of G with respect to $x_2$ can be found in terms of the molar Helmholtz free energy by differentiating equation 61 at constant T and P. That is,

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = \frac{\partial}{\partial x_2}\left[\left(\frac{\partial A}{\partial x_2}\right)_{T,V}\right]_{T,P} . \quad (62)$$

In a procedure analogous to that used to derive equation 61, the second derivative can be expressed as

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = \left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V} - \frac{\left(\frac{\partial^2 A}{\partial x_2 \, \partial V}\right)_T^{\,2}}{\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}} . \quad (63)$$

Since $\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = 0$ is the first critical state relation for binary mixtures, equation 63 can be used to define the critical state in terms of the molar Helmholtz free energy.

The role of the mechanical stability requirement, i.e.

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2} > 0$$

in determining the critical states of binary mixtures can be shown by considering the first critical state relation, equation 63 set equal to zero. If this critical state relation is to be satisfied, then the partial derivative $\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}$ cannot equal zero. Otherwise, $\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = -\infty$. Thus, the critical states of binary mixtures are not on the mechanical stability boundary as was the case for pure substances and the mechanical stability criterion plays no part in determining the critical states of binary mixtures.

The relationships between the mechanical stability boundary, diffusion stability boundary, and the critical point of a binary mixture can be visualized in a plot of volume versus composition at constant temperature as shown in Figure 4. The critical point K is located at the point of tangency of the two-phase equilibrium boundary, curve GKL and the diffusion stability boundary, also known as the "spinodal" curve, curve AKB, defined by equation 46. The mechanical stability boundary, curve ADB, is not related to the critical point of binary mixtures. Therefore, the critical point of binary mixtures cannot be found by using the simple mechanical stability criterion as was the

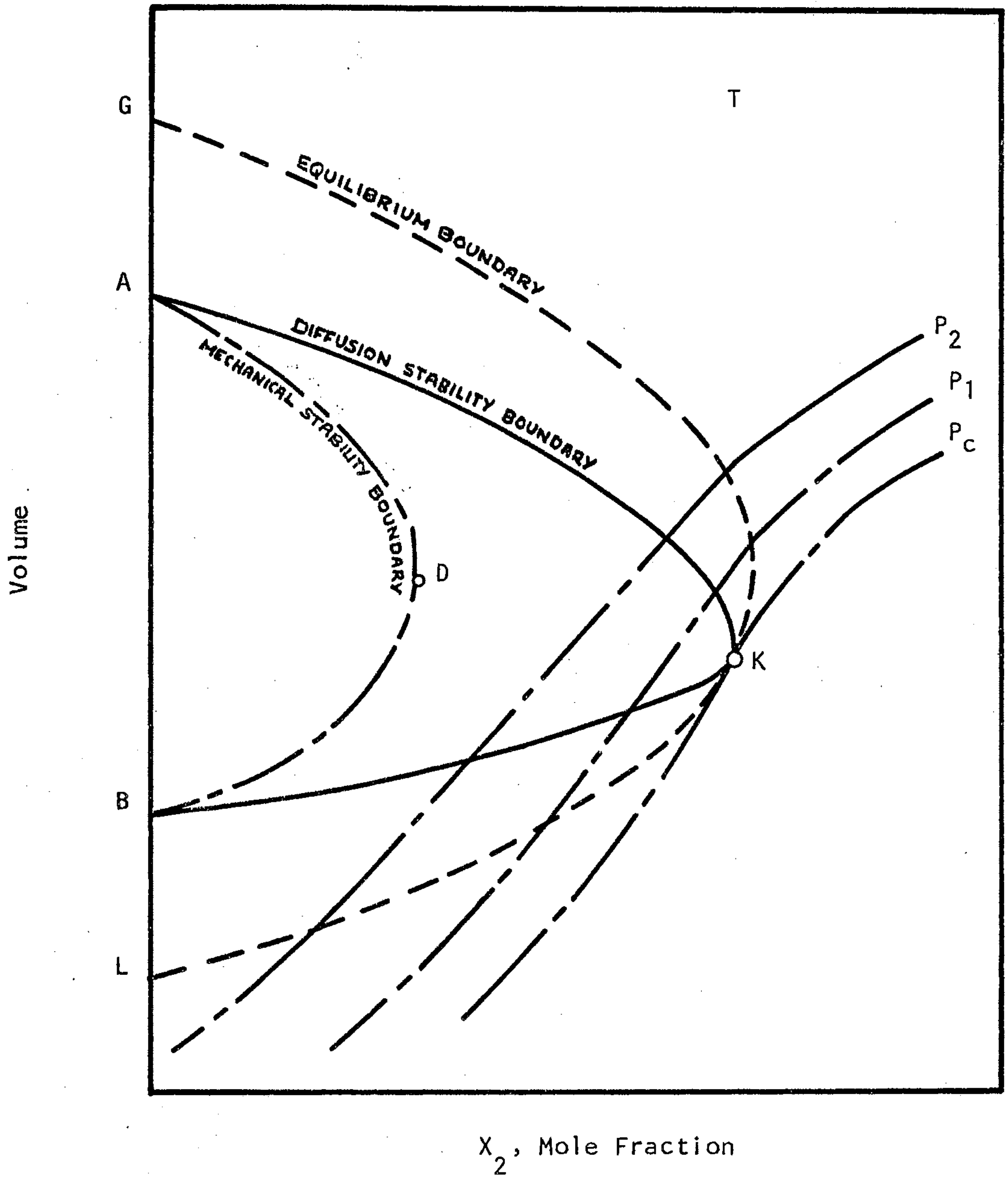

Figure 4. A Plot of Volume Versus Mole Fraction of Component 2 for a Typical Binary Mixture

case for pure substances.

The Gibbs phase rule as applied to binary mixtures at the critical point indicates that three independent variables are required to uniquely define the critical point. Thus, when one variable is specified, the two remaining variables can be determined from the two critical state relations. The choice of the variables to be specified and calculated was made after considering the critical state relations and the form of the equation of state. Since all the partial derivatives of the critical state relations are evaluated at constant temperature, the critical temperature was chosen as the variable to be specified. Either the variables P and $x_2$ or V and $x_2$ could be determined from the critical state relations. However, use of the variables P and $x_2$ would require a trial and error procedure to find the volume in all pressure explicit equations of state. Since most useful equations of state are pressure explicit, the variables V and $x_2$ were selected as the primary calculational variables.

The selection of V and $x_2$ as the primary calculational variables suggested that the critical state relations be expressed in terms of the molar Helmholtz free energy rather than the molar Gibbs free energy. The transformation of the first critical state relation has been followed in detail in the derivation of equation 63. The second critical state relation may be transformed in a similar procedure. The results of the transformation of the original critical state relations into the equivalent critical state relations in terms of the molar Helmholtz free energy appear below.

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}\left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V} - \left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_T^2 = 0 \qquad (64)$$

$$\left(\frac{\partial^3 A}{\partial x_2^3}\right)_{T,V} + \left(\frac{\partial V}{\partial x_2}\right)_{T,P} \left(\frac{\partial^3 A}{\partial x_2^2\,\partial V}\right)_T - \frac{\left(\frac{\partial^3 A}{\partial x_2^2\,\partial V}\right)_T \left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_T}{\left(\frac{{}^2A}{V^2}\right)_{T,x_2}}$$

$$- \frac{2\left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_T \left(\frac{\partial V}{\partial x_2}\right)_{T,P} \left(\frac{\partial^3 A}{\partial x_2\,\partial V^2}\right)_T}{\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}} + \frac{\left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_T^2 \left(\frac{\partial^3 A}{\partial x_2\,\partial V^2}\right)_T}{\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}^2}$$

$$+ \frac{\left(\frac{\partial^2 A}{\partial x_2\,\partial V}\right)_T^2 \left(\frac{\partial V}{\partial x_2}\right)_{T,P} \left(\frac{\partial^3 A}{\partial V^3}\right)_{T,x_2}}{\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x_2}^2} \qquad (65)$$

The two critical state relations in terms of the molar Helmholtz free energy can be simplified and put into a form convenient for a pressure explicit equation of state by substituting in the fundamental thermodynamic relationship $\left(\frac{\partial A}{\partial V}\right)_{T,x_2} = - P.$ (66) Equation 64 becomes

$$\left(\frac{\partial P}{\partial V}\right)_{T,x_2} \left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V} + \left(\frac{\partial P}{\partial x_2}\right)_{T,V} = 0 \qquad (66)$$

The second and more complicated of the two critical state relations, equation 65, could be simplified in a similar manner. However, for the special case of binary mixtures, the second critical state relation can be replaced with an equivalent but even simpler relation. Since the first critical state relation, equation 64, represents the diffusion stability boundary, then the second critical state relation, equation 65 locates the critical point at the point of tangency of the diffusion stability boundary and the two-phase equilibrium boundary. However, for well-behaved binary mixtures, as shown in Figure 5, the critical pressure is the maximum equilibrium pressure. Kuenen (49) proved that at the critical point of binary mixtures

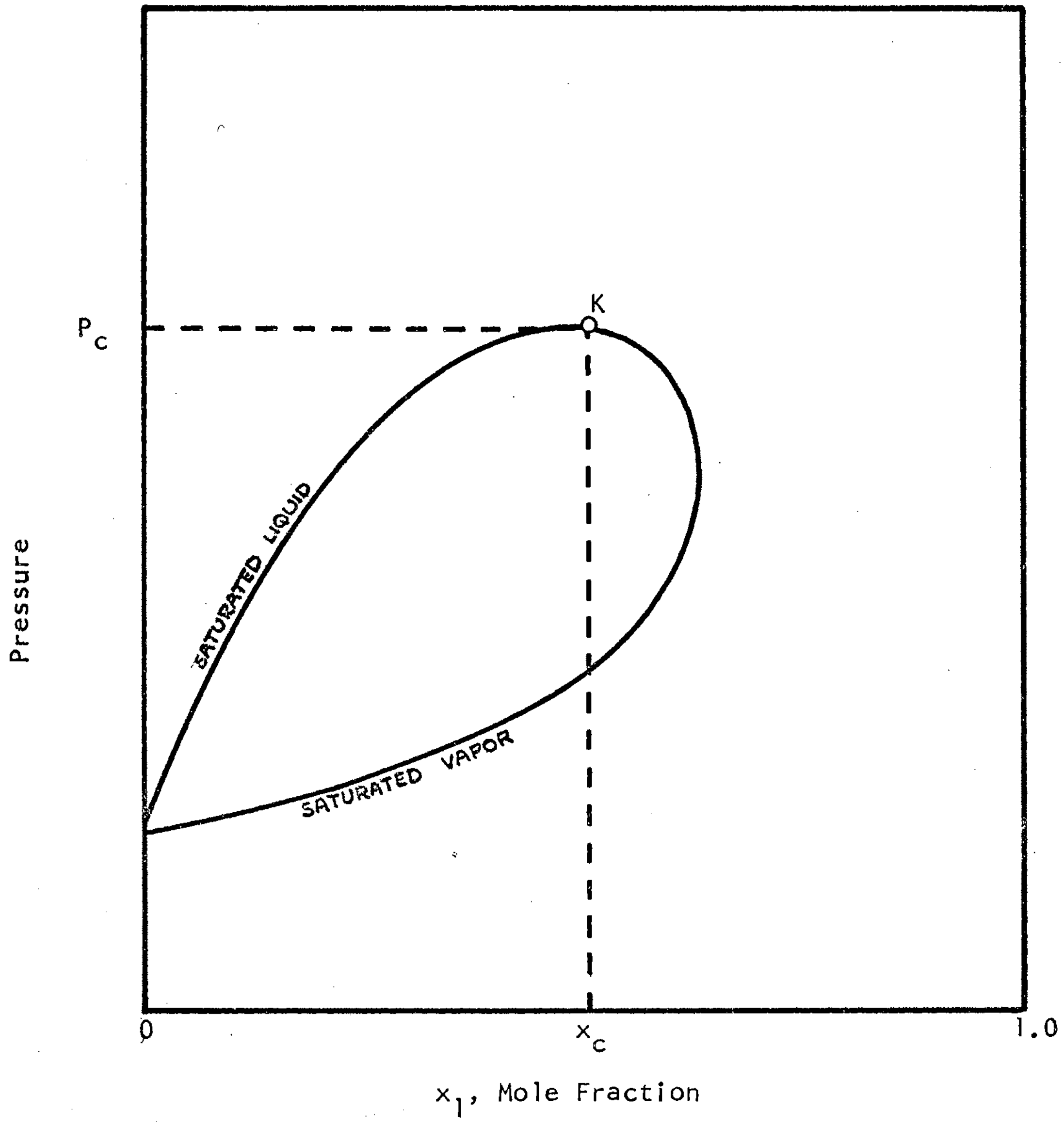

Figure 5. A Plot of Pressure Versus the Mole Fraction of Component 2 for a Well-Behaved Binary Mixture

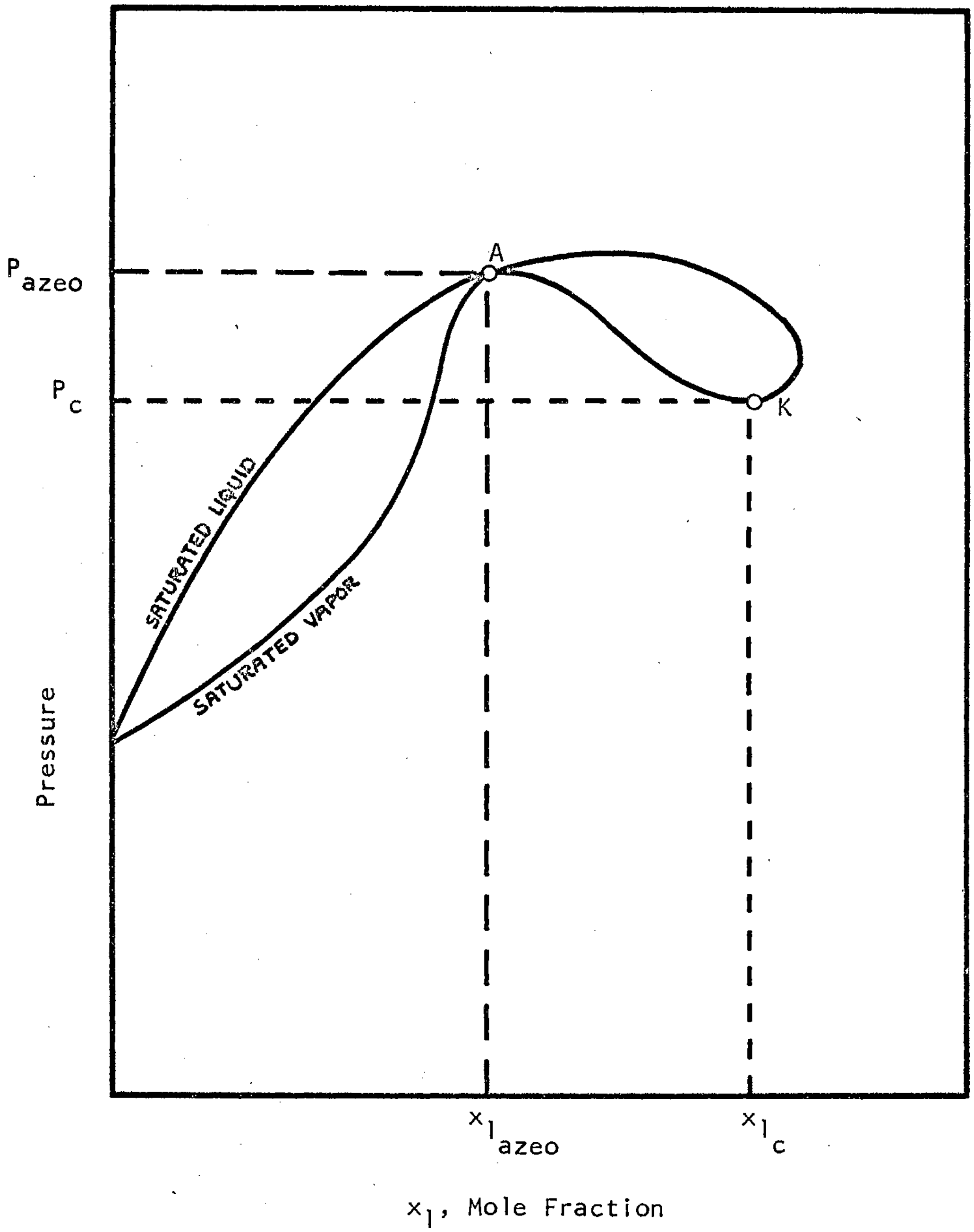

Figure 6. A Plot of Pressure Versus the Mole Fraction of Component 2 for an Azeotropic Binary Mixture

$$\left(\frac{\partial P}{\partial x_2}\right)_{T,\sigma'} = 0 \tag{67}$$

where $\sigma'$ indicates that the derivative is taken along the two-phase equilibrium boundary or the diffusion stability boundary. A maximum or minimum in the pressure-mole fraction loop would satisfy equation 67 but Rowlinson (77) has shown that the minimum condition is a result of an azeotropic mixture rather than well-behaved critical phenomena. An example of the behavior of the critical point and the $P$-$x_2$ loop for an azeotropic mixture is shown in Figure 6. Therefore, the critical point of well-behaved and azeotropic binary mixtures can be determined by solving equations 64 and 67 simultaneosly.

Much of the complexity encountered by Joffe and Zudkevitch (38) in using the critical state relations developed by Redlich and Kister (73) can be avoided by using the simpler critical state relations of equations 64 and 67. In addition, these simpler critical state relations are well suited for numerical calculations on the digital computer.

## B. Ternary Mixture Theory

With the addition of each new chemical species to the mixture the thermodynamic criteria for the critical state becomes increasingly complex. This increased complexity is a result of the correspondingly increased complexity in representing the condition of diffusion stability in the mixture system. Prigogine and Defay (66) used the general conditions for equilibrium in terms of the temperature, pressure, and the chemical potentials for an unperturbed ternary system to derive the general criteria for diffusion stability in a ternary system:

$$u_{11} > 0 \qquad u_{22} > 0 \qquad u_{33} > 0 \tag{68}$$

$$u_{11}\, u_{22} - u_{12}^2 \geq 0 \qquad u_{11}\, u_{33} - u_{13}^2 \geq 0 \qquad u_{22}\, u_{33} - u_{23}^2 \geq 0 \tag{69}$$

$$\begin{vmatrix} u_{11} & u_{21} & u_{31} \\ u_{12} & u_{22} & u_{32} \\ u_{13} & u_{23} & u_{33} \end{vmatrix} \geq 0 \tag{70}$$

where

$$u_{ij} = \left(\frac{\partial u_i}{\partial n_j}\right) = \left(\frac{\partial u_j}{\partial n_i}\right) = u_{ji} \ . \tag{71}$$

Equations 68, 69, and 70 represent the necessary and sufficient conditions for diffusion stability in a ternary system. Prigogine and Defay show that the sufficient conditions can be expressed in a much simpler form:

$$u_{11} > 0 \tag{72}$$

$$u_{22} > 0 \tag{73}$$

$$u_{11}\, u_{22} - u_{12}^2 \geq 0 \ . \tag{74}$$

Thus, the diffusion stability boundary separating the stable and unstable states of the system is given by

$$u_{11}\, u_{22} - u_{12}^2 = 0 \ . \tag{75}$$

Gibbs (29) related the diffusion stability boundary to the critical point of ternary mixtures by pointing out that

$$\left(\frac{\partial \mu_2}{\partial n_2}\right)_{T,P,n_3,\mu_1} = \frac{u_{11}\, u_{22} - u_{12}^2}{u_{11}} \ . \tag{76}$$

The relationship between this partial derivative of the chemical potential and the critical point is best shown in Figure 7, a plot of the chemical potential of the second component versus the moles of that component at constant T, P, $n_3$, and $\mu_1$. The critical point occurs at the point of inflexion (66) and in this respect is similar to the behavior of both pure substances and binary mixtures. Thus, the critical state equations for a ternary mixture can be expressed as

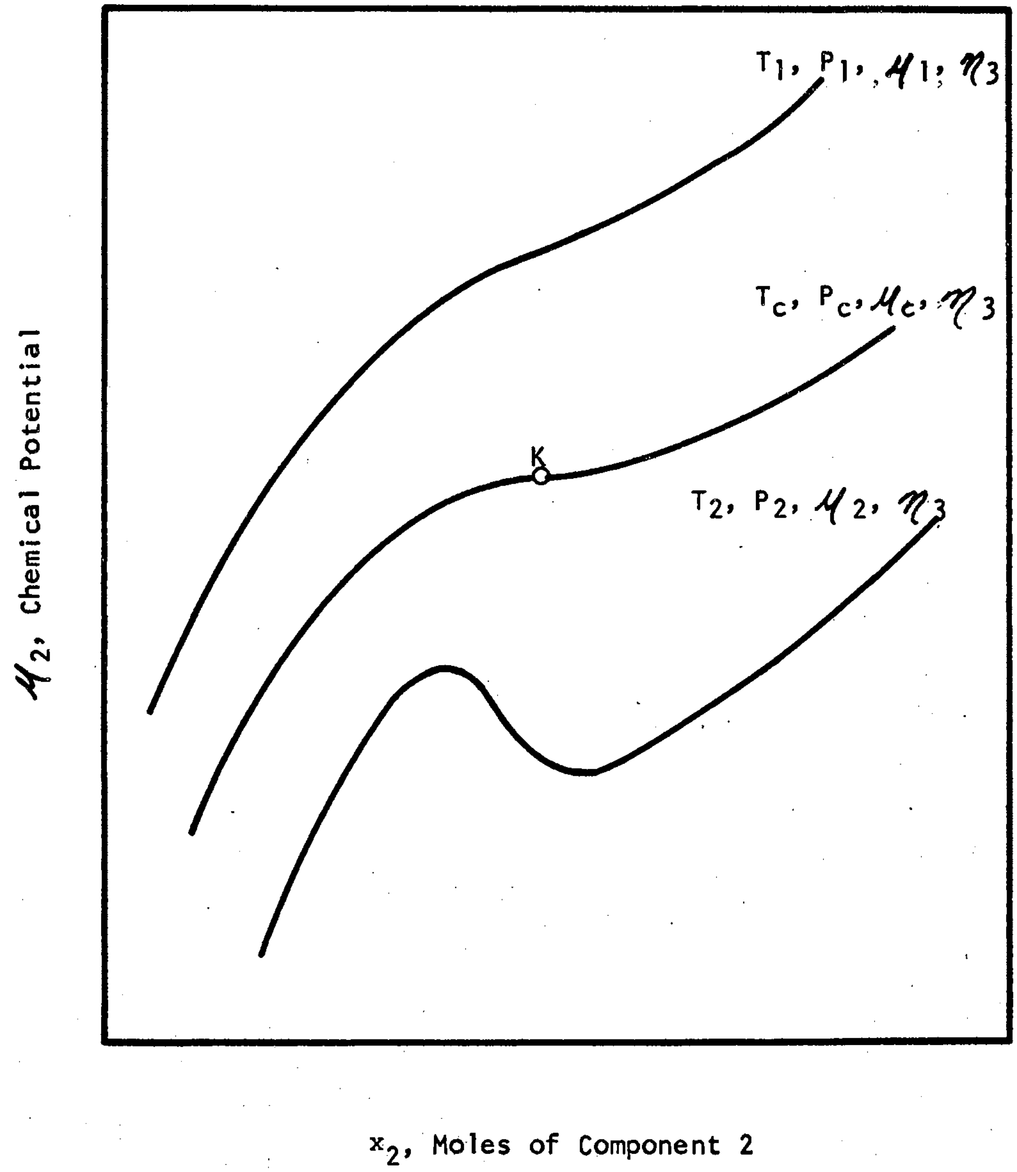

Figure 7. A Plot of the Chemical Potential of Component 2 Versus the Number of Moles of Component 2 at Constant T, P, $n_3$, and $\eta_1$ for a Ternary Mixture

$$\left(\frac{\partial \mu_2}{\partial n_2}\right)_{T,P,n_3,\mu_1} = 0 \tag{77}$$

$$\left(\frac{\partial^2 \mu_2}{\partial n_2^2}\right)_{T,P,n_3,\mu_1} = 0 \tag{78}$$

$$\left(\frac{\partial^3 \mu_2}{\partial n_2^3}\right)_{T,P,n_3,\mu_1} \neq 0 \quad . \tag{79}$$

These critical state equations are not in the most convenient form for practical manipulations. The first step in obtaining a critical state equation suitable for numerical calculations is to obtain an equivalent equation in terms of the chemical potential derivatives $\mu_{ij}$. By combining equation 76 and the critical state equation 77, the first critical state equation becomes

$$u_{11}\ u_{22} - u_{12}^2 = 0 \ . \tag{80}$$

The next step is to transform equation 80 into an even more useful critical state relation in terms of molal Gibbs free energy. This final transformation is presented in detail by Prigogine and Defay (66) and results in

$$\left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,x_3} - \left(\frac{\partial^2 G}{\partial x_2\, \partial x_3}\right)^2_{T,P} = 0 \tag{81}$$

Since equation 80 also defines the diffusion stability boundary, the critical point of ternary mixtures is on the diffusion stability boundary as was the case for binary mixtures.

The second of the critical state relations in terms of the chemical potential derivatives, equation 78, is transformed in a similar manner. The resulting critical state equations obtained from both these transformations can be summarized very concisely in the following determinant form suggested by Gibbs (29):

$$U = \begin{vmatrix} \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,x_3} & \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)_{T,P} \\ \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)_{T,P} & \left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} \end{vmatrix} = 0 \qquad (82)$$

$$M = \begin{vmatrix} \left(\frac{\partial U}{\partial x_2}\right)_{T,P,x_3} & \left(\frac{\partial U}{\partial x_3}\right)_{T,P,x_2} \\ \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)_{T,P} & \left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} \end{vmatrix} = 0 \qquad (83)$$

The critical state determinant M has been expressed in terms of the determinant U for convenience. By performing the indicated derivations the determinant M becomes

$$\begin{aligned} M = {} & \left(\frac{\partial^2 G}{\partial x_3^2}\right)^2_{T,P,x_2} \left(\frac{\partial^3 G}{\partial x_2^3}\right)_{T,P,x_3} - \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)_{T,P} * \\ & \left[ 3 \left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} \left(\frac{\partial^3 G}{\partial x_2^2\,\partial x_3}\right)_{T,P} + \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,x_3} \left(\frac{\partial^3 G}{\partial x_3^3}\right)_{T,P,x_2} \right] \\ & + \left(\frac{\partial^3 G}{\partial x_2\,\partial x_3^2}\right)_{T,P} \left[ \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,x_3} \left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} \right. \\ & \left. + 2 \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)^2_{T,P} \right] \end{aligned} \qquad (84)$$

All the terms in the critical state determinants U and M can be expressed in terms of the four independent variables T, P, $x_2$, and $x_3$. However, as was the case for binary mixtures, the critical state determinants U and M are better suited for calculations when written in terms of the molar Helmholtz free energy rather than the molal Gibbs free energy. This transforms the independent variables to T, V, $x_2$, and $x_3$ and eliminates the need for any trial and error procedure to determine the volume in a pressure explicit equation of state.

The various partial derivatives required in the critical state determinants U and M have been expressed in terms of the molar Helmholtz free energy and pressure using the thermodynamic relationship $\left(\frac{\partial A}{\partial V}\right)_{T,x_2} = -P$ and are presented below.

$$\left(\frac{\partial^3 G}{\partial x_2^3}\right)_{T,P,x_3} = \left(\frac{\partial^3 A}{\partial x_2^3}\right)_{T,V,x_3} + \frac{3\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial^2 P}{\partial x_2^2}\right)_{T,V,x_3}}{\frac{\partial P}{\partial V}\quad T,x_2,x_3}$$

$$- \frac{3\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial^2 P}{\partial x_2\,\partial V}\right)_{T,x_3}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$+ \frac{\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial^2 P}{\partial x_2\,\partial x_3}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)^3_{T,x_2,x_3}} \tag{85}$$

$$\left(\frac{\partial^3 G}{\partial x_2^2\,\partial x_3}\right)_{T,P} = \left(\frac{\partial^3 A}{\partial x_2^2\,\partial x_3}\right)_{T,V} + \frac{2\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial^2 P}{\partial x_2\,\partial x_3}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}}$$

$$+ \frac{\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2}\left(\frac{\partial^2 P}{\partial x_2^2}\right)_{T,V,x_3}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}}$$

$$- \frac{2 \left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3} \left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2} \left(\frac{\partial^2 P}{\partial x_2 \, \partial V}\right)_{T,x_3}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$- \frac{\left(\frac{\partial P}{\partial x_2}\right)^2_{T,V,x_3} \left(\frac{\partial^2 P}{\partial x_3 \, \partial V}\right)_{T,x_2}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$+ \frac{\left(\frac{\partial P}{\partial x_2}\right)^2_{T,V,x_3} \left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2} \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,x_2,x_3}}{\left(\frac{\partial P}{\partial V}\right)^3_{T,x_2,x_3}} \qquad (86)$$

$$\left(\frac{\partial^3 G}{\partial x_2 \, \partial x_3^2}\right)_{T,P} = \left(\frac{\partial^3 A}{\partial x_2 \, \partial x_3^2}\right)_{T,V} + \frac{\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3} \left(\frac{\partial^2 P}{\partial x_3^2}\right)_{T,V,x_2}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}}$$

$$+ \frac{2 \left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2} \left(\frac{\partial^2 P}{\partial x_2 \, \partial x_3}\right)_{T,V}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}}$$

$$- \frac{\left(\frac{\partial P}{\partial x_3}\right)^2_{T,V,x_2} \left(\frac{\partial^2 P}{\partial x_2 \, \partial V}\right)_{T,x_3}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$- \frac{2 \left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3} \left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2} \left(\frac{\partial^2 P}{\partial x_3 \partial V}\right)_{T,x_2}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$+\frac{\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2}\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,x_2,x_3}}{\left(\frac{\partial P}{\partial V}\right)^3_{T,x_2,x_3}} \tag{87}$$

$$\left(\frac{\partial^3 G}{\partial x_3^3}\right)_{T,P,x_2} = \left(\frac{\partial^3 A}{\partial x_3^3}\right)_{T,V,x_2} + \frac{3\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2}\left(\frac{\partial^2 P}{\partial x_3^2}\right)_{T,V,x_2}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}}$$

$$-\frac{3\left(\frac{\partial P}{\partial x_3}\right)^2_{T,V,x_2}\left(\frac{\partial^2 P}{\partial x_3\,\partial V}\right)_{T,x_2}}{\left(\frac{\partial P}{\partial V}\right)^2_{T,x_2,x_3}}$$

$$+\frac{\left(\frac{\partial P}{\partial x_3}\right)^3_{T,V,x_2}\left(\frac{\partial^2 P}{\partial x_3^2}\right)_{T,x_2,x_3}}{\left(\frac{\partial P}{\partial V}\right)^3_{T,x_2,x_3}} \tag{88}$$

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,x_3} = \left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V,x_3} + \frac{\left(\frac{\partial P}{\partial x_2}\right)^2_{T,V,x_3}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}} \tag{89}$$

$$\left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)_{T,P} = \left(\frac{\partial^2 A}{\partial x_2\,\partial x_3}\right)_{T,V} + \frac{\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3}\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}} \tag{90}$$

$$\left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,x_2} = \left(\frac{\partial^2 A}{\partial x_3^2}\right)_{T,V,x_2} + \frac{\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2}}{\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3}} \tag{91}$$

All derivatives of the molar Helmholtz free energy and pressure in equations 85 through 91 can be evaluated without difficulty from a pressure explicit equation of state and the corresponding equation defining the molar Helmholtz free energy for that equation of state.

The relative complexity of the critical state criteria for binary and ternary mixtures can be compared at this point. The two critical state determinants U and M for ternary mixtures require a total of sixteen derivatives, four third order, nine second order, and three first order, to calculate the critical point. The two critical state equations for binary mixtures require only four derivatives, one second order and three first order derivatives, to calculate the critical point. Thus, although each term in the critical state determinants U and M can be evaluated without difficulty, the expressions for the critical state relations are much more complex than the relations for binary mixtures.

## C. Multicomponent Mixture Theory

The general conditions for equilibrium can be used to derive the general criteria for the critical state of multicomponent mixtures in a manner completely analogous to the derivation presented for ternary mixtures. The result of this derivation for multicomponent mixtures, first presented by Gibbs (29), is two critical state determinants U and M. The general form of the determinants U and M are presented on the next page.

$$U = \begin{vmatrix} \left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P,X_j} & \left(\frac{\partial^2 G}{\partial x_2 \partial x_3}\right)_{T,P,X_j} & \cdots \\ \left(\frac{\partial^2 G}{\partial x_2 \partial x_3}\right)_{T,P,X_j} & \left(\frac{\partial^2 G}{\partial x_3^2}\right)_{T,P,X_j} & \cdots \\ \vdots & & \end{vmatrix} \qquad (92)$$

and M is equal to the determinant U with any row replaced by

$$\left(\frac{\partial U}{\partial x_2}\right)_{T,P,X_j} \quad \left(\frac{\partial U}{\partial x_3}\right)_{T,P,X_j} \quad \cdots$$

The subscript $X_j$ refers to all the remaining components of the mixture.

# CHAPTER IV

# EQUATIONS OF STATE

## A. "Suitable" Equations of State

The volumetric behavior of pure substances and mixtures can be determined by a number of different methods including charts of experimental data, graphical correlations, various modifications of the law of corresponding states, and equations of state. Since the critical state criteria can be expressed in terms of thermodynamic derivatives easily evaluated from an equation of state, equations of state are of particular importance in the quantitative prediction of the critical state.

The key to the accurate prediction of the critical state is finding a "suitable" equation of state. In general, there are three basic requirements which determine the suitability of an equation of state for critical state prediction. The first and by far the most important requirement is that the equation of state accurately describe the volumetric behavior of the vapor and liquid phases in the critical region. The second requirement to be considered is the difficulty in evaluating the critical state derivatives in terms of the equation of state. The third requirement is that the equation of state should be as simple as possible for the desired level of accuracy in the prediction of the volumetric behavior in the critical region. At the present time no truly suitable equation of state exists for the precise prediction of the critical state since no equation of state accurately describes the behavior of fluids in the critical region. Therefore, the selection of an equation of state to be used in these initial investigations of the prediction of critical states must come from considerations of the last two requirements.

Equations of state to be used in critical state studies can be chosen from a long list of available equations. Each equation of state differs in its accuracy, complexity, the amount of data required for the determination of its parameters, and in its general usefulness. The two equations of state finally selected for this investigation were developed by Redlich and Kwong and by Benedict, Webb, and Rubin.

## B. Redlich-Kwong Equation of State

The Redlich-Kwong equation of state (74) is a simple, two-parameter equation of state. The justification for its selection is a result of its simplicity, degree of approximation to actual P-V-T behavior, and general usefulness. Recent studies have shown that the Redlich-Kwong equation is the best two-parameter equation of state for the prediction of P-V-T behavior and derived thermodynamic properties. (2, 84, 93)

Redlich and Kwong proposed an equation of the form

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}\, V(V+b)} \quad . \tag{93}$$

The two parameters a and b for pure components are evaluated from the critical properties in the following relations derived to satisfy the thermodynamic criteria of the critical point:

$$a = 0.4278\ R^2T_c^{2.5} / P_c \tag{94}$$

$$b = 0.0867\ RT_c / P_c \quad . \tag{95}$$

The equation of state may be extended to mixtures by using appropriate mixing rules. The mixing rules proposed by Redlich and Kwong for binary mixtures were

$$a = a_1x_1^2 + 2a_{12}x_1x_2 + a_2x_2^2 \tag{96}$$

$$b = b_1x_1 + b_2x_2 \tag{97}$$

where $a_{12}$ is a binary interaction coefficient and is related to the pure component parameters by

$$a_{12} = \sqrt{a_1a_2} \quad . \tag{98}$$

Several modifications of the binary interaction mixing rules have been suggested. The mixing rules selected for this investigation were presented by Joffe and Zudkevitch (37) who showed that substantial improvement in the representation of the fugacity of gas mixtures could be obtained by using the mixing rules:

$$a = a_1x_1^2 + 2a_{12}x_1x_2 + a_2x_2^2 \tag{99}$$

$$b = b_1x_1^2 + 2b_{12}x_1x_2 + b_2x_2^2 \tag{100}$$

where $a_{12}$ and $b_{12}$ are related to the pure component parameters by

$$a_{12} = \theta \sqrt{a_1a_2} \tag{101}$$

$$b_{12} = \emptyset \sqrt{b_1b_2} \tag{102}$$

and $\theta$ and $\emptyset$ are treated as empirical parameters. The original mixing rules of Redlich and Kwong can be obtained by setting $\theta = 1$ and

$\phi = (b_1 + b_2)/(2\ b_1 b_2)$.

The principal disadvantage encountered in using the Redlich-Kwong equation of state in critical state predictions is that the predicted vapor and liquid volumes can show large deviations from experimental data, particularly at the critical point. The basic Redlich-Kwong equation and the definition of the parameters a and b require the pure component critical compressibility $Z_c$ to equal 0.333 for all substances. However, most substances of interest have a critical compressibility ranging from 0.23 to 0.30. Therefore, accurate critical volume predictions for mixtures should not be expected from the critical state calculations using the Redlich-Kwong equation of state.

## C. Benedict-Webb-Rubin Equation of State

The Benedict-Webb-Rubin equation of state (4) is an eight-parameter equation developed to accurately predict the phase behavior of pure substances and mixtures. The primary justification for its selection is a result of its accuracy in predicting the P-V-T behavior, the critical properties, and vapor pressure of pure light hydrocarbons. In addition, the B-W-R equation has been shown to accurately predict vapor-liquid equilibrium for several light hydrocarbon mixtures. (7)

The Benedict-Webb-Rubin equation of state is a pressure explicit equation of the form

$$P = \frac{RT}{V} + \frac{1}{V^2}(B_oRT - A_o - \frac{C_o}{T^2}) + \frac{1}{V^3}(bRT - a) + \frac{a\alpha}{V^6}$$

$$+ \frac{c(1 + \gamma/V^2)}{T^2V^2} \ \exp\ (-\gamma/V^2) \ . \qquad (103)$$

The eight coefficients of the equation were evaluated from experimental data for several light hydrocarbons (5) to accurately describe the volumetric behavior in the gas phase down to the critical region and at the bubble point.

The B-W-R equation of state may be extended to mixtures by using the following mixing rules (6):

$$A_o = \left[ \sum_{i=1}^{N} x_i \, (A_{o_i})^{\frac{1}{2}} \right]^2 \qquad (104)$$

$$B_o = \left[ \sum_{i=1}^{N} x_i \, (B_{o_i}) \right] \qquad (105)$$

$$C_o = \left[ \sum_{i=1}^{N} x_i \, (C_{o_i})^{\frac{1}{2}} \right]^2 \qquad (106)$$

$$\gamma = \left[ \sum_{i=1}^{N} x_i \, (\gamma_i)^{\frac{1}{2}} \right]^2 \qquad (107)$$

$$a = \left[ \sum_{i=1}^{N} x_i \, (a_i)^{1/3} \right]^3 \qquad (108)$$

$$b = \left[ \sum_{i=1}^{N} x_i \, (b_i)^{1/3} \right]^3 \qquad (109)$$

$$c = \left[ \sum_{i=1}^{N} x_i \, (c_i)^{1/3} \right]^3 \qquad (110)$$

$$\alpha = \left[ \sum_{i=1}^{N} x_i \, (\alpha_i)^{1/3} \right]^3 . \qquad (111)$$

Empirical interaction parameters can be introduced into the binary interaction mixing rules of the B-W-R equation. The three empirical parameters used in this investigation were defined by

$$A_{o_{12}} = \eta_1 \sqrt{A_{o_1} A_{o_2}} \qquad (112)$$

$$c_{o_{12}} = \eta_3 \sqrt{c_{o_1} c_{o_2}} \quad (113)$$

$$\gamma_{12} = \eta_4 \sqrt{\gamma_1 \gamma_2} . \quad (114)$$

The original mixing rules suggested by Benedict, Webb, and Rubin are obtained by setting $\eta_1 = \eta_3 = \eta_4 = 1$. In general, the B-W-R equation can accurately predict volumetric behavior of the mixture at temperatures and densities up to the critical temperature and density of the mixture. As a result, the B-W-R equation is superior to the simple, two-parameter Redlich-Kwong equation, particularly in the accurate representation of density.

The values of the coefficients for the B-W-R equation of state were obtained from considerations of the critical properties of the pure components. However, unlike the Redlich-Kwong equation of state, calculations of the critical point of pure substances were not required, in general, to give the exact pure component critical properties. The deviations in the critical properties predicted by the B-W-R equation are small but significant, as indicated in Table I. (61)

The principal limitation of the B-W-R equation of state in general calculations is that the volumetric behavior of the vapor and liquid phases and the vapor pressure of a pure substance cannot be described with equal accuracy. Parameters evaluated to accurately describe the liquid phase behavior do not accurately describe the vapor phase behavior and vice versa. The primary disadvantages of the B-W-R equation in critical state calculation of mixtures are the complexity of the derived critical state equations and the limited availability of coefficients for more than a few light hydrocarbon substances.

## TABLE I

### Deviation in Critical Properties Predicted by the B-W-R Equation of State (61)

| System | Deviations in Critical Properties | | |
|---|---|---|---|
| | Temperature (Deg F) | Pressure (psia) | Specific Weight (lb-mol/cu ft) |
| Methane | -0.54 | -22.0 | 0.0037 |
| Ethane | -0.45 | - 2.5 | 0.0037 |
| Propane | -0.29 | - 6.2 | 0 |
| n-Butane | -0.11 | - 0.7 | 0.0081 |
| n-Pentane | -2.88 | +12.1 | 0.0212 |
| n-Hexane | -0.72 | - 6.2 | 0.0106 |
| n-Heptane | -1.49 | - 2.9 | 0.0187 |
| Ethene | -0.54 | -10.3 | -0.0125 |
| Propene | -1.26 | -10.3 | -0.0281 |

# CHAPTER V

# BINARY MIXTURE CRITICAL STATE PREDICTIONS

## A. Critical State Search Procedure

The critical state criteria for binary and ternary mixtures were established from considerations of the diffusion stability requirements. Two equations of state, the simple Redlich-Kwong equation and the more complex Benedict-Webb-Rubin equation, were selected as suitable equations of state to describe the volumetric behavior of the mixtures. The major problem and purpose of this initial investigation of the equation of state approach to the prediction of the critical state was to integrate the rigorous thermodynamic criteria with an equation of state in some numerical search procedure.

The basic critical relations defining the critical point of binary mixtures,

$$\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{T,P} = 0 \qquad (115)$$

$$\left(\frac{\partial^3 G}{\partial x_2^3}\right)_{T,P} = 0 \qquad (116)$$

were transformed into two equivalent but more convenient critical relations better suited for practical calculations:

$$\left(\frac{\partial P}{\partial V}\right)_{T,x_2} \left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V} + \left(\frac{\partial P}{\partial x_2}\right)^2_{T,V} = 0 \tag{117}$$

$$\left(\frac{\partial P}{\partial x_2}\right)_{T,\sigma} = 0 \quad . \tag{118}$$

The critical state conditions have been written in terms of the independent variables T, V, and $x_2$. The isothermal restrictions on the two critical state relations suggested that the critical temperature be specified and the critical state equations, 117 and 118, be used in a search procedure to predict the critical volume and composition. The critical pressure was then determined by substituting the critical temperature, volume, and composition into the equation of state.

If only well-behaved binary mixtures are considered, equation 118 defines the critical point as the point of maximum pressure on both the two-phase equilibrium boundary and diffusion stability boundary. Therefore, the basis of the numerical search procedure for binary mixtures was to find the maximum pressure point on the isothermal diffusion stability boundary defined by equation 117. The two-phase equilibrium boundary need not be considered. Since the diffusion stability boundary can be calculated from an equation of state much more easily than the two-phase equilibrium boundary, the elimination of possible equilibrium calculations was a distinct advantage of this search procedure.

The general behavior of binary mixtures and the search procedure used to locate the critical point can best be illustrated on the isothermal volume-composition diagram of Figure 8. The critical point K is the maximum pressure point on both the diffusion stability boundary, curve AKB, and the two-phase equilibrium boundary, curve DKE.

A systematic search procedure to determine the maximum pressure could be conducted along either branch AK or BK of the diffusion stability boundary. However, Rowlinson (77) pointed out that the critical point lies on the upper half of the diffusion stability boundary, curve AM, only for azeotropic mixtures. For these mixtures a minimum in the pressure on the diffusion stability boundary occurs at the critical point. Thus, for well-behaved binary mixtures the search procedure need only be concerned with the lower half of the diffusion stability boundary, curve BKM.

The search procedure adopted for the calculation of the critical point was a simple four-step iterative procedure. The procedure began with the specification of the critical temperature and estimation of the critical composition. The specification of the critical temperature presented no problem since, in general, the critical temperatures of a mixture lie between the two pure component critical temperatures. Likewise, the initial estimate of the critical composition presented no problem. In most cases the critical temperature-mole fraction relationship of the mixture is approximated by

$$T_{c_m} = x_1 \, T_{c_1} + x_2 \, T_{c_2} \tag{119}$$

By rearranging this equation an initial estimate of the critical composition was obtained:

$$x_2^{(o)} = \frac{T_{c_m} - T_{c_1}}{T_{c_2} - T_{c_1}} \tag{120}$$

The calculation path of the iterative search procedure is described in detail below and can be visualized for a typical binary mixture in Figure 8. A systematic search using the initial estimate of the critical composition, $x_2^{(0)}$, was made for the molar volume which lies on the diffusion stability boundary defined by equation 117. At molar volumes less than the volume on the stability boundary, a condition which corresponds to a stable state, the stability equation is positive and approaches zero as the volume approaches the stability boundary. In the unstable region where the molar volumes are greater than the volume on the stability boundary, the stability equation is negative. When the volume on the stability boundary was found, $V^{(o)}$, the pressure was calculated from the equation of state and stored for future comparisons.

The initial composition estimate then was incremented by an arbitrary composition interval to provide a second trail value of the critical composition, $x_2^{(1)}$. A search for the molar volume on the stability boundary at this new composition estimate was carried out and the pressure at that point was calculated. The calculated pressures of the two iterations were compared and the composition was again incremented in the direction of increasing pressure. This procedure was repeated as many times as necessary until either one of two conditions arose: 1) the estimate for the critical composition was too high for any value of the molar volume to satisfy the diffusion stability boundary equation as is the case for $x_2^{(2)}$, or 2) the calculated pressure on the stability boundary was less than for the previous iteration, as is the case for $x_2^{(3)}$. If either of these two conditions were encountered, an upper limit on the composition was set and the search was confined to a smaller composition interval. For the example in Figure 8, the composition interval for the fourth iteration was between $x_2^{(1)}$ and $x_2^{(3)}$. The search procedure was continued within the smaller and smaller intervals, always in the direction of increasing pressure, until the interval becomes arbitrarily small. At this point the maximum pressure on the diffusion stability boundary and therefore, the critical

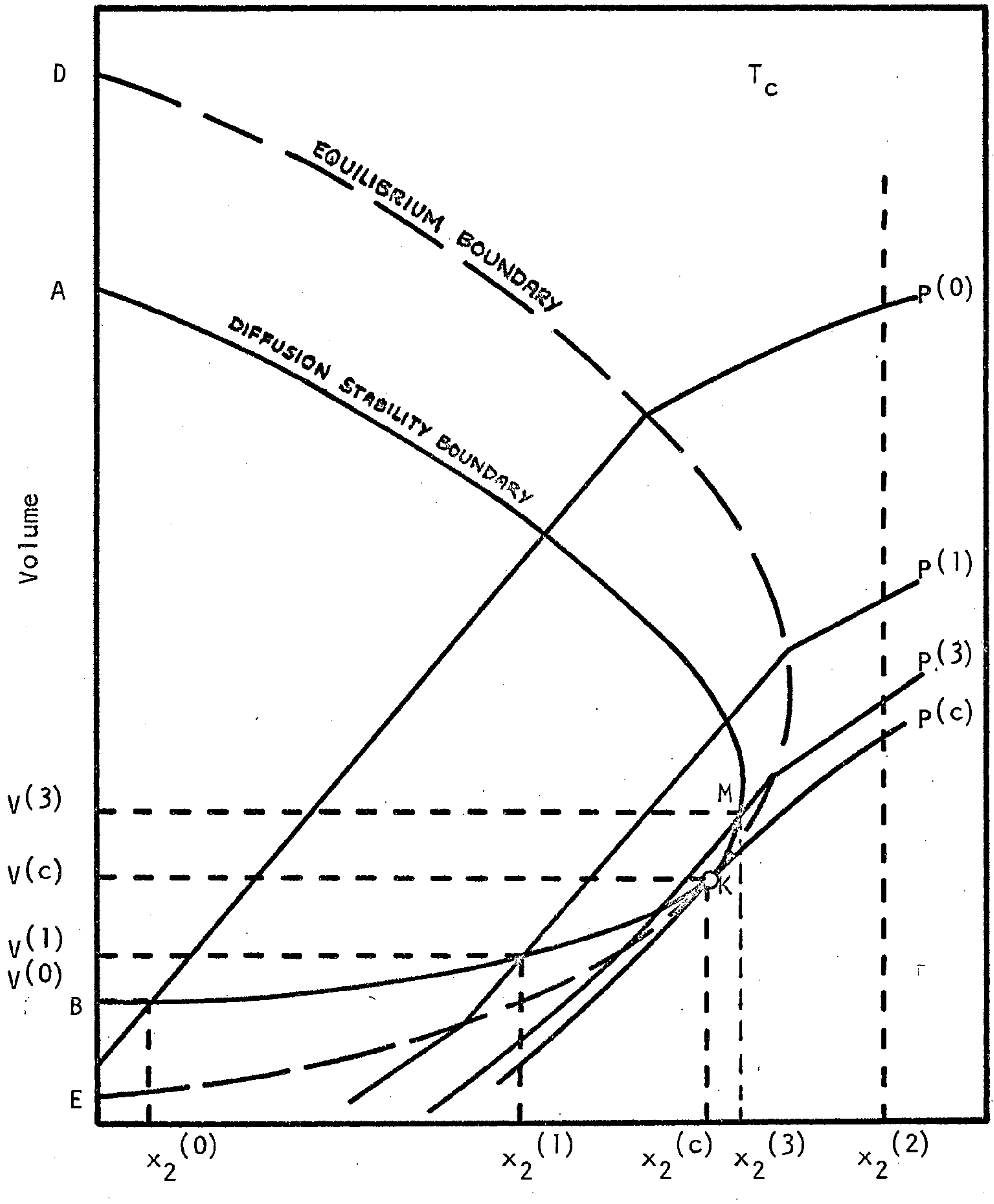

Figure 8. Isothermal Volume-Composition Diagram for a Binary Mixture

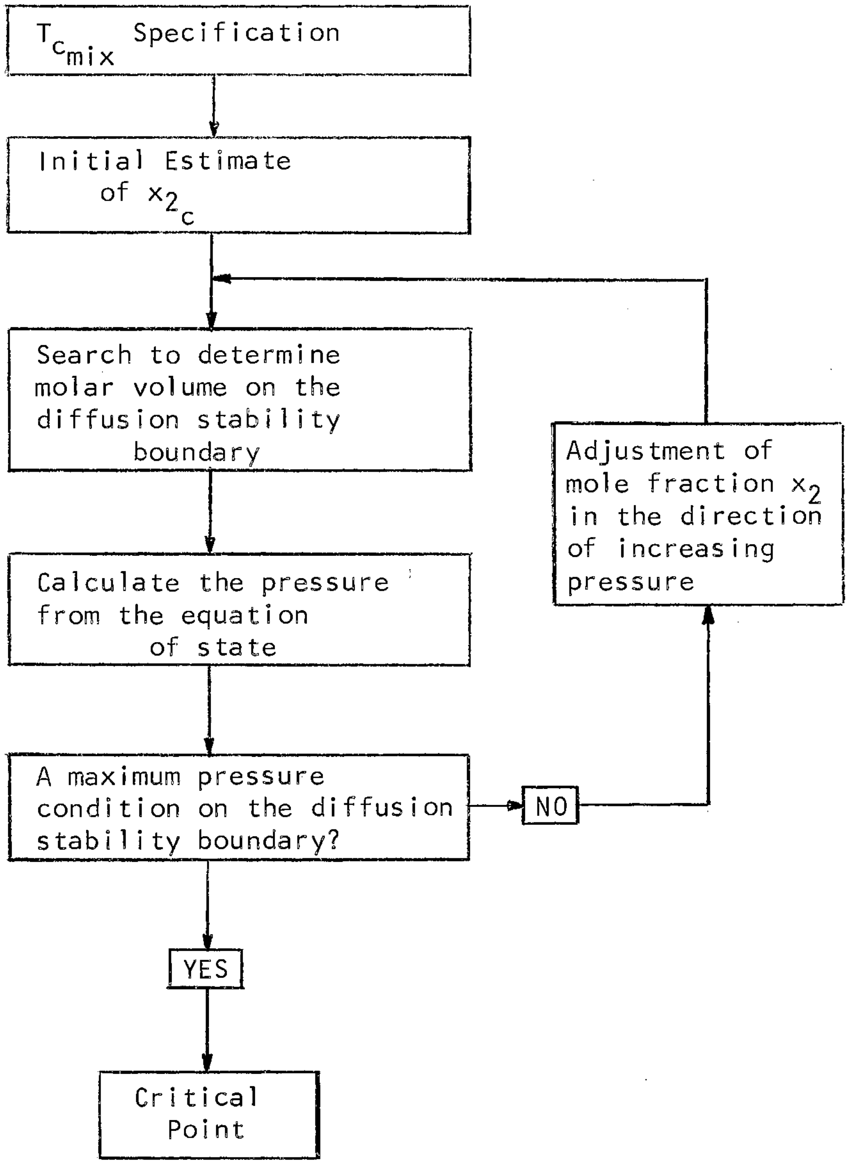

Figure 9. Critical State Search Procedure for Binary Mixtures

point for the specified critical temperature has been established.

The general computational logic for this search procedure is presented in the block diagram of Figure 9. This search procedure was developed for well-behaved binary mixtures and does not converge to the correct critical point for azeotropic mixtures. However, the critical state criteria is general so that a corresponding search procedure for azeotropic mixtures could be developed in a manner similar to the present procedure for well-behaved mixtures.

### B. Computer Program for Critical State Calculations

The critical state calculations must be carried out on a digital computer because of the complexity of the critical state equations and the calculations required by the iterative search procedure. The computer program developed for the prediction of the critical state of binary mixtures, designated by the name CRITCALC, was written for use on the Oklahoma State University Computing Center's IBM 7040 digital computer in FORTRAN IV. Because of the exploratory nature of these calculations, several special features were incorporated into the computer program. The first and most significant feature was the modular form of the program. The calculation was broken down into basic sub-calculations with specific and independent functions. Data input and output, evaluation of the critical state equations, and the search procedure were written as independent subroutines of the program. This was possible since the search procedure is independent of the equation of state. Likewise, the critical state equations are independent of the search procedure and depend only on the equation of state. This modular form also facilitates debugging and makes the program very versatile by allowing major changes, such as the substitution of the critical state relations evaluated in terms of a new equation of state, to be made without disturbing the over-all program.

The second special feature was the variable print-out facilities built into the program. An output control variable was used to specify whether the program was to print out the final results, an outline of the calculation path of the search procedure, or a detailed description of the calculation. This feature allowed individual sections or the entire calculation to be investigated in detail and with ease.

The third special feature was the inclusion of calculation safeguards and provisions for error messages. Each iterative sub-calculation and all convergence procedures were limited to insure convergence or to terminate the calculation should the calculation begin diverging. If the calculation did not converge and was terminated, appropriate error messages were printed out and the program automatically printed out a detailed description of the calculation up to the point of divergence.

A complete description of the computer program CRITCALC, the required input data and its format, and the control parameters for the operation of the program are presented in Appendix A.

### C. Application of the Redlich-Kwong Equation of State in Critical State Predictions

The Redlich-Kwong equation was the first equation of state to be used to test the equation of state approach to the prediction of the critical state. The simplicity of the Redlich-Kwong equation and the three partial derivatives defining the diffusion stability boundary in terms of the Redlich-Kwong equation were the primary reasons for its selection as a suitable equation of state.

The first step in the critical state calculations was to express the equation for the diffusion stability boundary in terms of the Redlich-Kwong equation of state and its parameters. The three partial derivatives required to numerically evaluate the diffusion stability equation are derived from the Redlich-Kwong equation defined by equation 93, the pure component parameters a and b, equations 94 and 95, the binary mixing rules, equation 99 and 100, and the two binary interaction parameters defined by equations 101 and 102. The resulting partial derivatives are presented below.

$$\left(\frac{\partial P}{\partial x_2}\right)_{T,V} = \frac{RTb'}{(V-b)^2} + \frac{1}{T^{\frac{1}{2}}V(V+b)}\left[\frac{a'b}{(V+b)} - a'\right] \tag{121}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,x_2} = \frac{a(2V+b)}{T^{\frac{1}{2}}V^2(V+b)^2} - \frac{RT}{(V-b)^2} \tag{122}$$

$$\frac{\left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V}}{RT} = \frac{(b')^2}{(V-b)^2} + \frac{b''}{(V-b)} - \frac{\ln\,(1+b/V)}{bRT^{1.5}}\left[a'' - \frac{2a'b'}{b} + \frac{2a(b')^2}{b} - \frac{ab''}{b}\right] - \frac{1}{bRT^{1.5}(V+b)}\left[ab'' + 2a'b' - \frac{2a(b')^2}{(V+b)}\right] + \frac{1}{x_1\,x_2} \tag{123}$$

where

$$a' = \left(\frac{da}{dx_2}\right) = 2x_2(a_2 - 2a_{12} + a_1) + 2(a_{12} - a_1) \tag{124}$$

$$b' = \left(\frac{db}{dx_2}\right) = 2x\ (b_2 - 2b_{12} + b_1) + 2(b_{12} - b_1) \tag{125}$$

$$a'' = \left(\frac{d^2a}{dx_2^2}\right) = 2\ (a_2 - 2a_{12} + a_1) \tag{126}$$

$$b'' = \left(\frac{d^2b}{dx_2^2}\right) = 2\ (b_2 - 2b_{12} + b_1)\ . \tag{127}$$

Equations 121, 122, and 124 through 127 were derived directly from the Redlich-Kwong equation and its binary mixing rules. Equation 123 was derived from the expression for the molar Helmholtz free energy in terms of the Redlich-Kwong equation of state (74) for a binary mixture:

$$\frac{A}{RT} = \ln \frac{RT}{V-b} - \frac{a}{bRT} \ln (1 + b/V) - 1 + x_1 \ln x_1 + x_2 \ln x_2 \ , \qquad (128)$$

Although the three partial derivatives in the diffusion stability boundary equation are of relatively simple form, extreme care was taken during this and all other critical state derivations to avoid minor errors such as missing terms and incorrect signs which usually plague simple but extended derivations of this nature. As an additional check on the accuracy of the derivations, values of the derived partial derivatives of the critical state relations were compared with the corresponding values obtained by numerical differentiation for that same derivative. The derived partial derivatives were assumed to be correct when the difference between the analytically and numerically obtained values was negligible.

The partial derivatives defining the diffusion stability boundary were programmed in the critical state equation subroutine of the CRITCALC computer program. The CRITCALC program was run, debugged, and tested to insure the search procedure was converging correctly. A sample calculation for the ethane-propane binary system is shown in the isothermal volume-composition diagram of Figure 10. Curve AKB is the diffusion stability boundary predicted by the Redlich-Kwong equation of state. The points on the lower half of the stability boundary and the critical point were calculated using the CRITCALC program. The points along the upper half of the stability boundary were calculated for test purposes only and do not represent the normal path of the automatic search procedure. The critical point predicted by the CRITCALC procedure, point K, is the maximum pressure on the stability boundary and thus, satisfies the thermodynamic criteria of the critical point.

Another test was made to determine the validity of the transformed critical state criteria and search procedure. If the second critical state relation were not transformed to the pressure extremum condition on the stability boundary, the more complicated second critical state relation, equation 65, would have to have been used to predict the critical point. Equation 65 was evaluated in terms of the Redlich-Kwong equation of state and is plotted in Figure 10 as curve DK. The critical point predicted by the simultaneous solution of the two basic critical state relations, i.e. the intersection of curves BK and DK, agreed with that obtained from the simpler maximum pressure condition used in the CRITCALC program. The results of this test indicated that the CRITCALC program was working correctly and could be applied to a variety of binary systems.

In order to test the equation of state approach, its applicability, accuracy, and limitations, critical state calculations using the Redlich-Kwong equation of state in the CRITCALC program were performed for a wide variety of mixtures. The mixtures used in this investigation were carefully selected from an extensive list of seventy-seven experimentally investigated binary systems summarized by Sutton. (86) The selected systems include a large cross-section of systems, including binaries containing carbon monoxide, carbon dioxide, hydrogen sulfide, and nitrogen, and make up four general classes of binary systems of interest in most engineering applications.

Critical temperatures of the mixtures were specified in the

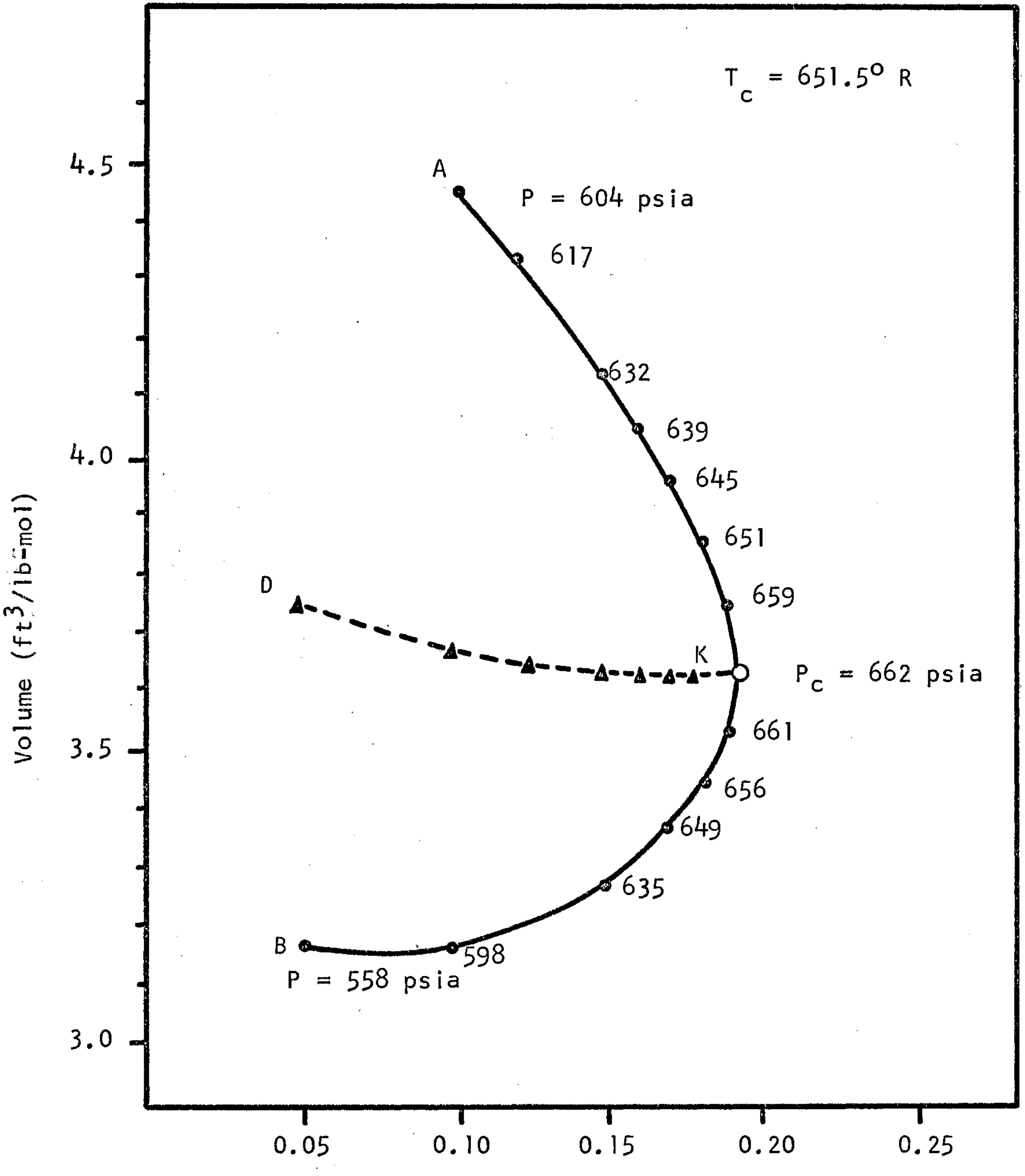

Figure 10. Isothermal Volume-Composition Diagram for the Ethane-Propane Mixture

CRITCALC program which then automatically determined the corresponding critical pressure, volume, and composition. To insure a uniform comparison of the results of a number of binary systems, five critical temperatures, approximately equally spaced between the two pure component critical temperatures, were specified for each binary system. This technique for selecting the critical temperatures to be specified provided critical points over the entire composition range as well, since in general, the critical temperature-mole fraction relationship is nearly linear. In the few cases where experimental data did not cover the entire composition range, such as in some methane systems, the critical state calculations were restricted to the critical temperature range of the experimental data.

## D. Results of Critical State Predictions Using the Redlich-Kwong Equation

The critical state calculations using the Redlich-Kwong equation of state were carried out for each binary system both with and without empirical adjustment of the binary interaction parameters $\theta$ and $\phi$. The general behavior of the calculated and experimental critical properties for several typical binary systems are presented in Figures 11-33. In general, qualitative results were obtained for the critical properties. A detailed comparison and discussion of the behavior of each of the calculated critical properties with respect to the corresponding experimental observations are presented in the following sections.

The variation of the calculated critical temperature with composition agreed both quantitatively and qualitatively with experimental data. Errors in the prediction of the critical temperature, as indicated in Figures 16-20, were in the neighborhood of one per cent. In almost every case the calculated critical temperature was greater than the experimental value at a given composition of the binary mixture. These observations agreed with the results obtained by Joffe and Zudkevitch (38) using the more complex, but equivalent, critical state equations developed by Redlich and Kister. (73)

The quantitative agreement between the calculated and experimental volumes was rather poor as shown in Figures 31-33. In general, consistently high deviations of 10 to 30 per cent were observed. However, these large deviations in the critical volume were expected since the Redlich-Kwong equation of state is known to fail to reproduce the critical density of pure substances. Nevertheless, the calculated critical volume-composition relationships are encouraging in showing that the predicted critical volumes of binary mixtures are no less accurate than those for pure substances. This observation indicates that an equation of state used in critical state calculations must correctly predict pure component critical volumes if accurate mixture critical volumes are to be obtained.

The critical pressure proved to be the most difficult of the critical properties to predict accurately. In general, qualitative, but not necessarily quantitative, agreement was obtained using the Redlich-Kwong equation. Figures 21-30 show the typical calculated and experimental critical pressure-composition behavior. The average error in the calculated critical pressure for the four general classes of binaries ranged from 0.3 to 18.5 per cent with an over-all average error of 5.2 per cent. A complete summary of the average and maximum errors for each binary system appears in Table II. As Figures 21-30 indicate, the calculated critical pressures generally were less than the experimental values at a given mixture composition.

A comparison of the accuracy of the predicted critical properties indicates that the $P_c$-$T_c$ relationships are predicted with greater accuracy than the $P_c$-$x_2$ or $T_c$-$x_2$ relationships. This result suggests that the mixing rules used with the Redlich-Kwong equation of state do not lead to accurate predictions of mixture behavior. Thus, improvements in existing mixing rules or the creation of completely new mixing rules may further increase the accuracy of the critical state predictions using the R-K equation of state.

The largest deviations in the prediction of the critical state properties occurred in the hydrocarbon/non-hydrocarbon class that includes the methane/hydrogen sulfide and ethene/carbon dioxide binaries and in the non-hydrocarbon/non-hydrocarbon class that includes the carbon dioxide/sulphur dioxide and methyl chloride/carbon dioxide binaries. Large deviations were not totally unexpected since the difference between the molecular species tends to be greatest for these two classes of mixtures. Empirical adjustments of the binary interaction parameters of the R-K equation seemed to be indicated for these latter systems.

The influence of the values of both binary interaction parameters on the accuracy of the prediction of the critical properties was investigated. Adjustment of $\phi$, the interaction parameter associated with the constant b of the Redlich-Kwong equation of state, had virtually no effect on the critical state calculations. Adjustment of $\theta$, the interaction parameter associated with the constant a, was observed to significantly improve the prediction of the critical properties, especially the critical pressure. Figure 34 shows the effect of the value of θ on the critical pressure-composition relationship for a typical binary mixture. A decrease in the value of θ from 1.0 corresponded to an increase in the critical pressure at a specified temperature and composition for most binary systems.

The optimum value of the interaction parameter θ giving the best representation of the critical pressure-composition relationship was determined for each binary mixture. The criterion selected for the best representation requirement was defined as the minimum in the sum of the squared deviations of the calculated minus the experimental critical pressure at a specified composition. In order to calculate these deviations the experimental critical pressure-mole fraction curves were required. Sutton (86) provided the necessary relationship in a very accurate three-parameter correlation of experimental data. The correlation,

$$P = x_1^2 + x_2^2 + x_1 x_2 \Big/ \left[ A + B(x_1 - x_2) + C(x_1 - x_2)^2 \right] \qquad (124)$$

was obtained by curve fitting the experimental critical pressure-mole fraction data of 77 binary systems. The CRITCALC computer program incorporated this correlation to calculate the deviations in the predicted critical pressure at the composition calculated by the program at the specified critical temperature.

Values of the optimum binary interaction parameter θ ranged from 1.095 to 0.775. A summary and comparison of the average and maximum errors in the critical pressure using the Redlich-Kwong equation with θ = 1.0 and with the optimum values of θ appear in Table II. The average error in the critical pressure was reduced from 5.2 per cent for θ = 1.0 to 3.2 per cent using the optimum values of θ. The errors in the critical state predictions for the non-hydrocarbon/non-hydrocarbon class of mixtures were surprisingly low even without the use of an optimum θ. Use of the optimum values of θ reduced the errors in the prediction of the critical properties to a level comparable to all other classes of mixtures. These two results indicated that critical state calculations using the Redlich-Kwong equation of state are capable of predicting the critical properties of all classes of binary mixtures with nearly equal accuracy if the optimum values of θ are used.

Use of the optimum θ designed to improve the critical pressure representations also improved the representations of the critical temperature and volume, but to a much smaller degree. The nature and extent of these improvements can be seen in Figures 11-33.

The optimum values of θ and accuracy of the critical state predictions for each class of mixture seemed to be dependent on the difference between the two pure component molecules. Figures 35 and 36, plots of the optimum values of θ and the average error in critical pressure versus the ratio of the molecular weights of the pure components, show the trend for the paraffin/paraffin class of mixtures. In general, the greater the difference between the pure components, the greater the optimum value of θ deviated from 1.0 and the greater the average error in the prediction of the critical pressure. No attempt was made to correlate the optimum value of θ with the ratio of the molecular weights because of the excessive scatter in the data points, particularly in the region where the correlation would be most useful.

## TABLE II

## COMPARISON OF CALCULATED AND EXPERIMENTAL CRITICAL PRESSURE AT SPECIFIED CRITICAL TEMPERATURES USING THE REDLICH-KWONG EQUATION OF STATE

| Binary System | R-K Eqn with $\theta = 1$ | | R-K Eqn with the Optimum $\theta$ | | | References |
|---|---|---|---|---|---|---|
| | Average Error (%) | Maximum Error (%) | Optimum $\theta$ ($\pm 0.005$) | Average Error (%) | Maximum Error (%) | |
| I. SYSTEMS OF PARAFFIN/PARAFFIN MIXTURES | | | | | | |
| Methane/Ethane | 2.0 | 4.4 | 0.948 | 1.5 | 3.0 | 10 |
| Methane/Propane | 5.1 | 9.2 | 0.939 | 1.9 | 3.5 | 67 |
| Methane/n-Butane | 11.0 | 17.2 | 0.911 | 6.8 | 11.7 | 81 |
| Methane/n-Pentane | 9.0 | 16.1 | 0.964 | 8.3 | 14.8 | 82 |
| Methane/n-Heptane | 18.5 | 26.1 | 0.939 | 17.3 | 23.0 | 70 |
| Ethane/Propane | 1.8 | 2.4 | 1.036 | 1.3 | 2.5 | 52 |
| Ethane/n-Butane | 1.5 | 2.5 | 0.973 | 1.2 | 2.0 | 18 |
| Ethane/n-Pentane | 5.4 | 10.5 | 0.875 | 3.8 | 5.6 | 71 |
| Ethane/n-Heptane | 7.9 | 12.2 | 0.875 | 3.5 | 6.6 | 42 |
| Propane/n-Butane | 1.9 | 2.8 | 1.050 | 1.3 | 2.0 | 58 |
| Propane/i-Pentane | 4.3 | 6.4 | 1.050 | 2.6 | 6.8 | 86 |
| Propane/n-Pentane | 1.5 | 3.5 | 1.005 | 1.2 | 3.6 | 83 |
| Propane/n-Hexane | 1.6 | 2.9 | 0.975 | 1.6 | 2.6 | 86 |
| Propane/n-Heptane | 3.2 | 7.1 | 0.962 | 3.2 | 5.8 | 86 |
| Propane/n-Octane | 3.7 | 9.2 | 0.970 | 4.4 | 7.2 | 86 |
| n-Butane/n-Pentane | 0.3 | 0.5 | 0.983 | 0.2 | 0.4 | 86 |
| n-Butane/n-Heptane | 1.9 | 3.4 | 1.020 | 1.8 | 3.4 | 43 |
| n-Butane/n-Octane | 2.4 | 4.3 | 0.992 | 2.3 | 4.1 | 86 |
| Averages | 4.6 | 7.8 | | 3.5 | 6.0 | |

TABLE II - Continued

| Binary System | R-K Eqn with θ = 1 | | R-K Eqn with the Optimum θ | | | References |
|---|---|---|---|---|---|---|
| | Average Error ( % ) | Maximum Error ( % ) | Optimum θ ($\pm$0.005) | Average Error ( % ) | Maximum Error ( % ) | |
| II. SYSTEMS OF PARAFFIN/NON-PARAFFIN MIXTURES | | | | | | |
| Ethane/Propene | 0.5 | 0.8 | 1.000 | 0.5 | 0.8 | 51 |
| Ethane/Benzene | 7.4 | 11.6 | 0.898 | 3.2 | 5.1 | 46 |
| Ethane/Cyclohexane | 9.1 | 13.8 | 0.867 | 3.9 | 7.2 | 45 |
| Propane/Benzene | 3.9 | 5.8 | 0.927 | 2.0 | 3.5 | 30 |
| n-Butane/Ethene | 4.6 | 10.1 | 0.911 | 2.9 | 7.3 | 86 |
| n-Hexane/Toluene | 3.3 | 4.8 | 1.086 | 1.3 | 2.1 | 90 |
| n-Heptane/Ethene | 10.5 | 15.3 | 0.898 | 5.3 | 12.0 | 44 |
| Ethene/Propene | 4.0 | 5.4 | 0.948 | 3.3 | 4.4 | 35 |
| Averages | 5.4 | 8.5 | | 2.8 | 5.3 | |
| III. SYSTEMS OF HYDROCARBON/NON-HYDROCARBON MIXTURES | | | | | | |
| Methane/Nitrogen | 2.1 | 4.9 | 0.961 | 1.8 | 3.0 | 13 |
| Methane/CO | 2.0 | 3.6 | 0.952 | 0.4 | 0.5 | 88 |
| Methane/$CO_2$ | 8.2 | 9.2 | 0.864 | 4.1 | 12.1 | 19 |
| Methane/$H_2S$ | 12.9 | 19.7 | 0.873 | 1.9 | 7.8 | 68 |
| Ethane/$H_2S$ | 2.8 | 5.6 | 0.889 | 1.2 | 2.5 | 47 |
| Propane/CO | 13.1 | 30.0 | 1.095 | 10.9 | 16.6 | 91 |
| Propane/$CO_2$ | 3.4 | 8.4 | 1.055 | 3.0 | 4.4 | 69 |

TABLE II - Continued

| Binary System | R-K Eqn with θ = 1 | | R-K Eqn with the Optimum θ | | | References |
|---|---|---|---|---|---|---|
| | Average Error ( % ) | Maximum Error ( % ) | Optimum θ ($\pm$0.005) | Average Error ( % ) | Maximum Error ( % ) | |
| III. - continued | | | | | | |
| n-Butane/$CO_2$ | 9.7 | 12.8 | 0.775 | 2.8 | 4.6 | 59 |
| n-Pentane/$CO_2$ | 11.0 | 18.1 | 0.783 | 5.4 | 11.5 | 65 |
| Ethene/$CO_2$ | 2.7 | 3.2 | 0.845 | 0.7 | 1.1 | 86 |
| Dimethyl Ether/$CO_2$ | 4.7 | 11.6 | 0.948 | 4.4 | 10.9 | 92 |
| Averages | 6.6 | 11.6 | | 3.3 | 6.8 | |
| IV. SYSTEMS OF NON-HYDROCARBON MIXTURES | | | | | | |
| $CO_2$/$SO_2$ | 1.9 | 3.6 | 0.967 | 1.7 | 2.4 | 12 |
| $CO_2$/$H_2S$ | 3.5 | 6.7 | 0.875 | 1.7 | 2.8 | 8 |
| HCl/Kr | 6.0 | 8.5 | 0.848 | 4.8 | 12.6 | 31 |
| Methyl Chloride/$CO_2$ | 4.2 | 6.6 | 0.889 | 0.2 | 0.4 | 12 |
| Averages | 3.9 | 6.3 | | 2.1 | 4.5 | |
| TOTAL AVERAGES (41 systems) | 5.2 | 8.8 | | 3.2 | 5.9 | |

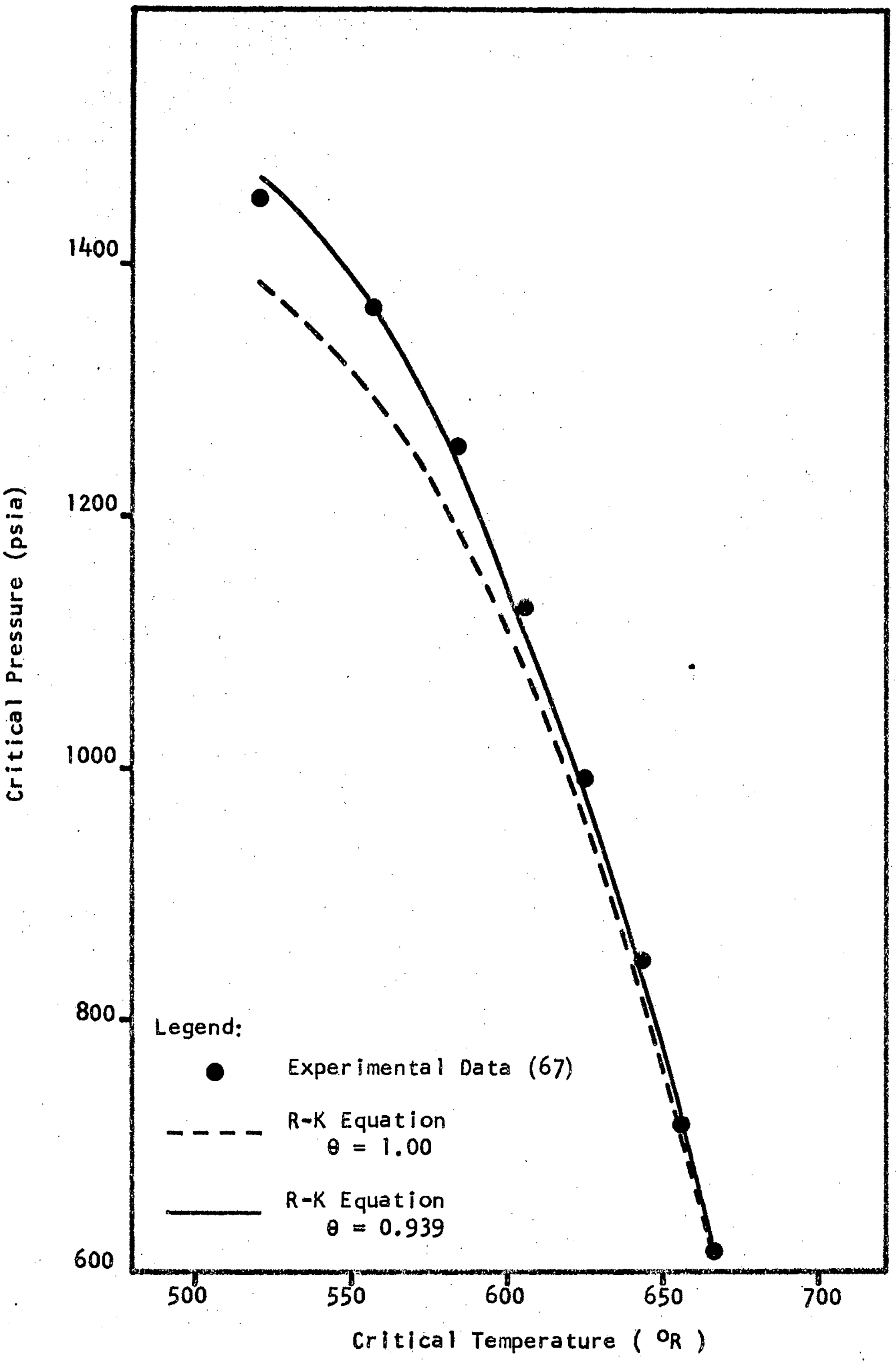

Figure 11. Critical Pressure-Critical Temperature Diagram for the Methane/Propane System

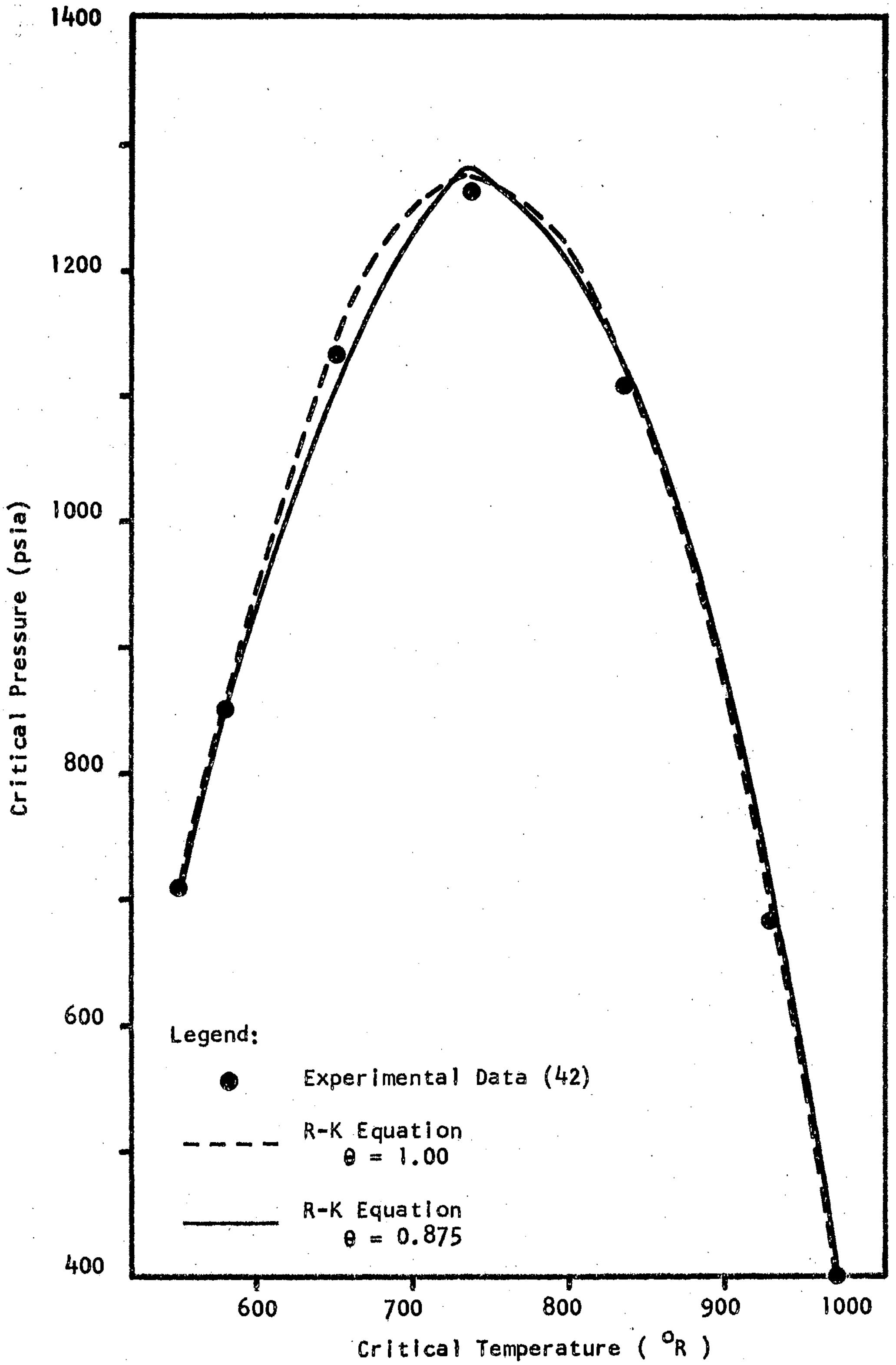

Figure 12. Critical Pressure-Critical Temperature Diagram for the Ethane/n-Heptane System

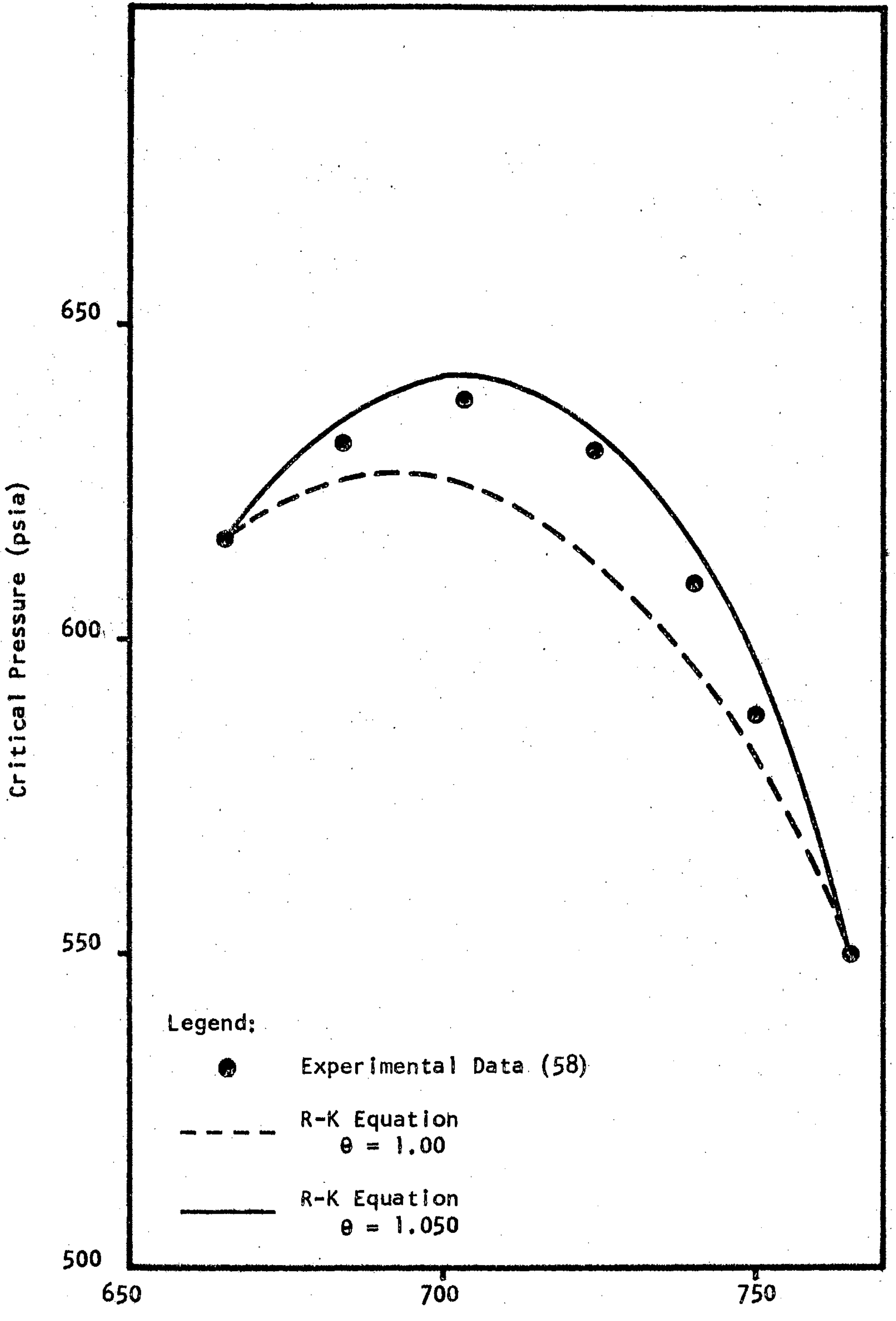

Figure 13. Critical Pressure-Critical Temperature Diagram for the Propane/n-Butane System

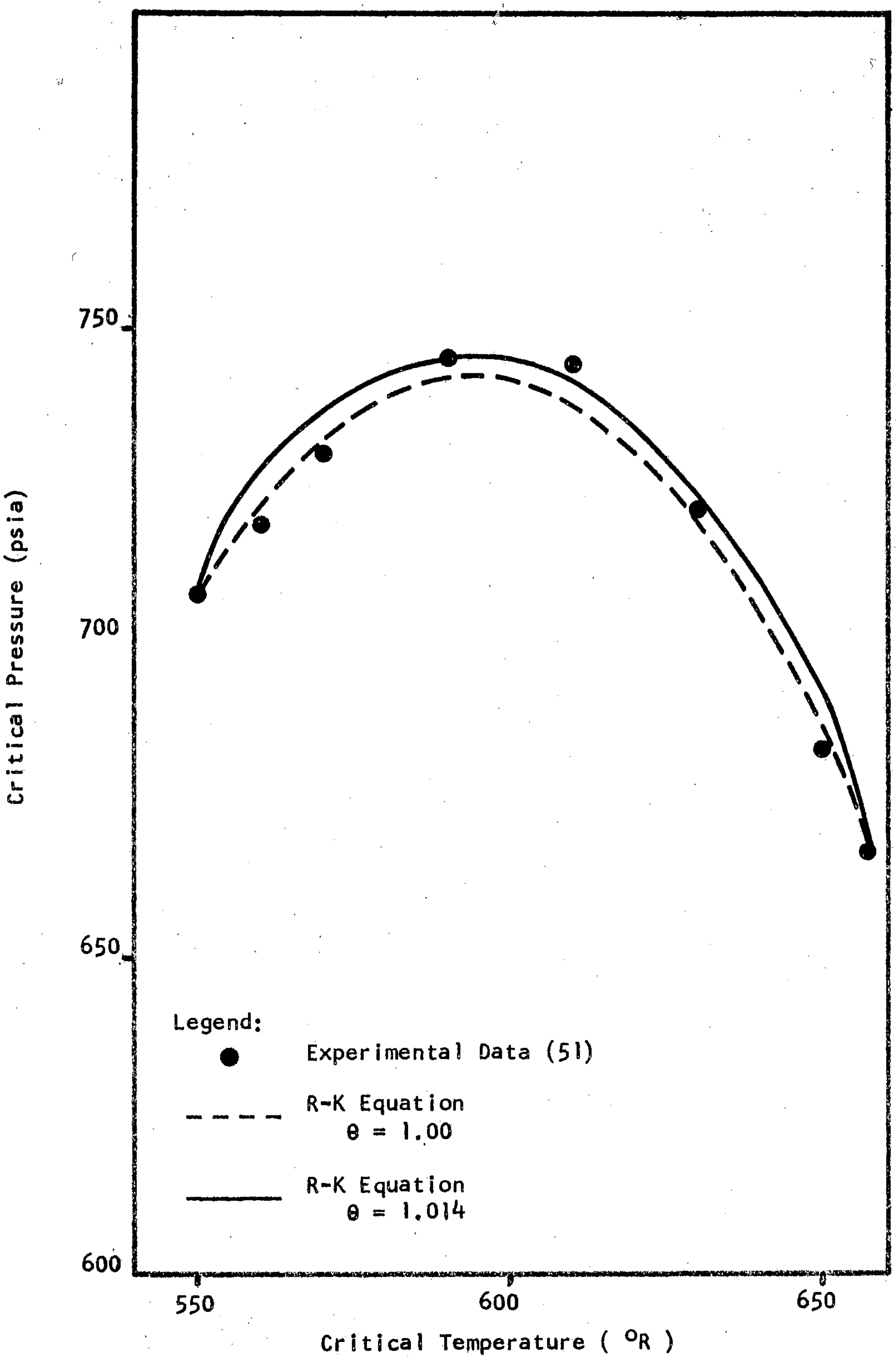

Figure 14. Critical Pressure-Critical Temperature Diagram for the Ethane/Propene System

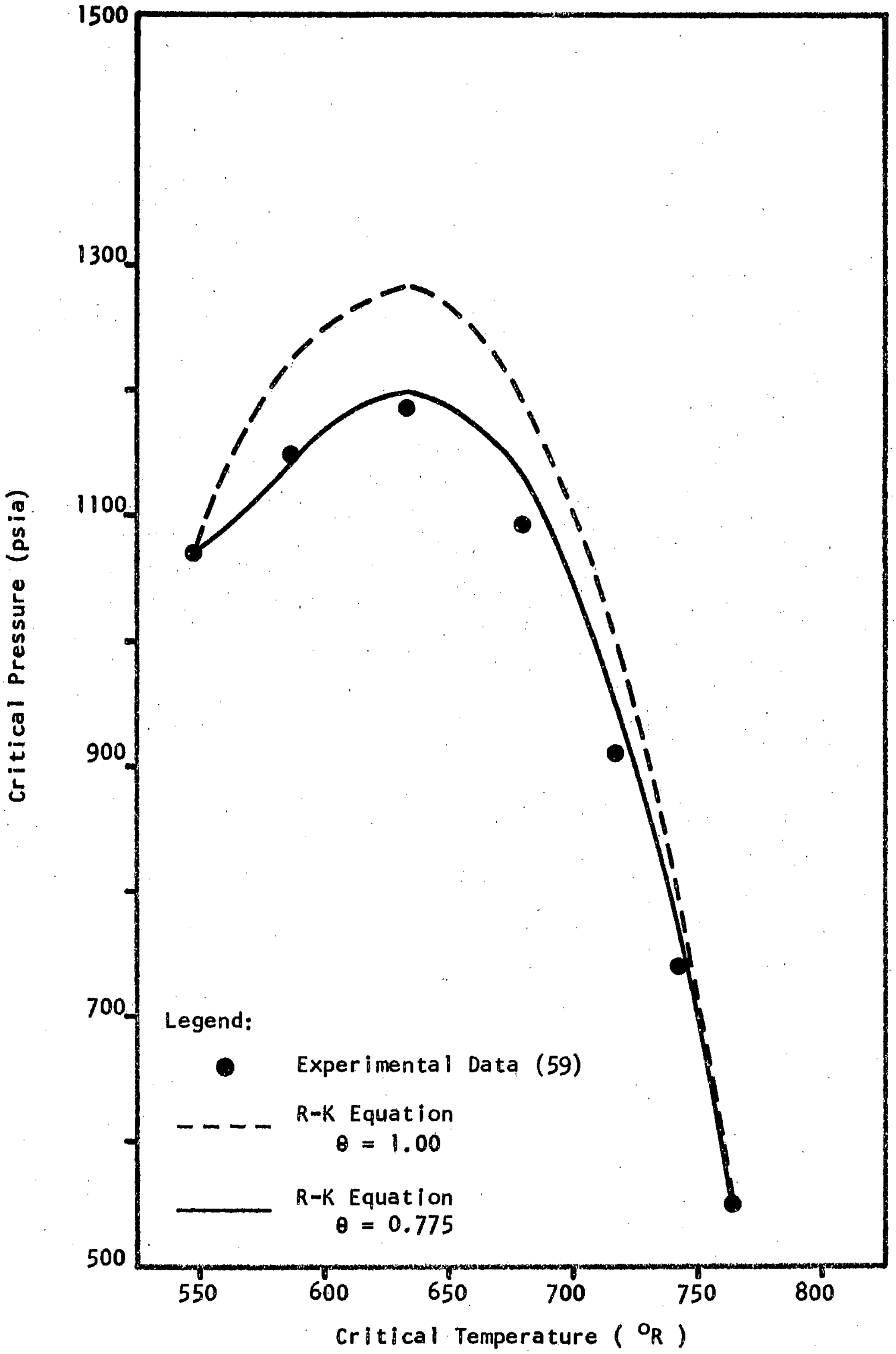

Figure 15. Critical Pressure-Critical Temperature Diagram for the n-Butane/Carbon Dioxide System

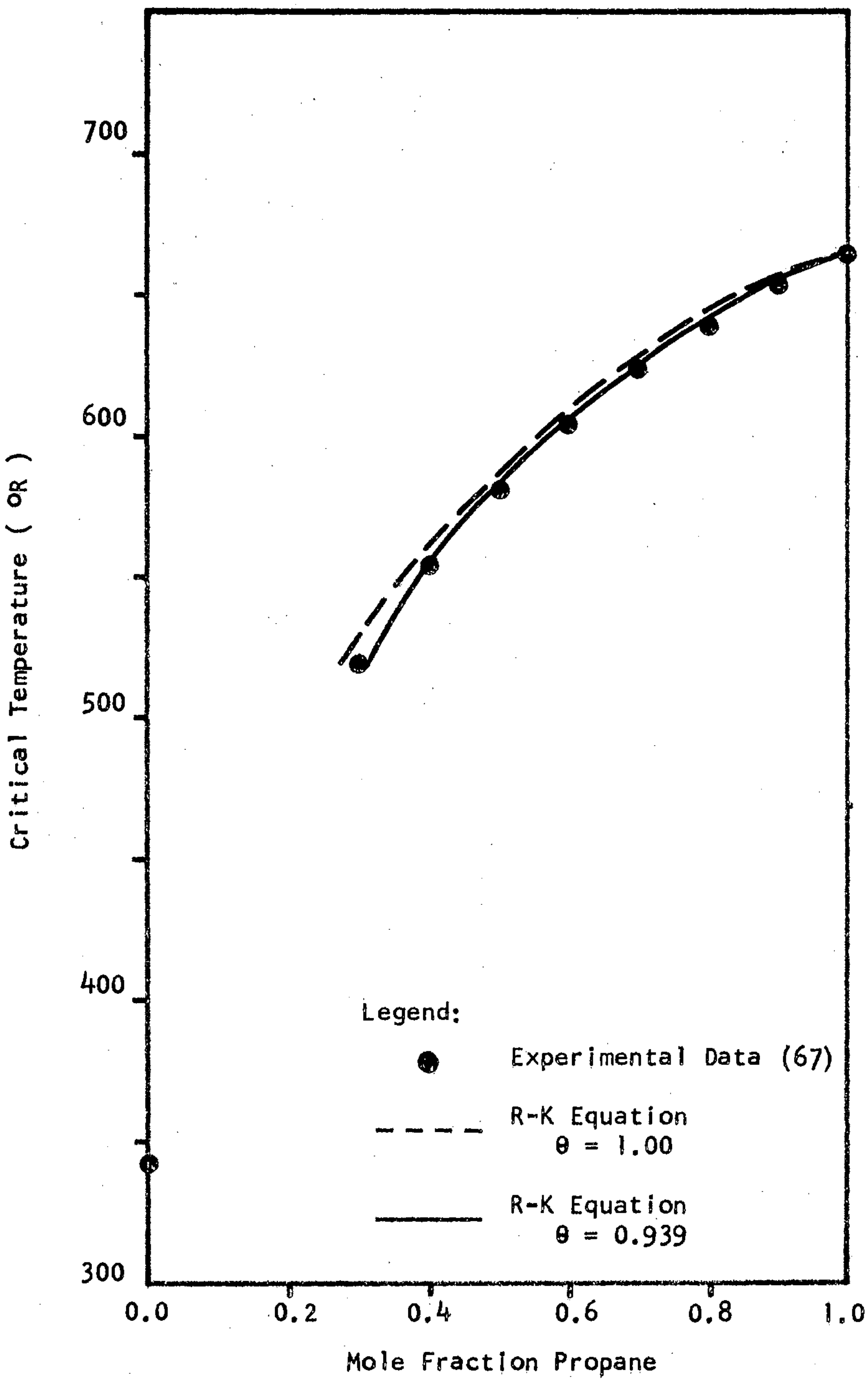

Figure 16. Critical Temperature-Composition Diagram for the Methane/Propane System

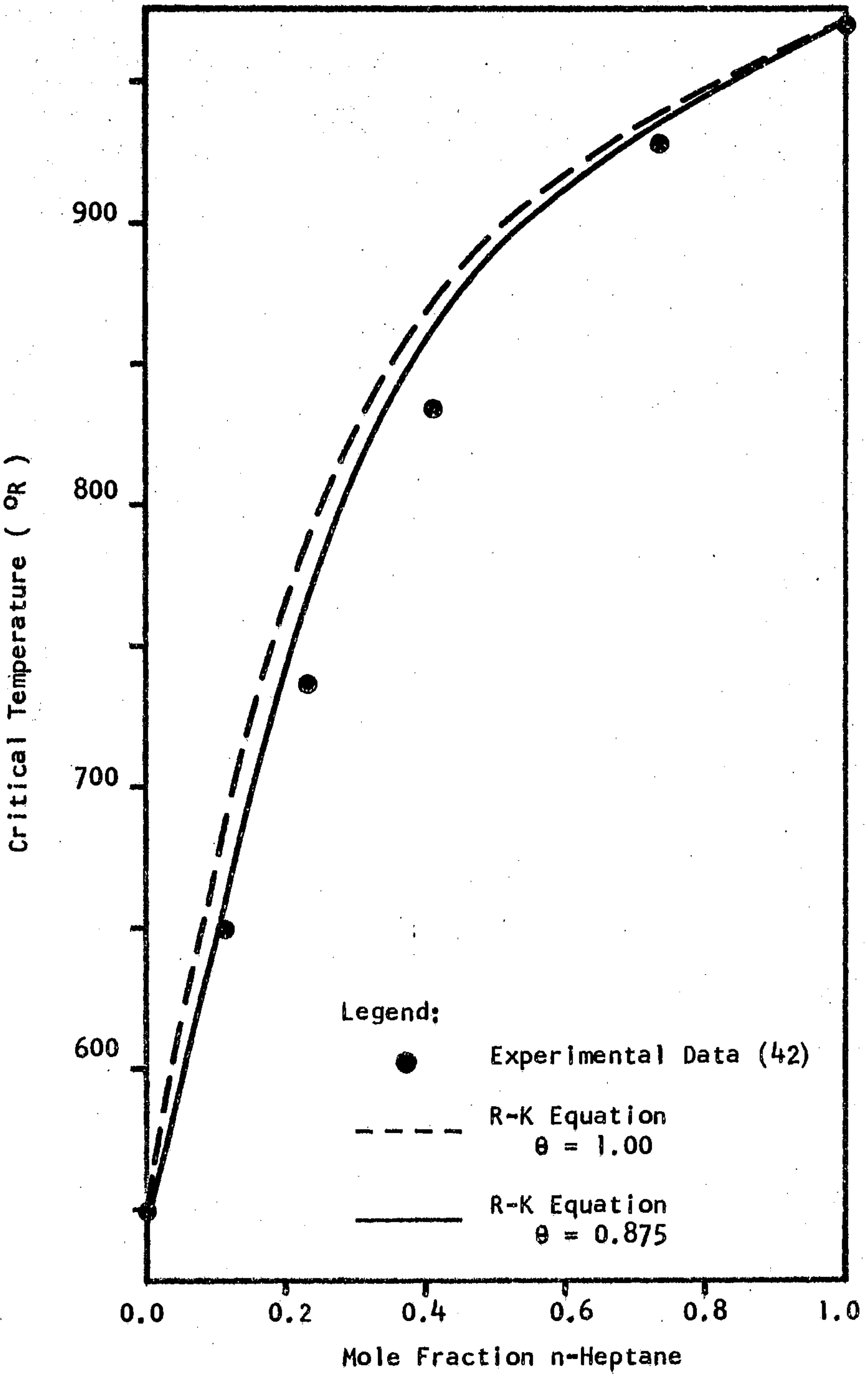

Figure 17. Critical Temperature-Composition Diagram for the Ethane/n-Heptane System

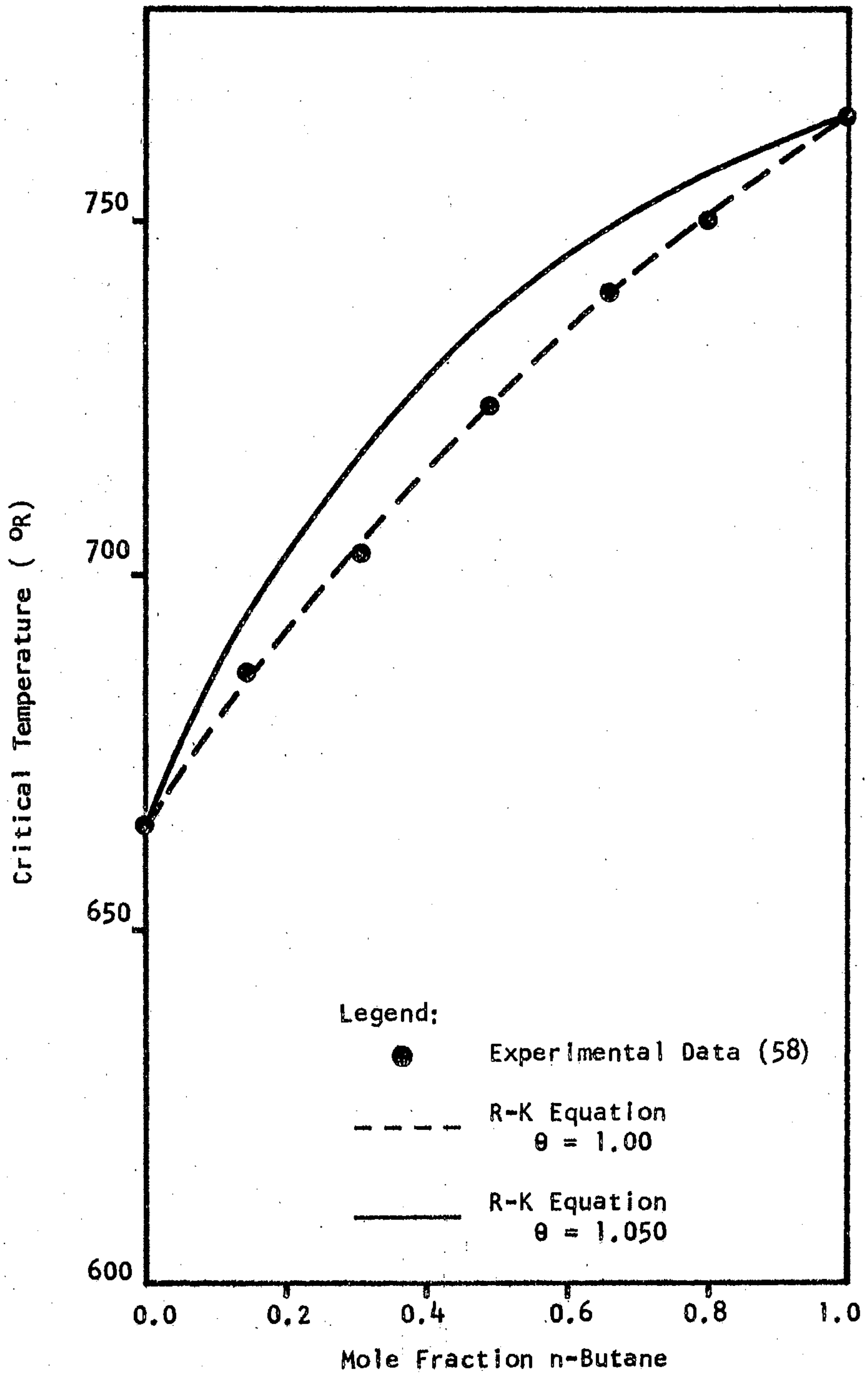

Figure 18. Critical Temperature-Composition Diagram for the Propane/n-Butane System

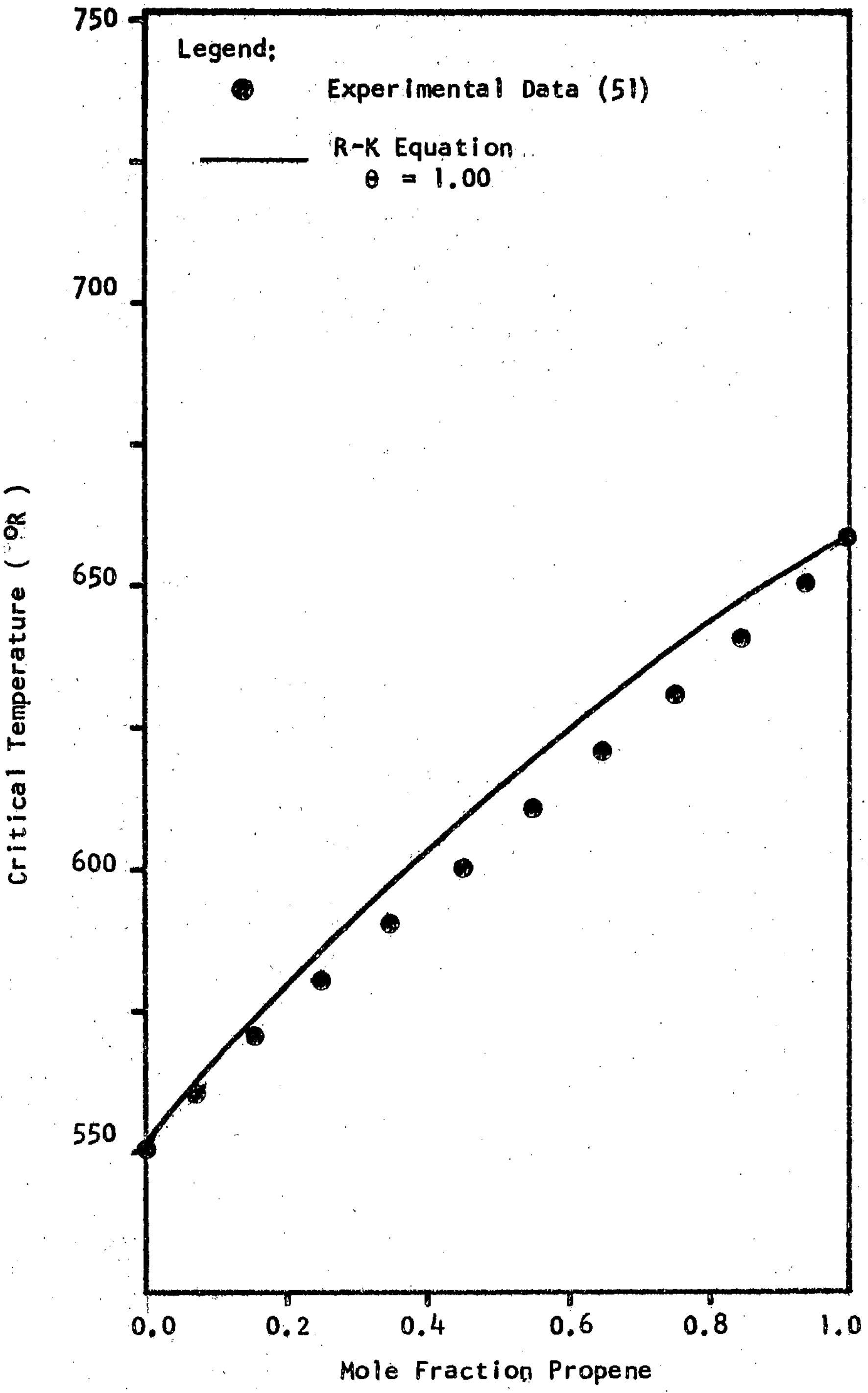

Figure 19. Critical Temperature-Composition Diagram for the Ethane/Propene System

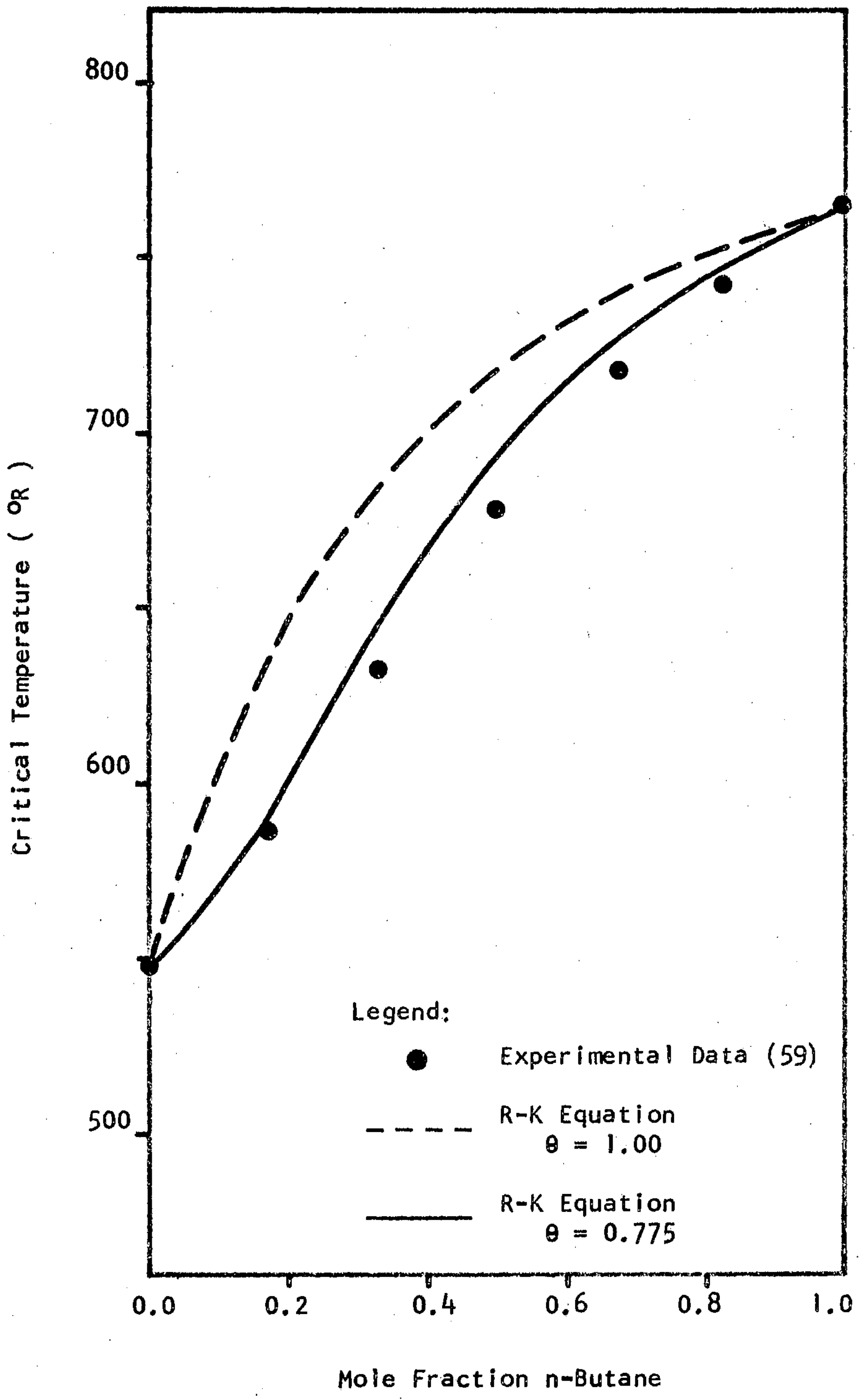

Figure 20. Critical Temperature-Composition Diagram for the n-Butane/Carbon Dioxide System

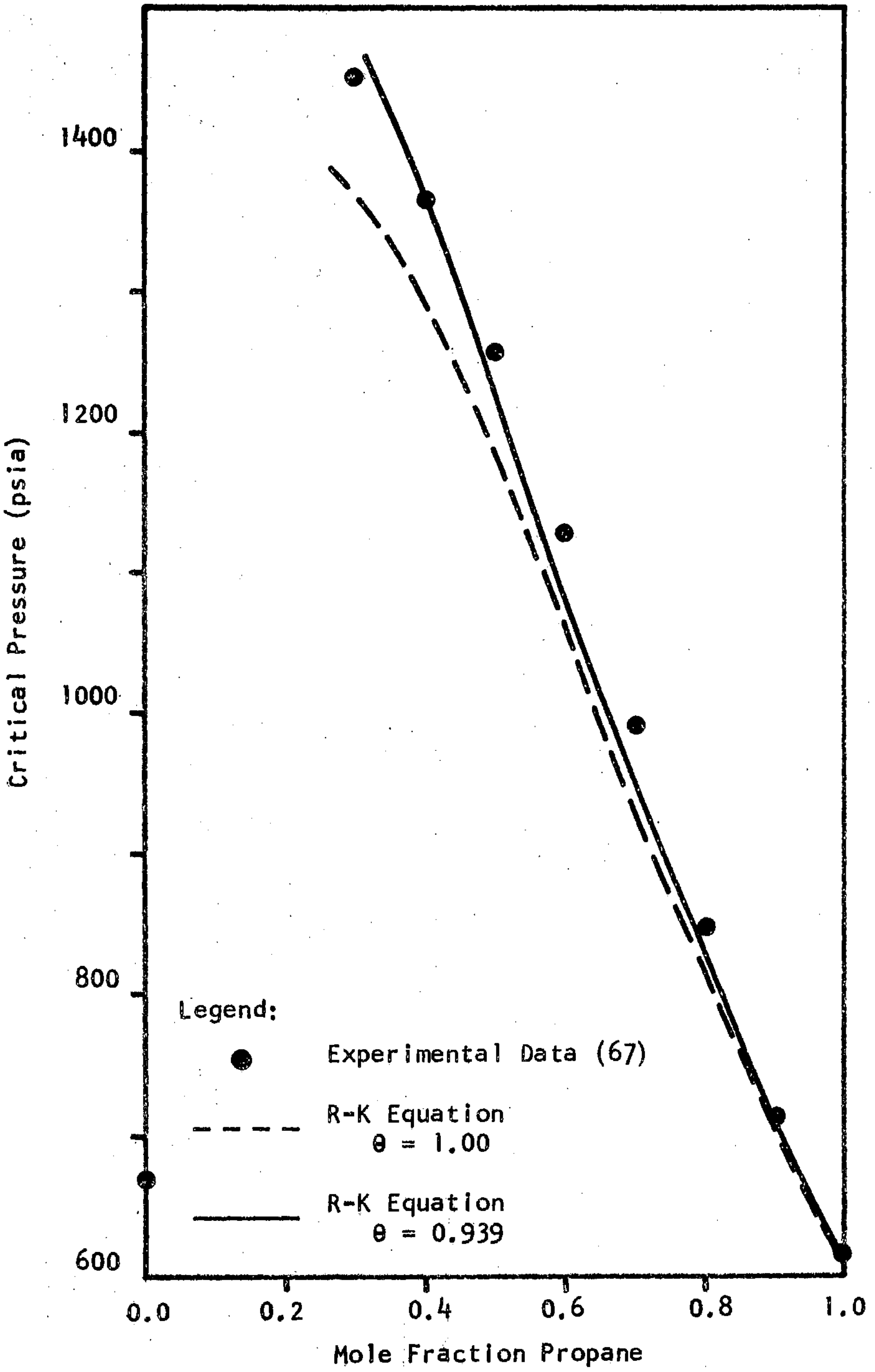

Figure 21. Critical Pressure-Composition Diagram for the Methane/Propane System

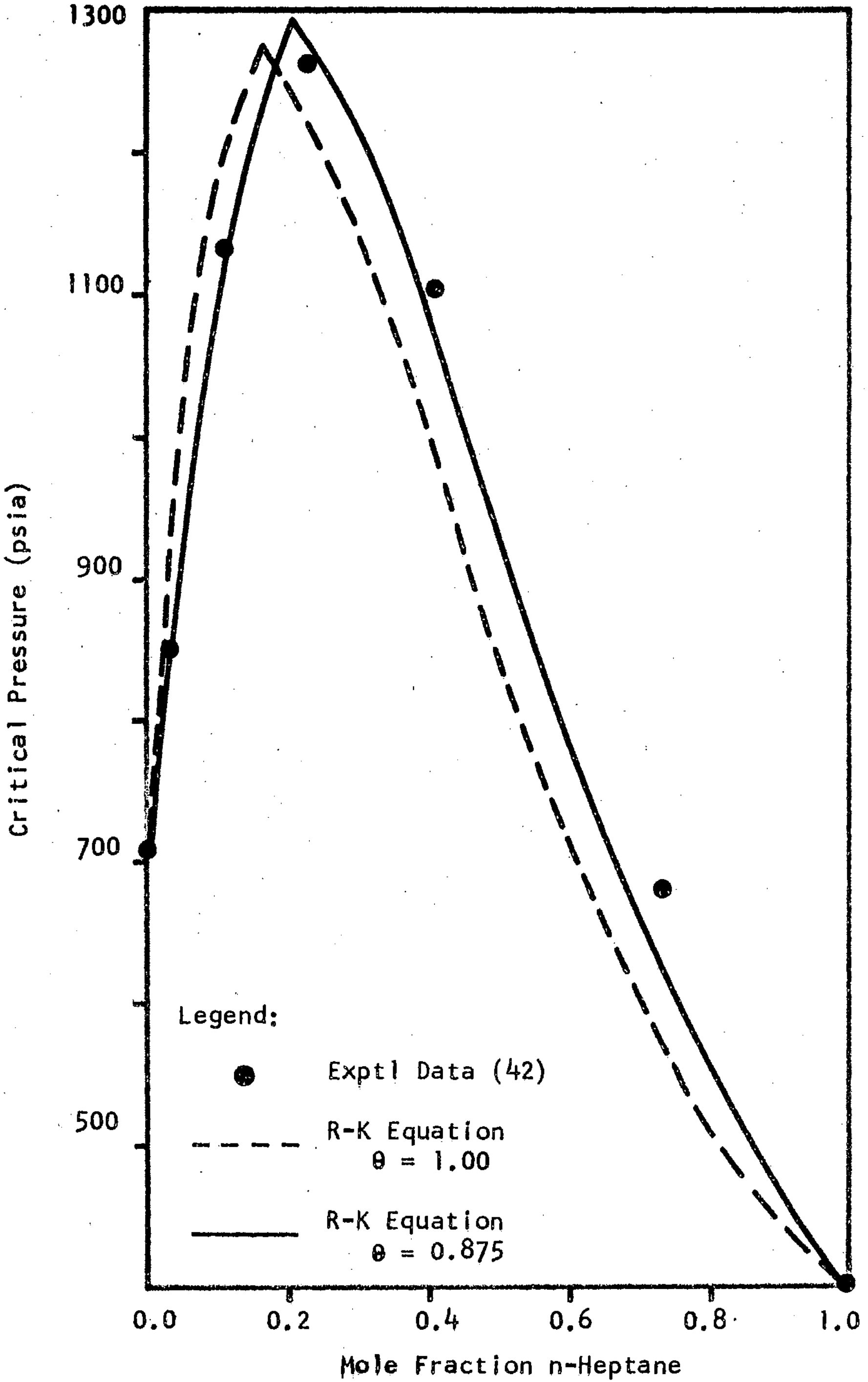

Figure 22. Critical Pressure-Composition Diagram for the Ethane/n-Heptane System

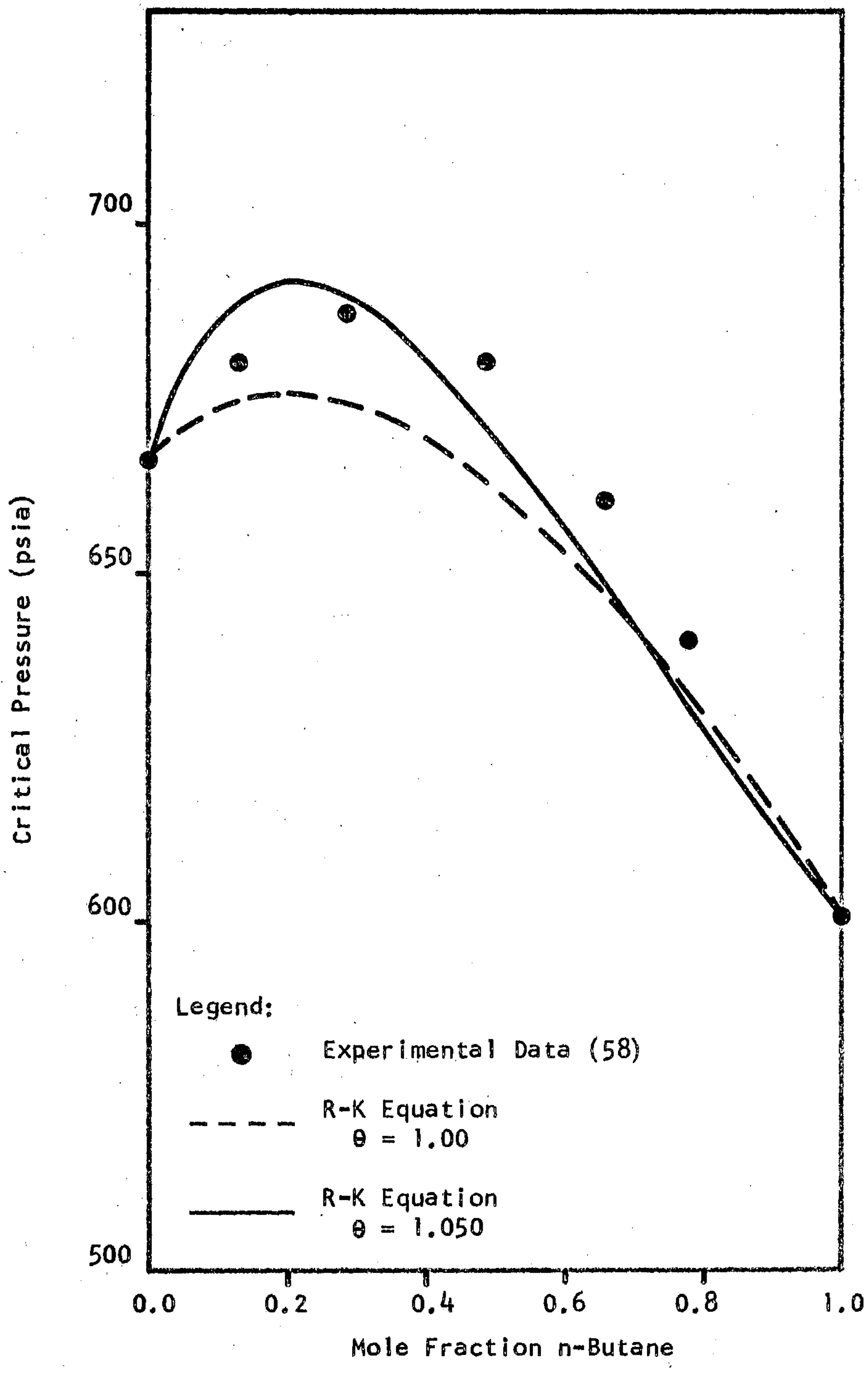

Figure 23. Critical Pressure-Composition Diagram for the Propane/n-Butane System

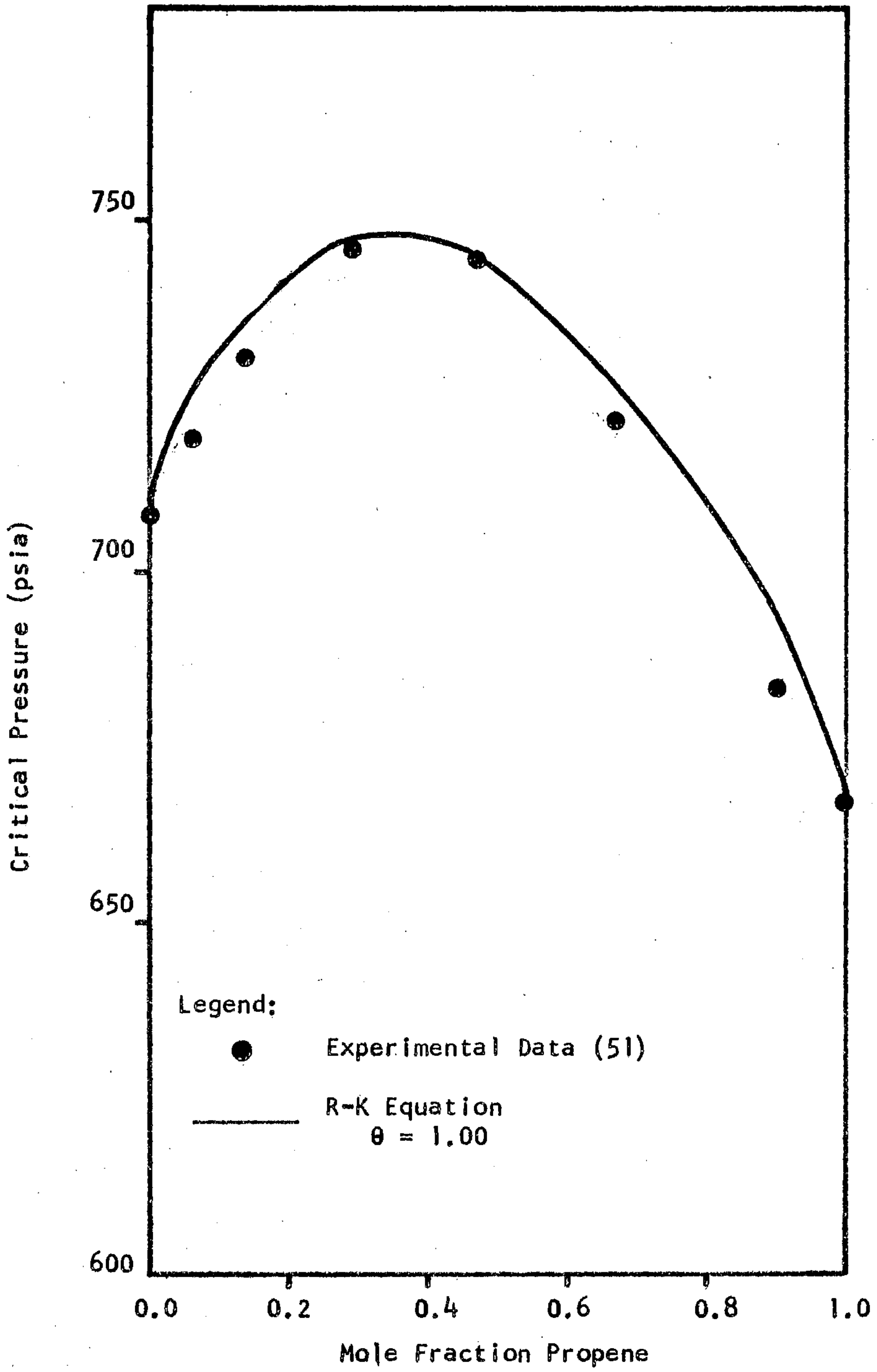

Figure 24. Critical Pressure-Composition Diagram for the Ethane/Propene System

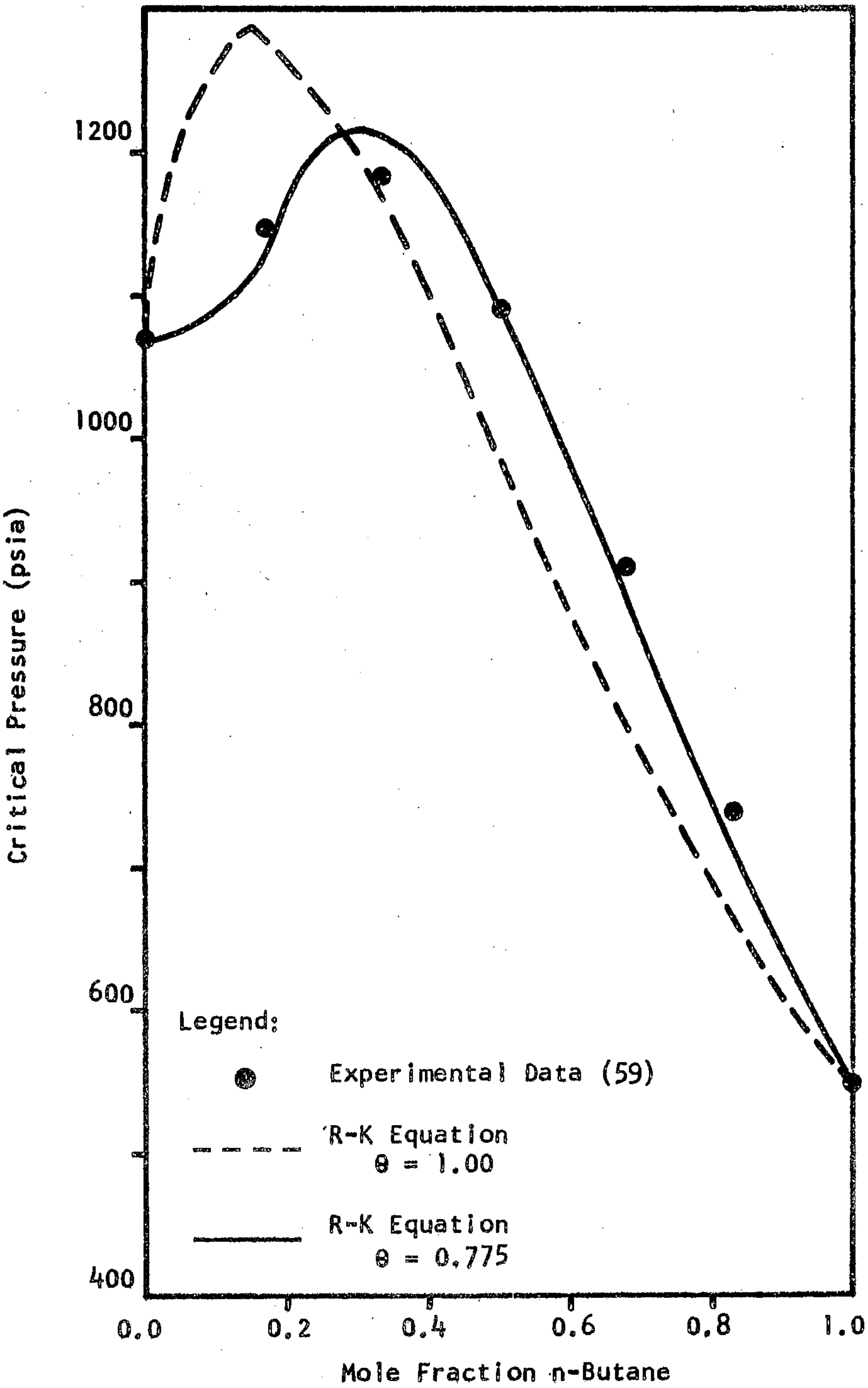

Figure 25. Critical Pressure-Composition Diagram for the n-Butane/Carbon Dioxide System

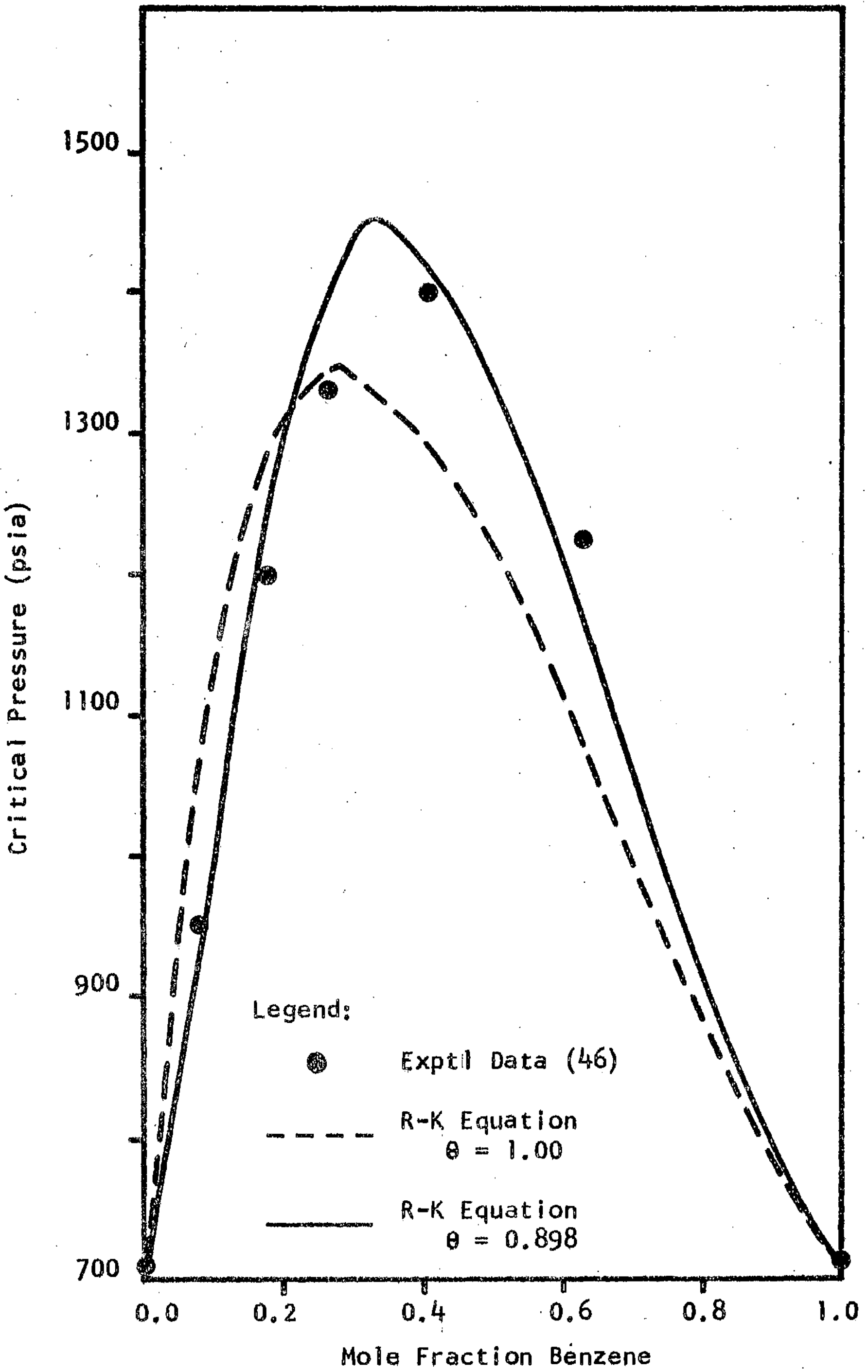

Figure 26. Critical Pressure-Composition Diagram for the Ethane/Benzene System

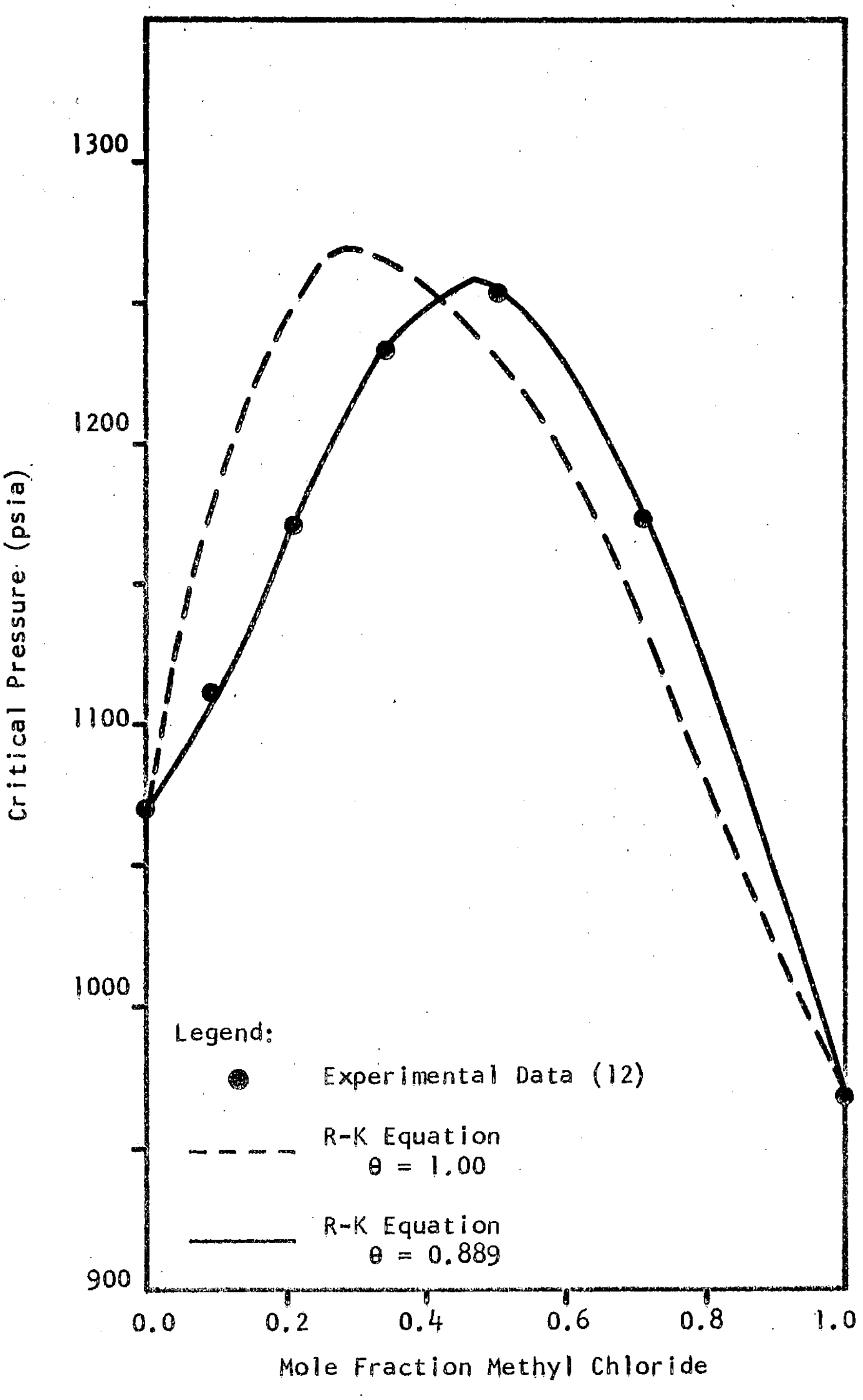

Figure 27. Critical Pressure-Composition Diagram for the Methyl Chloride/$CO_2$ System

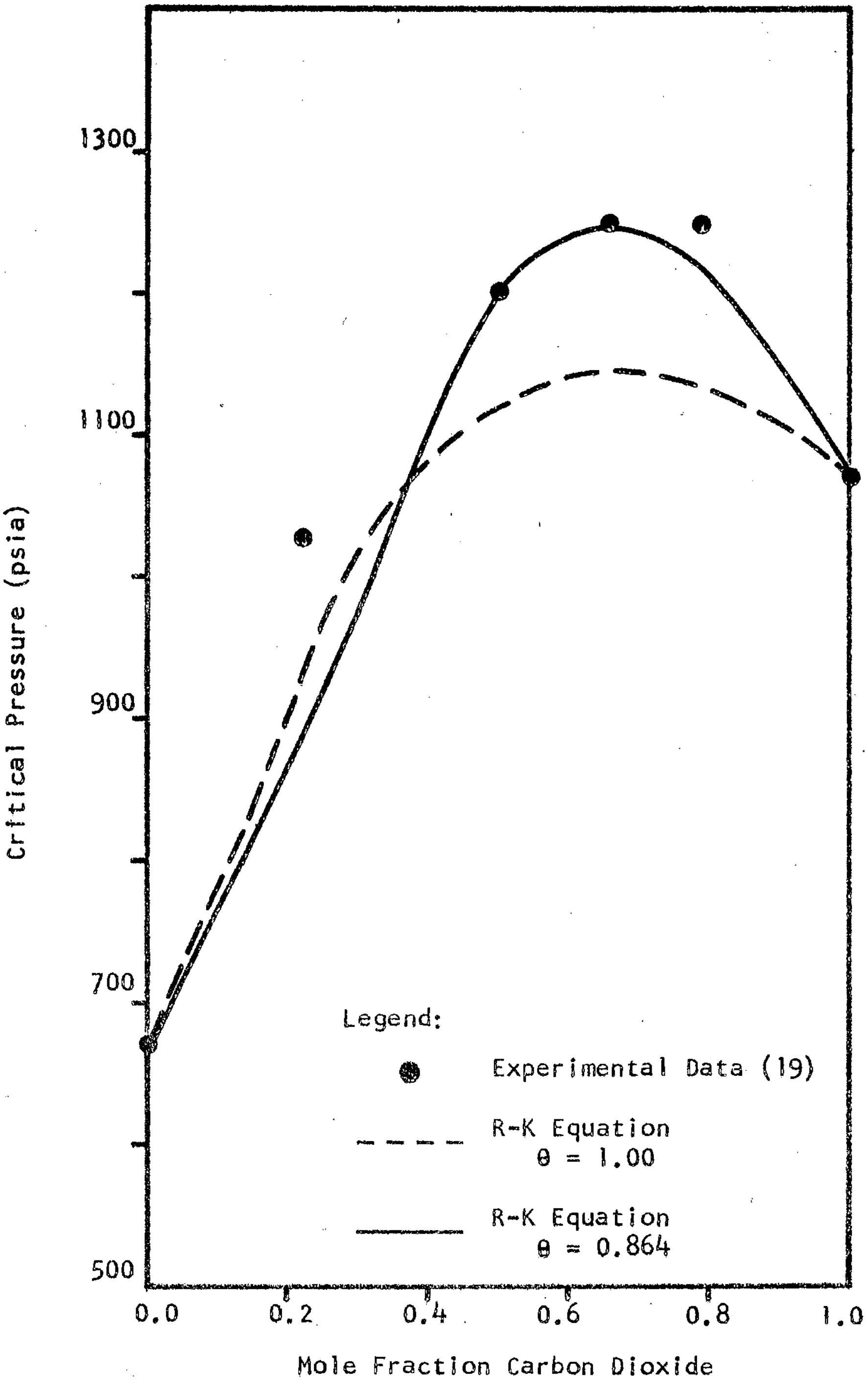

Figure 28. Critical Pressure-Composition Diagram for the Methane/Carbon Dioxide System

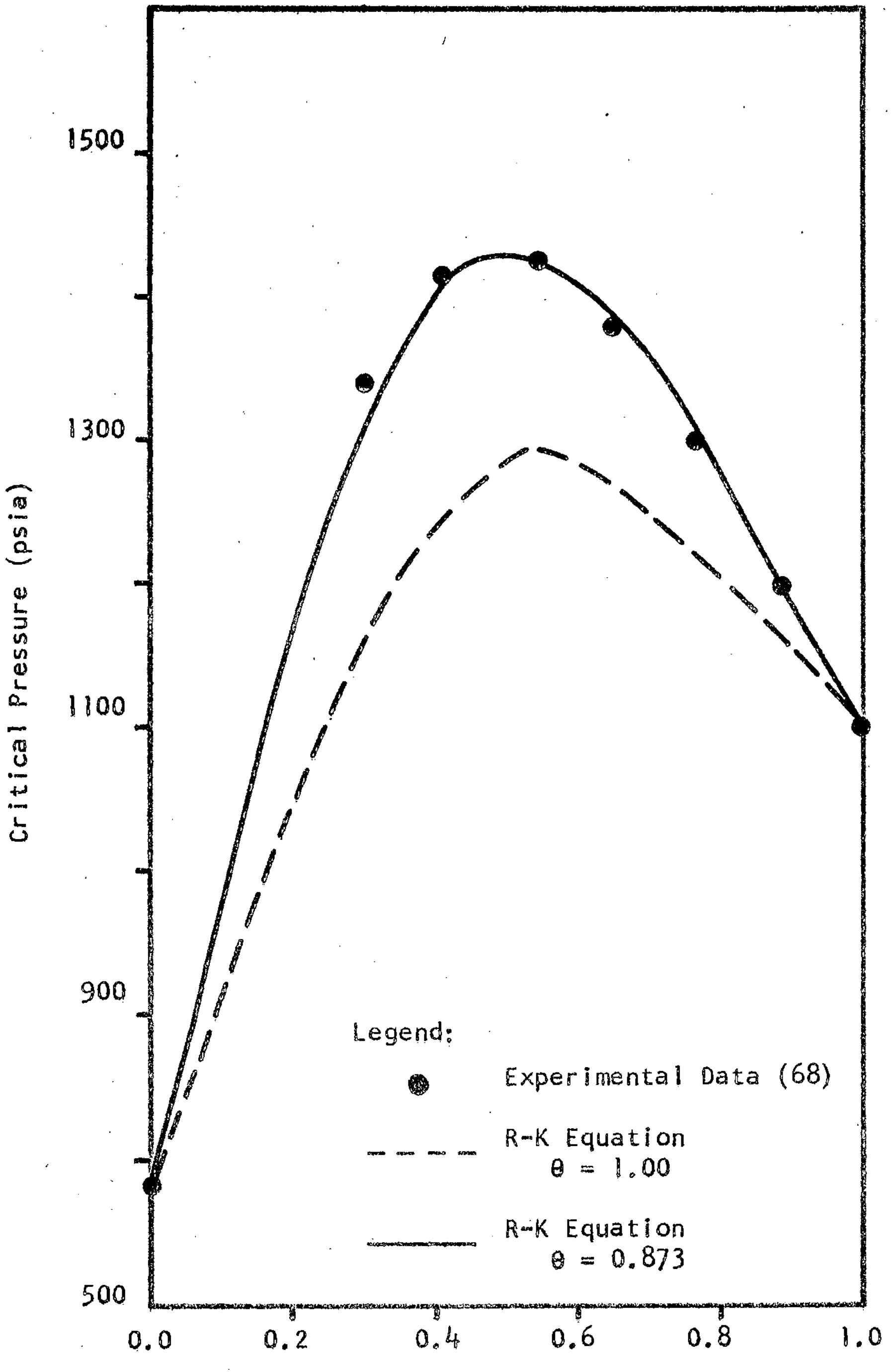

Figure 29. Critical Pressure-Composition Diagram for the Methane/Hydrogen Sulfide System

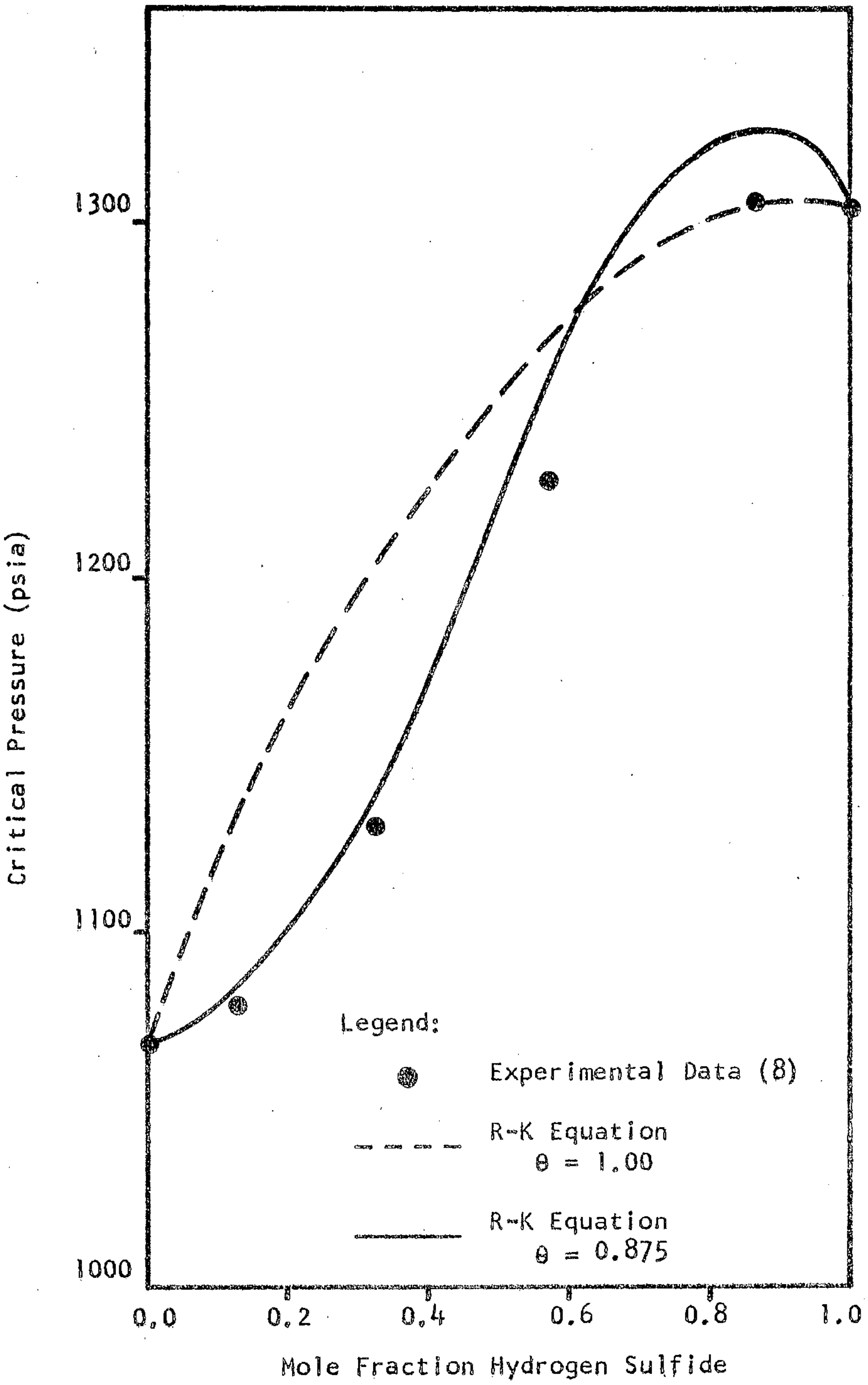

Figure 30. Critical Pressure-Composition Diagram for the Carbon Dioxide/Hydrogen Sulfide System

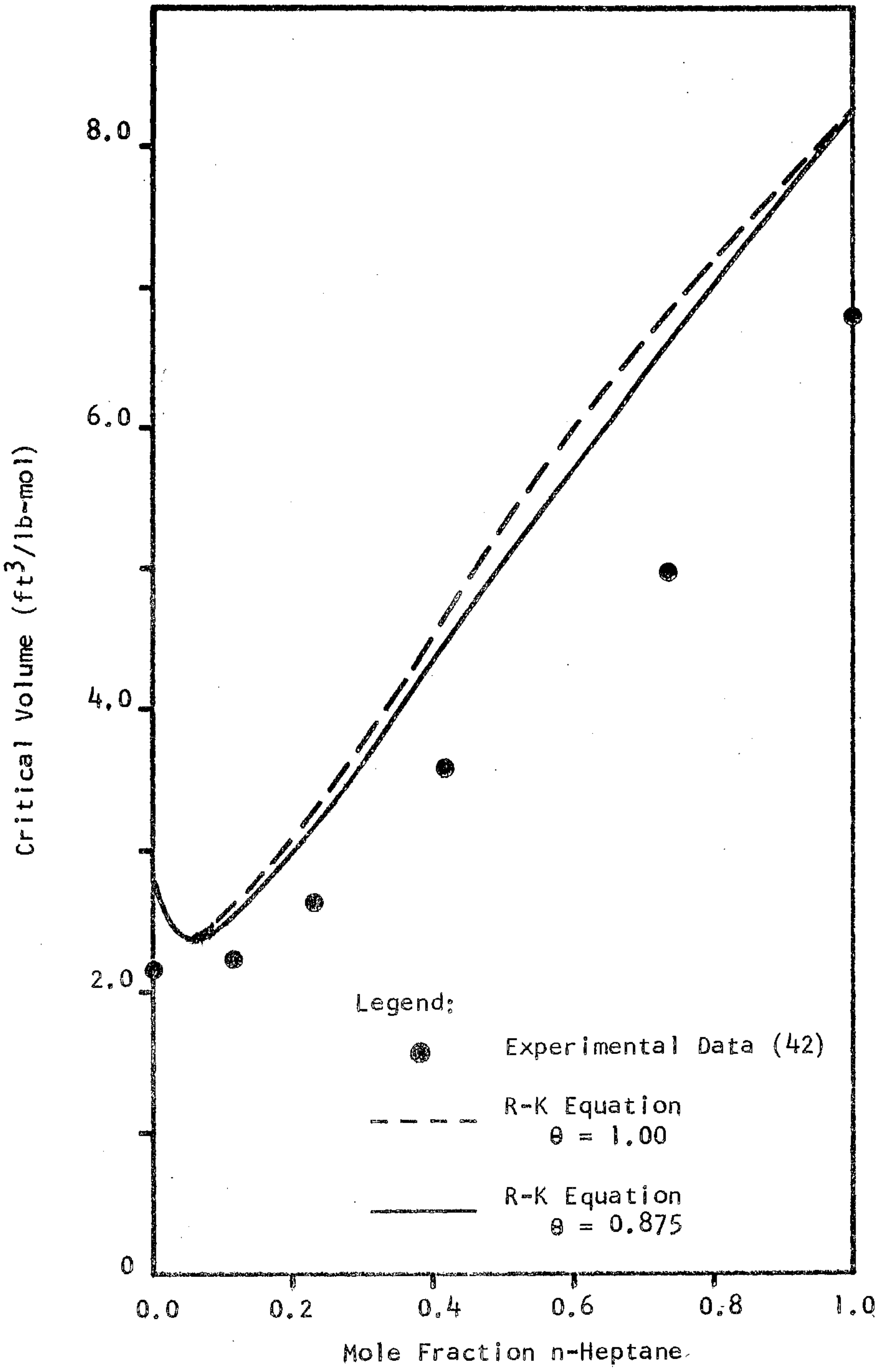

Figure 31. Critical Volume-Composition Diagram for the Ethane/n-Heptane System

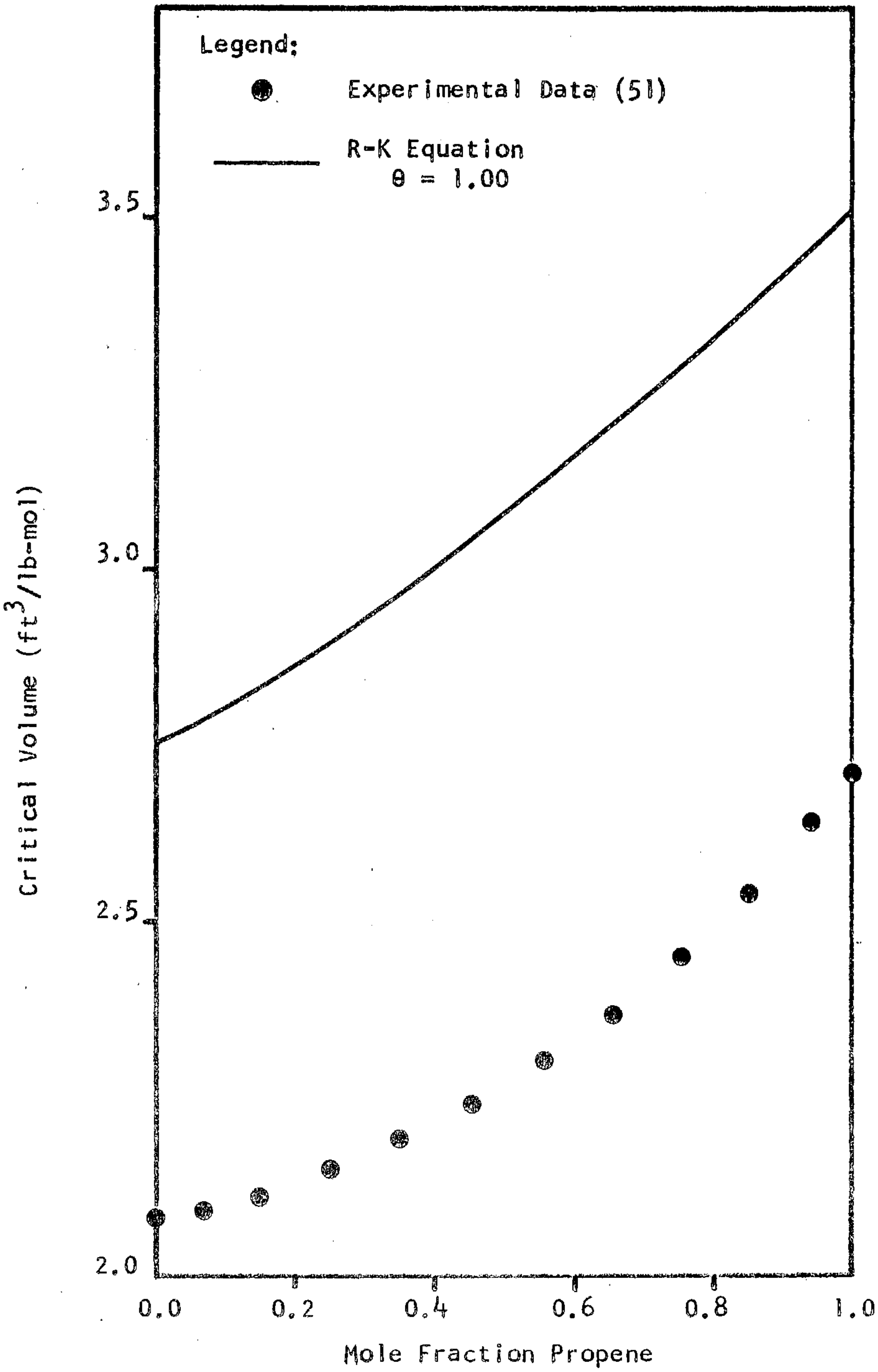

Figure 32. Critical Volume-Composition Diagram for the Ethane/Propene System

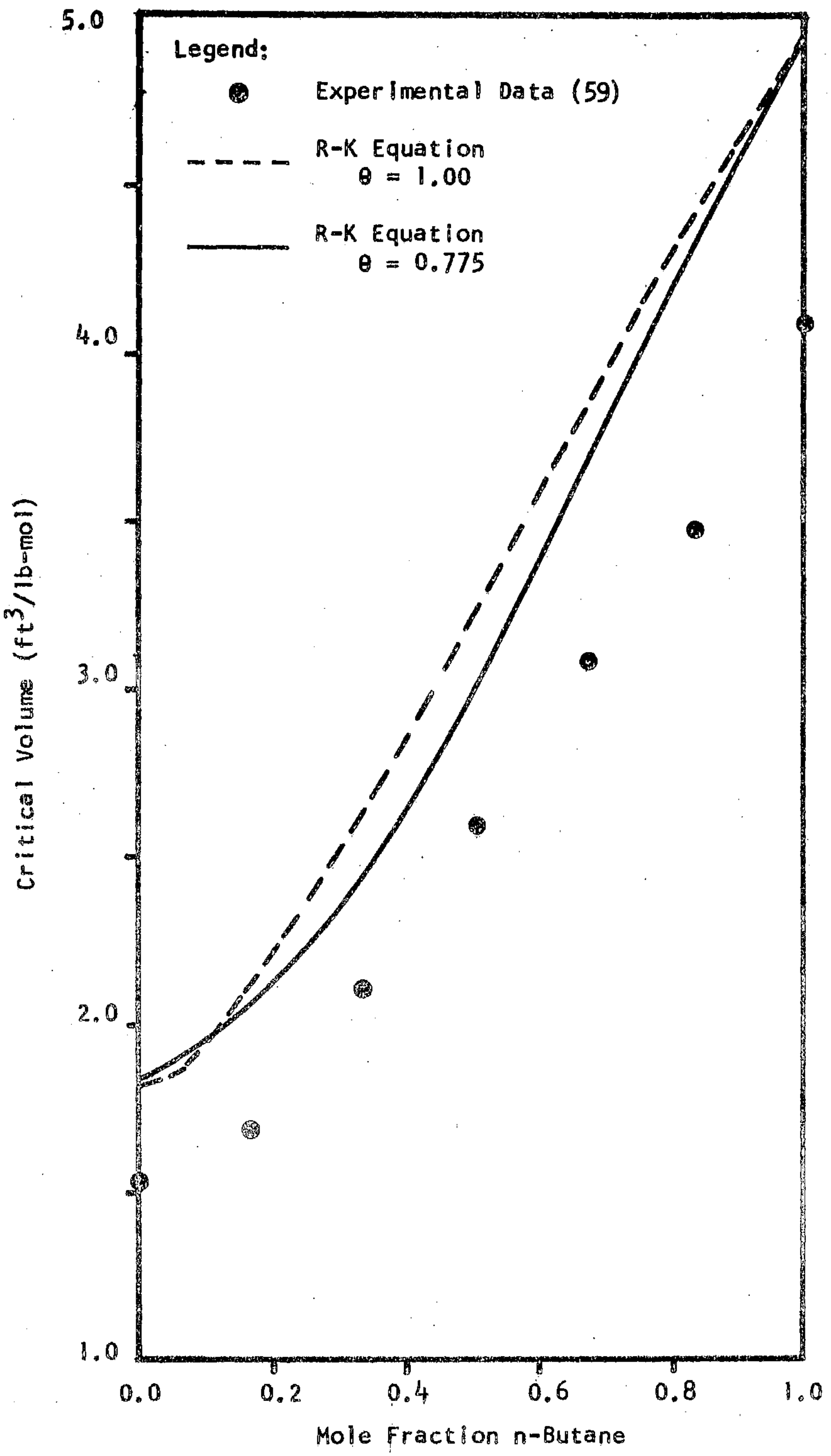

Figure 33. Critical Volume-Composition Diagram for the n-Butane/$CO_2$ System

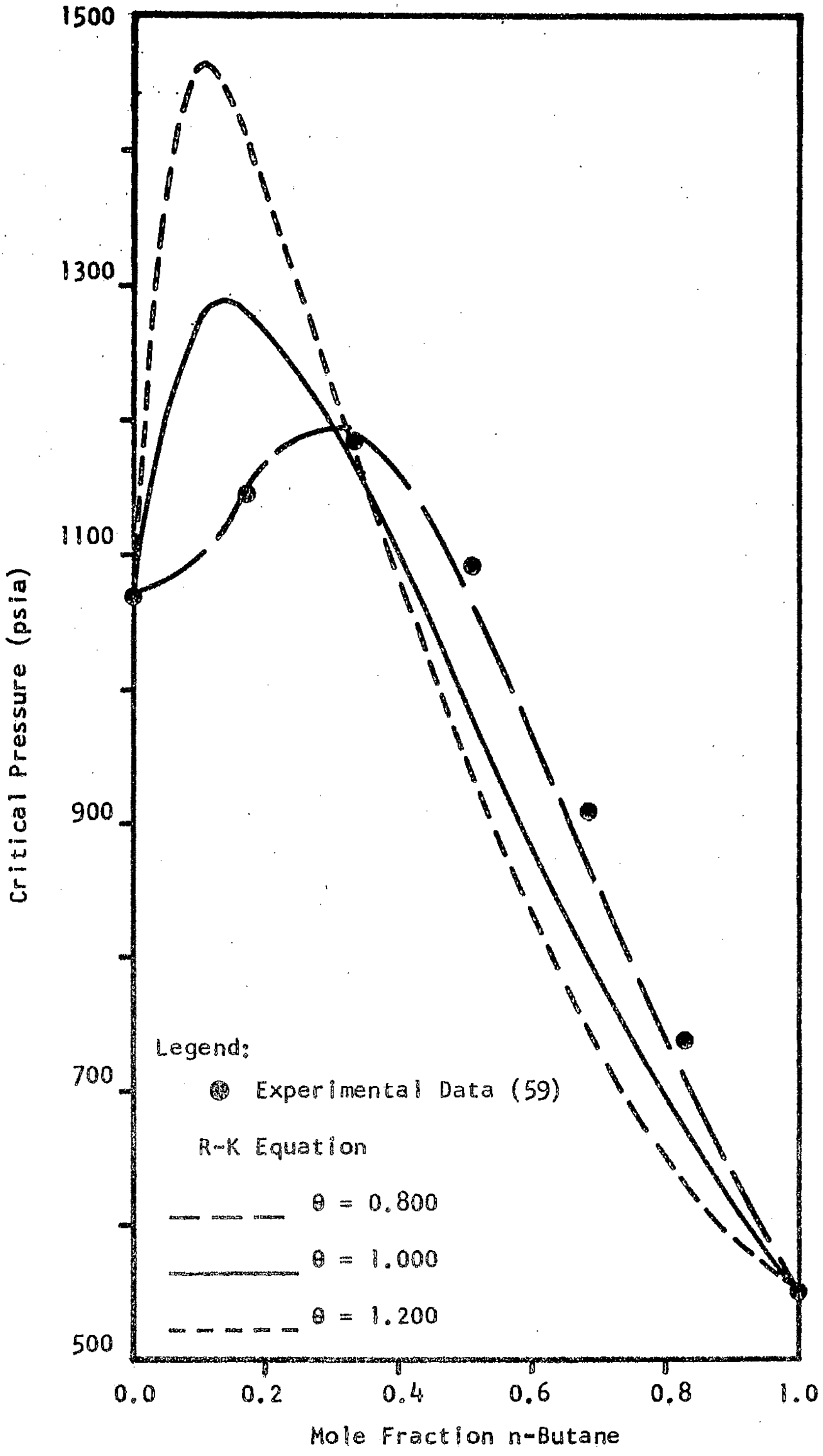

Figure 34. Critical Pressure-Composition Diagram for the n-Butane/$CO_2$ System

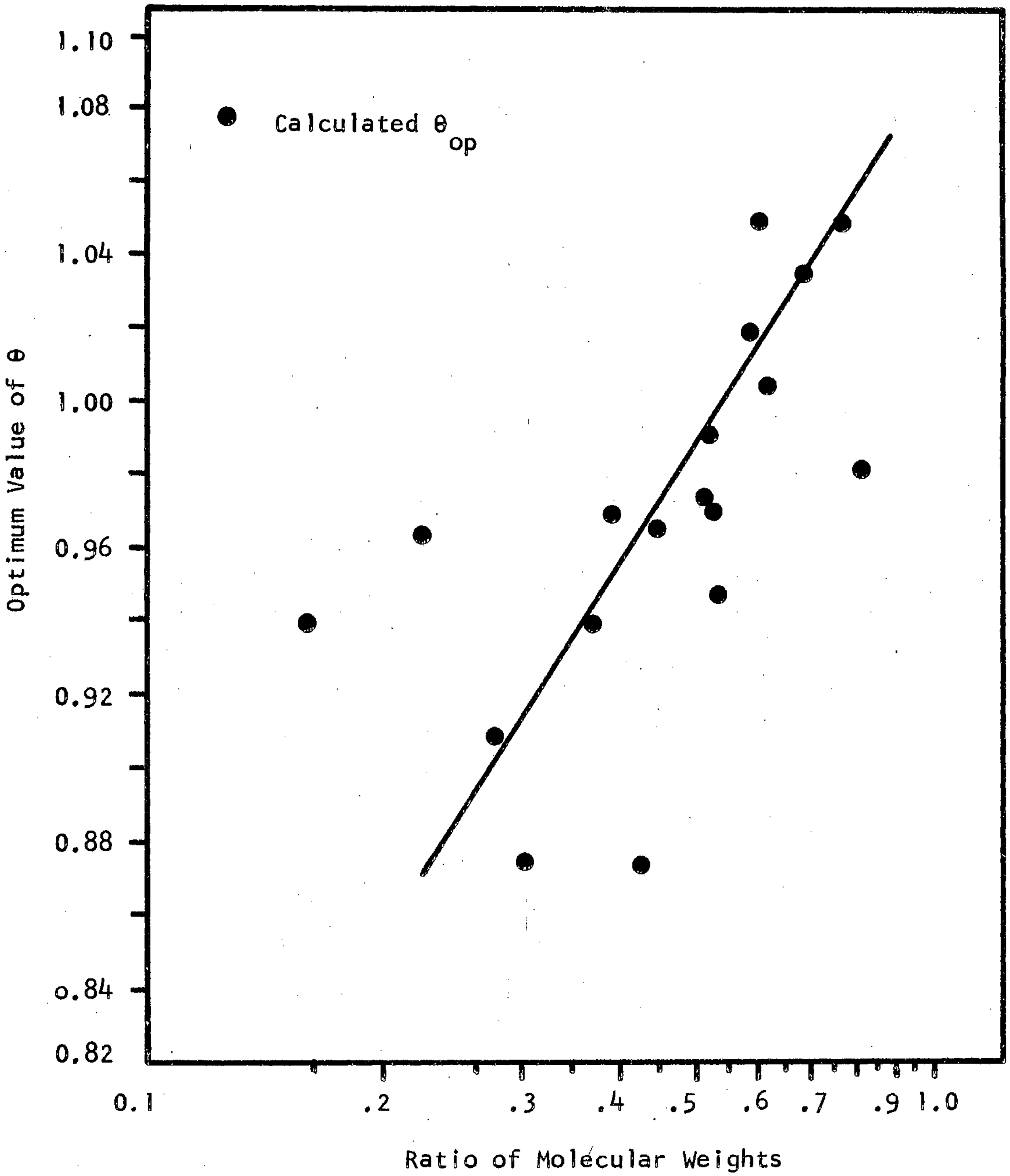

Figure 35. Plot of Optimum θ-Molecular Weight Ratio for Paraffin/Paraffin Mixtures

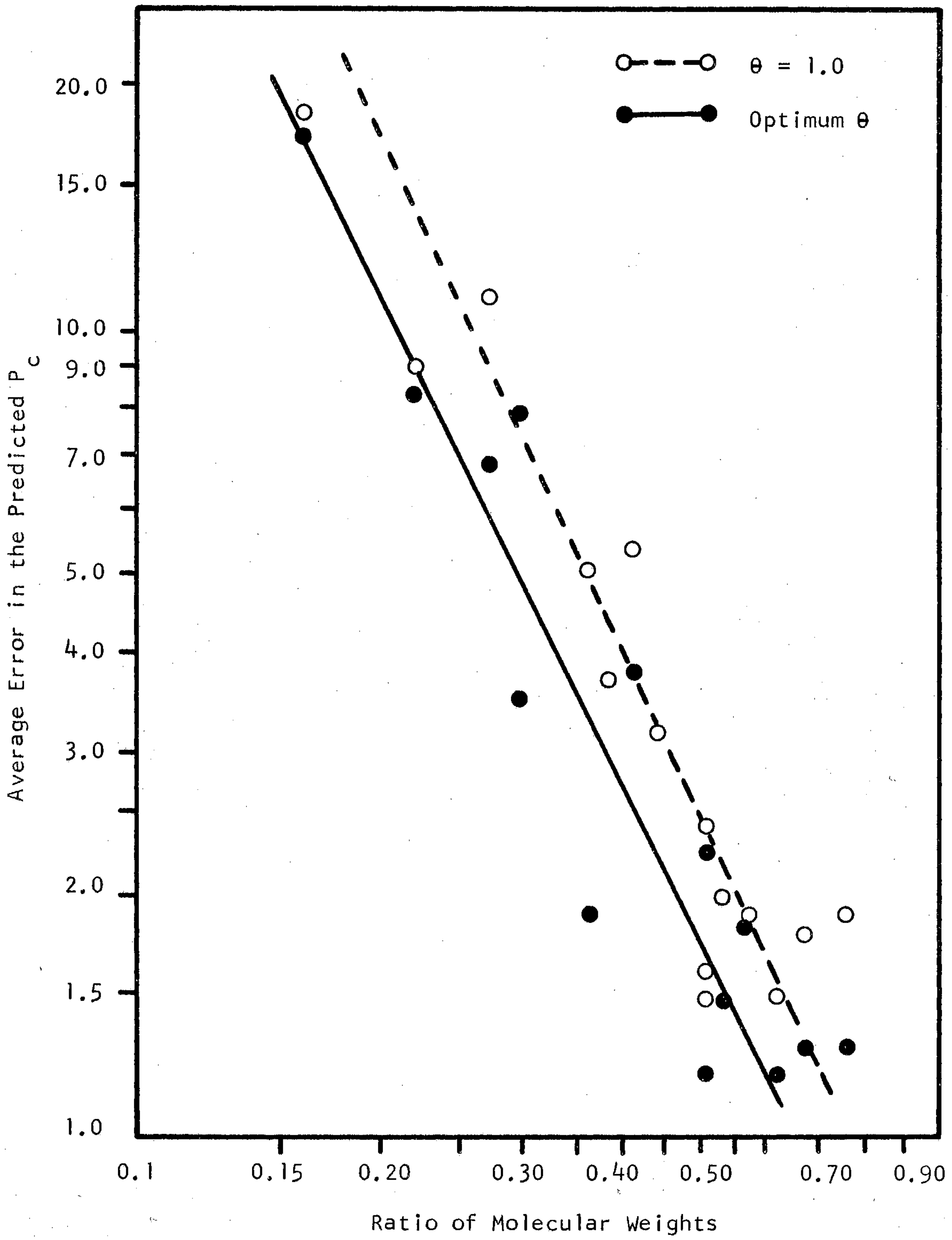

Figure 36. Plot of Average Error in the Critical Pressure versus Molecular Weight Ratio for Paraffin/Paraffin Mixtures

## E. Application of the Benedict-Webb-Rubin Equation of State in Critical State Predictions

The eight-parameter Benedict-Webb-Rubin equation of state (4) was selected as the second equation of state to be investigated with the critical state criteria for binary mixtures. The primary reason for the selection of the B-W-R equation of state was the improved accuracy of this equation over the two-parameter Redlich-Kwong equation of state in representing the general P-V-T behavior of mixtures.

Critical state calculations using the B-W-R equation of state require the critical state criteria to be expressed in terms of the B-W-R equation and its binary mixing rules. Because of the modular form of the CRITCALC computer program, only the critical state derivatives of the diffusion stability boundary, equation 64, needed to be re-evaluated in terms of the B-W-R equation. The three partial derivatives required to numerically evaluate the diffusion stability boundary equation are presented below in terms of the B-W-R equation of state.

$$\begin{aligned}\left(\frac{\partial P}{\partial x_2}\right)_{T,V} = {} & \frac{RT}{V^2}\left[B_o' + \frac{b'}{V}\right] - \frac{1}{V^2}\left[A_o' + \frac{a'}{V} + \frac{C_o'}{T^2}\right] \\ & + \frac{1}{V^6}\left[a\alpha' + a'\alpha\right] + \frac{c'\,e^{-\gamma/V^2}}{T^2\,V^3}\left[1 + \frac{\gamma}{V^2}\right] \\ & - \frac{c\gamma\gamma'\,e^{-\gamma/V^2}}{T^2\,V^7}\end{aligned} \tag{130}$$

$$\begin{aligned}-\left(\frac{\partial P}{\partial V}\right)_{T,x_2} = {} & \frac{RT}{V^2}\left[1 + \frac{2B_o}{V} + \frac{3b}{V^2}\right] - \frac{1}{V^3}\left[2A_o + \frac{3a}{V} + \frac{2C_o}{T^2}\right. \\ & \left. - \frac{6a}{V^4}\right] + \frac{c\,e^{-\gamma/V^2}}{T^2\,V^4}\left[3 + \frac{3\gamma}{V^2} - \frac{2\gamma^2}{V^4}\right]\end{aligned} \tag{131}$$

$$\begin{aligned}\left(\frac{\partial^2 A}{\partial x_2^2}\right)_{T,V} = {} & \frac{RT}{x_1 x_2} + \frac{1}{V}\left[B_o''RT - A_o'' - \frac{C_o''}{T^2}\right] + \frac{1}{2V^2}\left[b''RT - a''\right] \\ & + \frac{1}{5V^5}\left[a\alpha'' + 2a'\alpha' + a''\alpha\right] + \frac{1}{T^2\gamma}\left[c'' - \frac{2c'\gamma'}{\gamma}\right. \\ & \left. - \frac{c\gamma''}{\gamma} + \frac{2c(\gamma')^2}{\gamma^2}\right] - \frac{c''\, e^{-\gamma/V^2}}{T^2}\left[\frac{1}{\gamma} + \frac{1}{2V^2}\right] \\ & + \frac{e^{-\gamma/V^2}}{T^2}\left[c\gamma'' + 2c'\gamma'\right]\left[\frac{1}{\gamma^2} + \frac{1}{\gamma V^2} + \frac{1}{2V^4}\right] \\ & - \frac{c(\gamma')^2\, e^{-\gamma/V^2}}{T^2}\left[\frac{1}{\gamma V^4} + \frac{2}{\gamma^2 V^2} + \frac{2}{\gamma^3} + \frac{1}{2V^6}\right] . \end{aligned} \tag{132}$$

The first and second derivatives of the B-W-R constants $A_o$, $C_o$, and $\gamma$, designated collectively as Z in the following equations, are evaluated according to the relations:

$$z' = \left(\frac{dz}{dx_2}\right) = 2x_2\,(z_1 - 2z_{12} + z_2) + 2(z_{12} - z_1) \tag{133}$$

$$z'' = \left(\frac{d^2z}{dx_2^2}\right) = 2\,(z_1 - 2z_{12} + z_2) \tag{134}$$

where

$$z_{12} = \eta\sqrt{z_1 z_2} \ . \tag{135}$$

The first and second derivatives of the B-W-R constants a, b, c, and , designated collectively as Y in the following equations, are evaluated according to the relations:

$$\begin{aligned} Y' = \left(\frac{dY}{dx_2}\right) = {} & 3x_2^2\,(Y_2 - 3Y_{122} + 3Y_{112} - Y_1) + 6x_2\,(Y_{122} \\ & - 2Y_{112} + Y_1) + 3\,(Y_{112} - Y_1) \end{aligned} \tag{136}$$

$$\begin{aligned} Y'' = \left(\frac{d^2Y}{dx_2^2}\right) = {} & 6x_2\,(Y_2 - 3Y_{122} + 3Y_{112} - Y_1) + 6(Y_{122} \\ & - 2Y_{112} + Y_{111}) \end{aligned} \tag{137}$$

where

$$Y_{112} = \sqrt[3]{Y_1 Y_1 Y_2} \tag{138}$$

$$Y_{122} = \sqrt[3]{Y_1 Y_2 Y_2} \ . \tag{139}$$

The equation for the second derivative of the molar Helmholtz free energy, equation 132, was derived from the expression for the molar Helmholtz free energy of a binary mixture in terms of the B-W-R equation of state (7):

$$A = \sum_{i=1}^{2} x_i \left(RT \ln \frac{RT}{V} x_i + E_i^o - TS_i^o\right) + \frac{B_oRT}{V} - \frac{A_o}{V} - \frac{C_o}{T^2V} + \frac{bRT}{2V^2} - \frac{a}{2V^2} + \frac{a\alpha}{5V^5} + \frac{c}{T^2}\left[\frac{1 - e^{-\gamma/V^2}}{\gamma}\right] - \frac{c\, e^{-\gamma/V^2}}{2\, T^2\, V^2} \qquad (140)$$

The two remaining partial derivatives of the diffusion stability boundary equation have been derived from the B-W-R equation of state and the binary mixing rules of that equation of state and result in equations 130 and 131.

As a check on the accuracy of the derivations, values of the derived partial derivatives of the critical state relations in terms of the B-W-R equation of state were compared with the corresponding values obtained by numerical differentiation of that derivative. The derived partial derivatives were assumed to be correct when the difference between the analytically and numerically obtained values was negligible.

The equations defining the diffusion stability boundary in terms of the B-W-R equation of state and its binary mixing rules were programmed in subroutines DELTA and ABCAL respectively of the CRITCALC computer program. All other subroutines and the search procedure used in the program are independent of the equation of state and had been tested and used previously with the Redlich-Kwong equation of state. Thus, the calculations using the B-W-R equation of state in the CRITCALC program are entirely equivalent to those carried out using the simpler

Redlich-Kwong equation of state.

To test the applicability, accuracy, and limitations of the B-W-R equation in the prediction of the critical state, calculations were made for a variety of binary mixtures. The number of classes of mixtures investigated were necessarily limited to mixtures for which the coefficients of the B-W-R equation had been determined for the pure components and for which experimental critical state data was available. Five critical temperature, approximately equally spaced between the two pure component critical temperatures, were specified for each binary system. This technique for selecting the critical temperatures to be specified proved to be a successful method for obtaining critical points over the entire composition range of the mixture in the calculations using the Redlich-Kwong equation of state. In the cases where experimental data did not cover the entire composition range, the critical state calculations were restricted to the critical temperature range of the experimental data.

## F. Results of Critical State Predictions Using the Benedict-Webb-Rubin Equation

The critical state calculations using the B-W-R equation of state were carried out for each binary system with no empirical adjustment of the binary interaction parameters $\eta_1$, $\eta_3$, and $\eta_4$ associated with the constants $A_o$, $C_o$, and $\gamma$ respectively. The general behavior of the calculated and experimental critical properties for several binary systems are presented in Figures 37-56. In general, qualitative results similar to those obtained with the Redlich-Kwong equation were obtained for the critical properties using the B-W-R equation of state. A detailed comparison and discussion of the behavior of each of the calculated critical properties with respect to the corresponding experimental observations are presented in the following sections.

The variation of the calculated critical temperatures with composition agreed quantitatively and qualitatively with experimental data. Errors in the prediction of the critical temperature, as indicated in the $T_c$-$x_2$ plots in Figures 42-46, were in the neighborhood of one per cent. In general, the critical temperature-composition relationship and the magnitude of the errors using the B-W-R equation are very similar to those obtained using the Redlich-Kwong equation of state. However, in most cases the calculated critical temperatures were slightly less, not greater, than the experimental values at given compositions of the binary mixture using the B-W-R equation.

The quantitative agreement between the calculated and experimental critical volumes proved to be rather poor as shown in Figures 54-56. The large deviations in the prediction of the critical volume observed in some mixtures were not expected with the B-W-R equation. The reason for the large errors in the critical volume appeared to be the inability of the B-W-R equation of state to accurately predict the critical volumes of the pure components. This effect can best be seen in Figure 56. The calculated and experimental critical volume of pure n-butane ($x_2 = 1.0$) differ by more than 0.5 $ft^3$/lb-mol. However, the observation can again be made that the equation of state used in critical state calculations must accurately predict the pure component critical volume to accurately predict mixture critical volumes.

The critical pressure proved to be the next most difficult of the critical properties to predict accurately. In general, qualitative, but not necessarily quantitative, agreement was obtained using the B-W-R equation. Figures 47-53 show the typical calculated and experimental critical pressure-composition behavior. In general, the calculated critical pressures were greater than the experimental values at a given mixture composition. The average error in the calculated critical pressure for the three classes of binaries ranged from 0.6 to 28.8 per cent with an over-all average error of 7.4 per cent for the 27 systems. The errors encountered in the systems containing carbon dioxide and hydrogen sulfide increased the over-all average error by about two per cent. A complete summary of the average and maximum errors for each binary system using the B-W-R equation appears in Table III.

As was the case with the Redlich-Kwong equation of state, the critical pressure-critical temperature relationships are predicted with greater accuracy than the $T_c$-$x_2$ or $P_c$-$x_2$ relationships. This result suggests that the mixing rules used in the B-W-R equation do not accurately represent the mixture behavior. Thus, improvements in the existing mixing rules of either the Redlich-Kwong or B-W-R equation may further increase the accuracy of the critical state predictions.

The largest deviations in the prediction of the critical state properties occurred in the hydrocarbon/non-hydrocarbon class of binary mixtures. This class of mixtures included the paraffin/carbon dioxide and paraffin/hydrogen sulfide binaries. Empirical adjustments of the binary interaction parameters of the B-W-R equation seemed to be indicated for these latter systems.

The influence of the values of the binary interaction parameters $\eta_1$, $\eta_3$, and $\eta_4$ associated with the B-W-R constants $A_o$, $C_o$, and $\gamma$ was investigated. Adjustment of $\eta_3$ and $\eta_4$ did not consistently improve the accuracy of the critical state predictions. Adjustment of $\eta_1$, the binary interaction parameter associated with the constant $A_o$, was observed to signficantly improve the prediction of the critical properties, particularly the critical pressure.

The optimum value of the interaction parameter $\eta_1$ giving the best representation of the critical pressure-composition relationship was determined for each binary mixture. The criterion for the "best representation" was a minimum in the sum of the squared deviations of the calculated minus the experimental critical pressure at a specified composition. The optimization of $\eta_1$ was carried out in subroutine OPTP in the CRITCALC computer program in the same manner as the optimization of $\theta$ in the Redlich-Kwong equation of state.

Values of the optimum binary interaction parameter $\eta_1$ ranged from 0.887 to 1.511. A summary and comparison of the average and maximum errors in the critical pressure using the B-W-R equation of state with $\eta_1 = 1.0$ and with the optimum values of $\eta_1$ appear in Table III. The average error in the critical pressure was reduced from 7.4 per cent for $\eta_1 = 1.0$ to only 3.1 per cent using the optimum values of $\eta_1$ for the 27 binary systems investigated. Use of the optimum $\eta_1$ in the hydrocarbon/non-hydrocarbon class of binary mixtures resulted in the most signficant reduction in the error in predicting the critical pressure. The average error for this class was reduced from 15.4 per cent, the highest average error level encountered in the critical state calculations using either the Redlich-Kwong or B-W-R equations of state, to 5.7 per cent, a level comparable to the paraffin/paraffin class with $\eta_1 = 1.0$. Thus, optimizing the binary interaction parameter $\eta_1$ proved to be a necessity to obtain average error levels less than 6.0 per cent for all classes of binary mixtures using the B-W-R equation of state.

Use of the optimum $\eta_1$ designed to improve the representation of the critical pressure also improved the representations of the critical pressure-critical temperature and critical temperature-composition relationships, but to a much smaller degree. The nature and extent of these improvements can be seen in Figures 37-56.

The optimum values of $\eta_1$ and the accuracy of the critical state predictions for each class of mixture seemed to be dependent on the difference between the two pure component molecules. Figures 57 and 58, plots of the optimum values of $\eta_1$ and the average error in the critical pressure versus the ratio of the molecular weights of the pure components, show the trend for the paraffin/paraffin class of mixtures. In general and just as with the Redlich-Kwong equation of state, the greater the difference between the pure components, the greater the optimum value of $\eta_1$ deviated from 1.0 and the greater the average error in the prediction of the critical pressure. Once again no attempt was made to correlate the optimum values of $\eta_1$ with the ratio of the molecular weights because of the execessive scatter in the data points, particularly in the region where the correlation would be most useful.

## TABLE III

## COMPARISON OF CALCULATED AND EXPERIMENTAL CRITICAL PRESSURE AT SPECIFIED CRITICAL TEMPERATURES USING THE B-W-R EQUATION OF STATE

| Binary System | B-W-R Eqn with $\eta_1 = 0$ | | B-W-R Eqn with Optimum $\eta_1$ | | | |
|---|---|---|---|---|---|---|
| | Average Error ( % ) | Maximum Error ( % ) | Optimum (±0.005) | Average Error ( % ) | Maximum Error ( % ) | References |
| **I. SYSTEMS OF PARAFFIN/PARAFFIN MIXTURES** | | | | | | |
| Methane/Ethane | 2.9 | 5.3 | 0.948 | 2.4 | 4.1 | 10 |
| Methane/Propane | 3.1 | 4.7 | 1.023 | 1.6 | 2.6 | 67 |
| Methane/n-Butane | 6.0 | 16.3 | 1.010 | 5.2 | 15.3 | 81 |
| Methane/n-Pentane | 15.5 | 18.8 | 1.102 | 4.2 | 9.2 | 82 |
| Methane/n-Heptane | 22.7 | 33.6 | 1.087 | 10.6 | 22.2 | 70 |
| Ethane/Propane | 1.4 | 2.2 | 1.021 | 0.5 | 1.0 | 52 |
| Ethane/n-Butane | 0.6 | 0.9 | 1.005 | 0.6 | 0.8 | 18 |
| Ethane/n-Pentane | 5.2 | 8.3 | 0.987 | 5.1 | 8.5 | 71 |
| Ethane/n-Heptane | 5.2 | 8.1 | 1.044 | 2.9 | 5.8 | 42 |
| Propane/n-Butane | 1.3 | 2.1 | 1.012 | 0.8 | 1.2 | 58 |
| Propane/n-Pentane | 3.0 | 4.9 | 1.025 | 1.2 | 3.5 | 83 |
| Propane/n-Heptane | 1.1 | 2.1 | 1.012 | 0.8 | 2.3 | 86 |
| n-Butane/n-Pentane | 2.5 | 3.3 | 1.027 | 1.0 | 2.2 | 86 |
| n-Butane/n-Heptane | 3.0 | 4.2 | 1.039 | 1.0 | 2.0 | 43 |
| Averages | 5.2 | 8.2 | | 2.1 | 5.8 | |

TABLE III - continued

| Binary System | B-W-R Eqn with $\eta_1 = 0$ | | B-W-R Eqn with Optimum $\eta_1$ | | | |
|---|---|---|---|---|---|---|
| | Average Error ( % ) | Maximum Error ( % ) | Optimum (±0.005) | Average Error ( % ) | Maximum Error ( % ) | References |
| II. SYSTEMS OF PARAFFIN/NON-PARAFFIN MIXTURES | | | | | | |
| Ethane/Propene | 0.8 | 1.7 | 0.994 | 0.7 | 1.6 | 51 |
| Ethane/Benzene | 2.4 | 3.8 | 1.002 | 2.3 | 3.8 | 46 |
| Propane/Benzene | 1.4 | 2.3 | 1.012 | 0.7 | 1.1 | 30 |
| n-Butane/Ethene | 2.5 | 7.6 | 1.002 | 2.5 | 7.6 | 86 |
| n-Heptane/Ethene | 7.5 | 12.5 | 1.048 | 5.6 | 9.3 | 44 |
| Ethene/Propene | 4.0 | 5.4 | 0.942 | 3.3 | 4.4 | 35 |
| Averages | 3.2 | 5.6 | | 2.5 | 4.6 | |
| III. SYSTEMS OF HYDROCARBON/NON-HYDROCARBON MIXTURES | | | | | | |
| Methane/$H_2S$ | 3.4 | 4.6 | 0.961 | 0.5 | 1.1 | 68 |
| Ethane/$H_2S$ | 7.0 | 9.7 | 0.887 | 2.8 | 7.5 | 47 |
| n-Butane/$CO_2$ | 21.4 | 27.1 | 1.375 | 11.0 | 20.4 | 59 |
| n-Pentane/$CO_2$ | 28.8 | 37.7 | 1.511 | 8.3 | 10.9 | 65 |
| Propane/$CO_2$ | 21.9 | 24.0 | 1.312 | 2.1 | 4.7 | 69 |
| n-Pentane/$H_2S$ | 17.1 | 21.5 | 1.148 | 11.5 | 20.5 | 72 |
| $CO_2$/$H_2S$ | 8.1 | 14.0 | 1.169 | 3.7 | 10.0 | 8 |
| Averages | 15.4 | 19.4 | | 5.7 | 10.7 | |
| TOTAL AVERAGES (27 systems) | 7.4 | 10.5 | | 3.1 | 6.8 | |

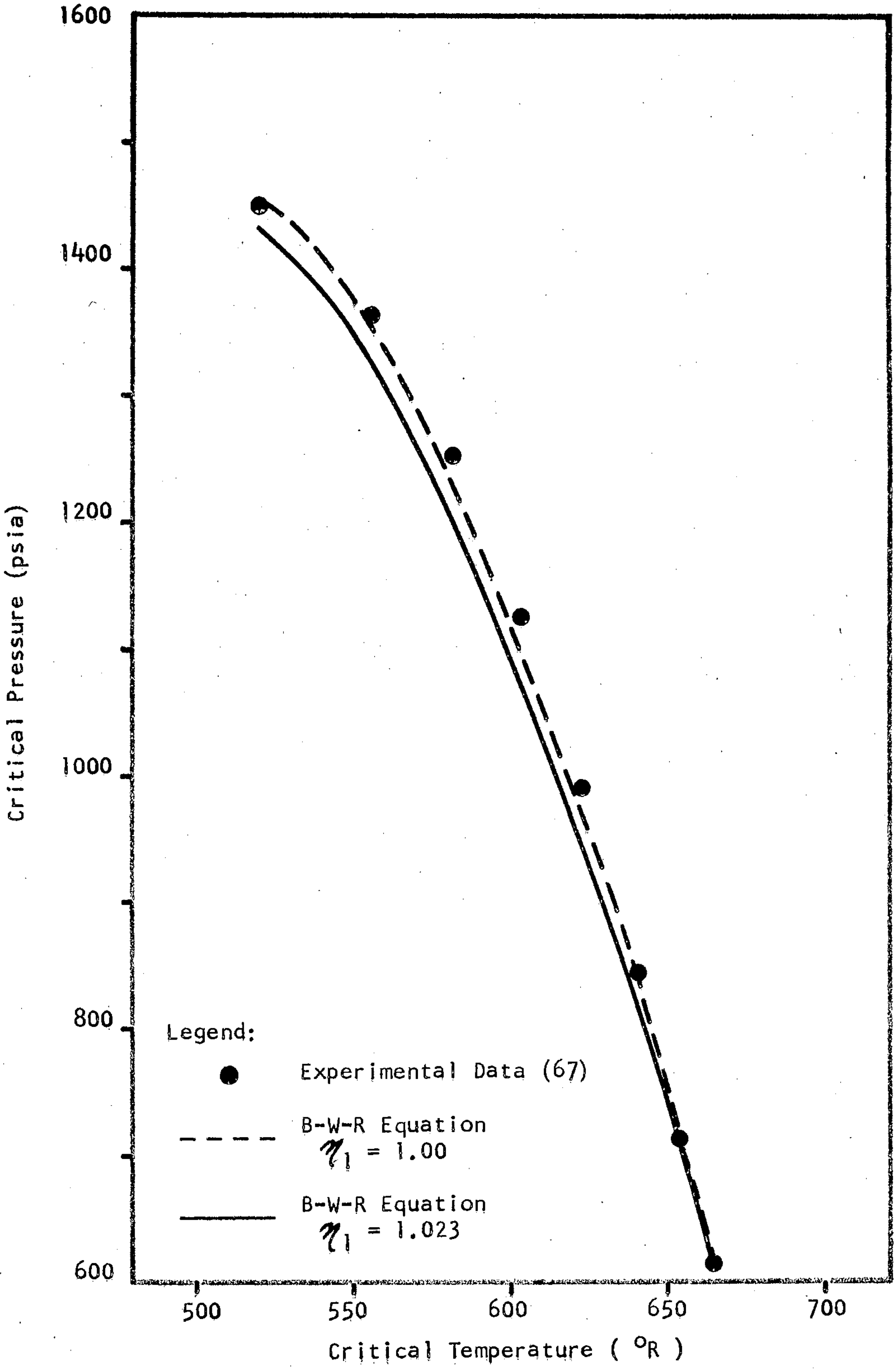

Figure 37. Critical Pressure-Critical Temperature Diagram for the Methane/Propane System

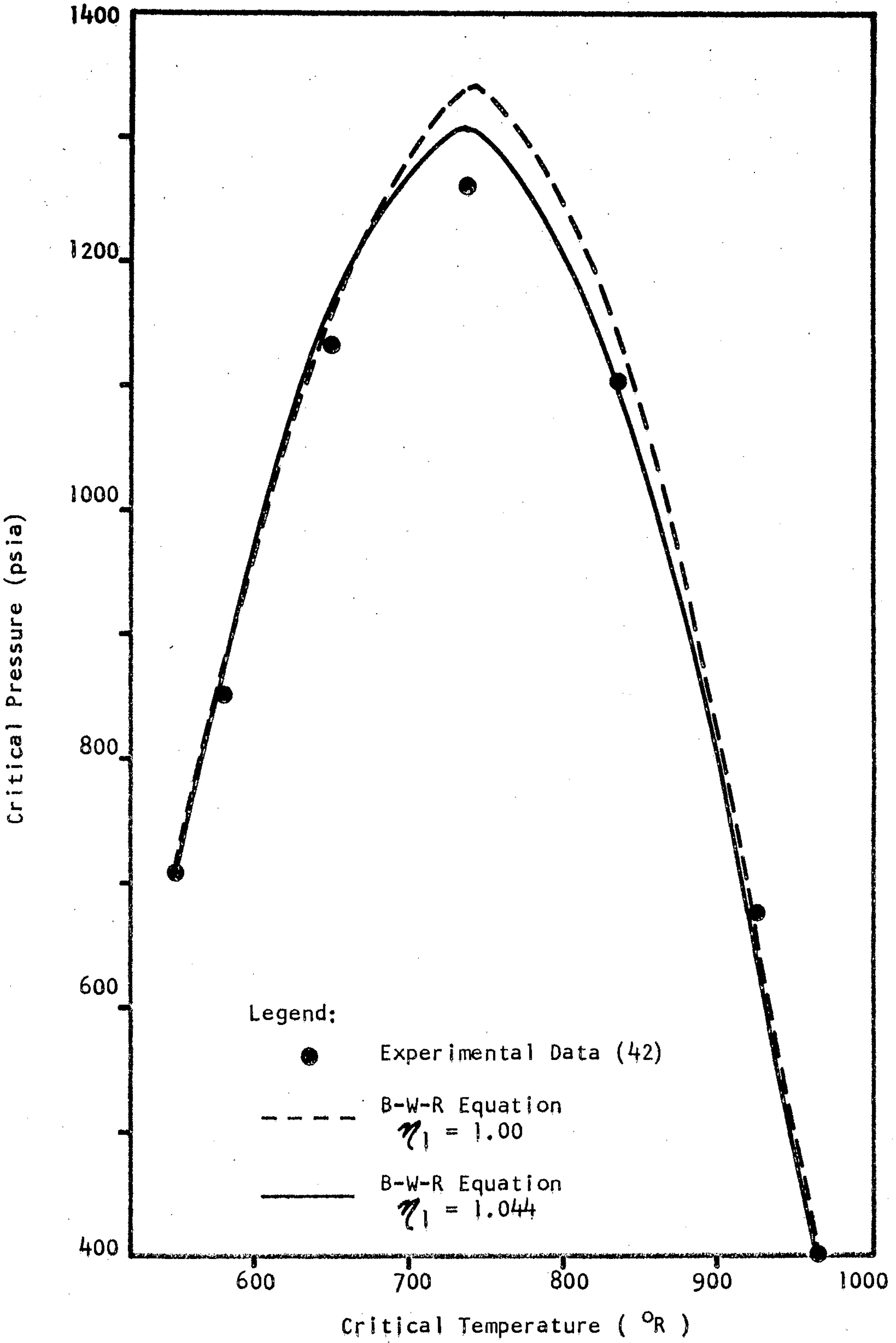

Figure 38. Critical Pressure-Critical Temperature Diagram for the Ethane/n-Heptane System

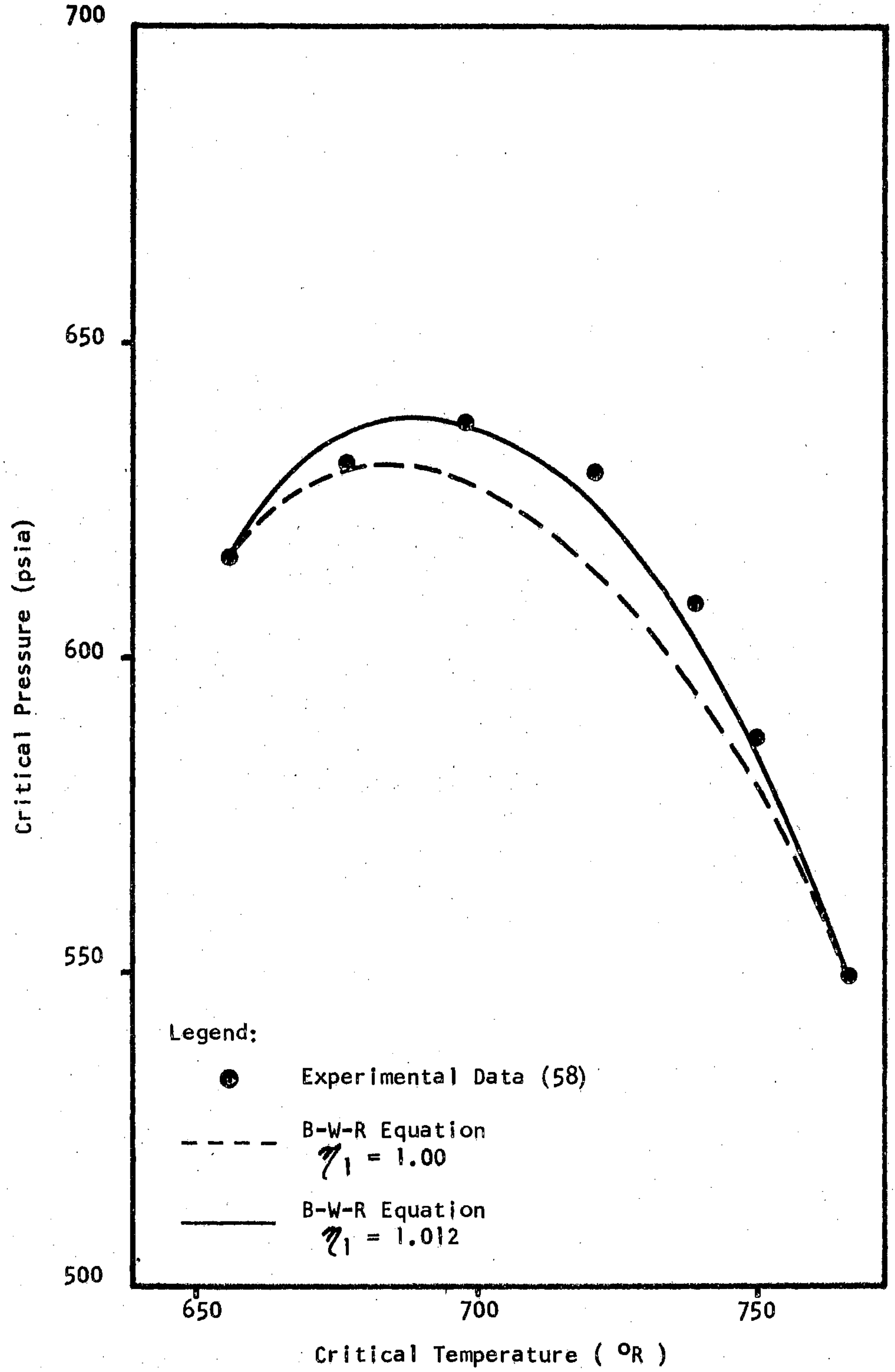

Figure 39. Critical Pressure-Critical Temperature Diagram for the Propane/n-Butane System

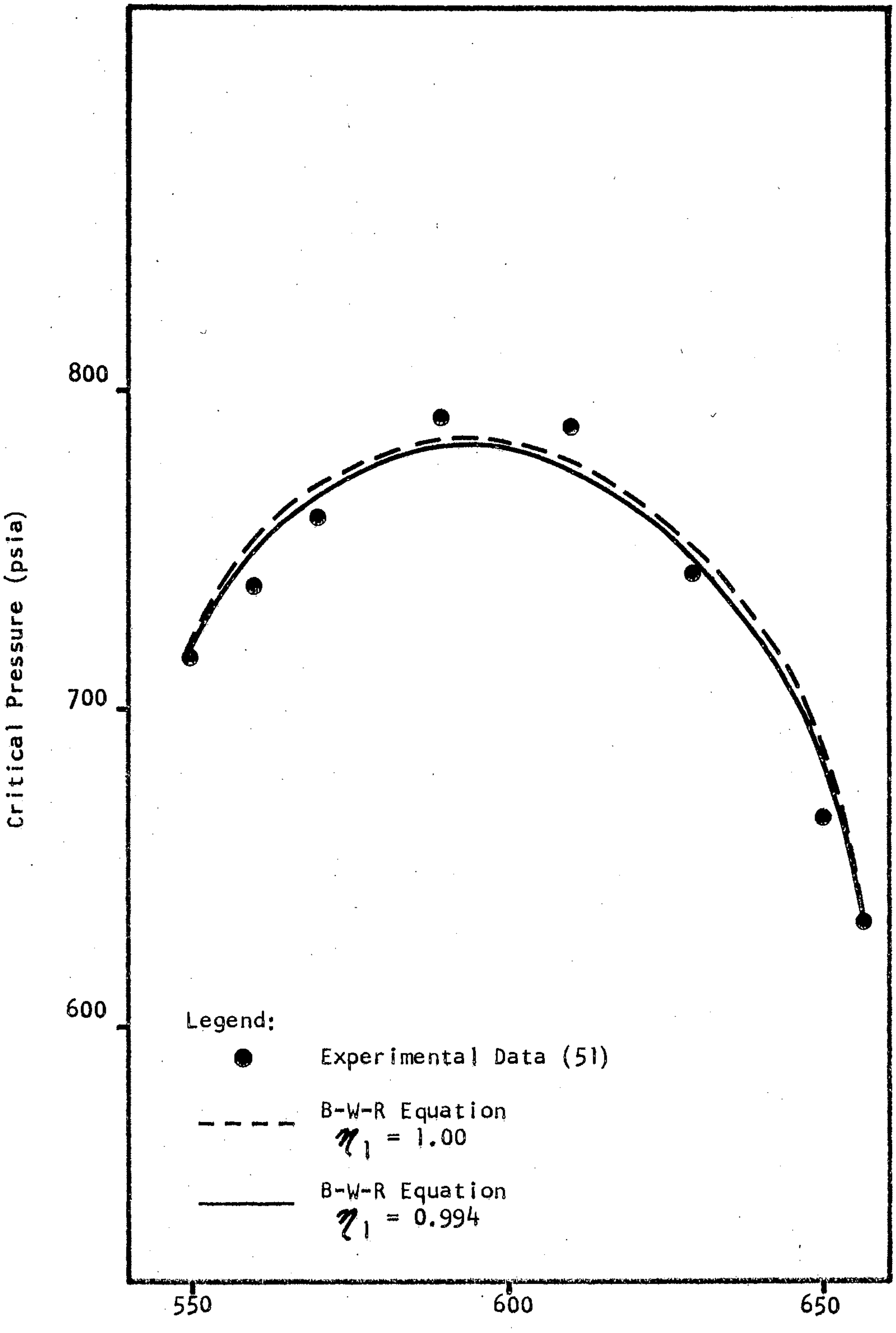

Figure 40. Critical Pressure-Critical Temperature Diagram for the Ethane/Propene System

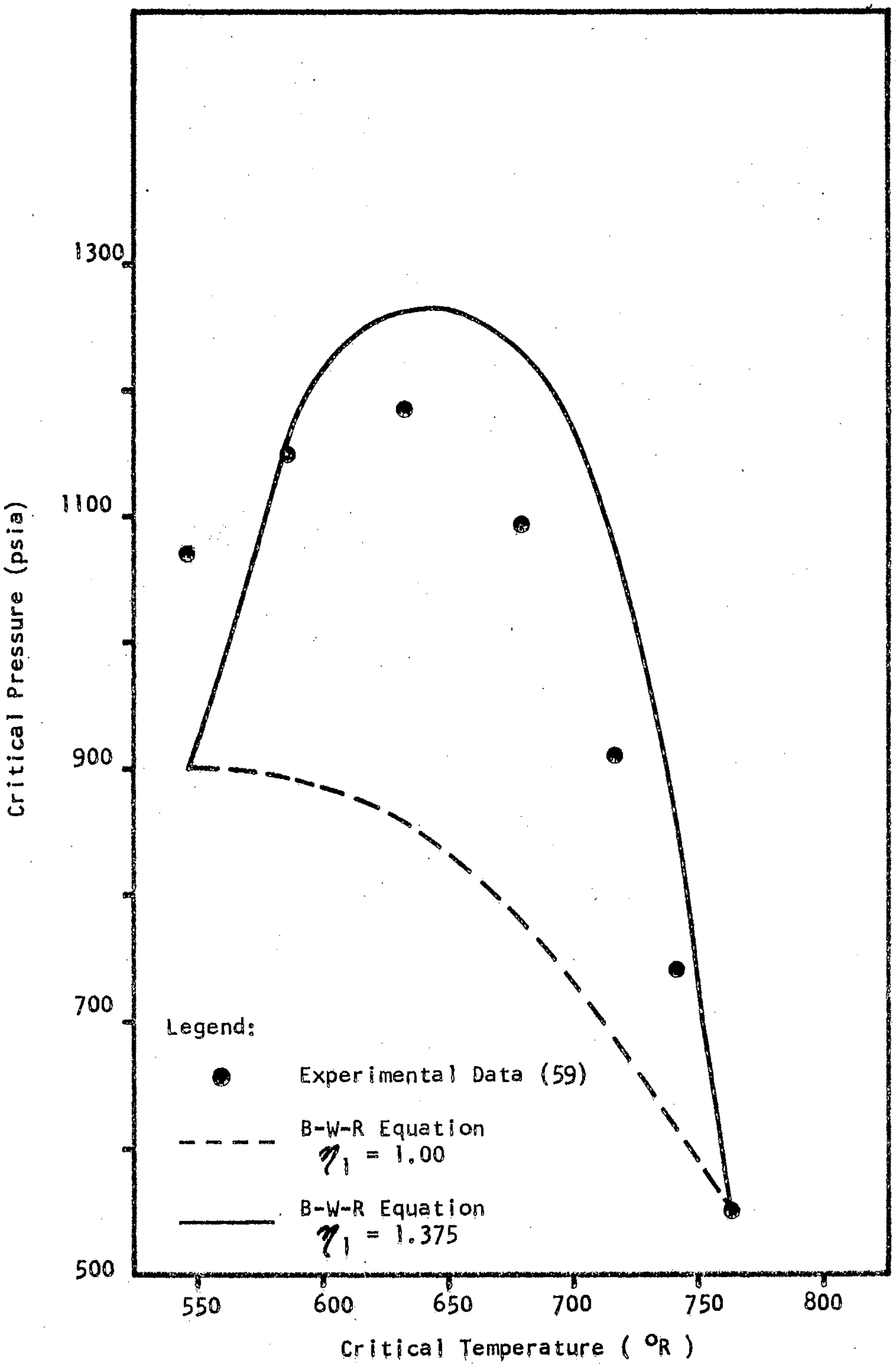

Figure 41. Critical Pressure-Critical Temperature Diagram for the n-Butane/$CO_2$ System

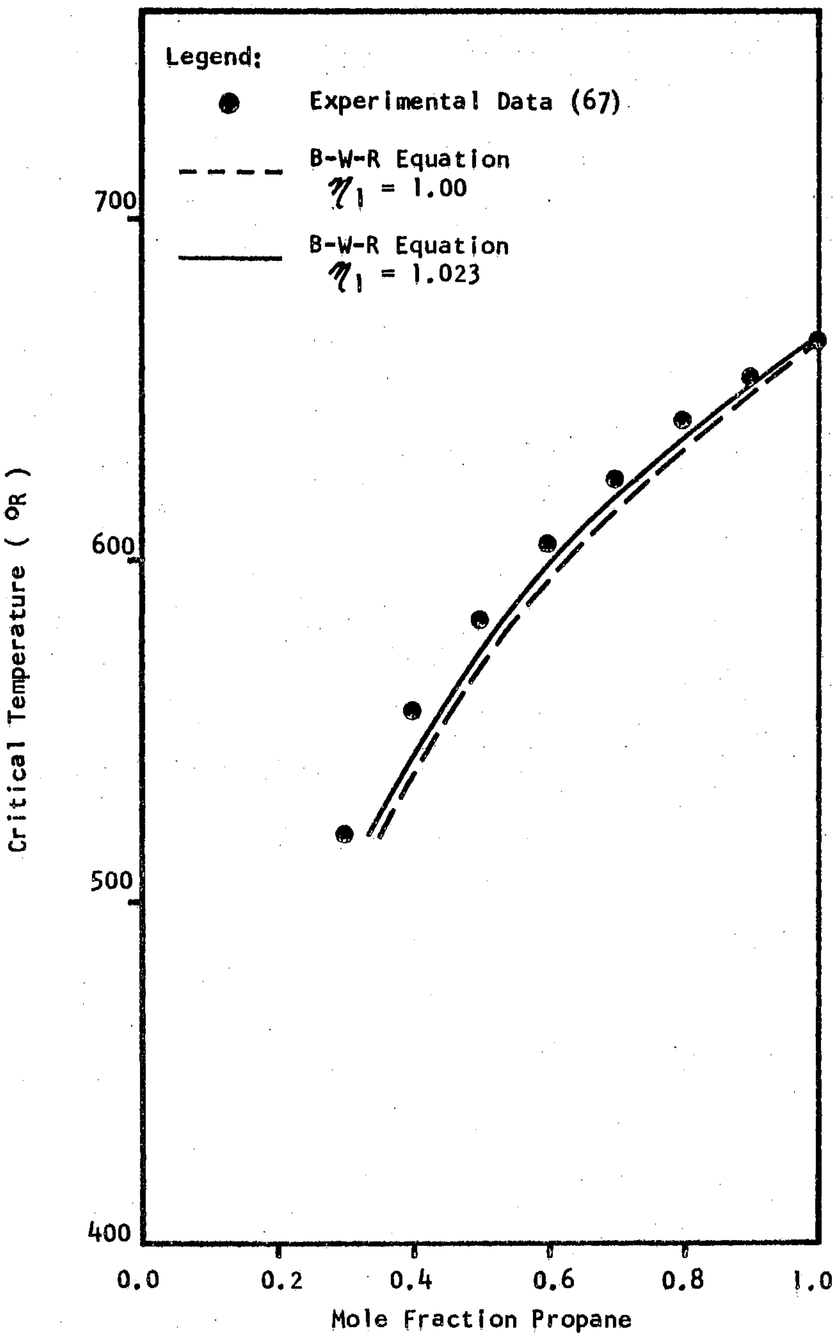

Figure 42. Critical Temperature-Composition Diagram for the Methane/Propane System

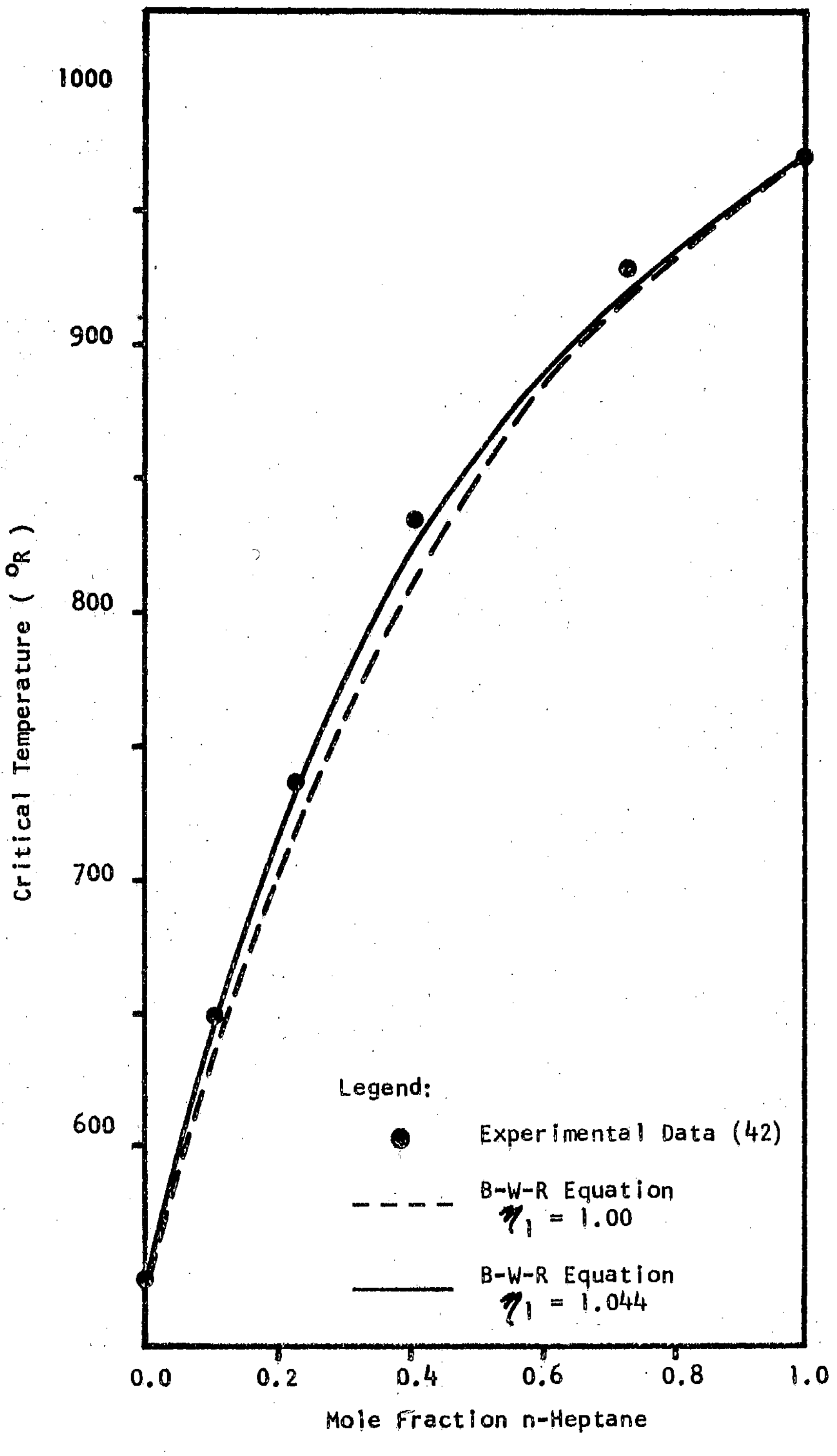

Figure 43. Critical Temperature-Composition Diagram for the Ethane/n-Heptane System

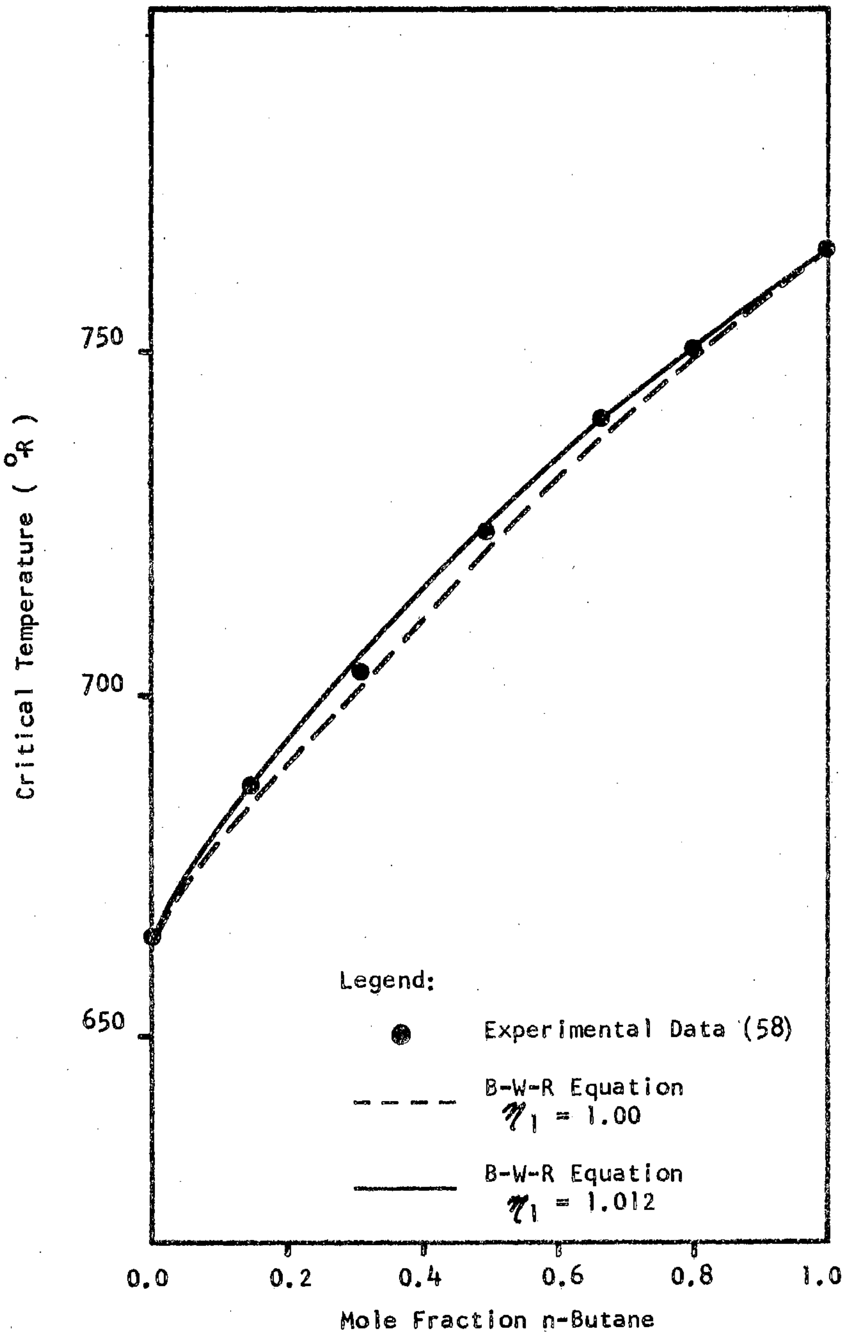

Figure 44. Critical Temperature-Composition Diagram for the Propane/n-Butane System

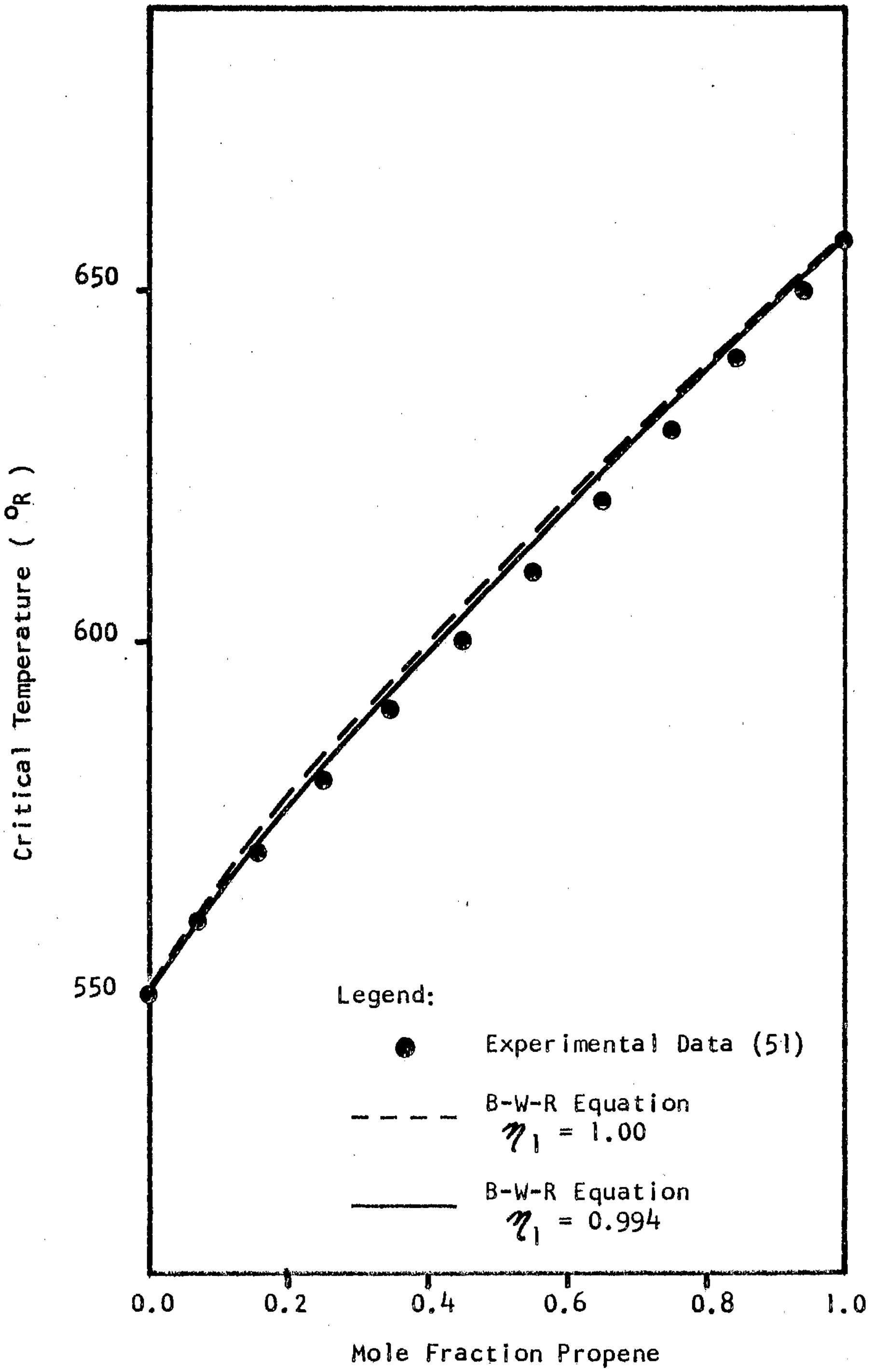

Figure 45. Critical Temperature-Composition Diagram for the Ethane/Propene System

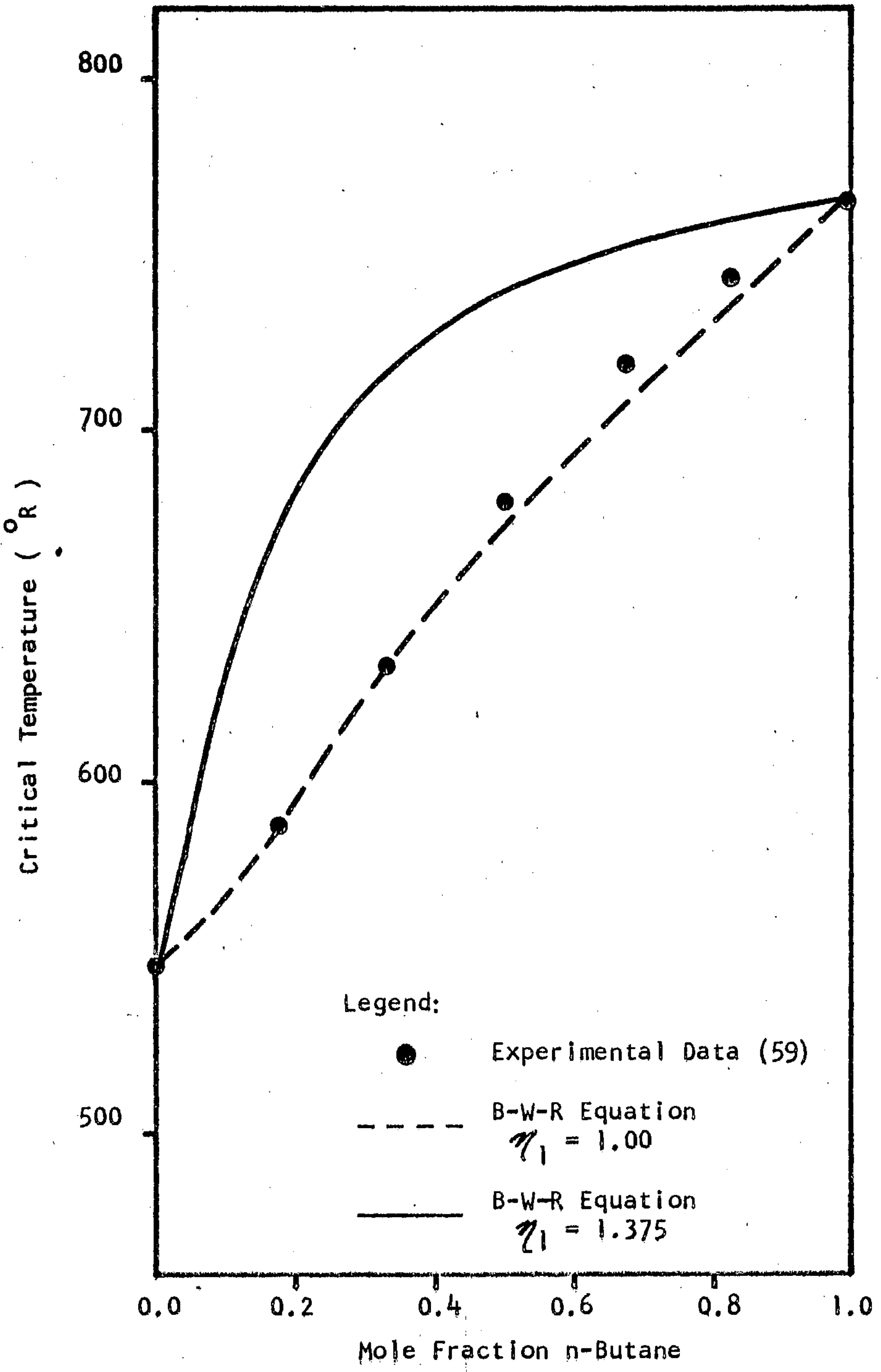

Figure 46. Critical Temperature-Composition Diagram for the n-Butane/$CO_2$ System

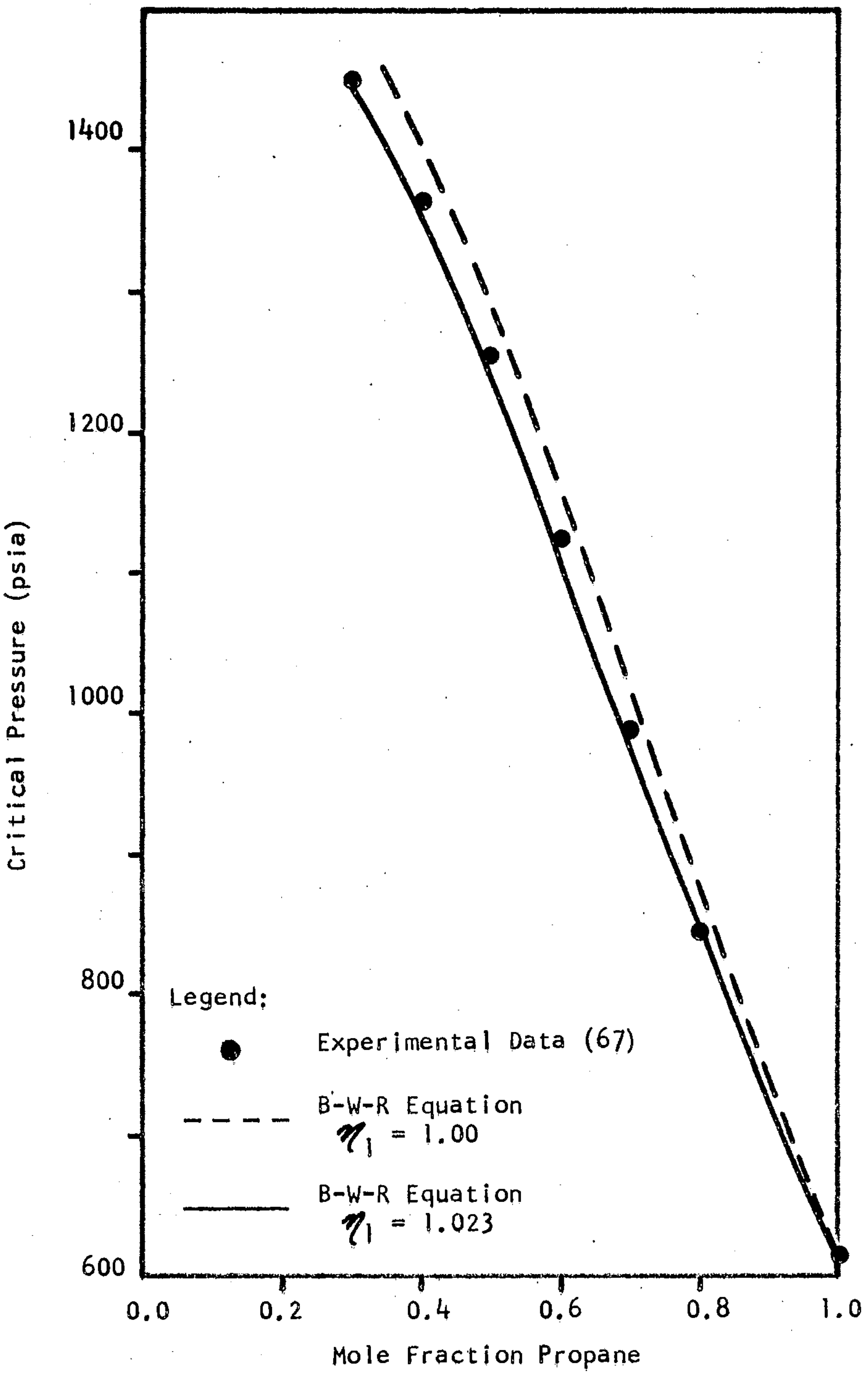

Figure 47. Critical Pressure-Composition Diagram for the Methane/Propane System

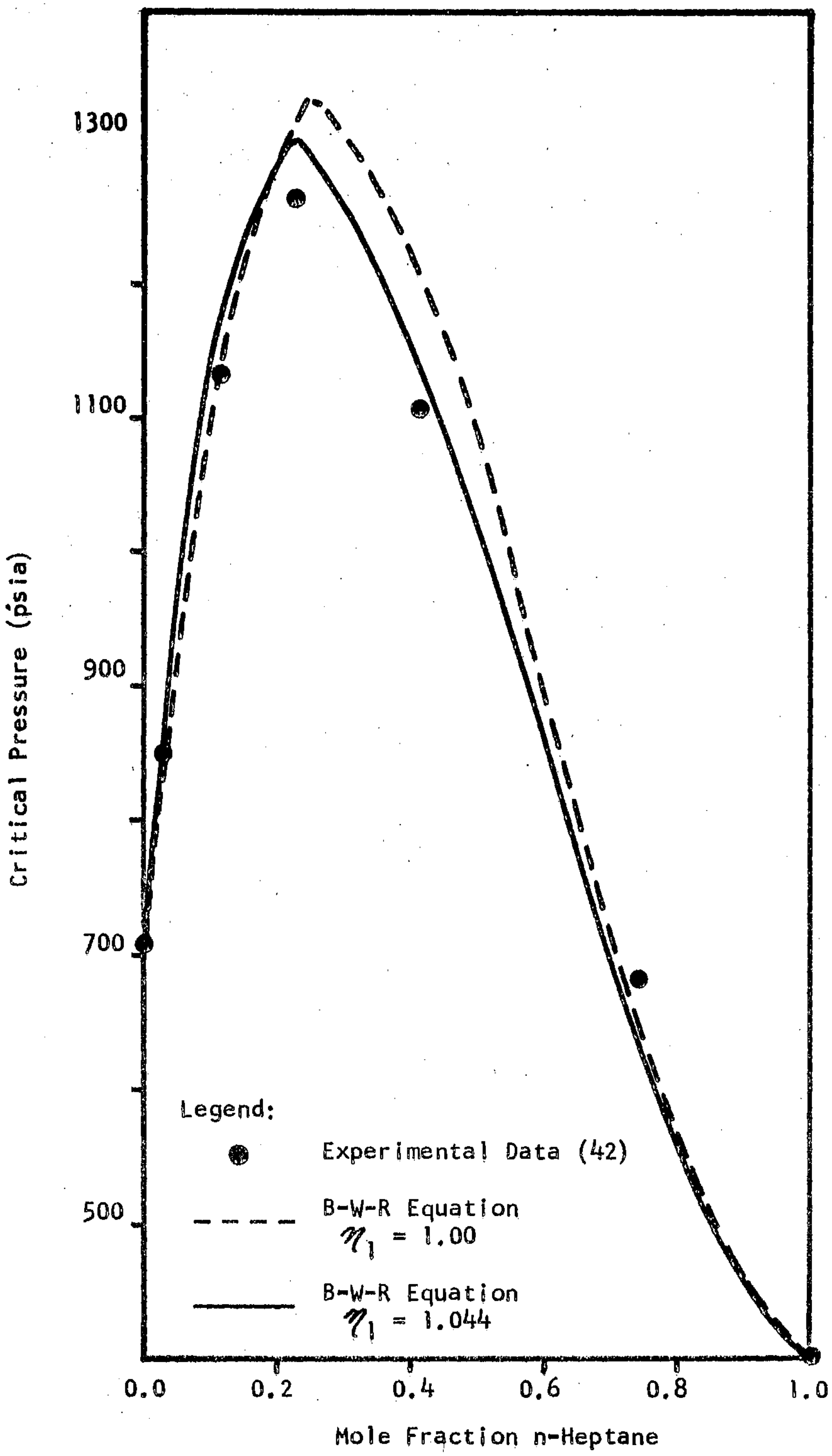

Figure 48. Critical Pressure-Composition Diagram for the Ethane/n-Heptane System

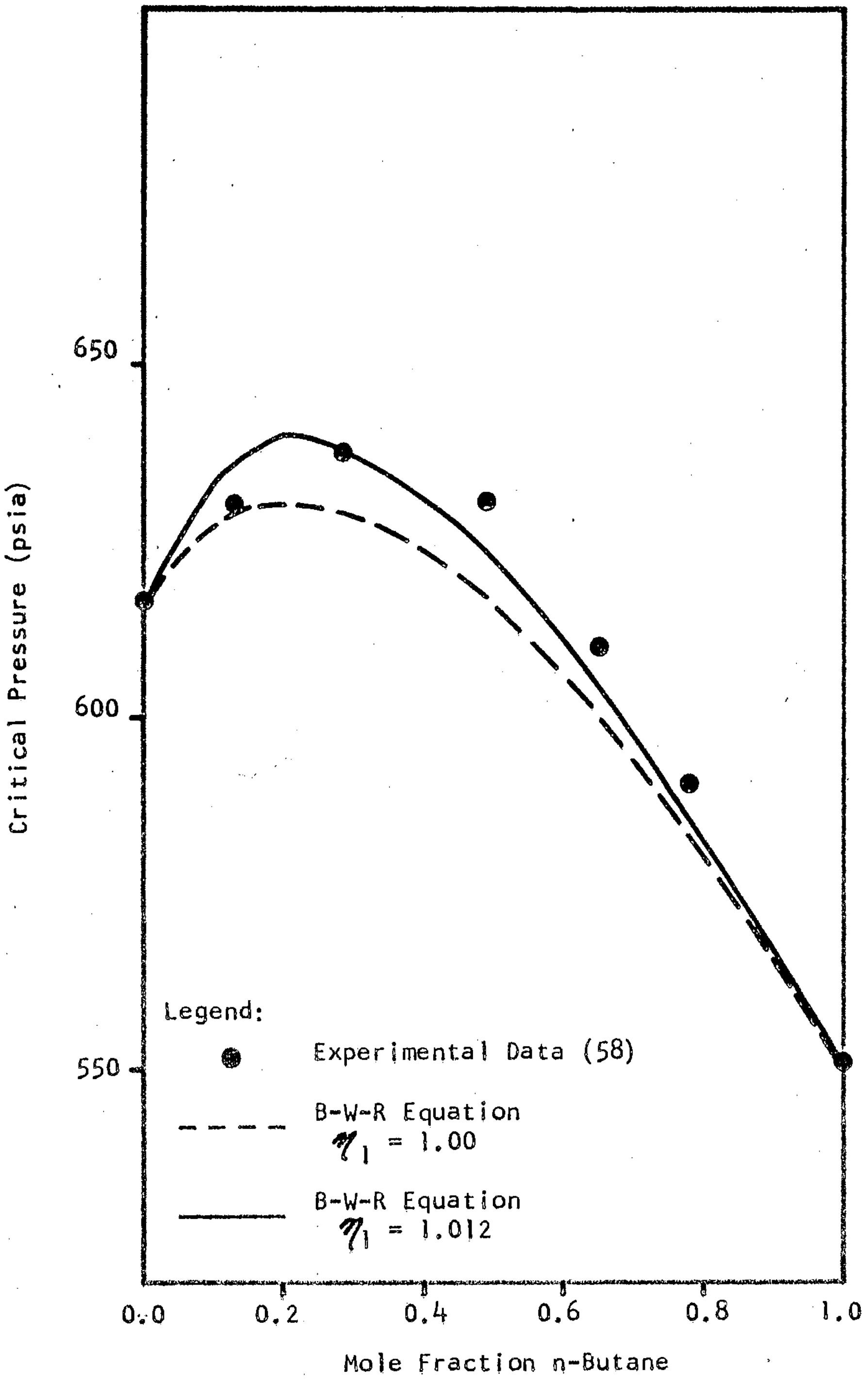

Figure 49. Critical Pressure-Composition Diagram for the Propane/n-Butane System

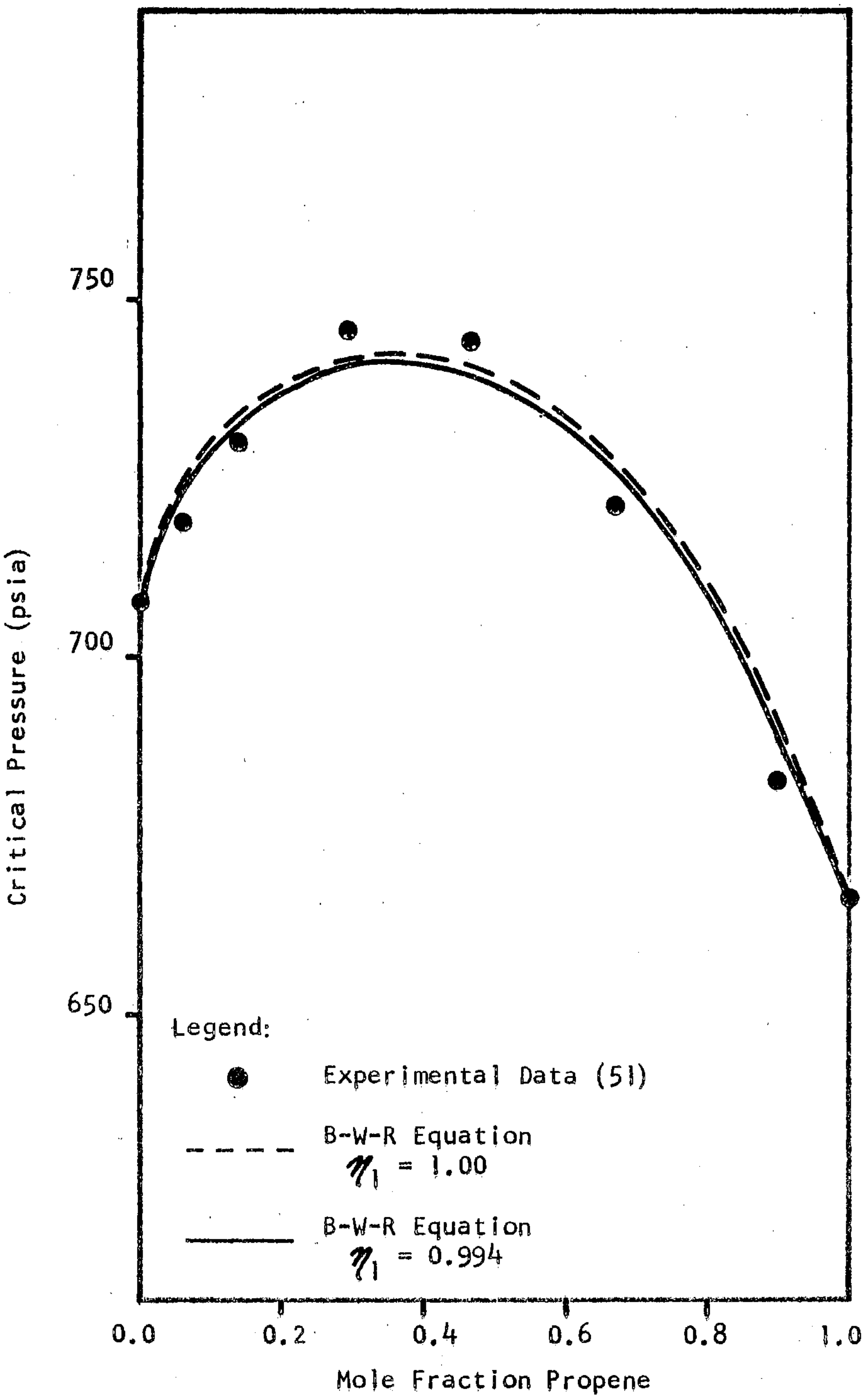

Figure 50. Critical Pressure-Composition Diagram for the Ethane/Propene System

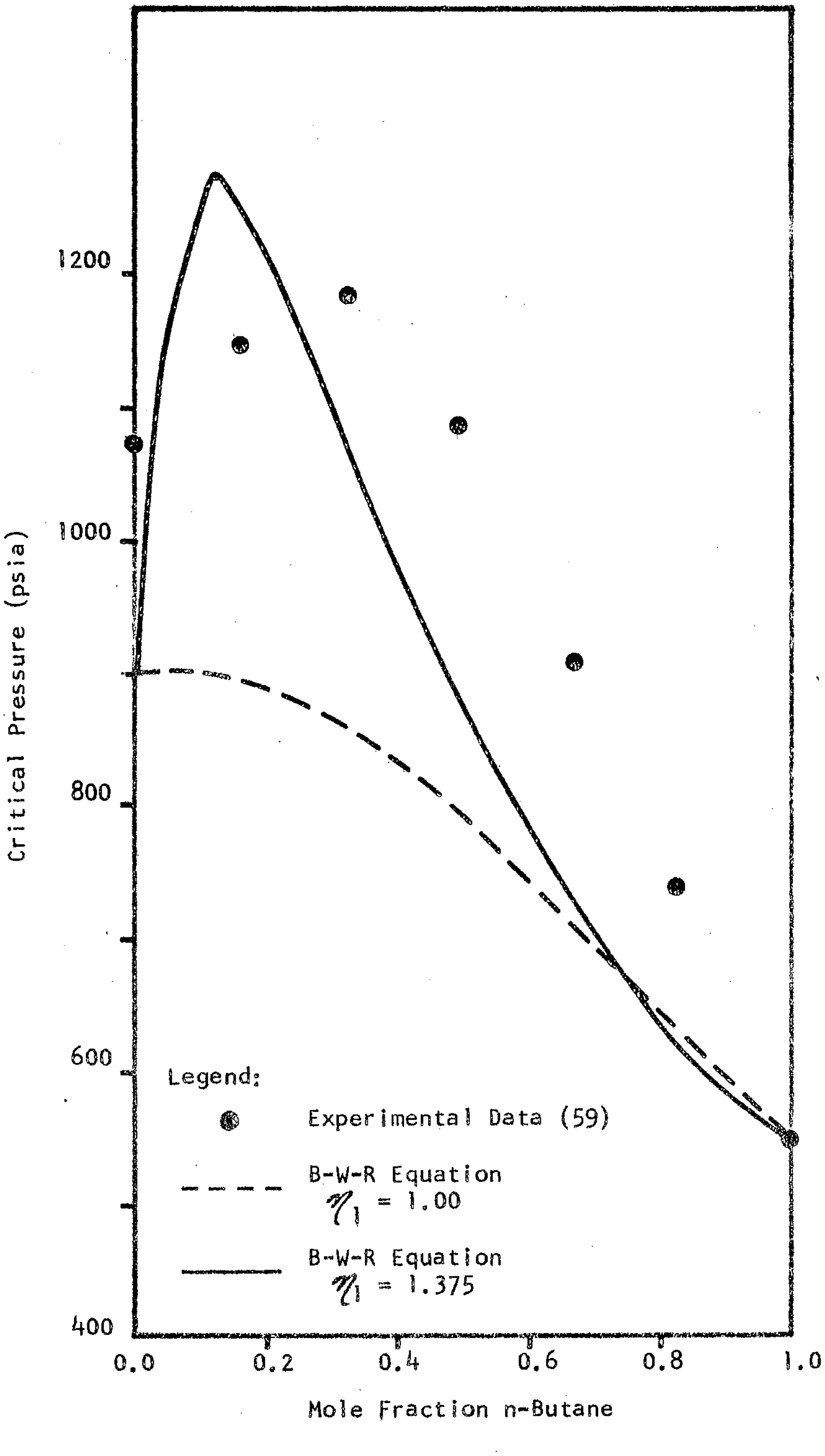

Figure 51. Critical Pressure-Composition Diagram for the n-Butane/$CO_2$ System

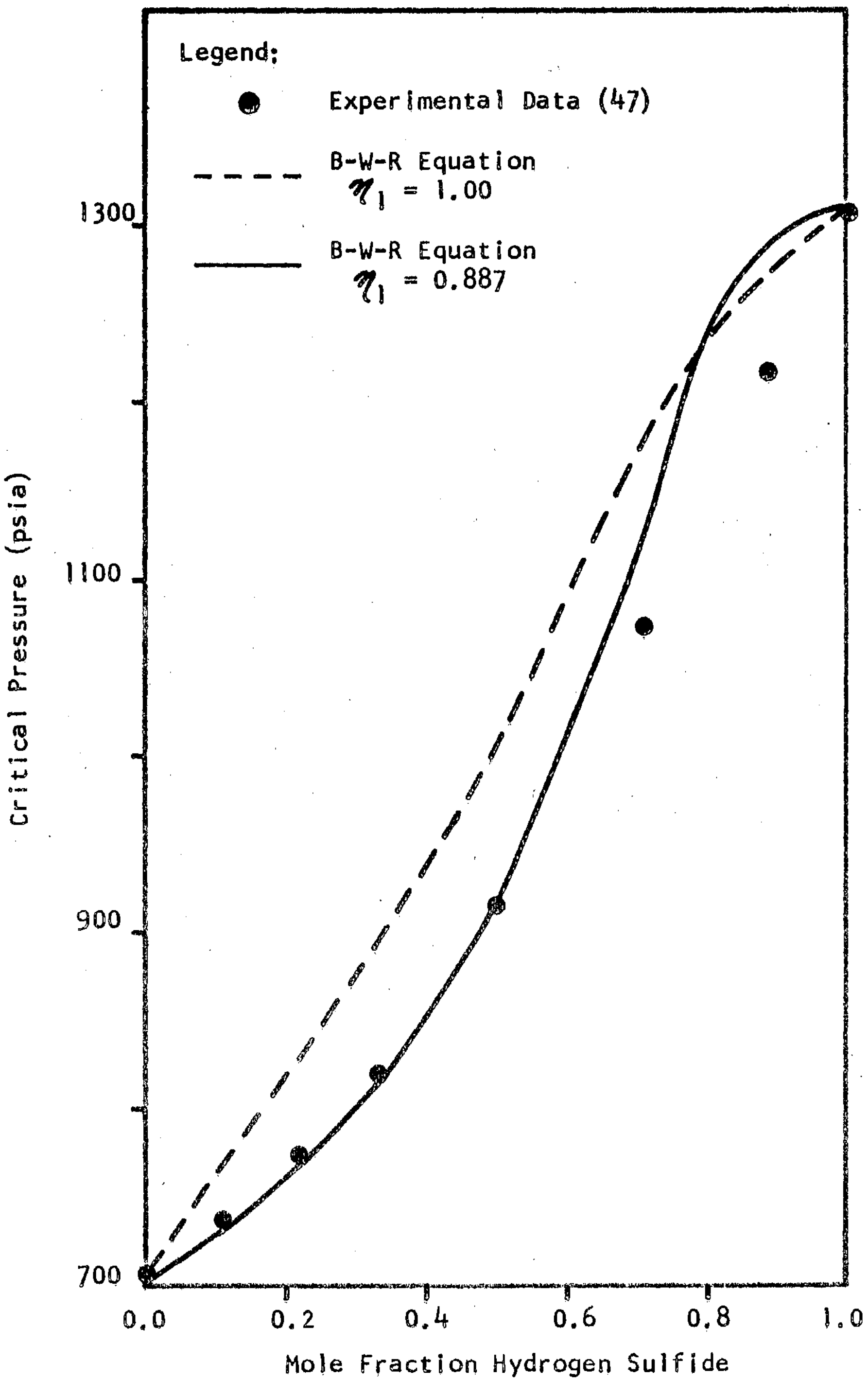

Figure 52. Critical Pressure-Composition Diagram for the Ethane/$H_2S$ System

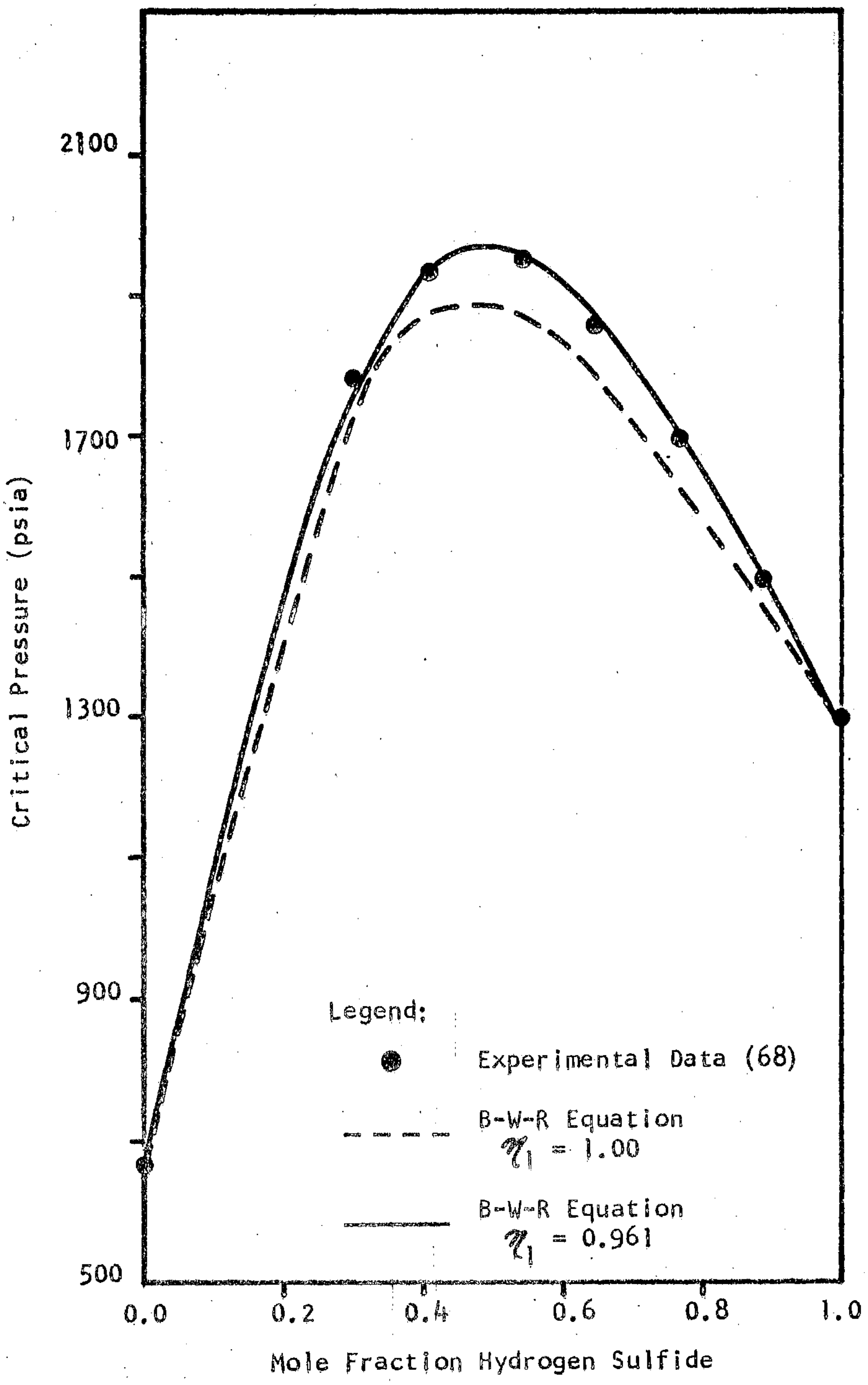

Figure 53. Critical Pressure-Composition Diagram for the Methane/$H_2S$ System

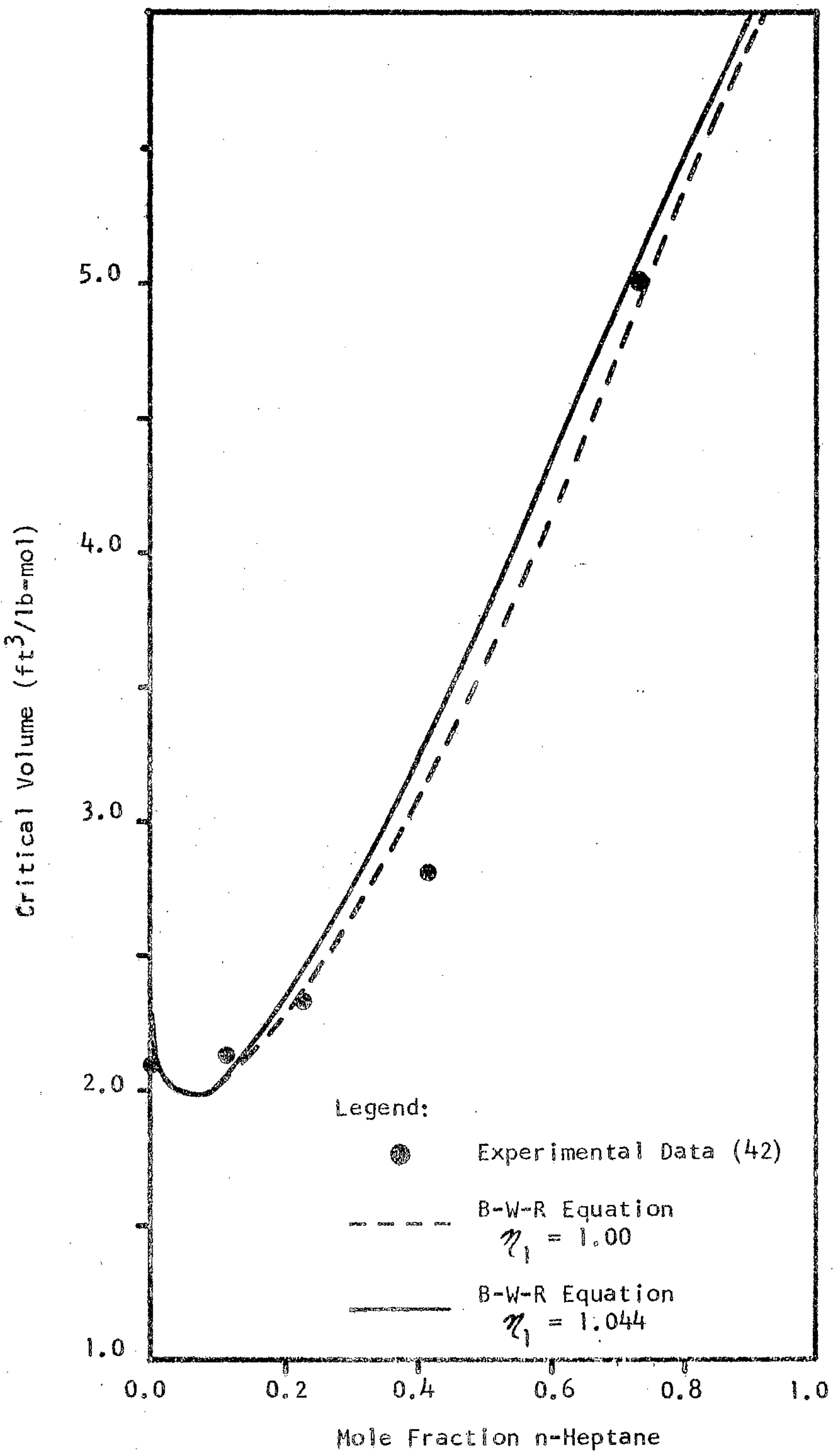

Figure 54. Critical Volume-Composition Diagram for the Ethane/n-Heptane System

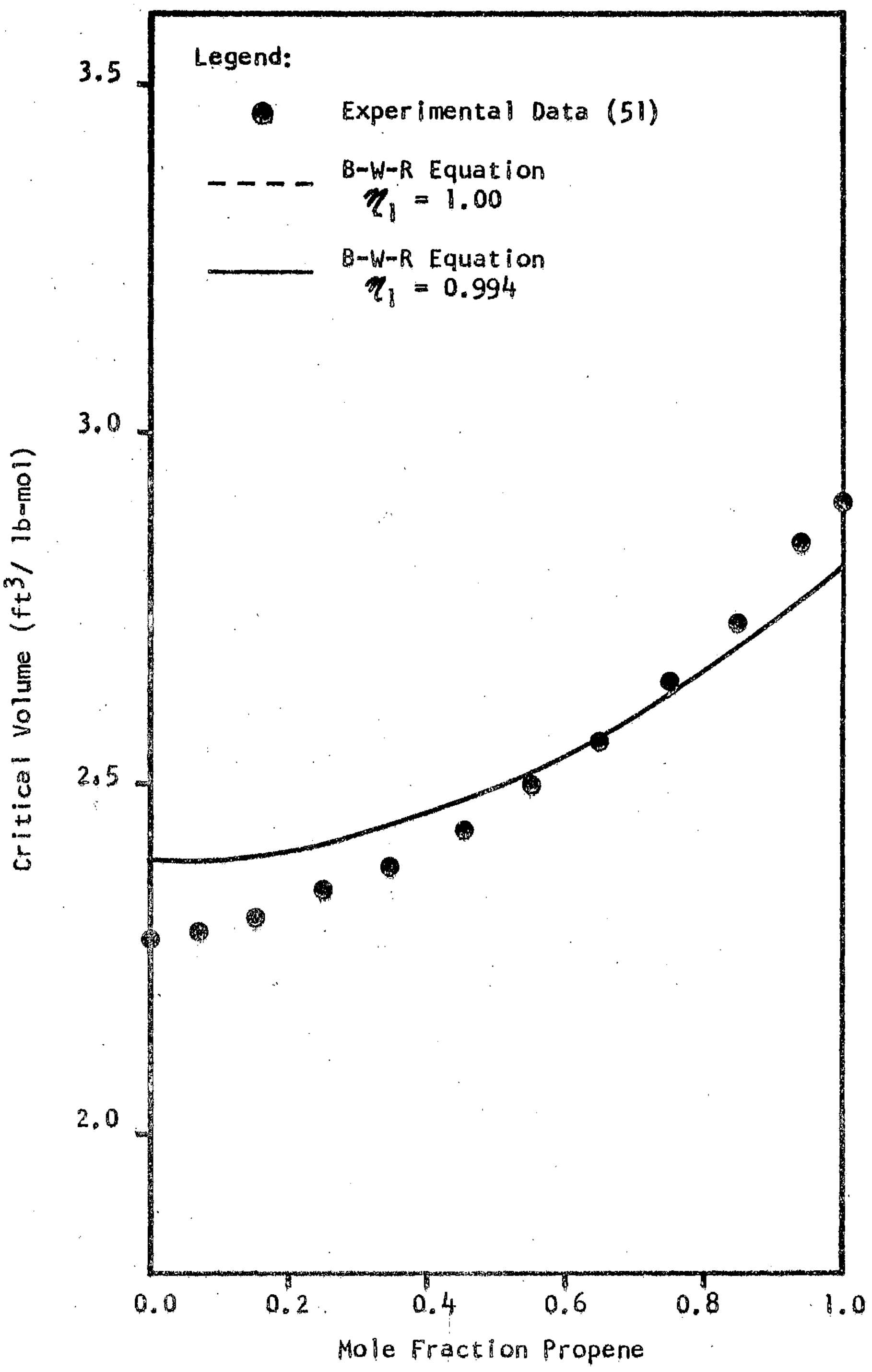

Figure 55. Critical Volume-Composition Diagram for the Ethane/Propene System

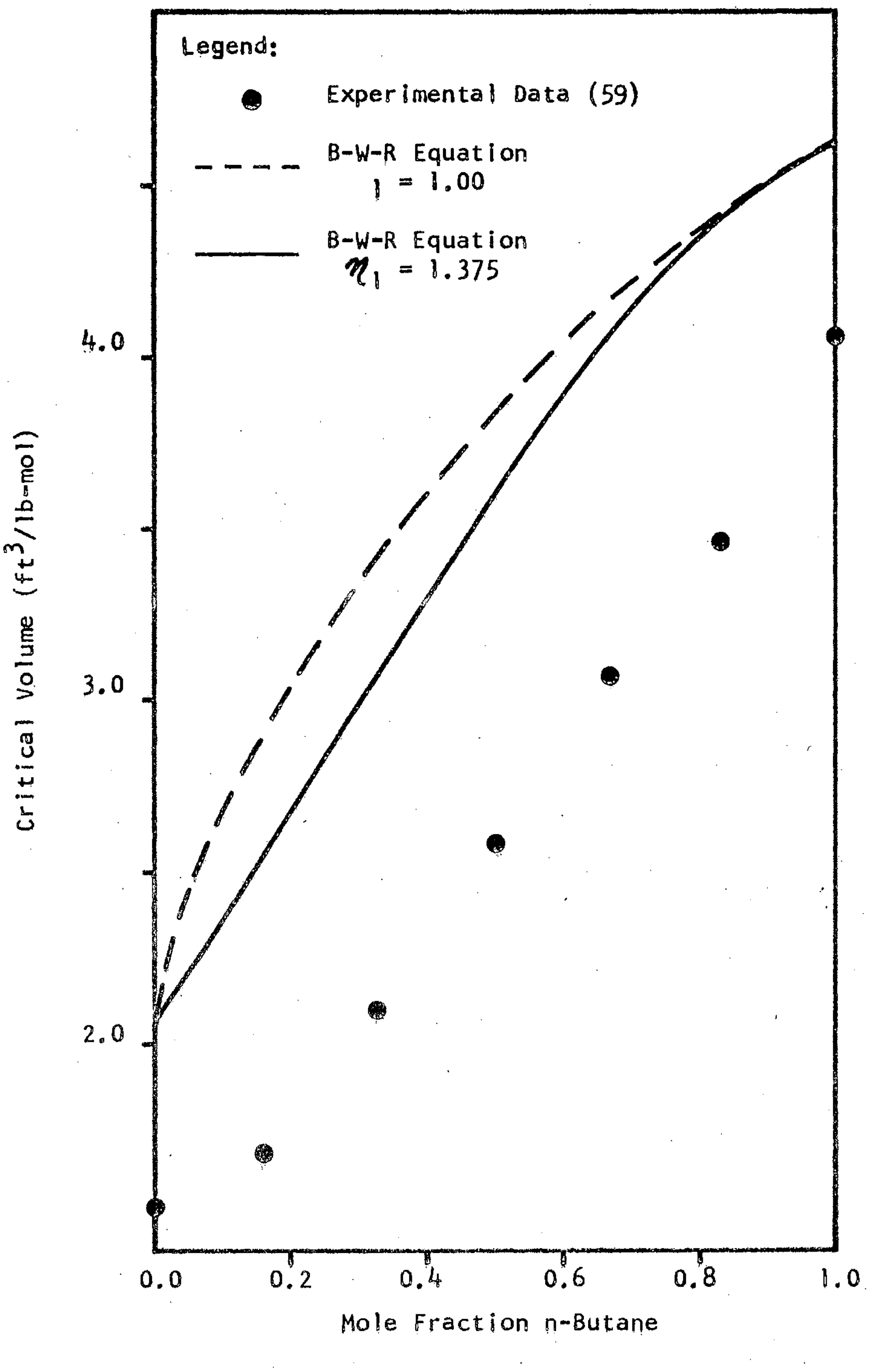

Figure 56. Critical Volume-Composition Diagram for the n-Butane/$CO_2$ System

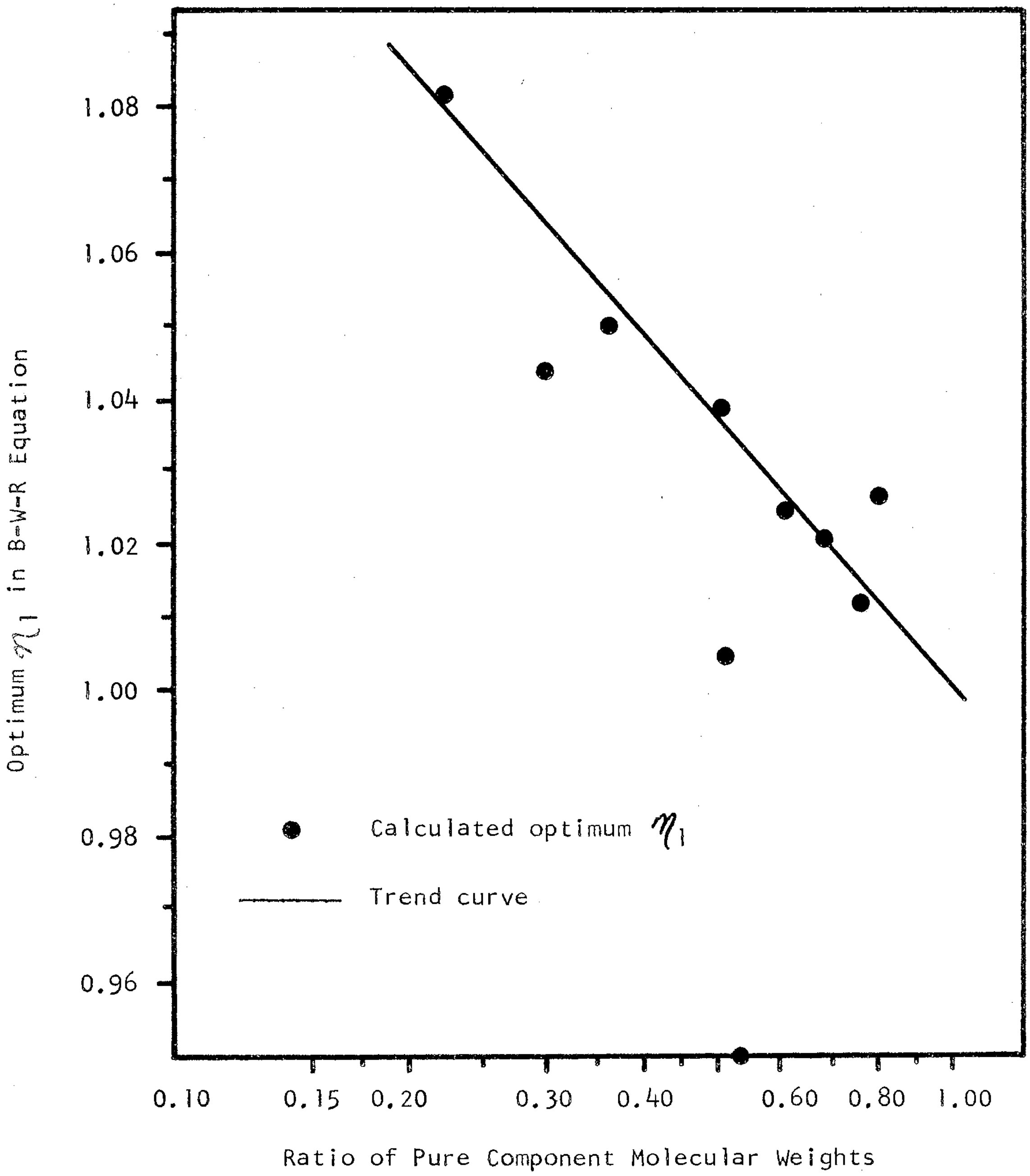

Figure 57. Plot of Optimum $\eta_1$-Molecular Weight Ratio for Paraffin/Paraffin Mixtures

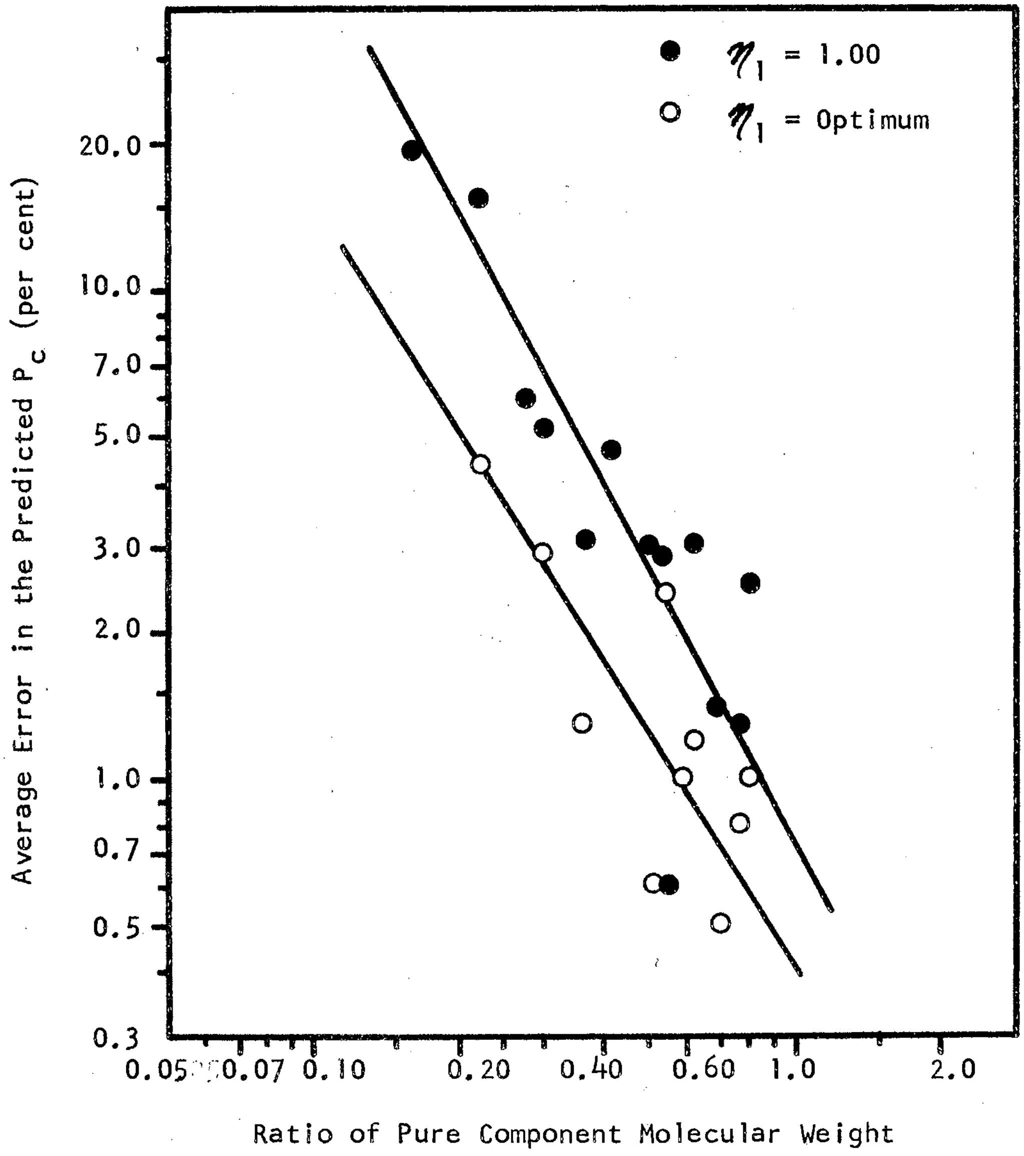

Figure 58. Plot of Average Error in the Critical Pressure versus Molecular Weight Ratio for Paraffin/Paraffin Mixtures

## G. Comparison of Critical State Calculation Results

A comparison of the results of the critical state predictions using the Redlich-Kwong and the B-W-R equations of state was necessary to provide guidelines for critical state predictions of higher multicomponent mixtures. The most important factor to be considered was the relationship between the complexity of the equations of state used in the critical state equations and the accuracy of the predictions of the critical properties. The critical state equations in terms of the B-W-R equation of state proved to be considerably more complex and difficult to derive than was the case for the Redlich-Kwong equation of state. However, the results of the critical state predictions proved to be surprisingly similar.

The most comprehensive comparison of the critical state predictions of the two equations of state can be made for the critical pressure calculations for each class of binary mixture. For the paraffin/paraffin class of mixture the B-W-R equation predicted a more accurate critical pressure-mole fraction relationship than did the Redlich-Kwong equation in eight out of fourteen binaries in the basic calculations (no adjustment of binary interaction parameters) and in ten of fourteen binaries in the optimized calculations. However, the increased accuracy of the B-W-R equation amounted to only 0.6% for the basic calculations and 1.4% for the optimized calculations. For the paraffin/non-paraffin class of mixture the B-W-R equation predicted a more accurate $P_c$-$x_2$ relationship in four out of six binaries for the basic calculations and in three out of six binaries for the optimized calculations. The increased accuracy of the B-W-R equation amounted to 1.9% for the basic calculations and only 0.4% for the optimized calculations. For the hydrocarbon/non-hydrocarbon class of mixture the B-W-R equation was more accurate in only one of six binaries for the basic and optimized calculations. The increased accuracy of the Redlich-Kwong equation was 8.2% for the basic calculations and 3.0% for the optimized calculations. A comparison of the total over-all error averages using the Redlich-Kwong and B-W-R equations of state indicated that the more complex B-W-R equation is not greatly superior in predicting the critical pressure than the simple Redlich-Kwong equation. In fact, the Redlich-Kwong equation proved to be far superior to the B-W-R equation when a polar molecule such as carbon dioxide or hydrogen sulfide was present in the binary mixture. The major conclusion to be drawn from this comparison is that for exploratory calculations without optimization of the binary interaction parameters the Redlich-Kwong equation is superior to the B-W-R equation in terms of both accuracy and simplicity of the critical state equation derivations. This somewhat surprising result is supported by the findings of Ackerman and Redlich (1) who came to the same conclusion using both the Redlich-Kwong and B-W-R equations of state in the "limiting slope" calculation method developed by Redlich and Kister. (73)

Graphical comparisons of the calculated critical properties of two binary systems, the ethane/n-heptane and n-butane/carbon dioxide binaries, are presented in Figures 59-66. The critical state relationships of the ethane/n-heptane system show that the $P_c$-$T_c$ and $P_c$-$x_2$ relationships were best described by the Redlich-Kwong equation while the $T_c$-$x_2$ and $V_c$-$x_2$ relationships were best described by the B-W-R equation. Thus, one particular equation of state did not necessarily describe all the critical property relationships better than the other equation of state.

In the hydrocarbon/non-hydrocarbon class of mixtures, however, the Redlich-Kwong equation generally predicted all critical property relationships better than the B-W-R equation. The n-butane/carbon dioxide system, shown in Figures 62-65, shows that even the critical volume-composition relationship was predicted better by the Redlich-Kwong equation. The reason for the extreme critical volume deviations using the B-W-R equation appeared to be the inability of the B-W-R equation to accurately predict the pure component critical volume. For pure n-butane the deviation of the calculated and experimental critical volume was over 0.6 $ft^3$/lb-mol or a deviation of 15%. Thus, the mixture critical volume predictions using the B-W-R equation with the original B-W-R constants were no worse than the predictions for pure components.

One of the most striking features of the critical state calculations is that the values of the optimized interaction parameters are not equal to 1.0 as suggested in the original binary mixing rules of the Redlich-Kwong and B-W-R equations of state. The assignment of a value of 1.0 to the binary interaction parameters is equivalent to assuming that the intermolecular energy can be described by the geometric mean of the pure-component energies. Chueh and Prausnitz(14) point out that the geometric mean relationship is accurate only for simple, spherically-symmetric molecules of nearly equal size. Thus, for most binary systems, the "best" value of the interaction parameter will not equal 1.0 which agrees with the results of the semi-theoretical critical state correlation of Chueh and Prausnitz and with this investigation.

A comparison of the accuracy of the critical state predictions using the equation of state approach and two of the most significant and useful empirical calculation methods appears in Table IV. In general, the accuracy of critical pressure predictions from the empirical calculation methods of Eilerts (23) and Chueh and Prausnitz (14) was comparable to that obtained with the equation of state approach using either the Redlich-Kwong or B-W-R equations of state. However, the Eilerts correlation is generally restricted to the paraffin/hydrocarbon binary systems. The Chueh and Prausnitz correlation, the most general and accurate of the available empirical correlations, is comparable to the equation of state approach in terms of both accuracy and applicability for all classes of binary mixtures. The advantages of the equation of state approach are that the critical properties are determined simultaneously, including the critical volume, and are not restricted to any particular equation of state. Thus, as improvements in equations of state are made, particularly in the region near the critical point, the accuracy of all the predicted critical properties will be improved simultaneously.

# TABLE IV

## A COMPARISON OF THE AVERAGE ERROR IN THE PREDICTION OF THE CRITICAL PRESSURE FROM THE $P_c$-$x_2$ RELATIONSHIP

| Method | Number of Systems | Average Error in $P_c$-$x_2$ (%) | Type of Mixture Systems* |
|---|---|---|---|
| Eilerts, et al | 44 | 11.1 | Par/HC |
| Chueh-Prausnitz | 36 | 3.6 | Par/Par<br>Par/n-Par<br>HC/n-HC<br>n-HC/n-HC |
| Eqn of state | | | |
| R-K Equation | | | Par/Par<br>Par/n-Par |
| Basic | 41 | 5.2 | HC/n-HC |
| Optimized | 41 | 3.2 | n-HC/n-HC |
| B-W-R Equation | | | Par/Par<br>Par/n-Par |
| Basic | 27 | 7.4 | HC/n-HC |
| Optimized | 27 | 3.1 | |

| *Mixture Systems | |
|---|---|
| Par/Par | Paraffin/Paraffin |
| Par/n-Par | Paraffin/non-Paraffin |
| HC/n-HC | Hydrocarbon/non-Hydrocarbon |
| n-HC/n-HC | non-Hydrocarbon/non-Hydrocarbon |

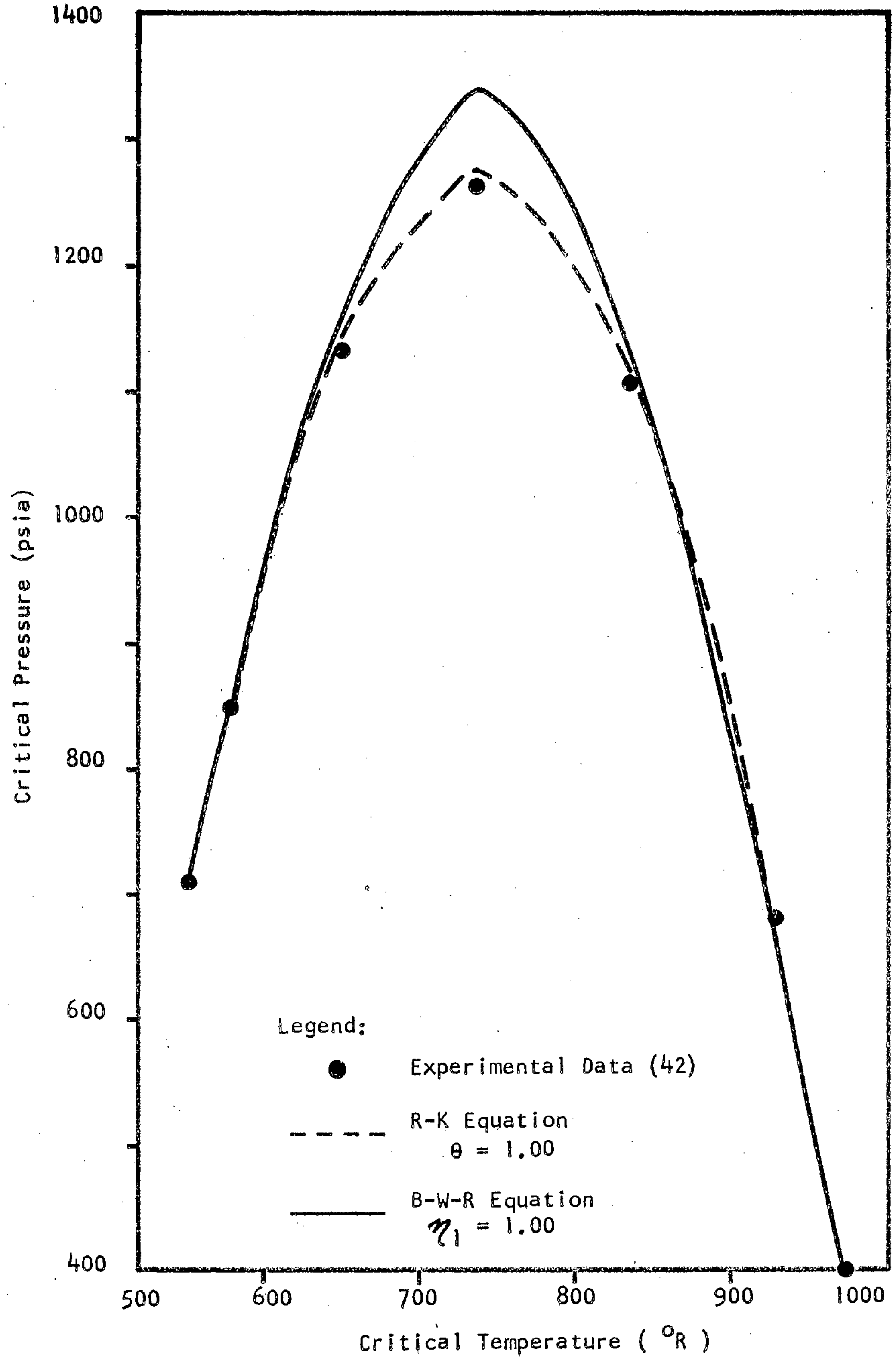

Figure 59. Critical Pressure-Critical Temperature Diagram for the Ethane/n-Heptane System

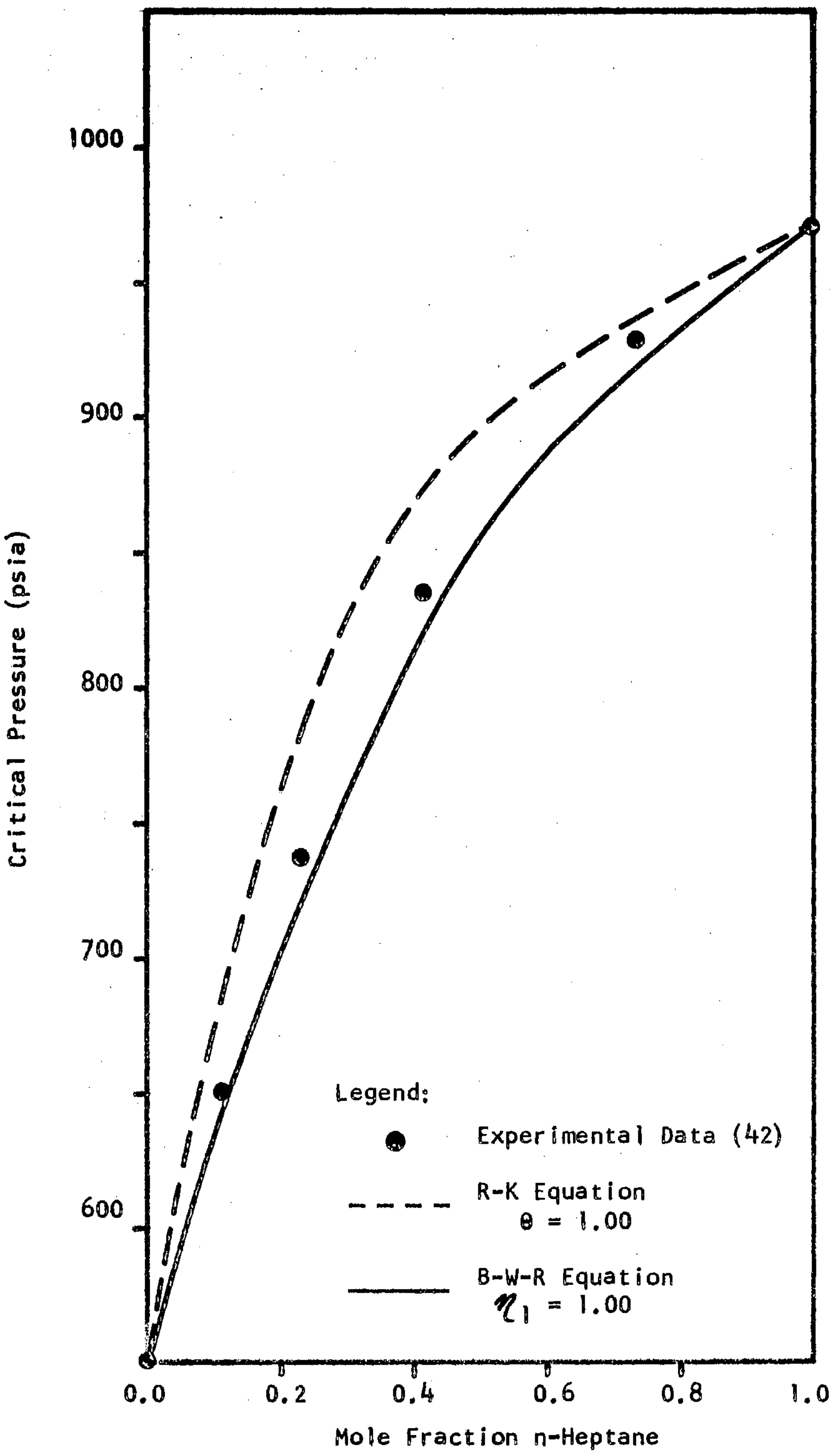

Figure 60. Critical Pressure-Composition Diagram for the Ethane/n-Heptane System

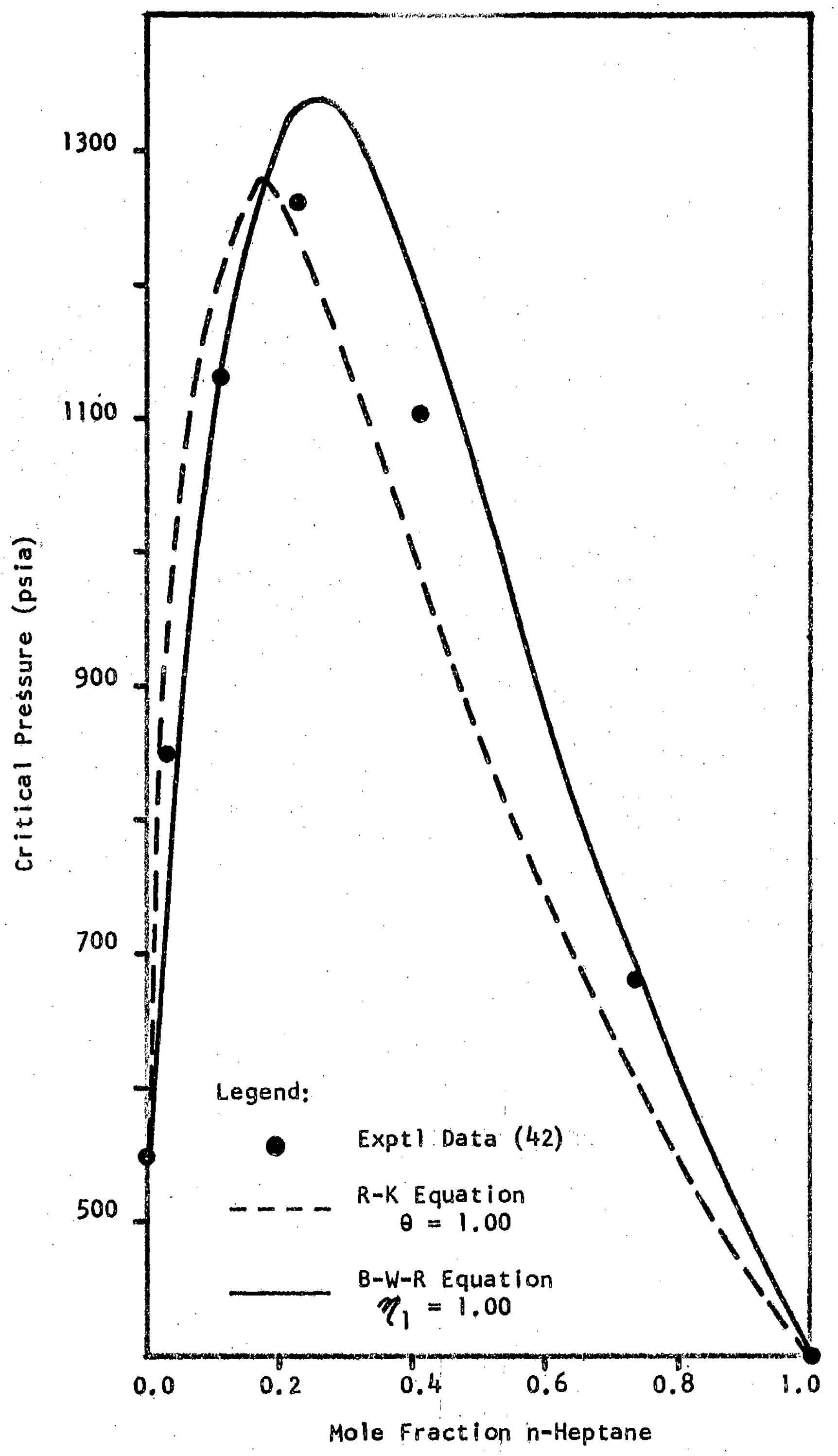

Figure 61. Critical Pressure-Composition Diagram for the Ethane/n-Heptane System

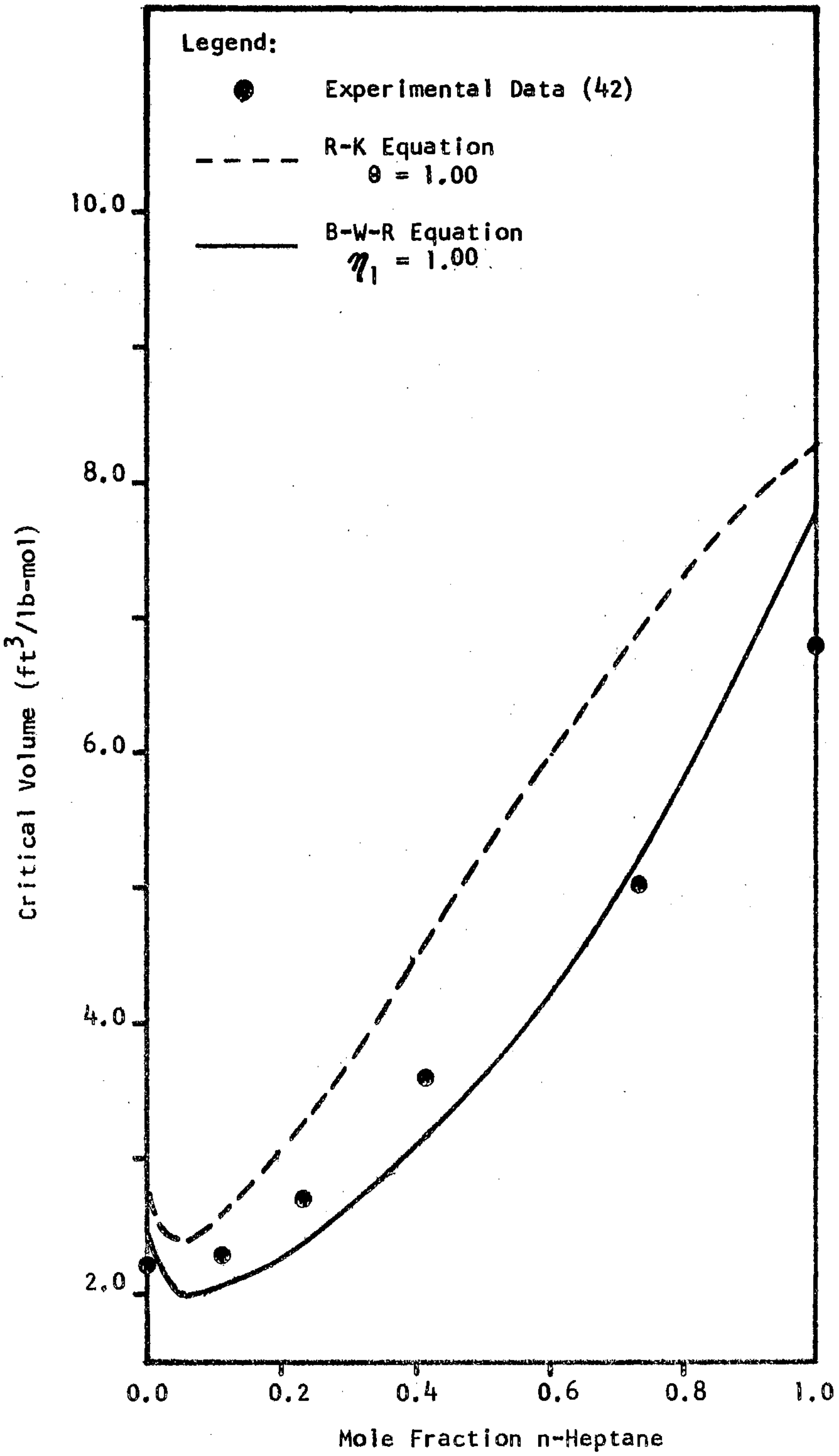

Figure 62. Critical Volume-Composition Diagram for the Ethane/n-Heptane System

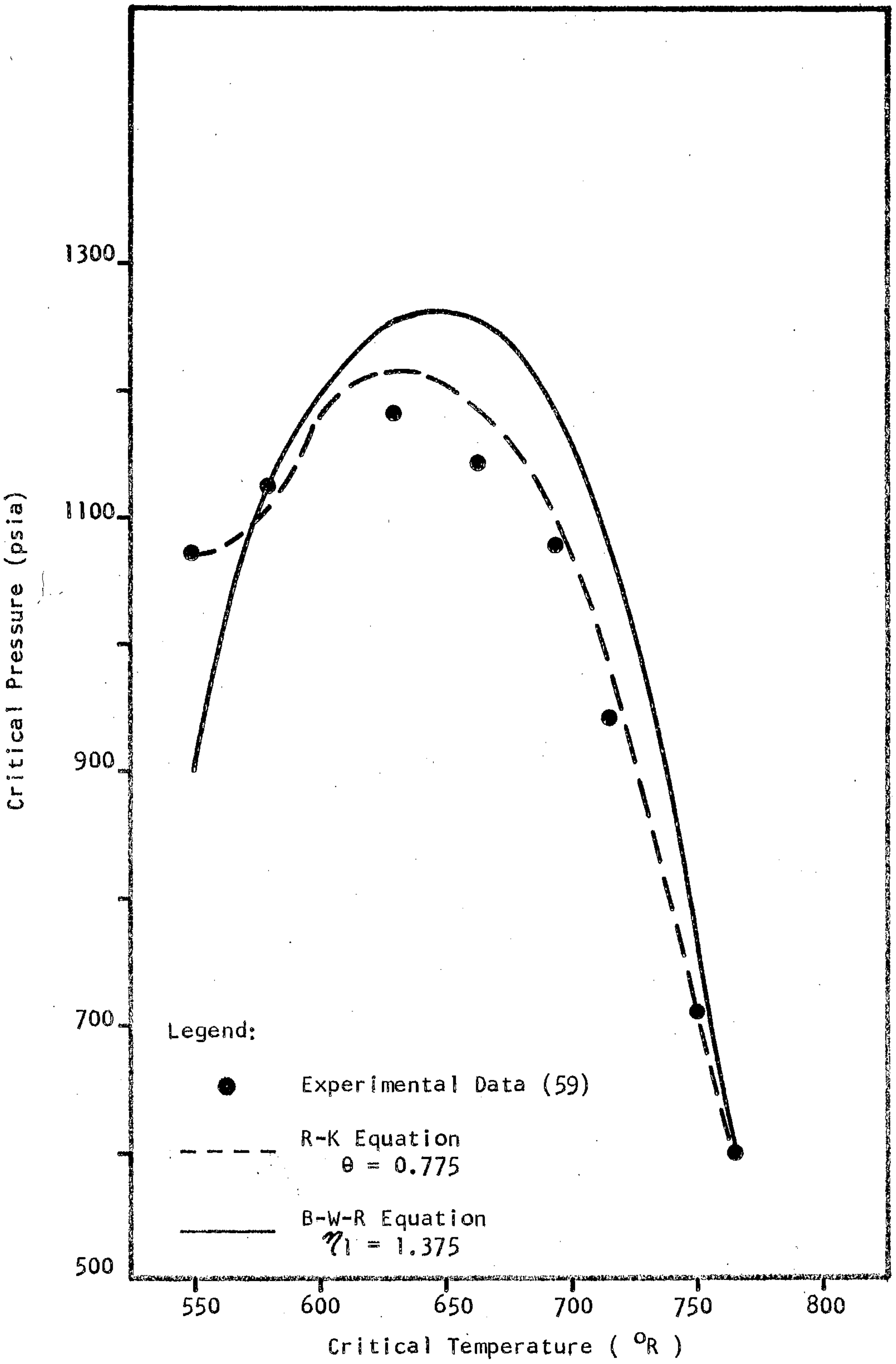

Figure 63. Critical Pressure-Critical Temperature Diagram for the n-Butane/$CO_2$ System

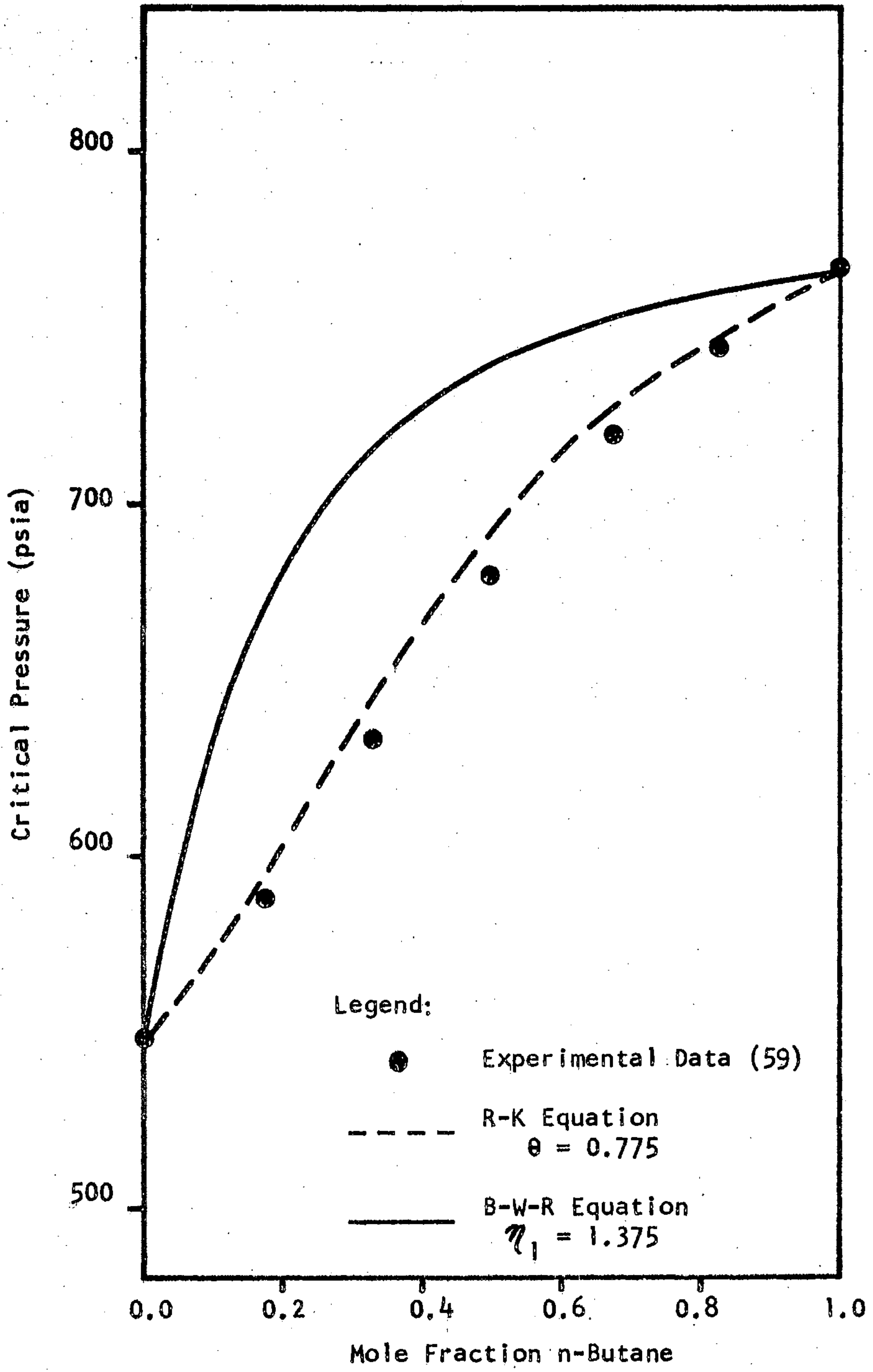

Figure 64. Critical Pressure-Composition Diagram for the n-Butane/$CO_2$ System

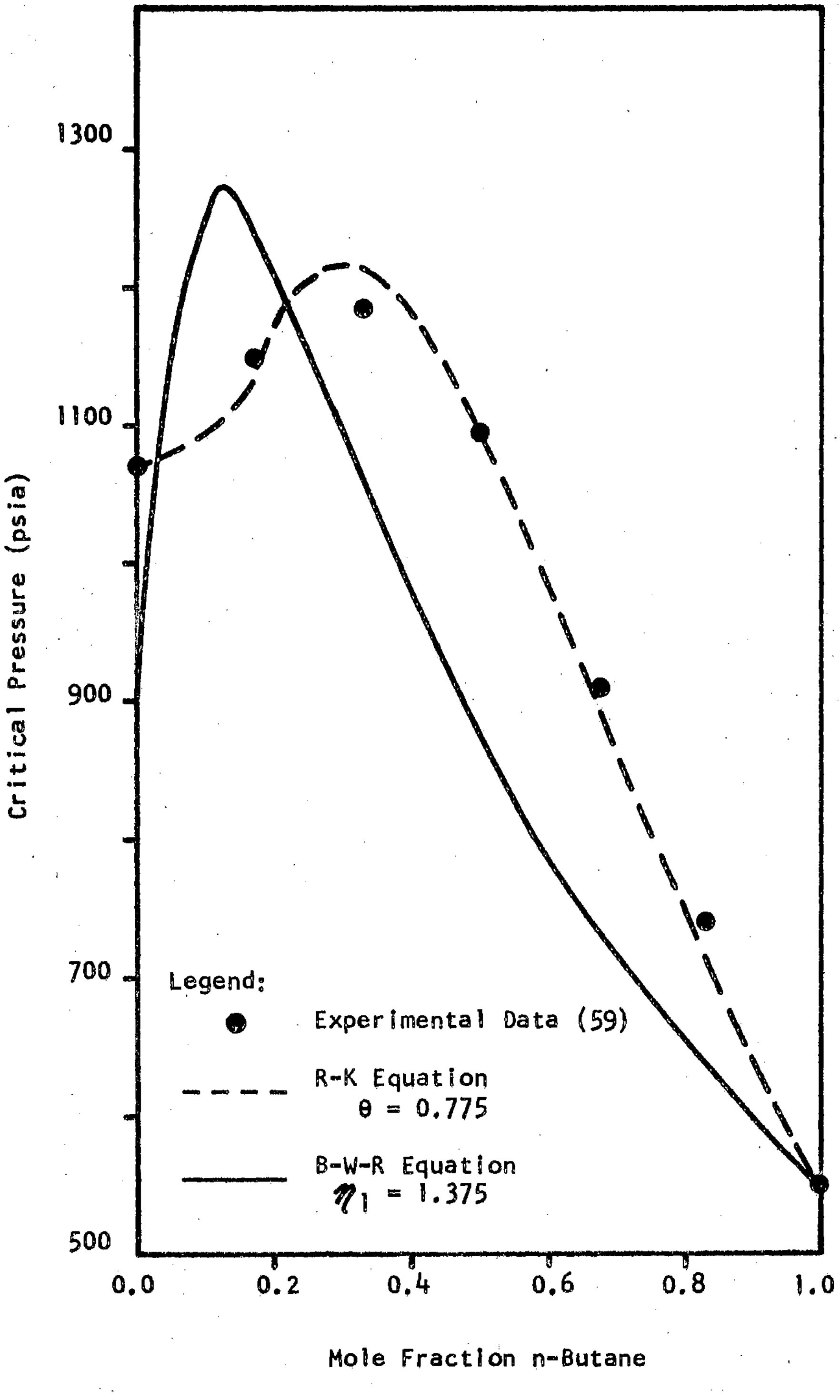

Figure 65. Critical Pressure-Composition Diagram for the n-Butane/$CO_2$ System

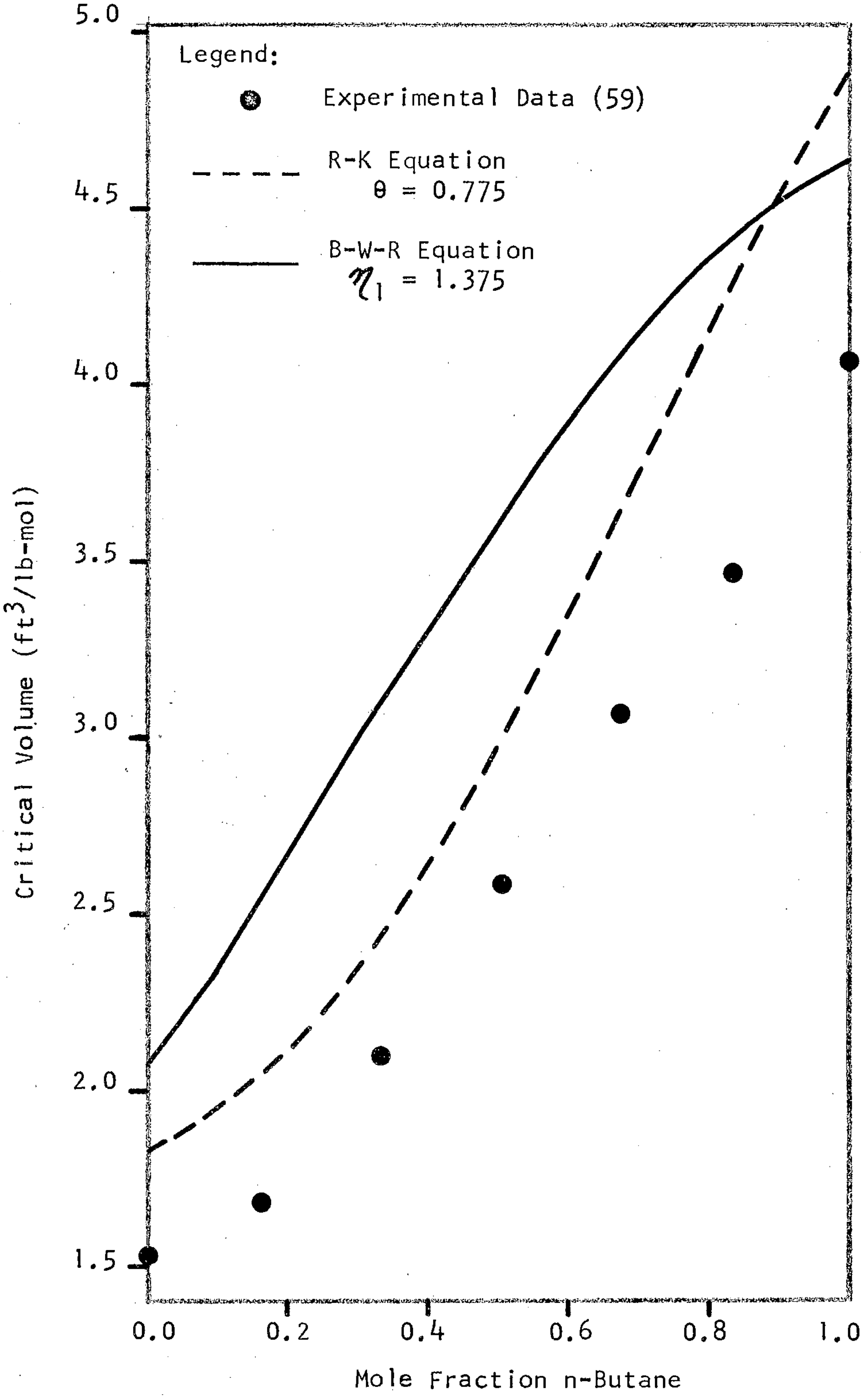

Figure 66. Critical Volume-Composition Diagram for the n-Butane/$CO_2$ System

# CHAPTER VI

# TERNARY MIXTURE CRITICAL STATE PREDICTIONS

## A. Critical State Search Procedure

The results of the study of critical state predictions for binary mixtures indicated that the equation of state approach can be used successfully to predict the critical properties of binary mixtures. The next logical step in the investigation was to determine if this theoretical approach could be extended to ternary and higher multicomponent mixtures. Unfortunately, the equation of state approach and search procedure used for binary mixtures can not be extended directly to ternary mixtures because of the simplifying transformation of the second critical state equation used in the search procedure for binary mixtures. Therefore, an investigation of the equation of state approach for ternary mixtures is particularly important since the critical state criteria and calculational techniques required for ternary mixtures are directly extendible to all higher multicomponent mixtures.

The first step in developing a new search procedure for ternary mixtures was to decide which of the four independent variables were to be specified and which were to be calculated from the critical state relations. The thermodynamic theory of the critical state of multicomponent mixtures has shown that only two critical state relations, the determinants U and M equal to zero, exist regardless of the number of components in the mixture. Since n + 1 independent variables are required to completely describe an n-component mixture, the most convenient calculational set of independent variables is T, V, $x_2$, $x_3$, • • • $x_n$. If n - 1 of these variables are specified, the remaining two can be calculated from the two critical state relations. Considerations of a general procedure for ternary and higher multicomponent mixtures suggest that the composition be specified and the critical state relations be used to calculate the critical temperature and volume. In addition, practical calculations are usually concerned with determining the critical state for some specified composition of the mixture. However, in principle any two variables may be specified for ternary mixtures. For this initial investigation of the accuracy and limitations of the equation of state approach the critical temperature and pressure were specified to facilitate comparisons of the calculated and experimentally determined critical points of ternary mixtures. The result of this specification of $T_c$ and $P_c$ was that the search procedure and computer program developed for calculating the critical points of ternary mixtures is somewhat less general than it might be.

The development of a search procedure used in a computer program to automatically calculate the critical point of a ternary mixture at a specified critical temperature and pressure required a knowledge of the variation of the values of the determinants U and M with the mixture composition. To determine these variations a small computer program was used to calculate the values of U and M evaluated in terms of the Redlich-Kwong equation of state over a wide range of compositions at the specified $T_c$ and $P_c$. The results of these calculations for the methane/ethane/n-butane ternary mixture at 700$^o$ R and 905 psia are presented in Figure 67. The calculated critical composition of the mixture, $x_{C_2} = 0.29$ and $x_{C_4} = 0.55$, is the point of intersection of the U = 0 and M = 0 loci. The most interesting features in Figure 67 were that the curves of constant values of M were nearly linear in the critical region and the U = 0 and M = 0 loci intersect at only one point in the critical region.

The critical temperature and pressure obtained by graphically interpolating the experimental data of Forman and Thodos (26) at the calculated composition of $x_{C_2} = 0.29$ and $x_{C_4} = 0.55$ were 688° R and 1010 psia, respectively. Thus, the errors in the calculated critical properties were less than 2% in the critical temperature and 11% in the critical pressure. The magnitude of both these errors is comparable to the errors obtained for the same components in binary mixture critical calculations.

A search procedure based on the general characteristics of the constant U and M loci of Figure 67 was developed. The temperature and pressure of the mixture were specified. The search procedure began by estimating the critical composition. In general, a reasonable estimate of the critical composition was obtained by using a linear pure component critical temperature-composition relationship. For example, if the specified temperature T lay between the pure component critical temperatures $T_{c_1}$ and $T_{c_2}$, the initial estimate of the composition of component 1 was given by

$$x_1^{(o)} = 1 - \frac{T - T_{c_1}}{T_{c_2} - T_{c_1}} \quad . \tag{141}$$

To insure analogous behavior for all ternary systems, component 1 was defined as the component having the lowest pure component critical

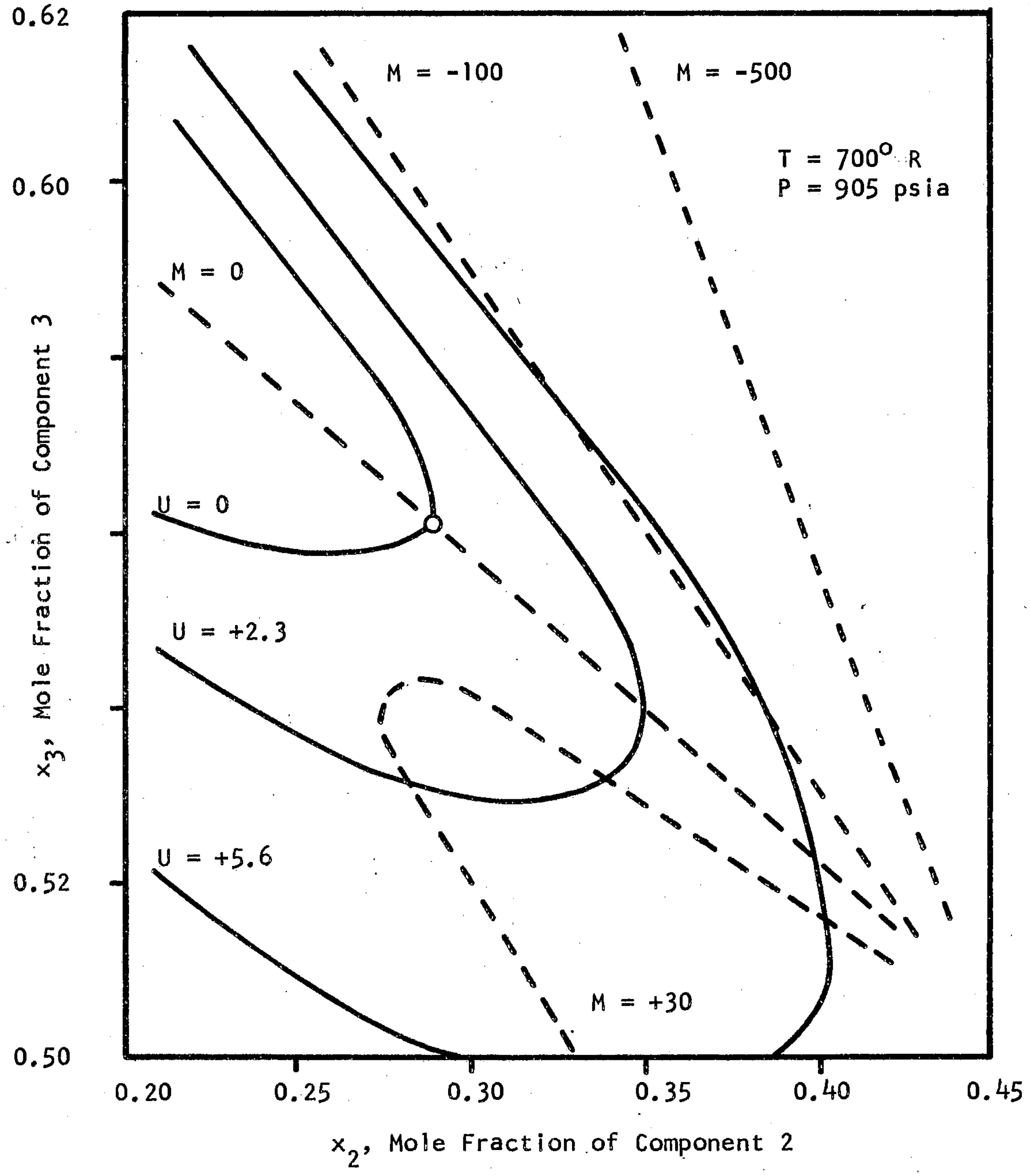

Figure 67. The Constant U and M Curves in a Ternary Mixture

temperature. Component 3 was defined as the component having the highest pure component temperature.

The calculation path of the search procedure for a typical ternary mixture is illustrated in Figure 68 and is described in detail below. The first step in the search procedure was to continuously increment the value of $x_3$ from the initial composition estimate, point A in Figure 68, in the direction of decreasing values of M until M = 0, point B. The value of U was then calculated at this point. If U was greater than zero, the value of $x_2$ was decreased by some arbitrary increment. Again $x_3$ was continuously incremented in the direction of decreasing M until M = 0, point D. If U was still greater than zero at this point, the value of $x_2$ was decreased again. If U was less than zero, as is the case in Figure 67, $x_2$ was increased by a smaller increment. This procedure was repeated, along path EFGHIK, until both U and M equalled zero at the critical point K.

The search procedure is straightforward and does not, in general, require a large number of iterations to find the critical point. However, care was taken to determine if the initial composition estimate was in the region where the curves of constant M are no longer linear. In this region the search procedure would not converge to the critical point. Appropriate safeguards were incorporated into the computer program to eliminate this possible divergence or to terminate the calculation if the search procedure did not converge quickly.

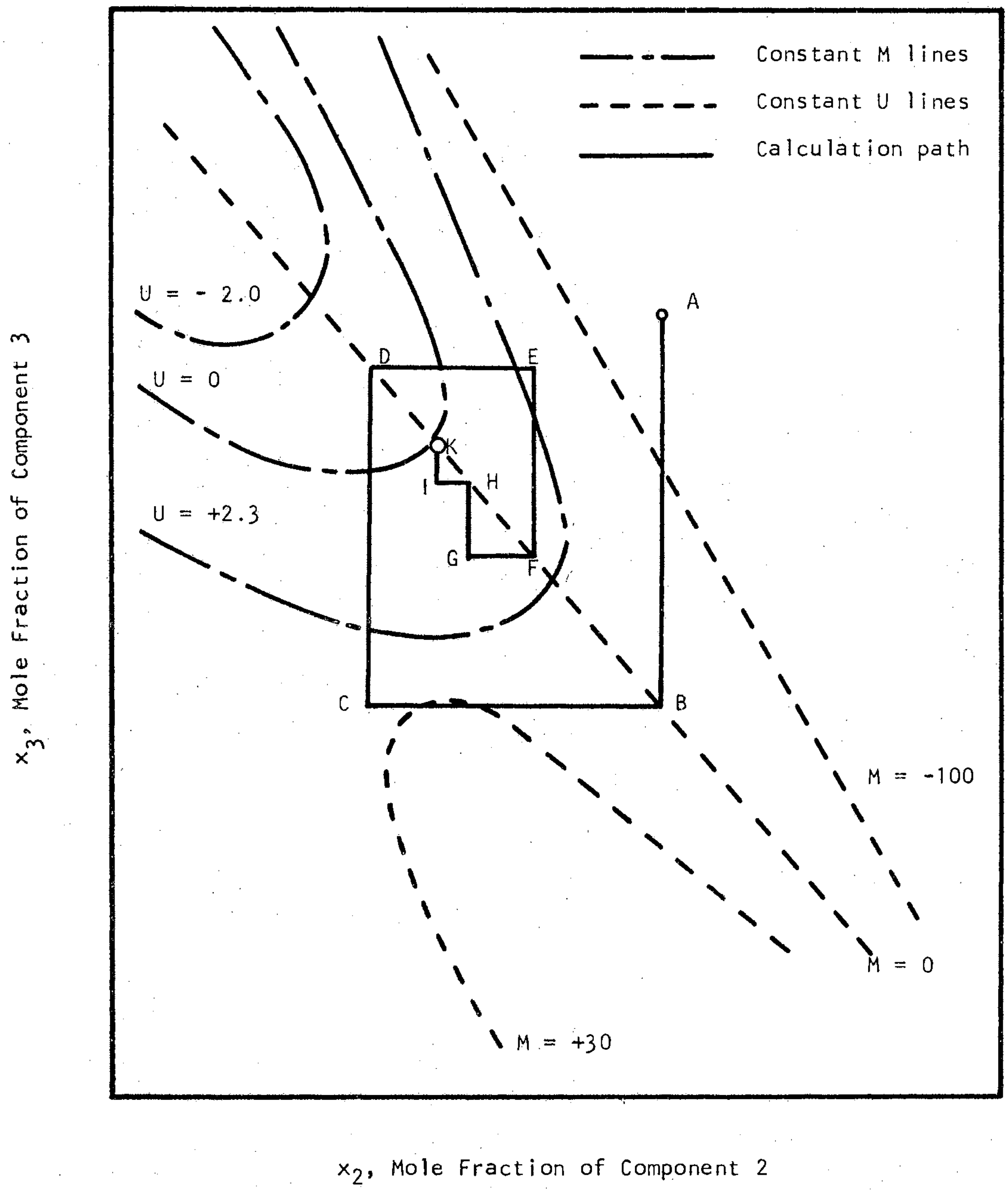

Figure 68. Calculation Path of Search Procedure for Ternary Mixtures

## B. Computer Program for Critical State Calculations for Ternary Mixtures

A computer program, designated as TERNCALC, was developed for the prediction of the critical state of ternary mixtures. The critical state relations, the determinants U and M equal to zero, and the generalized search procedure were incorporated in the program in a modular form. The concept of a modular program allowed the calculations to be broken down into basic sub-calculations: 1) a main program to control the search procedure, 2) independent subroutines for data input and output, and 3) a subroutine for the evaluation of the critical state relations. The modular form of the program facilitated debugging and kept the program versatile by allowing major changes to be made in any subroutine without disturbing the over-all program.

One of the important features of the TERNCALC program was the use of double precision arithmetic in the critical state equation calculations. Double precision was necessary because of the extremely large number of individual arithmetic calculations in the sixteen critical state derivatives required for the evaluation of U and M. As a result, round-off errors were kept at a minimum.

Other special features were included in the TERNCALC program. A variable print-out facility was built into the program which allowed either the final results or the entire calculation path of the search procedure to be printed out. Appropriate safeguards and provisions for error messages in case of divergence in the search procedure were included. A complete description of the computer program TERNCALC, its features, the required data input and output, and the control parameters for the operation of the program are presented in Appendix B.

### C. Application of the Redlich-Kwong Equation of State in Ternary Mixture Critical State Calculations

Reports of previous attempts at applying the equation of state approach to ternary mixtures could not be found in the literature. In fact, very little information on the experimental measurement of critical temperatures and pressures for multicomponent mixtures was available. Critical temperature and pressure measurements have been reported for only a few systems and were almost entirely restricted to paraffin mixtures. Generally, one to six critical points covered the entire composition range of the ternary mixtures. As a result, the experimental measurements used in evaluating the equation of state approach for ternary mixtures were much less extensive than was the case for binary mixtures.

The complexity of the critical state relations for ternary mixtures made the choice of a suitable equation of state much more important than was the case for binary mixtures. The two-parameter Redlich-Kwong equation or the eight-parameter B-W-R equation could have been selected for use in the ternary mixture critical state calculations. The complexity of the B-W-R equation, and therefore, of the resulting critical state derivatives, suggested that the simpler Redlich-Kwong equation be used in the initial investigation of the equation of state approach for predicting the critical properties of ternary mixtures. The choice of the Redlich-Kwong equation was not considered to be particularly limiting since the results of the binary mixture critical calculations showed that the more complex B-W-R equation did not consistently produce better predictions of the critical temperature and pressure than did the Redlich-Kwong equation. Therefore, use of the Redlich-Kwong equation should give a qualitative and quantitative estimate of the general accuracy and limitations of the equation of state approach for multicomponent mixtures.

The first step in applying the Redlich-Kwong equation of state to ternary mixture critical state calculations was to evaluate the sixteen derivatives of the critical state determinants U and M. The derivations are straightforward but required extreme care and repeated checking to insure complete accuracy. The final form for each of the derivatives appears in the following equations.

$$\frac{\left(\frac{\partial^3 A}{\partial x_2^3}\right)_{T,V,x_3}}{RT} = \frac{3b_2'b_2''}{(V-b)^2} + \frac{2(b_2')^3}{(V-b)^3} + \frac{3}{b^2RT}\ln(1+b/V)\Bigg[a_2''b_2' + a_2'b_2'' - \frac{2b_2'}{b}\left(a_2'b_2' + ab_2'' - \frac{a(b_2')^2}{b}\right)\Bigg] - \frac{1}{bRT(V+b)} \ast \Bigg[3(a_2''b_2' + a_2'b_2'') - \frac{6b_2'}{b}\left(a_2'b_2' + ab_2'' - \frac{a(b_2')^2}{b}\right) - \frac{3b_2'}{(V+b)}\left(a_2'b_2' + ab_2'' - \frac{a(b_2')^2}{b}\right) + \frac{2a(b_2')^3}{(V+b)^2}\Bigg] + \frac{1}{x_1^2} - \frac{1}{x_2^2} \qquad (142)$$

$$\frac{\left(\frac{\partial^3 A}{\partial x_3^3}\right)_{T,V,x_2}}{RT} = \frac{3b_3'b_3''}{(V-b)^2} + \frac{2(b_3')^3}{(V-b)^3} + \frac{3}{b^2RT}\ln(1+b/V)\Bigg[a_3''b_3' + a_3'b_3'' - \frac{2b_3'}{b}\left(a_3'b_3' + ab_3'' - \frac{a(b_3')^2}{b}\right)\Bigg] - \frac{1}{bRT(V+b)} \ast \Bigg[3(a_3''b_3' + a_3'b_3'') - \frac{6b_3'}{b}\left(a_3'b_3' + ab_3'' - \frac{a(b')^2}{b}\right) - \frac{3b_3'}{(V+b)}\left(a_3'b_3' + ab_3'' - \frac{a(b_3')^2}{b}\right) + \frac{2a(b_3')^3}{(V+b)^2}\Bigg] + \frac{1}{x_1^2} - \frac{1}{x_3^2} \qquad (143)$$

$$\begin{aligned}
\frac{\left(\dfrac{\partial^2 A}{\partial x_2^2}\right)_{T,V,x_3}}{RT} = {} & \frac{(b'_2)^2}{(V-b)^2} + \frac{b''_2}{(V-b)} - \frac{1}{bRT} \ln\,(1+b/V) \Bigg[ a''_2 - \frac{2a'_2 b'_2}{b} \\
& + \frac{2a(b'_2)^2}{b^2} - \frac{ab''_2}{b} \Bigg] - \frac{1}{bRT(V+b)} \Bigg[ ab''_2 + 2a'_2 b'_2 - \frac{2a(b'_2)^2}{b} \\
& - \frac{a(b'_2)^2}{(V+b)} \Bigg] + \frac{1}{x_2} + \frac{1}{x_1}
\end{aligned} \qquad (144)$$

$$\begin{aligned}
\frac{\left(\dfrac{\partial^2 A}{\partial x_2\,\partial x_3}\right)_{T,V}}{RT} = {} & \frac{b''_{23}}{(V-b)} + \frac{b'_2 b'_3}{(V-b)^2} - \frac{1}{bRT} \ln\,(1+b/V) \Bigg[ a''_{23} - \frac{a'_2 b'_3}{b} \\
& - \frac{a'_3 b'_2}{b} - \frac{ab''_{23}}{b} + \frac{2ab'_2 b'_3}{b^2} \Bigg] - \frac{1}{bRT(V+b)} \Bigg[ a'_2 b'_3 - \frac{2ab'_2 b'_3}{b} \\
& + a'_3 b'_2 + ab''_{23} - \frac{ab'_2 b'_3}{(V+b)} \Bigg] + \frac{1}{x_1}
\end{aligned} \qquad (145)$$

$$\begin{aligned}
\frac{\left(\dfrac{\partial^2 A}{\partial x_3^2}\right)_{T,V,x_2}}{RT} = {} & \frac{(b'_3)^2}{(V-b)^2} + \frac{b''_3}{(V-b)} - \frac{1}{bRT} \ln\,(1+b/V) \Bigg[ a''_3 - \frac{2a'_3 b'_3}{b} \\
& + \frac{2a(b'_3)^2}{b^2} - \frac{ab''_3}{b} \Bigg] - \frac{1}{bRT(V+b)} \Bigg[ ab''_3 + 2a'_3 b'_3 \\
& - \frac{2a(b')^2}{b} - \frac{a(b'_3)^2}{(V+b)} \Bigg] + \frac{1}{x_3} + \frac{1}{x_1}
\end{aligned} \qquad (146)$$

$$\begin{aligned}
\frac{\left(\dfrac{\partial^3 A}{\partial x_2^2\,\partial x_3}\right)_{T,V}}{RT} = {} & \frac{1}{(V-b)^2} \left[ 2b'_2 b''_{23} + b''_2 b'_3 \right] + \frac{2(b'_2)^2 b'_3}{(V-b)^3} \\
& + \frac{1}{bRT} \ln\,(1+b/V) \Bigg[ \frac{1}{b}(2a''_{23} b'_2 + 2a'_2 b''_{23} + a'_3 b''_2 + a''_2 b'_3) \\
& - \frac{2}{b^2}(2a'_2 b'_2 b'_3 + a'_3 (b'_2)^2 + 2ab'_2 b''_{23} + ab''_2 b'_3) + \frac{6a(b'_2)^2 b'_3}{b^3} \Bigg] \\
& - \frac{1}{bRT(V+b)} \Bigg[ (a''_2 b'_3 + a_3 b''_2 + 2a'_2 b''_{23} + 2a''_{23} b'_2) \\
& - \frac{2}{b}(2a'_2 b'_2 b'_3 + ab''_2 b'_3 + a'_3 (b'_2)^2 + 2ab'_2 b''_{23}) + \frac{6a(b'_2)^2 b'_3}{b^2} \\
& - \frac{1}{(V+b)} (a'_3 (b'_2)^2 + 2ab'_2 b''_{23} + ab''_2 b'_3 + 2a'_2 b'_2 b'_3)
\end{aligned}$$

$$+ \frac{2a(b'_2)^2 b'_3}{(V+b)^2} + \frac{3a(b'_2)^2 b'_3}{b(V+b)} \Bigg] + \frac{1}{x_1^2} \qquad (147)$$

$$\frac{\left(\dfrac{\partial^3 A}{\partial x_2 \partial x_3^2}\right)_{T,V}}{RT} = \frac{1}{(V-b)^2}\left[2b'_3 b''_{23} + b'_2 b''_3\right] + \frac{2b'_2(b'_3)^2}{(V-b)^3}$$

$$+ \frac{1}{bRT} \ln\,(1+b/V) \Bigg[\frac{1}{b}(2a''_{23}b'_3 + a'_2 b''_3 + a''_3 b'_2 + 2a'_3 b''_{23})$$

$$- \frac{2}{b^2}(a'_2(b'_3)^2 + 2a'_3 b'_2 b'_3 + 2ab'_3 b''_{23} + ab'_2 b''_3 )$$

$$+ \frac{6ab'_2(b'_3)^2}{b^3}\Bigg] - \frac{1}{bRT(V+b)} \Bigg[(2a''_{23}b'_3 + a'_2 b''_3 + a''_3 b'_2$$

$$+ 2a'_3 b''_{23}) - \frac{2}{b}(a'_2(b'_3)^2 + 2a'_3 b'_2 b'_3 + 2ab'_3 b''_{23} + ab'_2 b''_3)$$

$$+ \frac{6ab'_2(b'_3)^2}{b^2} - \frac{1}{(V+b)} \Big(2a'_3 b'_2 b'_3 + 2ab'_3 b''_{23} + ab'_2 b''_3$$

$$+ a'_2(b'_3)^2\Big) + \frac{2ab'_2(b'_3)^2}{(V+b)^2} + \frac{3ab'_2(b'_3)^2}{b(V+b)}\Bigg] + \frac{1}{x_1^2} \qquad (148)$$

$$\left(\frac{\partial^2 P}{\partial x_2^2}\right)_{T,V,x_3} = \frac{RT}{(V-b)^2}\left[b''_2 + \frac{2(b')^2}{(V-b)}\right] + \frac{1}{V(V+b)^2}\Bigg[2a'_2 b'_2 - \frac{2a(b'_2)^2}{(V+b)}$$

$$+ ab''_2 - a''_2(V+b)\Bigg] \qquad (149)$$

$$\left(\frac{\partial^2 P}{\partial x_2\,\partial x_3}\right)_{T,V} = \frac{RT}{(V-b)^2}\left[b''_{23} + \frac{2b'_2 b'_3}{(V-b)}\right] - \frac{a''_{23}}{V(V+b)}$$

$$+ \frac{a'_2 b'_3 + a'_3 b'_2 + ab''_{23}}{V(V+b)^2} - \frac{2ab'_2 b'_3}{V(V+b)^3} \qquad (150)$$

$$\left(\frac{\partial^2 P}{\partial x_3^2}\right)_{T,V,x_2} = \frac{RT}{(V-b)^2}\left[b'' + \frac{2(b')^2}{(V-b)}\right] + \frac{1}{V(V+b)^2}\Bigg[2a'b' - \frac{2a(b'_3)^2}{(V+b)}$$

$$+ ab''_3 - a''_3(V+b)\Bigg] \qquad (151)$$

$$\left(\frac{\partial^2 P}{\partial x_2\,\partial V}\right)_{T,x_3} = \frac{2a'_2 V + a'_2 b - ab'_2}{V^2(V+b)^2} - \frac{2ab'_2}{V(V+b)^3} - \frac{2RTb'_2}{(V-b)^3} \qquad (152)$$

$$\left(\frac{\partial^2 P}{\partial x_3\,\partial V}\right)_{T,x_2} = \frac{2a_3'V + a_3'b - ab_3'}{V^2(V+b)^2} - \frac{2ab_3'}{V(V+b)^3} - \frac{2RTb_3'}{(V-b)^3} \tag{153}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,x_2,x_3} = \frac{2RT}{(V-b)^3} + \frac{2a}{V^2(V+b)^2} - \frac{2a(2V+b)^2}{V^3(V+b)^3} \tag{154}$$

$$\left(\frac{\partial P}{\partial x_2}\right)_{T,V,x_3} = \frac{RTb_2'}{(V-b)^2} + \frac{1}{V(V+b)}\left[\frac{ab_2'}{(V+b)} - a_2'\right] \tag{155}$$

$$\left(\frac{\partial P}{\partial x_3}\right)_{T,V,x_2} = \frac{RTb_3'}{(V-b)^2} + \frac{1}{V(V+b)}\left[\frac{ab_3'}{(V+b)} - a_3'\right] \tag{156}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,x_2,x_3} = \frac{a(2V+b)}{V^2(V+b)^2} - \frac{RT}{(V-b)^2} \tag{157}$$

The constants a and b of the Redlich-Kwong equation of state for ternary mixtures were determined from the following rules (74):

$$a = a_1x_1^2 + a_2x_2^2 + a_3x_3^2 + 2a_{12}x_1x_2 + 2a_{13}x_1x_3 + 2\,a_{23}x_2x_3 \tag{158}$$

$$b = b_1x_1^2 + b_2x_2^2 + b_3x_3^2 + 2b_{12}x_1x_2 + 2b_{13}x_1x_3 + 2\,b_{23}x_2x_3 \tag{159}$$

where the binary interaction parameters $\theta_{ij}$ and $\phi_{ij}$ are defined by

$$a_{ij} = \theta_{ij}\sqrt{a_ia_j} \tag{160}$$

$$b_{ij} = \phi_{ij}\sqrt{b_ib_j}\;. \tag{161}$$

The derivatives of the constants a and b with respect to the mole fraction of a component were calculated from the relations below where z equals either the constant a or b:

$$z_2' = \left(\frac{\partial z}{\partial x_2}\right)_{x_3} = 2x_3(z_1 - z_{12} + z_{23} - z_{13}) + 2x_2(z_1 - 2z_{12} + z_2) + 2(z_{12} - z_1) \tag{162}$$

$$z_3' = \left(\frac{\partial z}{\partial x_3}\right)_{x_2} = 2x_3(z_1 - 2z_{13} + z_3) + 2x_2(z_1 - z_{12} + z_{23} - z_{13}) + 2(z_{13} - z_1) \tag{163}$$

$$z''_2 = \left(\frac{\partial^2 z}{\partial x_2^2}\right)_{x_3} = 2(z_1 - 2z_{12} + z_2) \qquad (164)$$

$$z''_3 = \left(\frac{\partial^2 z}{\partial x_3^2}\right)_{x_2} = 2(z_1 - 2z_{13} + z_3) \qquad (165)$$

$$z''_{23} = \left(\frac{\partial^2 z}{\partial x_2 \, \partial x_3}\right) = 2(z_1 - z_{12} + z_{23} - z_{13}) \qquad (166)$$

As a final check on the derivatives required for the ternary mixture critical calculations, values of the derived partial derivatives were compared with the corresponding values obtained by numerical differentiation of that derivative. The derived partial derivatives were assumed to be correct when the difference between the analytically and numerically obtained values was negligible.

The partial derivatives of the critical state relations were programmed in the critical state equation subroutine of the TERNCALC computer program. The TERNCALC program was then run, debugged, and tested to insure the search procedure was converging to the critical point correctly.

## D. Results of the Critical State Predictions Using the Redlich-Kwong Equation of State

Two general sets of calculations to determine the critical properties of seven ternary mixtures of paraffins were made using the TERNCALC computer program and the Redlich-Kwong equation of state. The first set of calculations were made with the binary interaction parameters of the Redlich-Kwong equation, $\theta_{ij}$ and $\emptyset_{ij}$, equal to 1.0. The second set of calculations were made using the values of the optimum binary interaction parameters $\theta_{ij}$ giving the best representation of the critical pressure in the study of binary mixtures. In this second set the binary interaction parameters $\phi_{ij}$ were maintained at a value of 1.0. The calculated results from both sets of critical state calculations were compared with the experimental results for the corresponding ternary mixtures.

The results of the first set of calculations with all six binary interaction parameters equal to 1.0 indicated that a qualitative and semi-quantitative agreement existed between the calculated and experimental critical temperatures and pressures of the ternary systems.

The variation of the critical temperature with the mixture composition are shown in the triangular composition diagrams of Figures 69-75. A summary of the average errors in predicting the critical temperature for the seven ternary systems appears in Table V. For the seven systems investigated, the calculated curve connecting the mixture compositions for a given critical temperature was linear across the entire composition range of the system. These lines of constant critical temperature terminated at the calculated compositions of the two binary systems having that same critical temperature. The complexity of the ternary mixture critical state relations used to calculate the critical compositions makes this simple linear relationship somewhat surprising. However, a linear relationship of this type has been reported for similar hydrocarbon systems and was used as the basis for a method to predict the critical temperature of ternary mixtures of hydrocarbons (33). The agreement between the calculated and observed linear critical temperature curves and the agreement of the ternary mixture calculations with the limiting binary mixture calculations was added assurance that the critical state relations and the TERNCALC program for ternary mixtures were functioning correctly.

The magnitude of the error in the prediction of the critical temperature was found to be dependent on the components of the mixture. For example, the ternary systems containing both methane and n-butane had much greater errors than did the other ternary systems. The methane/n-butane binary system was also quite difficult to predict in the critical state studies of binary mixtures using the Redlich-Kwong equation of state. No reasonable explanation can be presented for the unusual calculational behavior of the methane/n-butane binary systems using the Redlich-Kwong equation of state.

The magnitude of the errors in predicting the critical temperatures of ternary mixtures were approximately twice as great as the corresponding errors encountered in the binary mixture calculations when all six binary interaction parameters, both $\theta_{ij}$ and $\phi_{ij}$, were equal to 1.0. However, changes in the values of the binary interaction parameters resulted in a shift of the curves of constant critical temperature which generally improved the accuracy of the critical temperature predictions. When the optimum values of the binary interaction parameters were used, the errors were reduced to less than two per cent for those systems not containing both methane and n-butane. This two per cent error level was only slightly greater than the level encountered in the binary system critical state calculations.

A summary of the average errors in predicting the critical pressures for the seven ternary systems appears in Table VI. The range of the errors for the ternary systems was approximately the same as for the corresponding binary systems. The variation of the critical pressures with the mixture composition are shown in the triangular composition diagrams of Figures 76-82. A good example of the behavior of the critical pressure over the entire ternary composition range appears in Figure 76. The curves of constant critical pressure are non-linear and become increasingly so as the concentration of component 2 (the component with the second highest molecular weight, ethane for the system in Figure 76) increases. As was the case for the critical temperature predictions for ternary mixtures, the curves of constant pressure terminated at the critical compositions determined in the critical state calculations for binary mixtures.

The magnitude of the error for a particular ternary system seemed to be dependent on the similarity of the molecules of the components as was the case for binary mixtures. Figure 83 shows the definite trend in the relationship between the magnitude of the error in the predicted critical pressure and the total molecular weight of the components of the ternary system. Thus, as the complexity of the components of the ternary mixture increases, the accuracy of the critical state predictions can be expected to decrease accordingly.

The accuracy of the critical pressure prediction was generally improved by using the optimum values of the binary interaction parameters. Changes in the values of these parameters resulted in a shift of the curves of constant critical pressure. The best example of this shifting effect and the importance of the binary interaction parameters is the ethane/n-pentane/n-heptane ternary system shown in Figure 81. As the values of the binary interaction parameters changed from 1.0, the curves of constant pressure shifted downward in the direction of decreasing ethane concentration and slightly forward in the direction of increasing n-pentane concentration. The average error in the critical pressure was reduced from 3.5 per cent to less than 1.0 per cent for this system when the optimum values of the binary interaction parameters were used. Similar results were obtained for the other ternary systems.

The general limitation encountered in attempts to improve the critical state predictions using the optimum binary interaction parameters also can be demonstrated with the ethane/n-pentane/n-heptane ternary system. The experimentally determined critical pressures for this ternary system have been plotted in Figure 81. Although both sets of curves of constant critical pressure were qualitatively correct, the limiting binary critical pressure predictions did not agree with those determined experimentally even with the use of the optimum values of the binary interaction parameters. Therefore, the accuracy of the prediction of the critical properties for ternary mixtures is primarily limited by the accuracy of the binary mixture predictions. Thus, improvements in the representation of binary critical properties, such as those resulting from the development of a more suitable equation of state or modifications of the mixing rules or interaction parameters, will result in corresponding improvements in the representation of ternary mixture critical properties.

### TABLE V

### Average Errors in the Prediction of the Critical Temperature of Ternary Systems

| System | Absolute Average Percentage Errors | | Ref |
|---|---|---|---|
| | $\theta_{ij} = 1.0$ | Optimum $\theta_{ij}$ | |
| methane/ethane/n-butane | 7.4 | 4.8 | 18,26 |
| methane/ethane/n-pentane | 6.2 | 1.5 | 9 |
| methane/propane/n-butane | 6.1 | 5.2 | 75 |
| methane/propane/n-pentane | 2.8 | 2.1 | 20,55 |
| ethane/propane/n-pentane | 3.2 | 2.2 | 25 |
| ethane/n-pentane/n-heptane | 3.4 | 0.7 | 24 |
| propane/n-butane/n-pentane | 0.8 | 0.6 | 25,57 |
| TOTALS | 4.3 | 2.4 | |

# TABLE VI

## Average Errors in the Prediction of the Critical Pressure of Ternary Systems

| System | Absolute Average Percentage Errors | | Ref |
|---|---|---|---|
| | $\theta_{ij} = 1.0$ | Optimum $\theta_{ij}$ | |
| methane/ethane/n-butane | 17.7 | 15.2 | 18,26 |
| methane/ethane/n-pentane | 10.8 | 7.2 | 9 |
| methane/propane/n-butane | 5.9 | 6.1 | 75 |
| methane/propane/n-pentane | 5.3 | 1.5 | 20,55 |
| ethane/propane/n-pentane | 2.5 | 2.5 | 25 |
| ethane/n-pentane/n-heptane | 3.5 | 1.0 | 24 |
| propane/n-butane/n-pentane | 1.1 | 1.0 | 25,57 |
| TOTALS | 6.7 | 4.9 | |

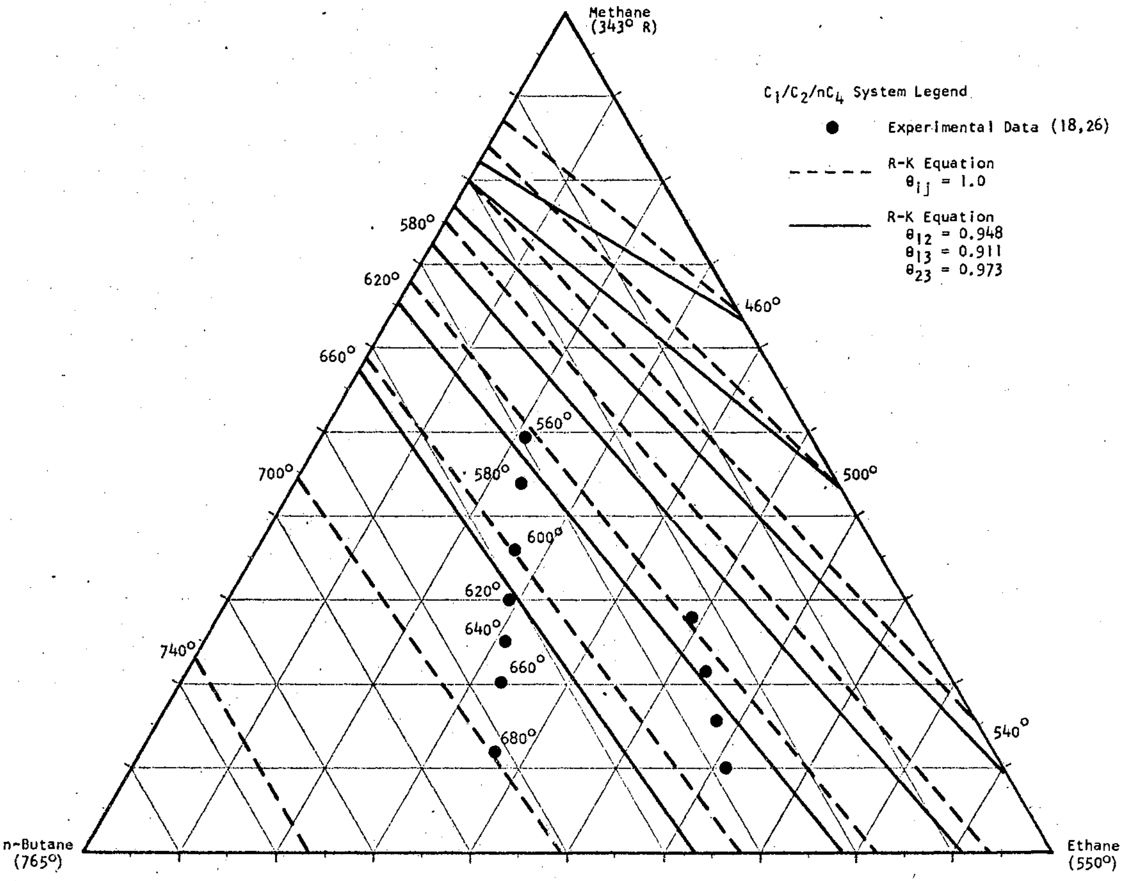

Figure 69. Critical Temperature-Composition Diagram for the Methane/Ethane/n-Butane System

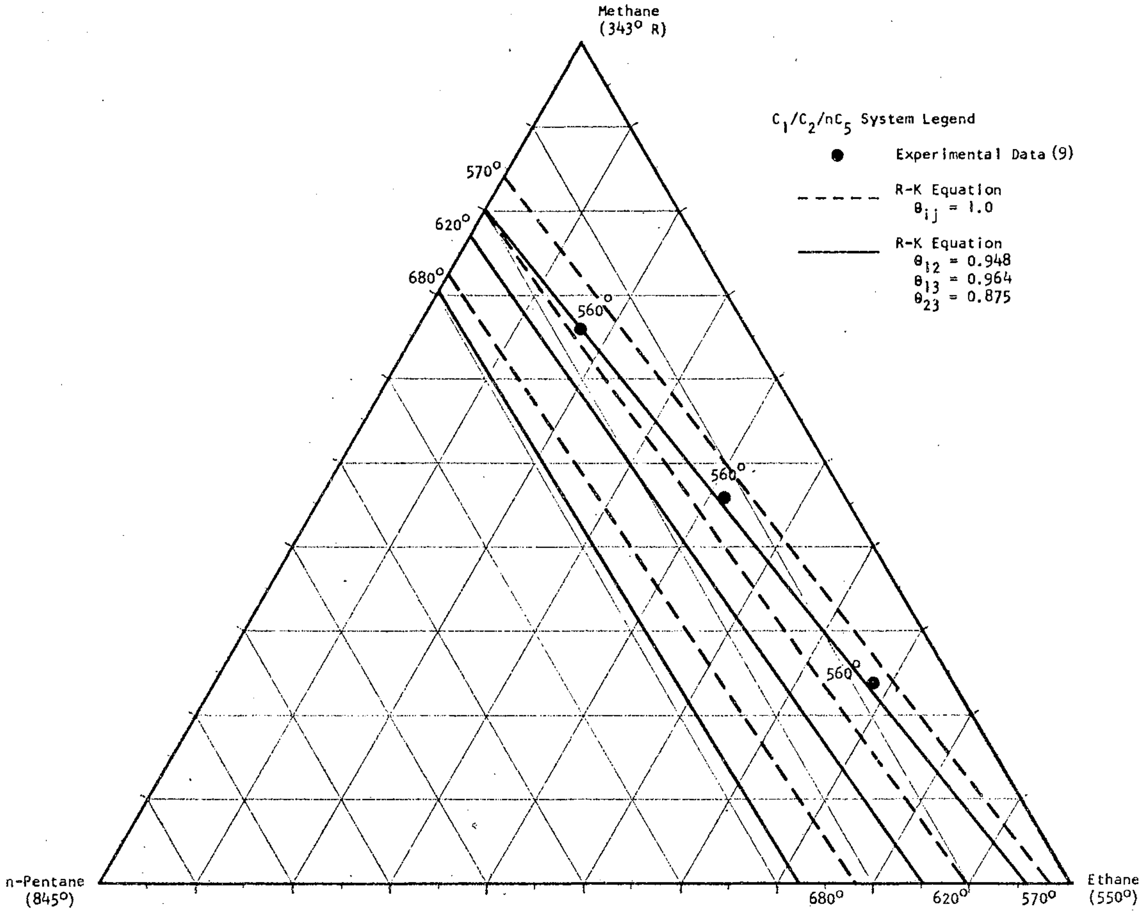

Figure 70. Critical Temperature-Composition Diagram for the Methane/Ethane/n-Pentane System

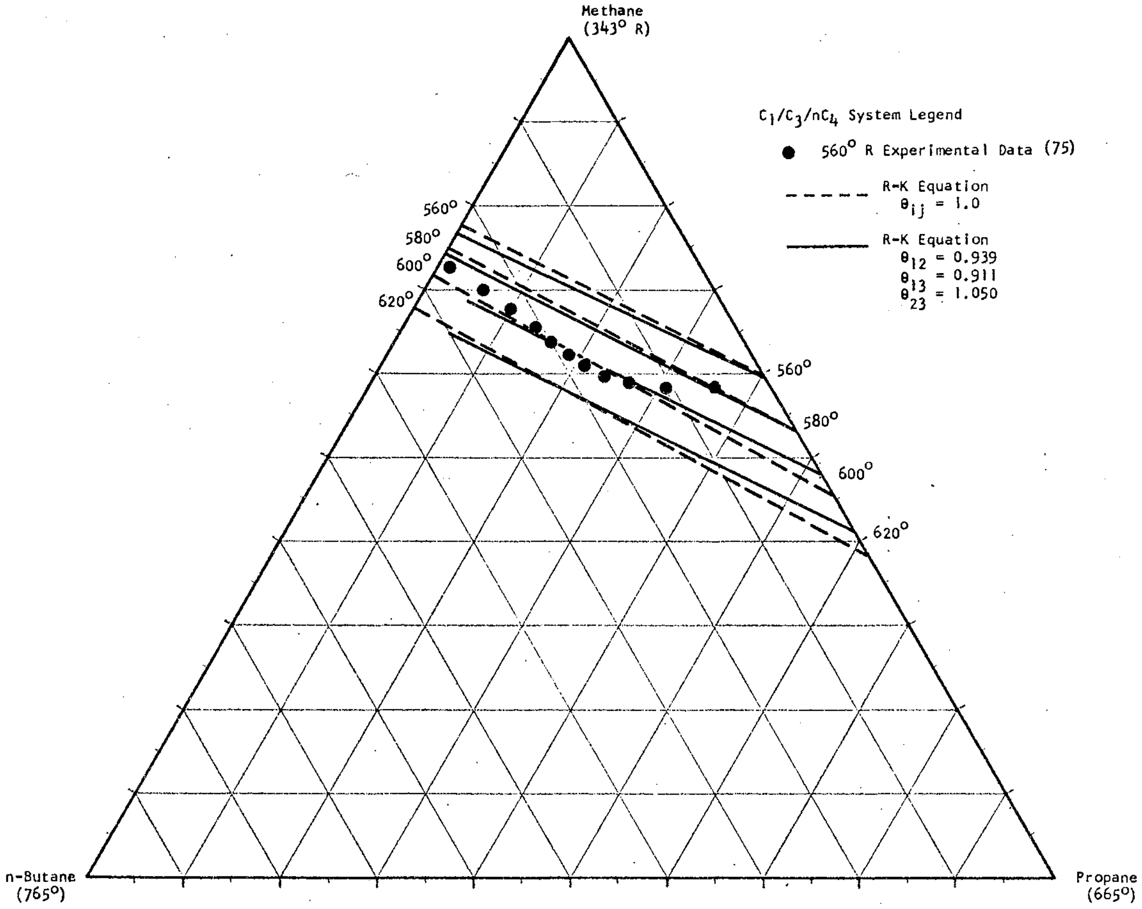

Figure 71. Critical Temperature-Composition Diagram for the Methane/Propane/n-Butane System

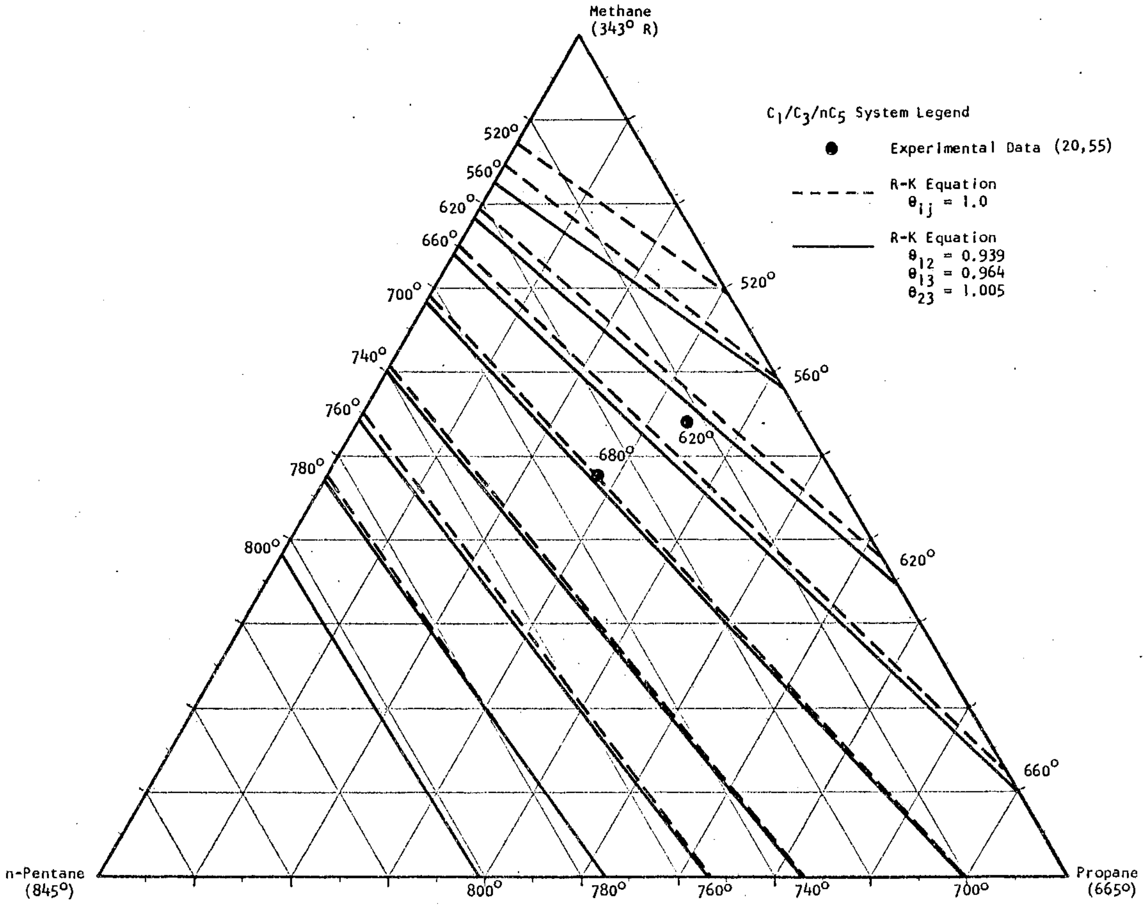

Figure 72. Critical Temperature-Composition Diagram for the Methane/Propane/n-Pentane System

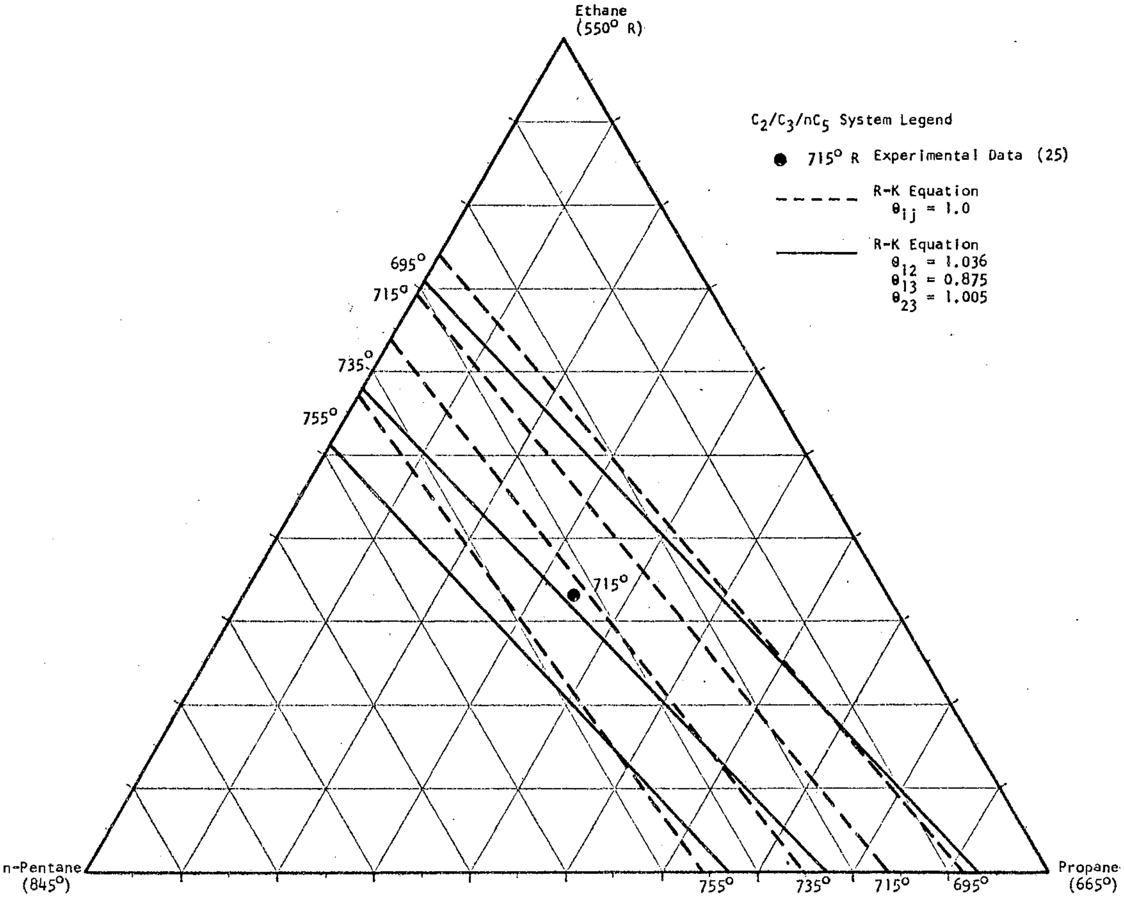

Figure 73. Critical Temperature-Composition Diagram for the Ethane/Propane/n-Pentane System

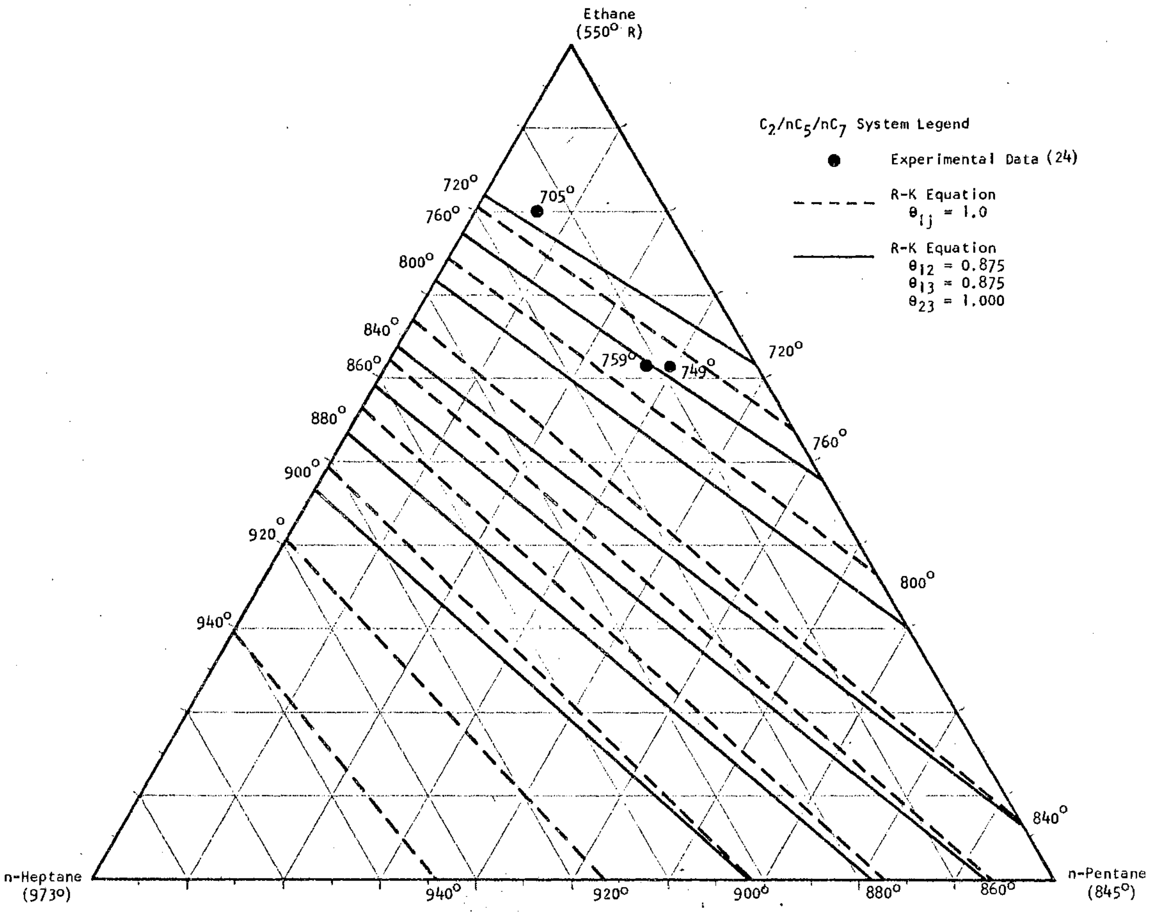

Figure 74. Critical Temperature-Composition Diagram for the Ethane/n-Pentane/n-Heptane System

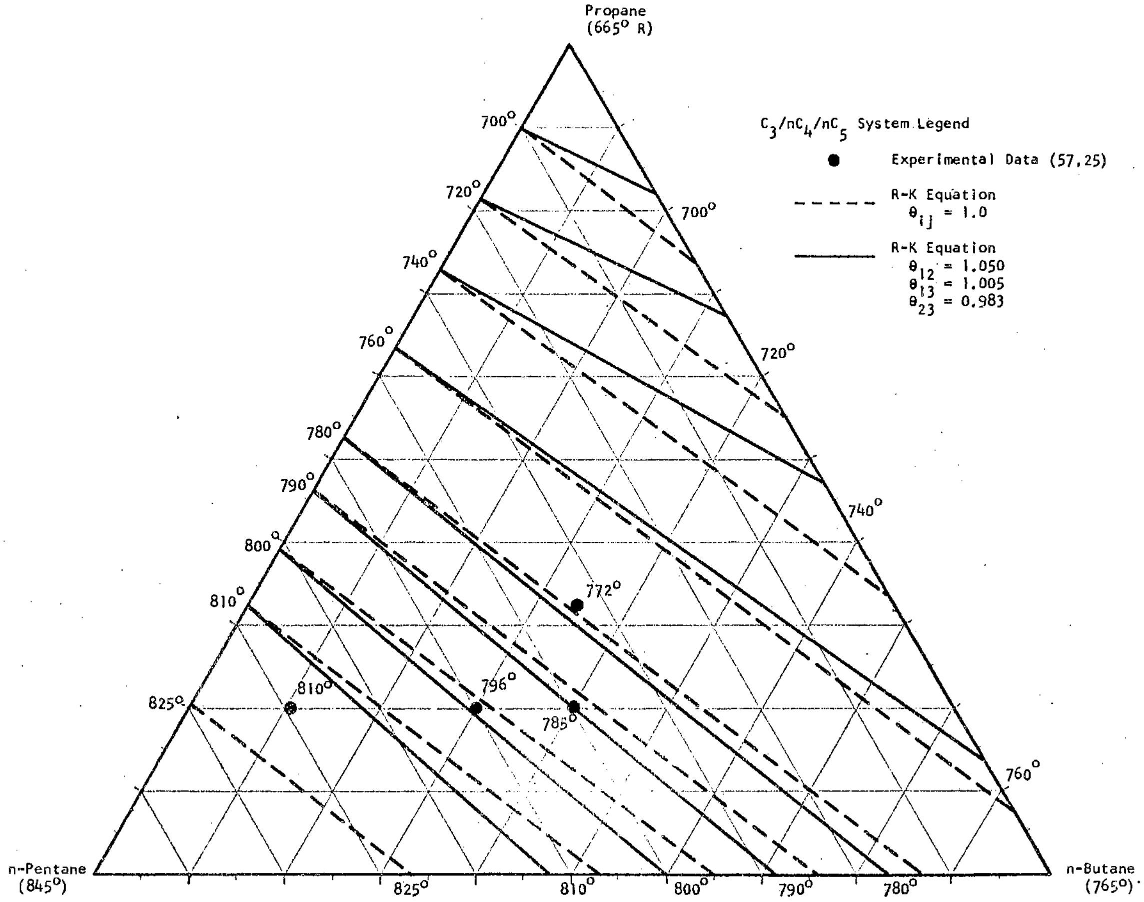

Figure 75. Critical Temperature-Composition Diagram for the Propane/n-Butane/n-Pentane System

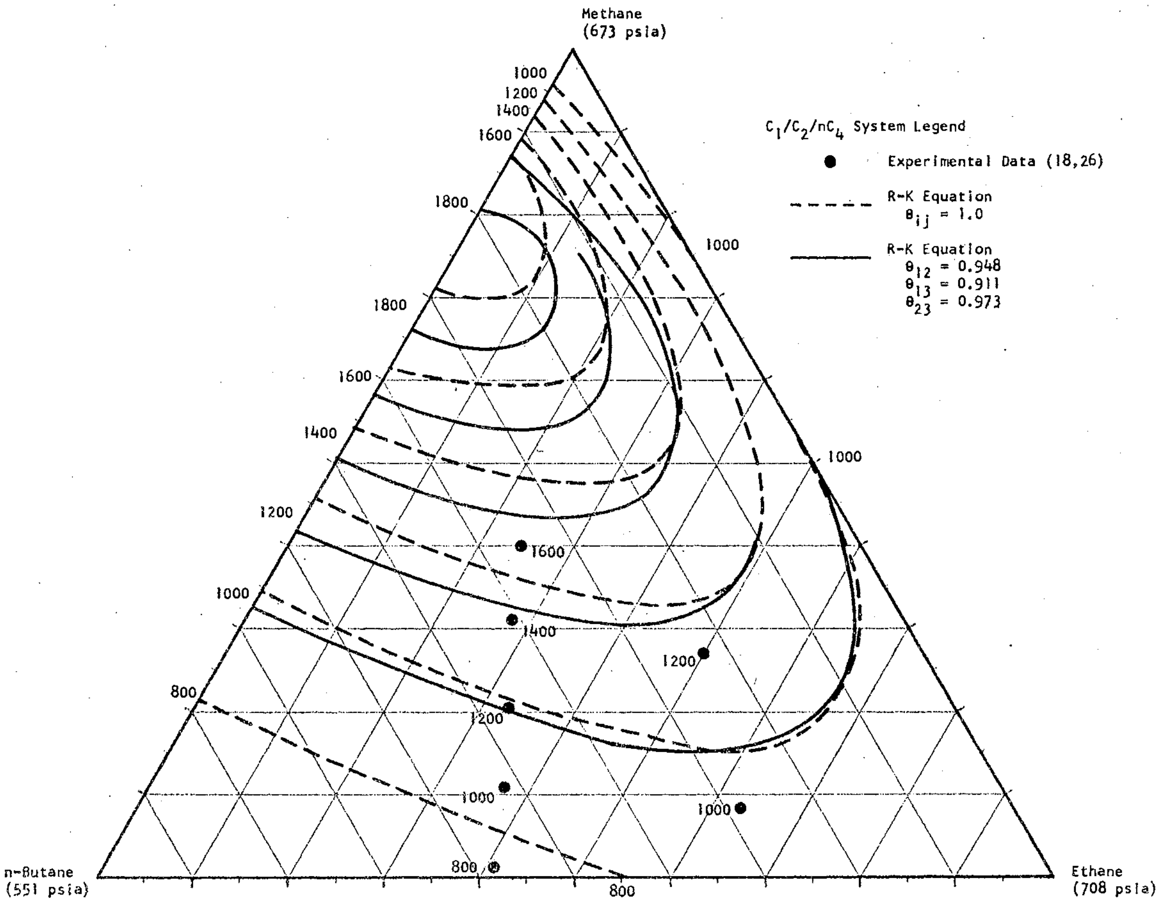

Figure 76. Critical Pressure-Composition Diagram for the Methane/Ethane/n-Butane System

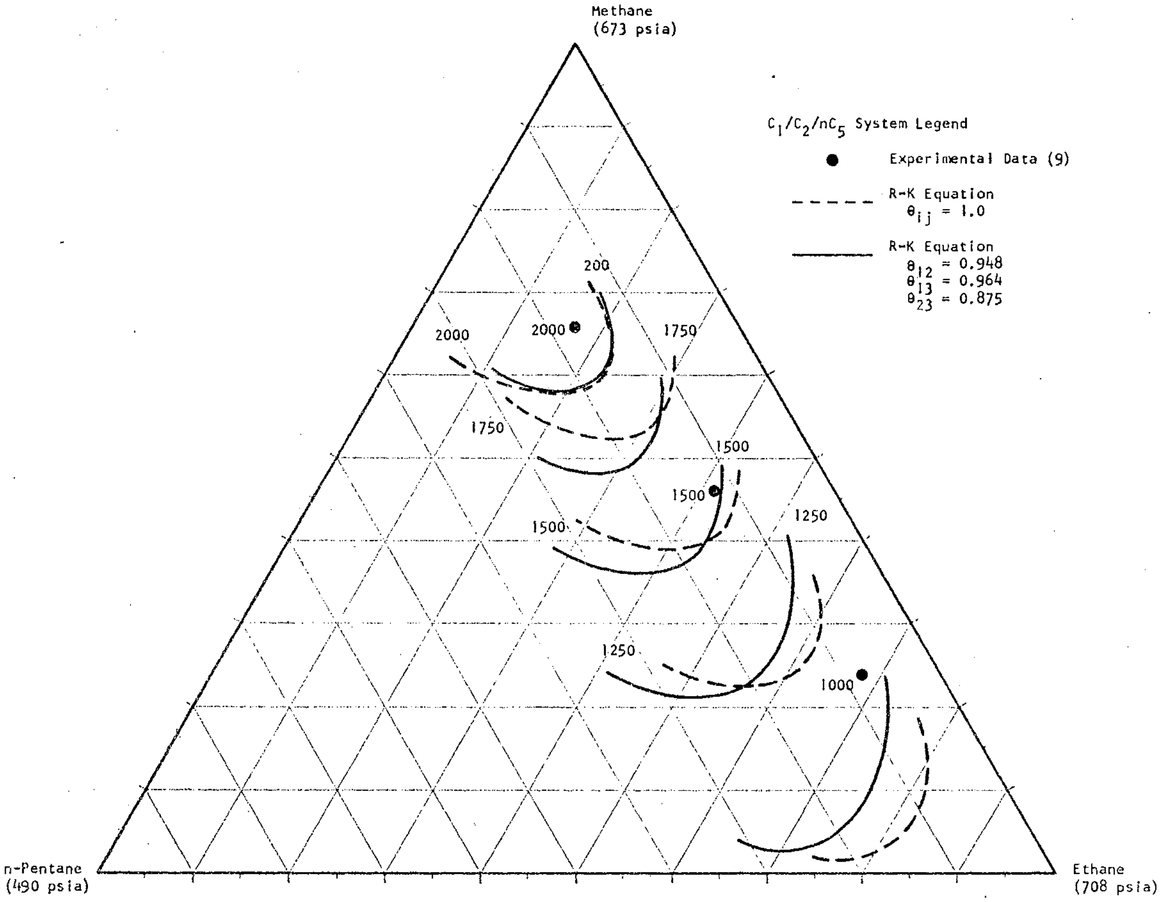

Figure 77. Critical Pressure-Composition Diagram for the Methane/Ethane/n-Pentane System

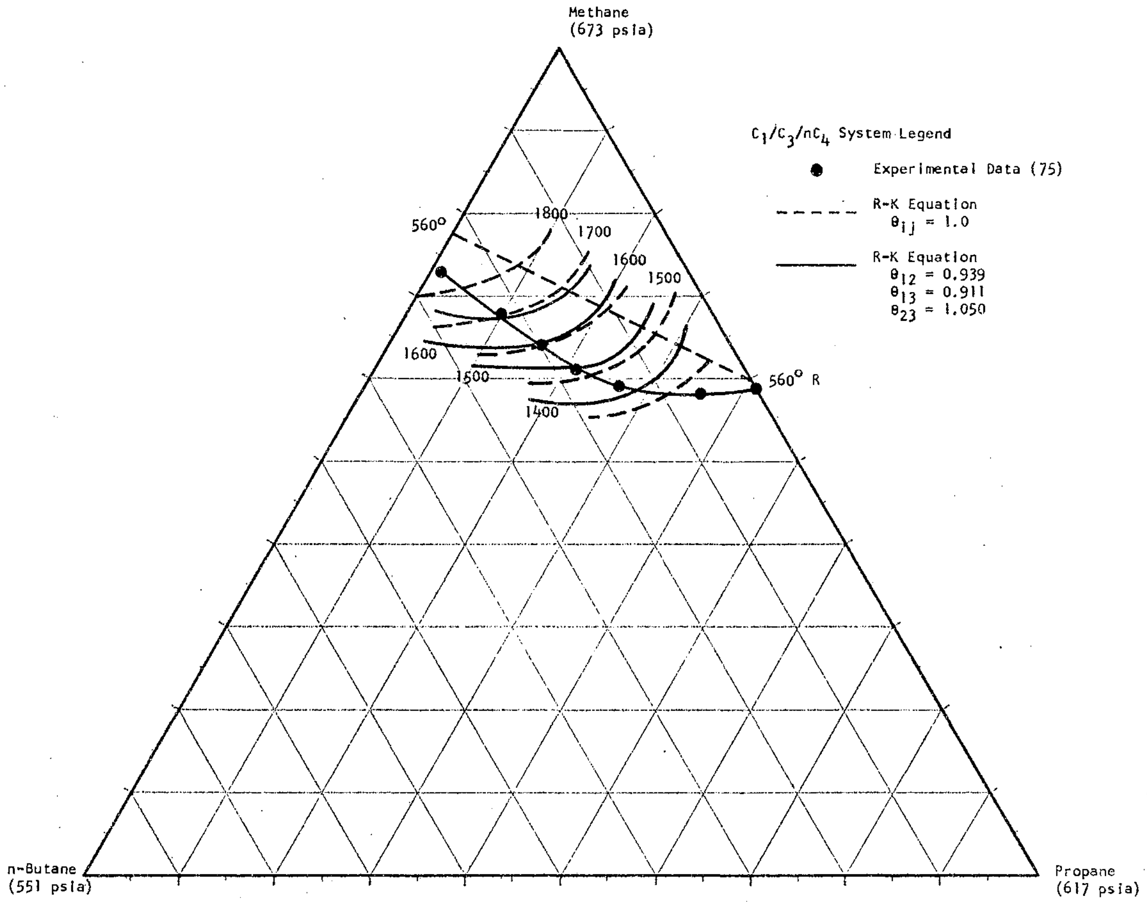

Figure 78. Critical Pressure-Composition Diagram for the Methane/Propane/n-Butane System

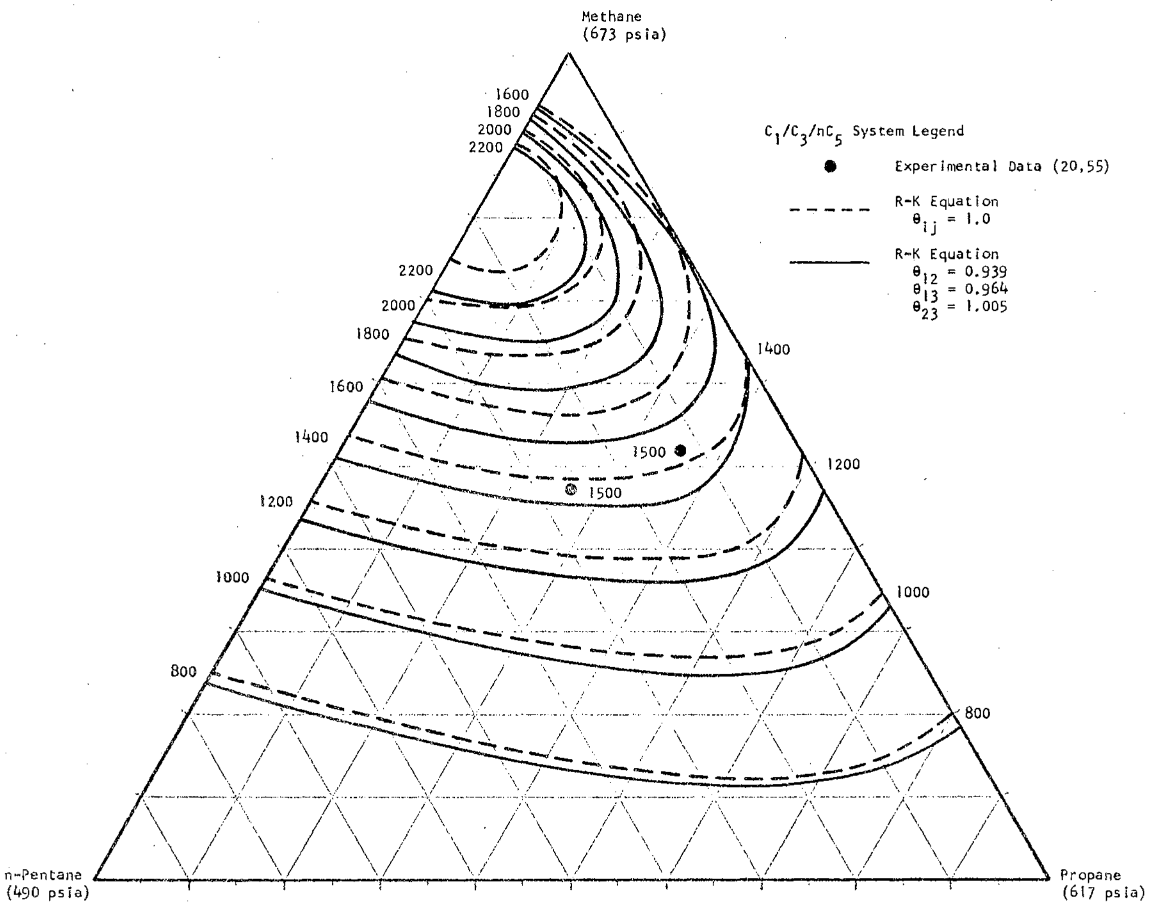

Figure 79. Critical Pressure-Composition Diagram for the Methane/Propane/n-Pentane System

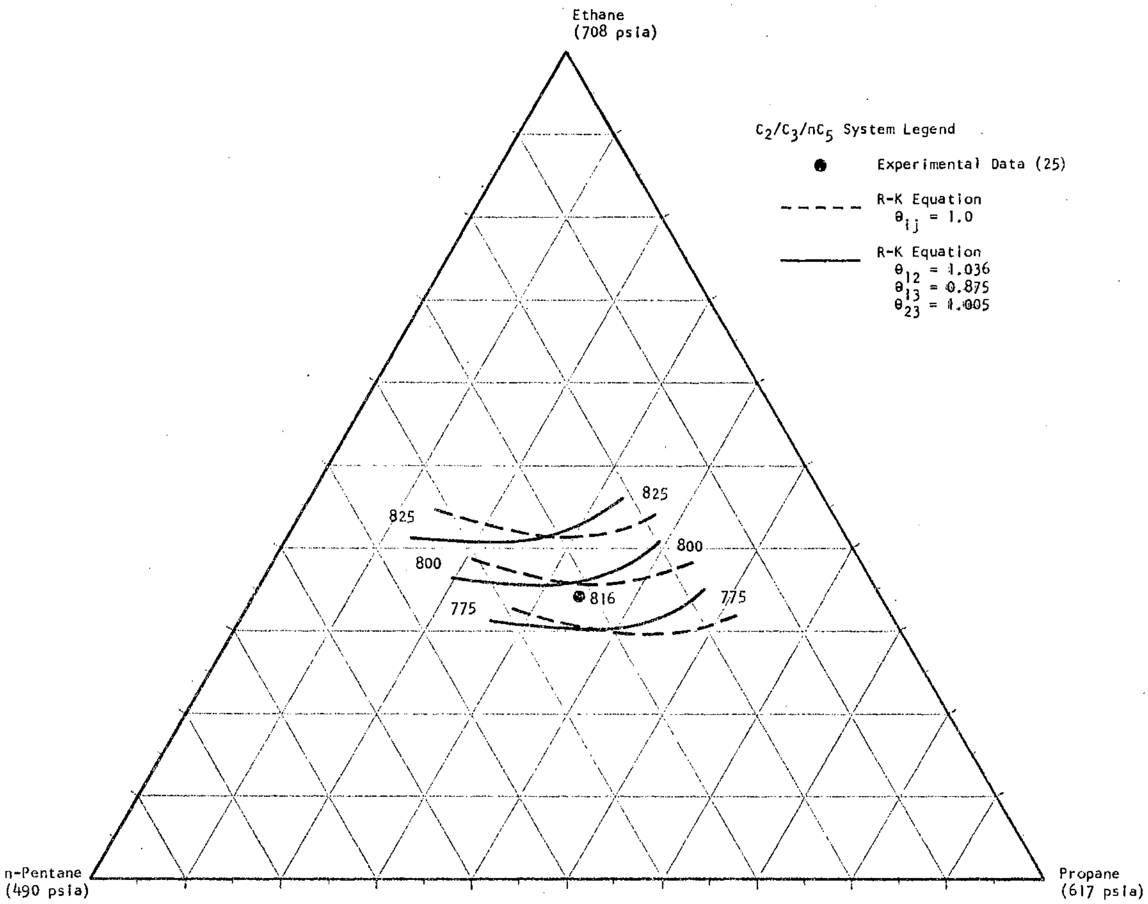

Figure 80. Critical Pressure-Composition Diagram for the Ethane/Propane/n-Pentane System

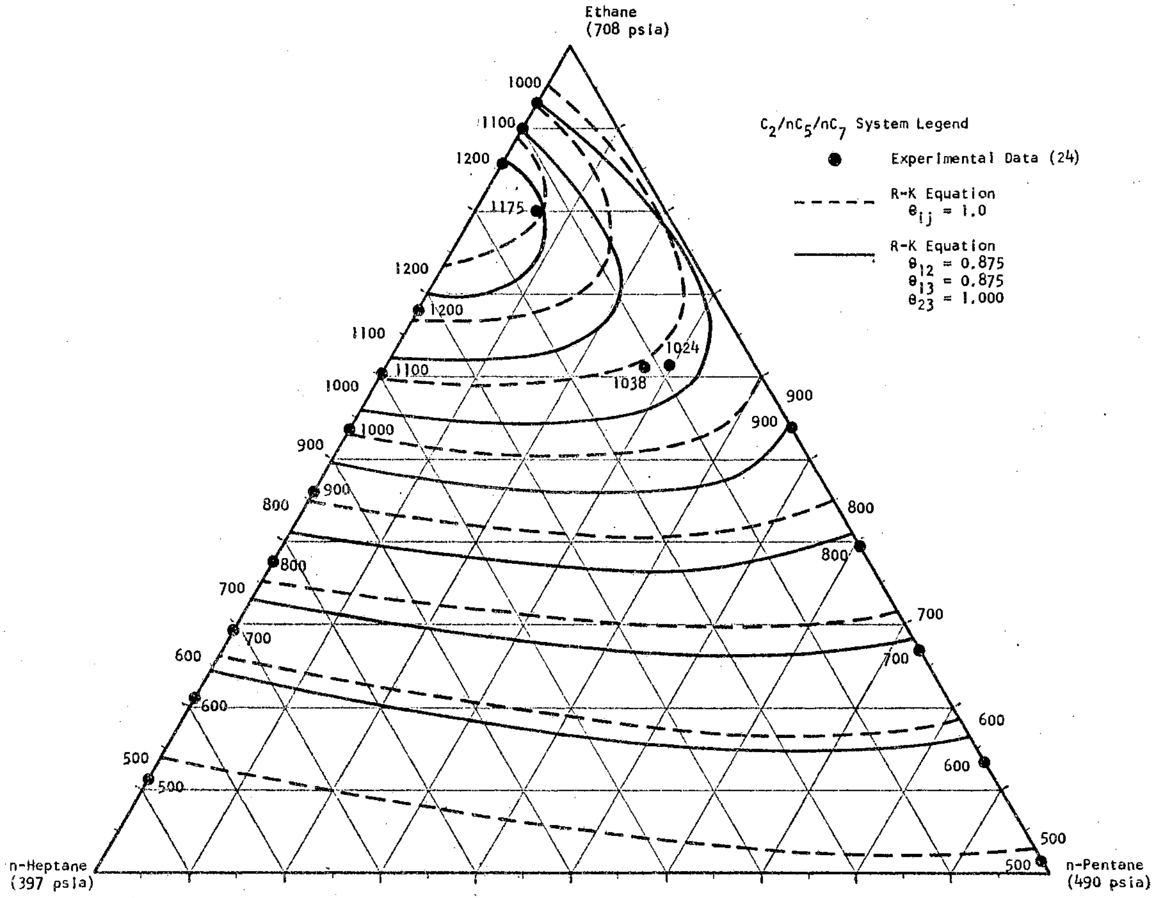

Figure 81. Critical Pressure-Composition Diagram for the Ethane/n-Pentane/n-Heptane System

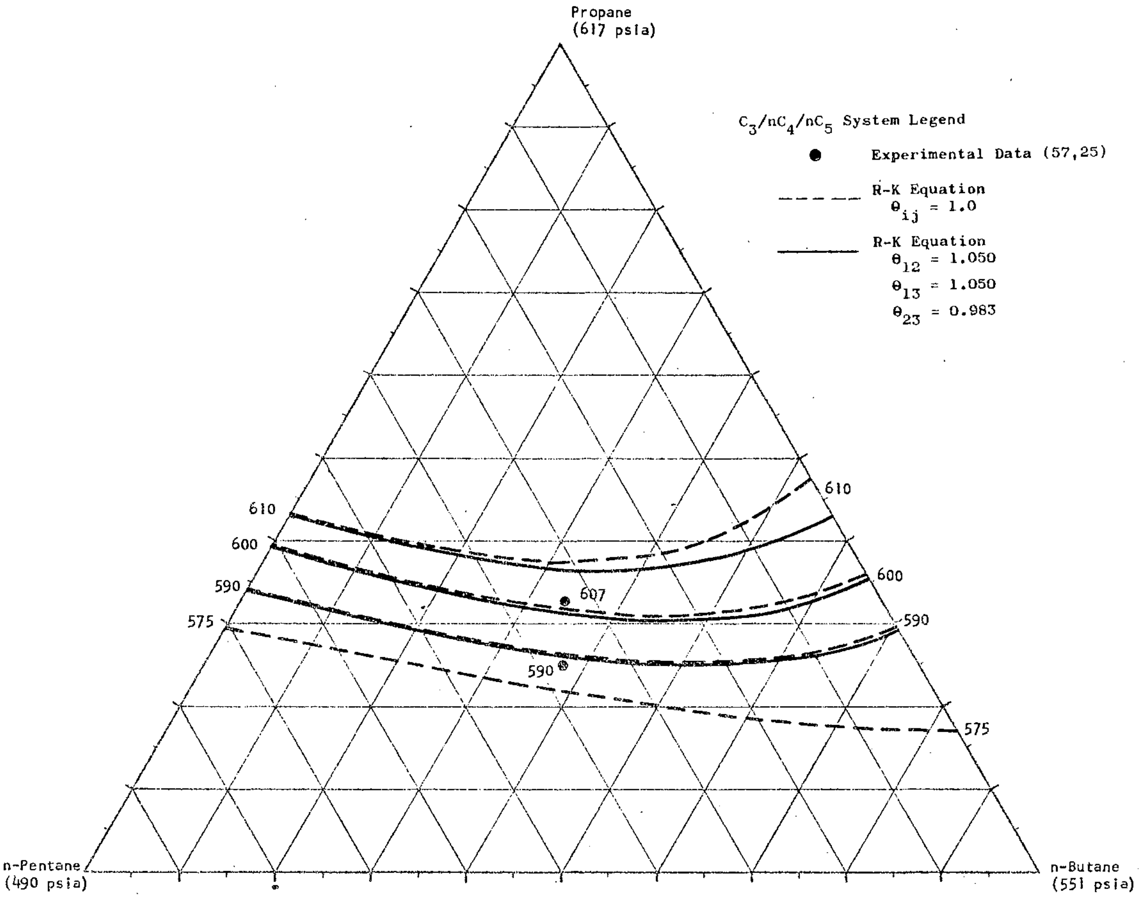

Figure 82. Critical Pressure-Composition Diagram for the Propane/n-Butane/n-Pentane System

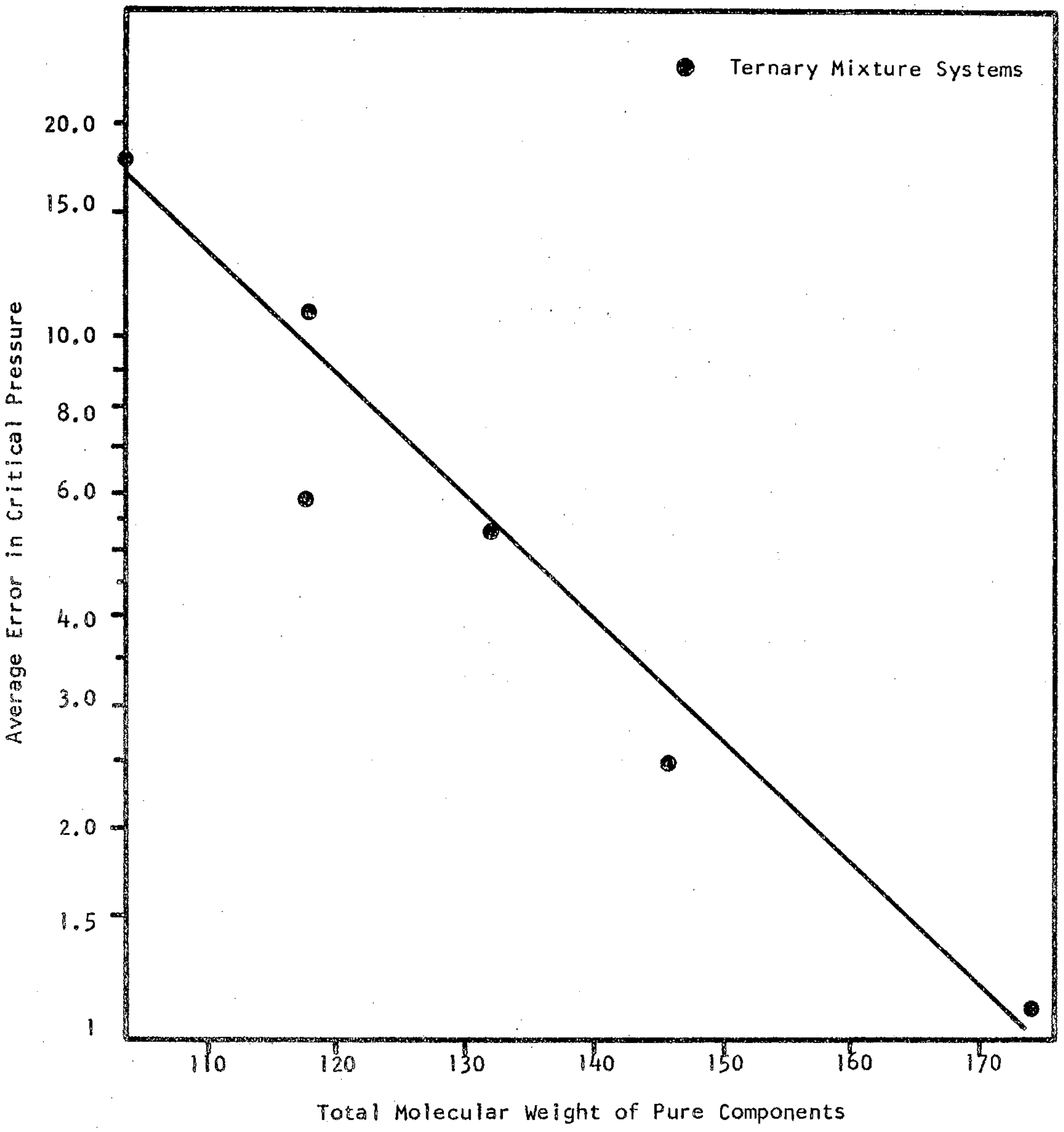

Figure 83. Plot of Average Error in the Critical Pressure versus the Total Molecular Weight of the Pure Components of the Ternary Mixture

# CHAPTER VII

# VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

## A. Vapor-Liquid Equilibrium State Theory

The equation of state approach has proved to be a highly successful and valuable tool in the prediction of various P-V-T properties of mixture systems. However, the P-V-T relationships calculated from equations of state in the high temperature-pressure region near the critical point show significant deviations from experimental data. The results of the critical state predictions for binary and ternary mixtures indicated that modifications of the binary interaction parameters in the mixing rules of the equations of state might result in significantly better predictions of the critical properties. Thus, the next logical objective of this investigation was to determine the effect of the optimum binary interaction parameters on the accuracy of the vapor-liquid equilibrium calculations in the critical region.

The vapor-liquid equilibrium boundary defines the limits of the region in which a vapor and liquid phase can exist together in an equilibrium state. The vapor-liquid equilibrium relationship for a binary mixture is shown in the isothermal pressure-composition diagram of Figure 84. The vapor-liquid equilibrium boundary, curve ABKDA, separates the single phase region from the two-phase region. The bubble point branch, curve ABK, and the dew point branch, curve ADK, of the vapor-liquid equilibrium boundary coincide at the critical point of the system, point K.

Each point on the bubble and dew point branches must satisfy the thermodynamic requirements of an equilibrium state. The first and second laws of thermodynamics indicate that the entropy must be a maximum and the internal energy a minimum in an equilibrium state. In practical physical systems the additional restraints of invariant total mass and volume can also be applied. Thus, any finite changes in an n-component system at equilibrium can be expressed as (61)

$$\delta S \leq 0 \qquad (167)$$

$$\delta E \geq 0 \qquad (168)$$

$$\delta V = 0 \qquad (169)$$

$$\delta m = \sum_{i=1}^{N} \delta m_i \quad . \qquad (170)$$

Combining these equilibrium relationships into the equation for the internal energy in variation form,

$$\delta E = T\ \delta S - P\ \delta V + \sum_{i=1}^{N} \mu_i \delta m_i \quad . \qquad (171)$$

results in the following identities at an equilibrium state:

$$T_{I} = T_{II} \qquad (172)$$

$$P_{I} = P_{II} \qquad (173)$$

$$\mu_{i_{I}} = \mu_{i_{II}} \quad . \qquad (174)$$

The equivalence of the chemical potentials between phases for all components can be expressed in terms of fugacities. Since fugacity is defined by (61)

$$f_i = e^{\frac{\mu_i - \beta_k}{RT}} \quad . \tag{175}$$

where $\beta_K$ is purely a temperature dependent function for a given component i, then equation 174 can be expressed equivalently for a binary mixture as

$$f_{i_I} = f_{i_{II}} \quad . \tag{176}$$

Therefore, the fundamental equilibrium relationships for a binary mixture suitable for VLE (vapor-liquid equilibrium) calculations are

$$T_g = T_l \tag{177}$$

$$P_g = P_l \tag{178}$$

$$f_{i_g} = f_{i_l} \quad . \tag{179}$$

These equilibrium requirements can be related quite easily to the isothermal pressure-composition diagram of Figure 84. At a specified temperature $T_o$ and pressure $P_o$, the equilibrium composition of component 2 in the vapor phase, $x_{2_g}$, and in the liquid phase, $x_{2_l}$, occur at the compositions for which the liquid and vapor fugacities are equal, points D and B. Thus, through a series of VLE calculations the vapor-liquid equilibrium boundary may be constructed.

Gibbs phase rule, as applied to binary mixtures in a two-phase region, indicates two independent variables are required to completely define the thermodynamic state of the system. If the equilibrium temperature and pressure are specified, then only the liquid and vapor phase fugacities need to be evaluated in order to determine the equilibrium state. Pressure explicit equations of state can be used to determine fugacities of system (7) since

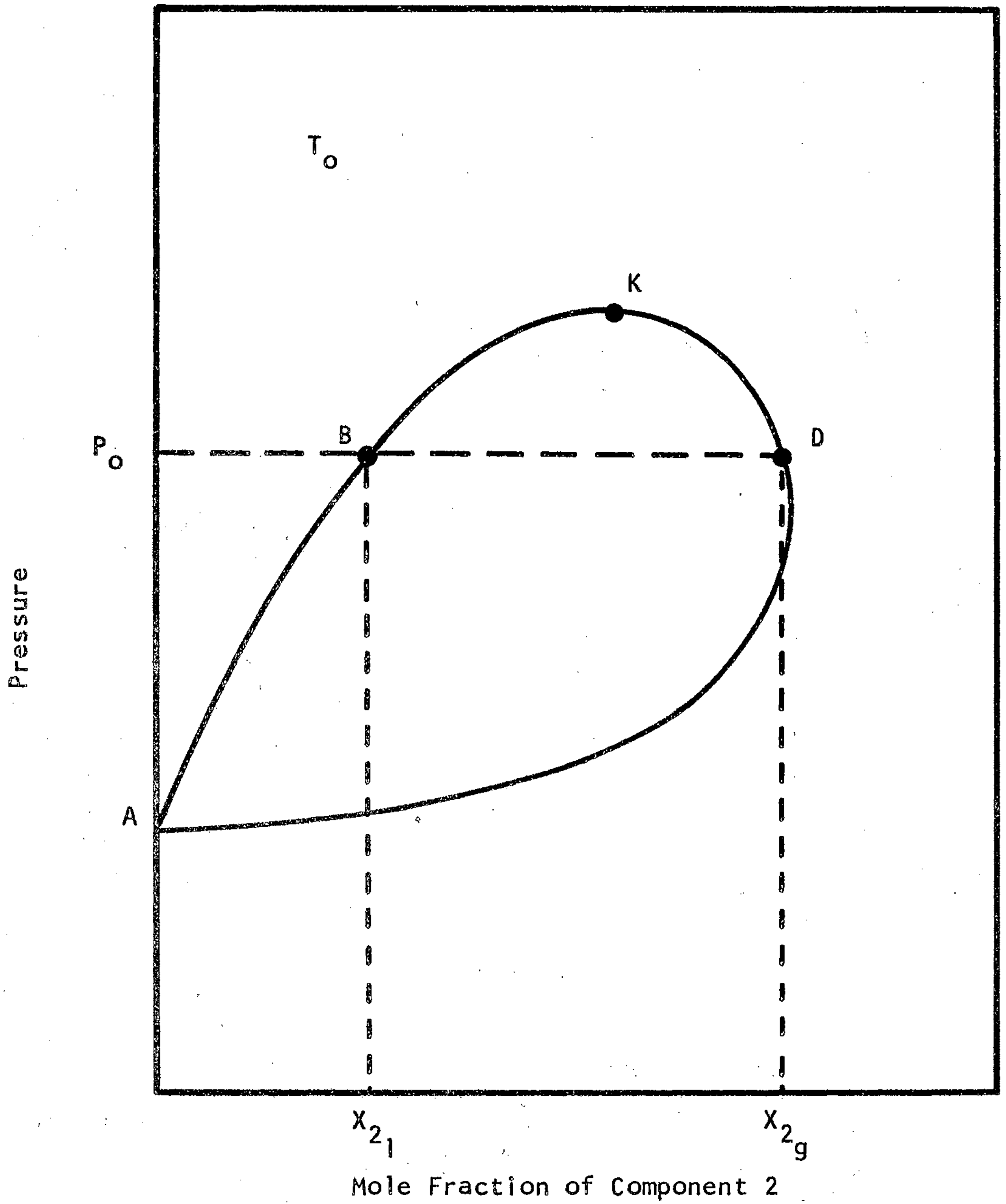

Figure 84. An Isothermal Pressure-Composition Diagram for a Binary Mixture

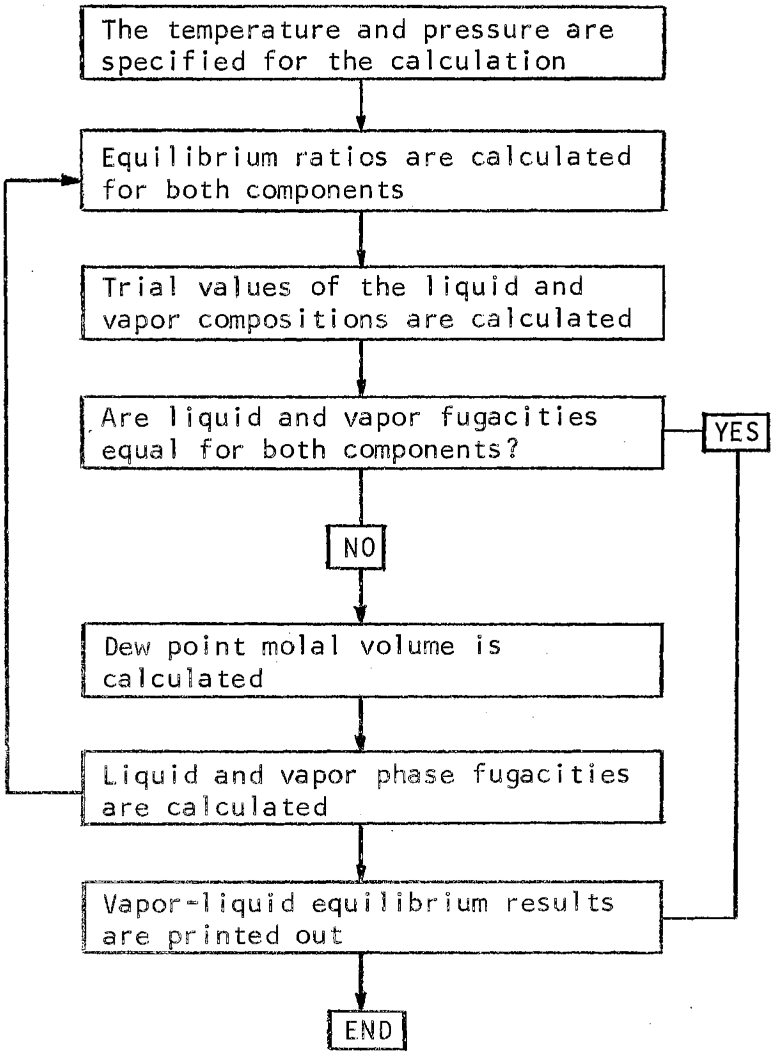

Figure 85. Block Diagram for VLE Calculations

$$RT \ln \frac{f_i}{x_i} = RT \ln \frac{RT}{V} + \int_0^{1/V} \left[ \left( \frac{\partial PV}{\partial n_i} \right)_{n_j,T,V} - RT \right] d \ln \frac{1}{V} \qquad (180)$$

The use of the volume and phase composition in the equation of state and the corresponding equation for the fugacity indicates that an iterative solution is required. The basic logic for the iterative solution for the vapor and liquid equilibrium state in a VLE calculation is shown in the block diagram of Figure 85.

## B. Application of the Benedict-Webb-Rubin Equation of State in Vapor-Liquid Equilibrium Calculations

The B-W-R equation was selected as the equation of state to be used to represent the properties of binary systems in the VLE calculations in this investigation. The B-W-R equation of state and its associated mixing rules and binary interaction parameters are presented in equations 103-114 of Chapter IV. The fugacity for either the liquid or vapor phase was derived from equation 180 using the B-W-R equation. The result of this derivation (7) is

$$\begin{aligned} RT \ln \frac{f_i}{x_i} = {} & RT \ln \frac{RT}{V} + \frac{1}{V}\left[ (B_o + B_{o_i})RT - 2(A_oA_{o_i})^{\frac{1}{2}} - \frac{2(C_oC_{o_i})^{\frac{1}{2}}}{T} \right] \\ & + \frac{3}{2V^2}\left[ RT(b^2b_i)^{1/3} - (a^2a_i)^{1/3} \right] + \frac{3}{5V^5}\left[ a(\alpha^2\alpha_i)^{1/3} \right. \\ & \left. + \alpha(a^2a_i)^{1/3} \right] + \frac{3(c^2c_i)^{1/3}}{T^2\,V^2}\left[ \frac{(1 - e^{-\gamma/V^2})V^2}{\gamma} - \frac{e^{-\gamma/V^2}}{2} \right] \\ & - \frac{2c}{T^2V^2}\left( \frac{\gamma_i}{\gamma} \right)^{\frac{1}{2}} \left[ \frac{(1 - e^{-\gamma/V^2})V^2}{\gamma} - e^{-\gamma/V^2} - \frac{\gamma e^{-\gamma/V^2}}{2V^2} \right] \end{aligned} \qquad (181)$$

The B-W-R equation of state and the equation for the fugacity of a binary mixture were programmed with the iterative procedure shown in Figure 85 in the VLECALC computer program. Each subcalculation of the iteration procedure was written as a subroutine of the program. This modular concept in the program permitted easy debugging and facilitates any future changes or modifications in the total program, such as the use of another equation of state. A complete description of the computer program VLECALC, the required input data and its format, and the control parameters for the operation of the program are presented in Appendix C.

Both the VLECALC computer program and the effect of adjusting the binary interaction parameter $\eta_1$ associated with the mixture coefficient $A_o$ of the B-W-R equation of state were tested with a series of VLE calculations with $\eta_1$ = 0.939, 1.000, and 1.100. The results of these calculations are shown in Figure 86. The VLE calculations using $\eta_1$ = 1.000, no adjustment of the usual binary interaction parameter, showed both qualitative and quantitative agreement with experimental data, particularly for the liquid phase. In general, a decrease in the value of $\eta_1$ resulted in a shift in the entire VLE boundary leftward and upward. A comparison of the VLE curves for $\eta_1$ = 1.000 and $\eta_1$ = 1.100 indicates, as previously mentioned as a characteristic of the B-W-R equation of state, that accurate predictions of both the liquid and vapor equilibrium phases over the complete range of temperature and pressure is not possible with one set of coefficients of the B-W-R equation of state. However, use of the optimum binary interaction parameter $\eta_1$ may result in a shift that increases the accuracy of either the liquid or vapor phase equilibrium calculations.

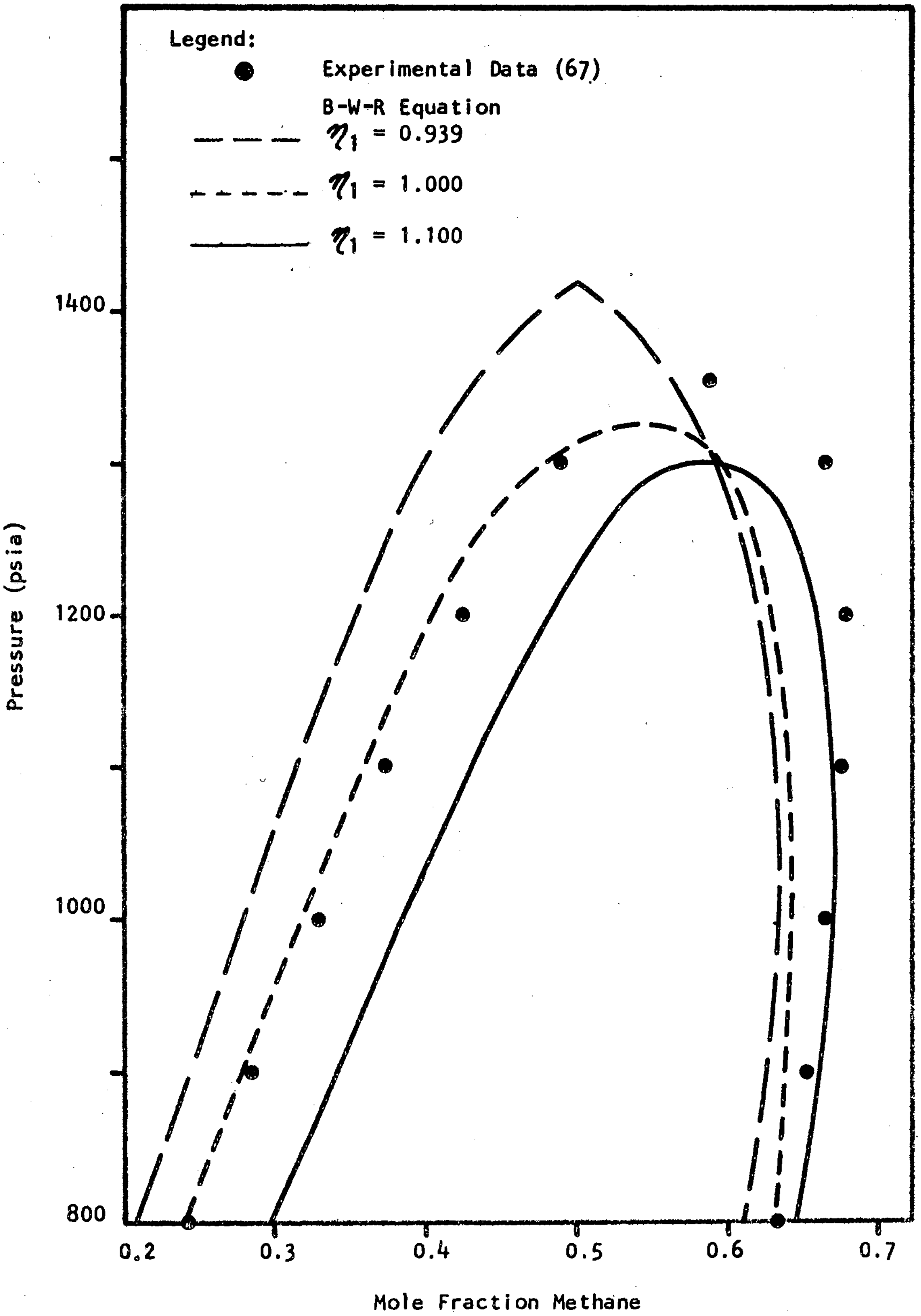

Figure 86. Vapor-Liquid Equilibrium Pressure-Composition Diagram

### C. Results of the Benedict-Webb-Rubin Equation of State in Vapor-Liquid Equilibrium Calculations

Two sets of vapor-liquid equilibrium calculations were performed on the methane/propane, ethane/n-pentane, propane/n-pentane, and propane/benzene binary systems to determine the effect of using the optimum binary interaction parameters $\eta_1$ on the accuracy of VLE calculations in the high temperature-pressure region near the critical point. The first set of VLE calculations used the usual mixing rules with no adjustment in the optimum binary interaction parameters in the mixing rules of the B-W-R equation of state. The second set of calculations used the optimum binary interaction parameters $\eta_1$ that gave the most accurate representation of the critical pressure-composition relationship for the corresponding binary system. Both sets of calculations were compared graphically with each other and with available experimental data. The results of both sets of VLE calculations for all four binary systems are shown in Figures 87-102 and discussed in detail in the following sections.

The methane/propane binary was the first system to be investigated at four approximately equally spaced isotherms between two pure component critical temperatures. Figure 86 indicated that a change in the value of $\eta_1$ had a significant effect on both the liquid and vapor phase equilibrium curves. The results of both the basic and optimized VLE predictions and experimental data points are plotted in the four isothermal pressure-composition diagrams of Figures 87-90. For the first set of VLE calculations with $\eta_1 = 1.000$ the vapor phase predictions, the right branch of the VLE boundaries in the figures, generally were poor in the high temperature-pressure region near the critical point.

However, good VLE predictions for the vapor phase could be obtained at pressure levels below 70% of the critical pressure. The liquid phase VLE predictions showed good agreement with experimental data. Approximately a two per cent error in the equilibrium pressure at a given mixture composition was observed to pressures up to 95% of the critical pressure.

The second set of VLE calculations using the optimum value of $\eta_1$ for the methane/propane system, $\eta_{1_{op}} = 1.023$, produced only a slight shift in both the liquid and vapor branches of the VLE boundary. This shift increased the accuracy of the vapor phase predictions only very slightly at pressures greater than 70% of the critical pressure. The error in the liquid phase predictions was reduced from approximately two per cent to one per cent. Table VII shows the reduction in the liquid phase equilibrium pressure error for each of the four isotherms investigated. The average reduction in the error using the optimum $\eta_1$ was from 1.9 to 1.3%. Thus, the increase in the accuracy of the VLE predictions was small and limited to the liquid phase.

Four isotherms of the ethane/n-pentane binary mixture were investigated. The results of both the basic and optimized VLE calculations are shown graphically in Figures 91-94. The basic VLE calculations with $\eta_1 = 1.000$ were much more accurate than the corresponding results for the methane/propane system. The average error level in the equilibrium pressure at a given composition for both the liquid and vapor phases was approximately two per cent. The $500^{\circ}$ and $560^{\circ}$ R isotherms form a cusp at the critical point. In this situation the VLE predictions were accurate up to the critical point for both the liquid and vapor phases. For the more typical rounded VLE boundary at the critical point, the vapor phase predictions were accurate only up to 80% of the critical pressure. The second set of VLE calculations using the optimum value of 0.987 for $\eta_1$ did not significantly improve the accuracy of either the liquid or vapor phase equilibrium predictions.

Four isotherms of the propane/n-pentane binary mixture were investigated. The results of both the basic and optimized VLE calculations are shown in Figures 95-98. The basic VLE calculations with $\eta_1 = 1.00$ were quite similar to those obtained for the ethane/n-pentane system. The average error level was approximately three per cent for the equilibrium pressure in the liquid and vapor phase predictions up to 95% of the critical pressure. Use of the optimum value of $\eta_1$ of 1.025 shifted the VLE boundary to the right and generally decreased the accuracy of the VLE predictions of both the liquid and vapor phases. The propane/n-pentane mixture was the only system of the four studied in detail that showed a decrease in the accuracy of VLE predictions using the optimum value of $\eta_1$.

Four isotherms of the propane/benzene binary system were investigated. The results of both the basic and optimized VLE calculations are shown graphically in Figures 99-102. The basic VLE calculations with $\eta_1 = 1.00$ were similar to those obtained for the methane/propane system. The vapor phase predictions were poor in the high temperature-pressure region near the critical point. However, good VLE predictions for the vapor phase could be obtained at pressure levels below 70% of the critical pressure. The average error level in the equilibrium pressure for the liquid phase was approximately three per cent up to pressures equal to 95% of the critical pressure. Use of the optimum value of $\eta_1$ of 1.012 in the second set of VLE calculations resulted in a shift to the right in the VLE boundaries. This shift significantly decreased the average error in the liquid phase predictions from approximately three per cent to two per cent. The effect of the optimum $\eta_1$ on the vapor phase predictions was negligible.

The results of the investigation of vapor-liquid equilibrium calculations in the region near the critical point indicated that predictions for the vapor phase generally are not accurate at pressures above 70% of the critical pressure for that isotherm. The liquid phase equilibrium predictions generally were more accurate than those for the vapor phase. The average error level in the equilibrium pressure of the liquid phase was two to three per cent to pressures up to 95% of the critical pressure. A noticeable exception to these error level statements occurred when the VLE boundary is cusped, rather than rounded, at the critical point. If a cusp existed at the critical point, both the liquid and vapor phase predictions had average error levels of two to three per cent at pressure up to the critical pressure.

Use of the optimum binary interaction parameter $\eta_1$ in the VLE calculations for the four binary systems investigated indicated that a slight increase in the accuracy of the liquid phase may be produced, but not necessarily so. If the VLE boundary at the critical point was rounded, the optimum $\eta_1$ generally produced only a one per cent reduction in the average error of the equilibrium pressure. An exception to the general rule of increased accuracy of the optimized VLE calculations was the propane/n-pentane system in which the accuracy was significantly reduced. If the VLE boundary is cusped at the critical point, the effect of the optimum $\eta_1$ was negligible since the basic ($\eta_1$ = 1.00) calculations were accurate up to the critical point. Thus, the conclusion to be drawn from this investigation is that use of the optimum binary interaction parameter $\eta_1$ in VLE calculations does not, in general, greatly improve the accuracy of VLE predictions in the region near the critical point in spite of the fact that use of the optimum $\eta_1$ substantially improves the accuracy of the critical pressure-composition relationships for the same binary systems.

This seemingly contradictory observation can be explained by a close examination of the nature of the improvements in the critical properties of binary mixtures when the optimum values of the binary interaction parameters were used. For the paraffin/paraffin binary systems used in the VLE calculations, the critical pressure improvements were limited to a relatively narrow composition range near the maximum critical pressure on the critical locus. Thus, significant improvements in the VLE calculations in the retrograde region will also be limited to a correspondingly narrow composition range for these paraffin/paraffin systems. However, for systems such as the n-butane/carbon dioxide binary, the use of optimum binary interaction parameters will undoubtedly have a very significant effect.

## TABLE VII

## COMPARISON OF EQUILIBRIUM PRESSURE ERRORS IN THE LIQUID PHASE USING THE B-W-R EQUATION OF STATE IN VLE CALCULATIONS FOR THE METHANE/PROPANE SYSTEM

| Isotherm ( °R ) | Equilibrium Pressure Errors | |
|---|---|---|
| | Basic = 1.0 | Optimized = 1.023 |
| 560 | 2.6 | 1.1 |
| 590 | 1.9 | 1.6 |
| 620 | 1.4 | 1.2 |
| 650 | 1.7 | 1.5 |
| Average | 1.9 | 1.3 |

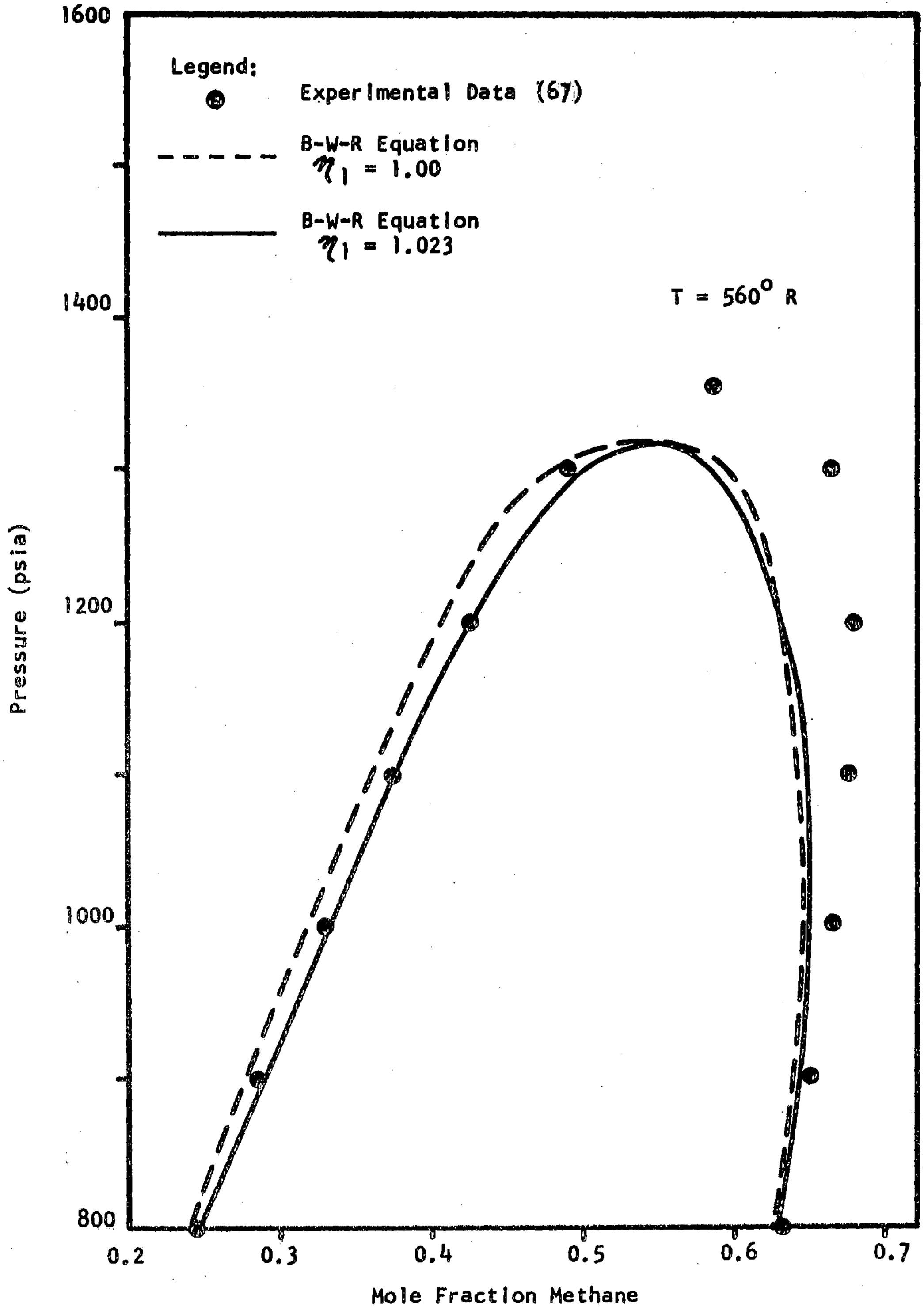

Figure 87. Pressure-Composition Diagram for the 560° R Isotherm for the Methane/Propane System

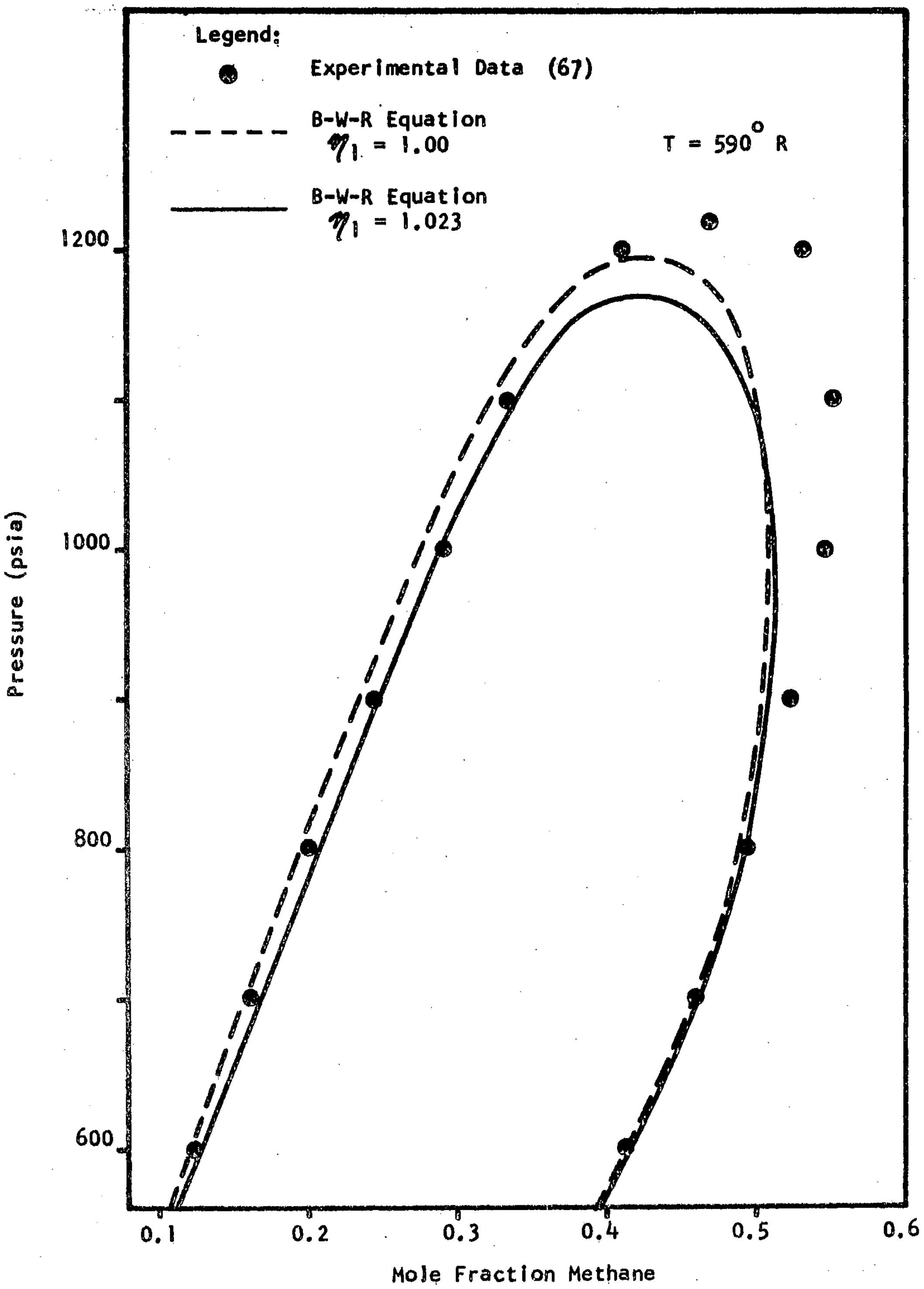

Figure 88. Pressure-Composition Diagram for the 590° R Isotherm for the Methane/Propane System

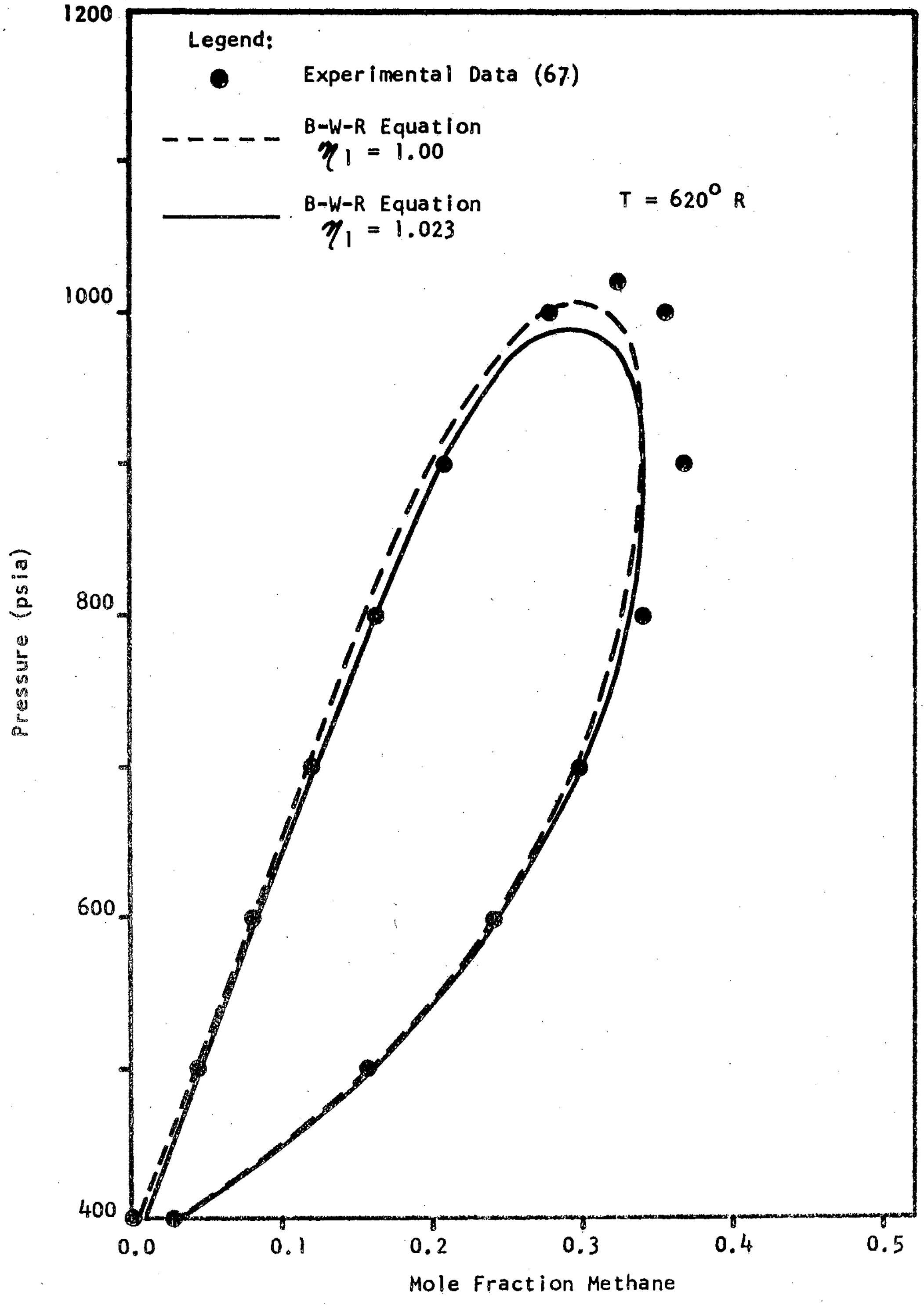

Figure 89. Pressure-Composition Diagram for the 620° R Isotherm for the Methane/Propane System

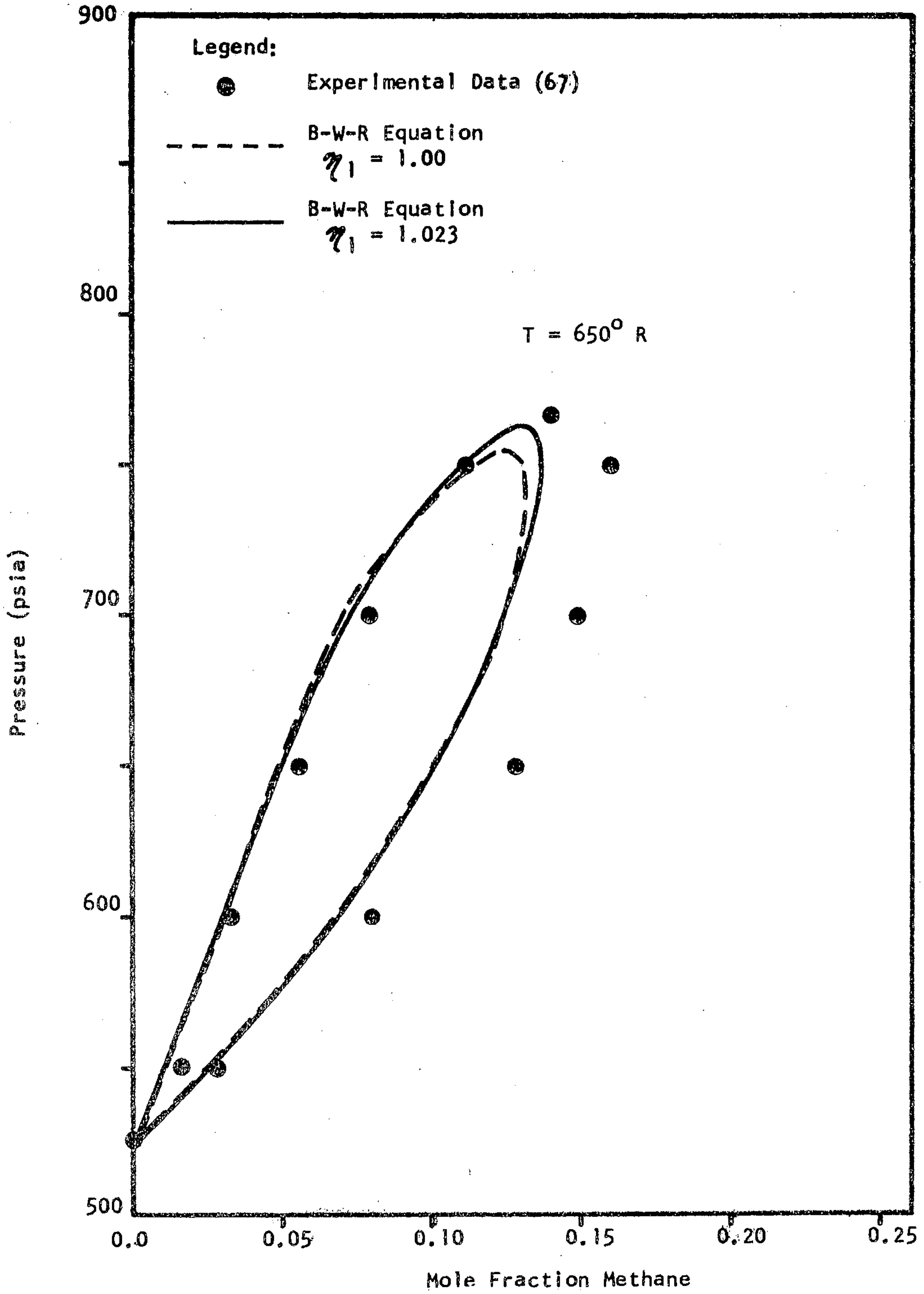

Figure 90. Pressure-Composition Diagram for the 650° R Isotherm for the Methane/Propane System

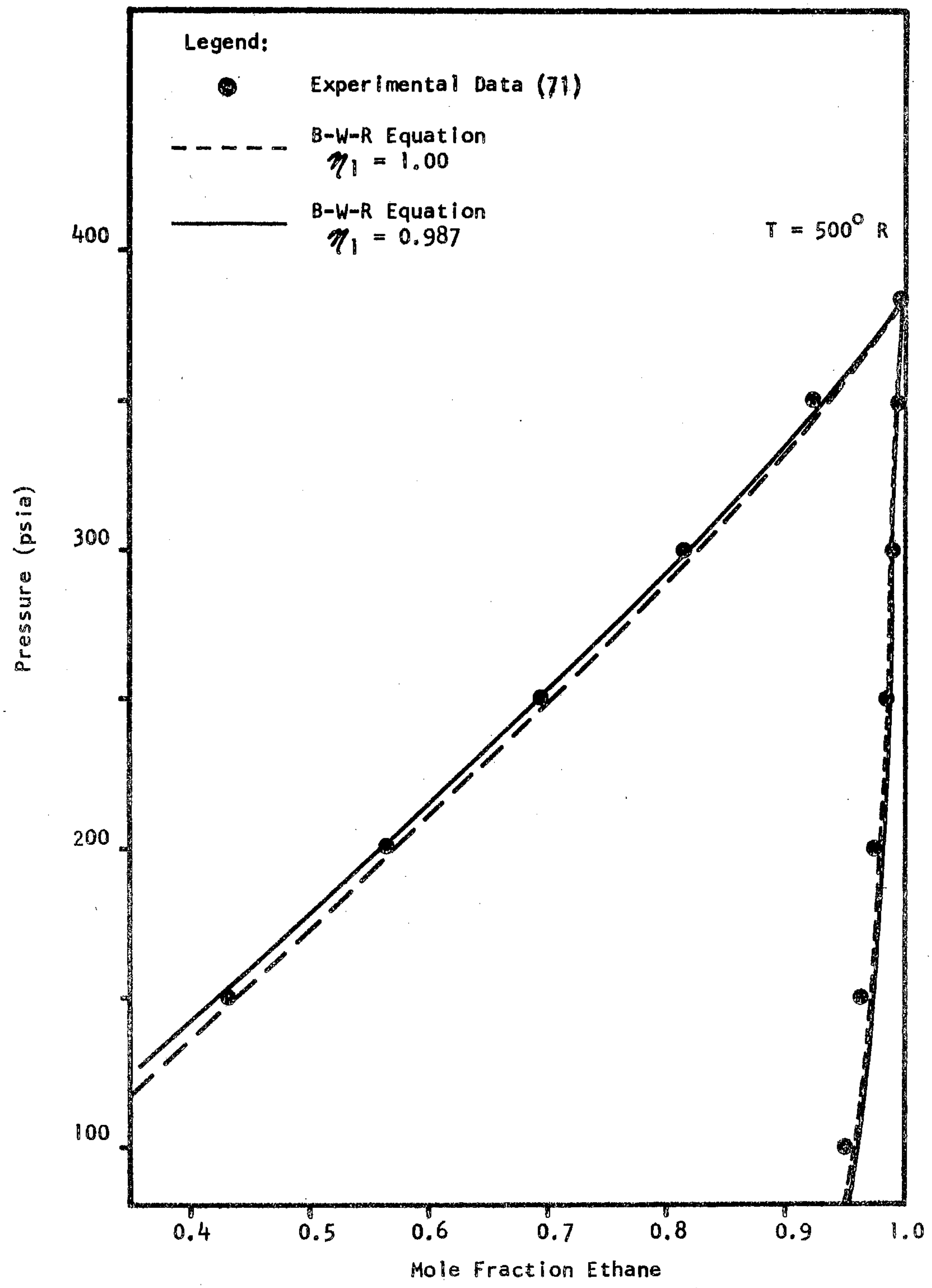

Figure 91. Pressure-Composition Diagram for the 500° R Isotherm for the Ethane/n-Pentane System

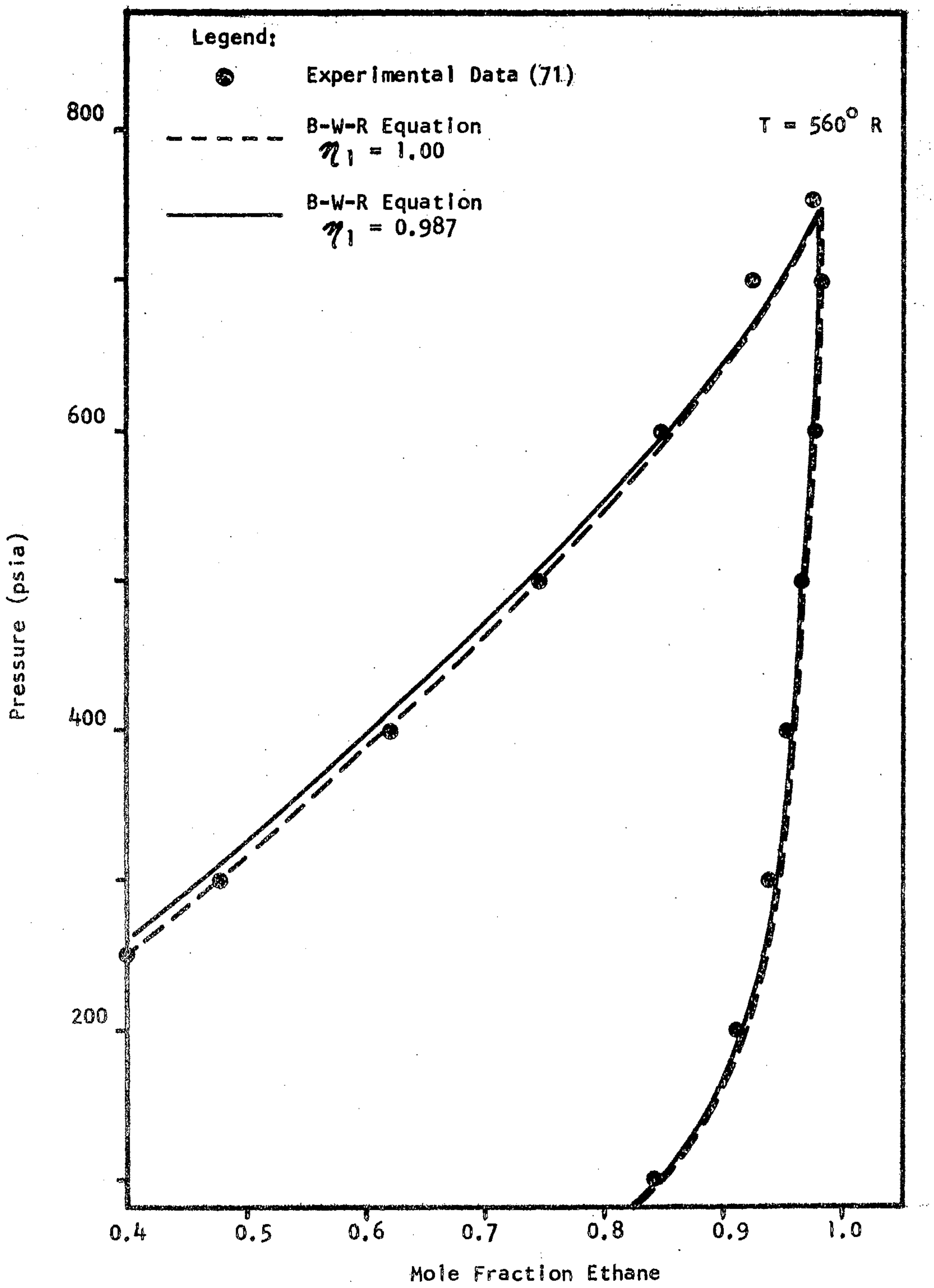

Figure 92. Pressure-Composition Diagram for the 560° R Isotherm for the Ethane/n-Pentane System

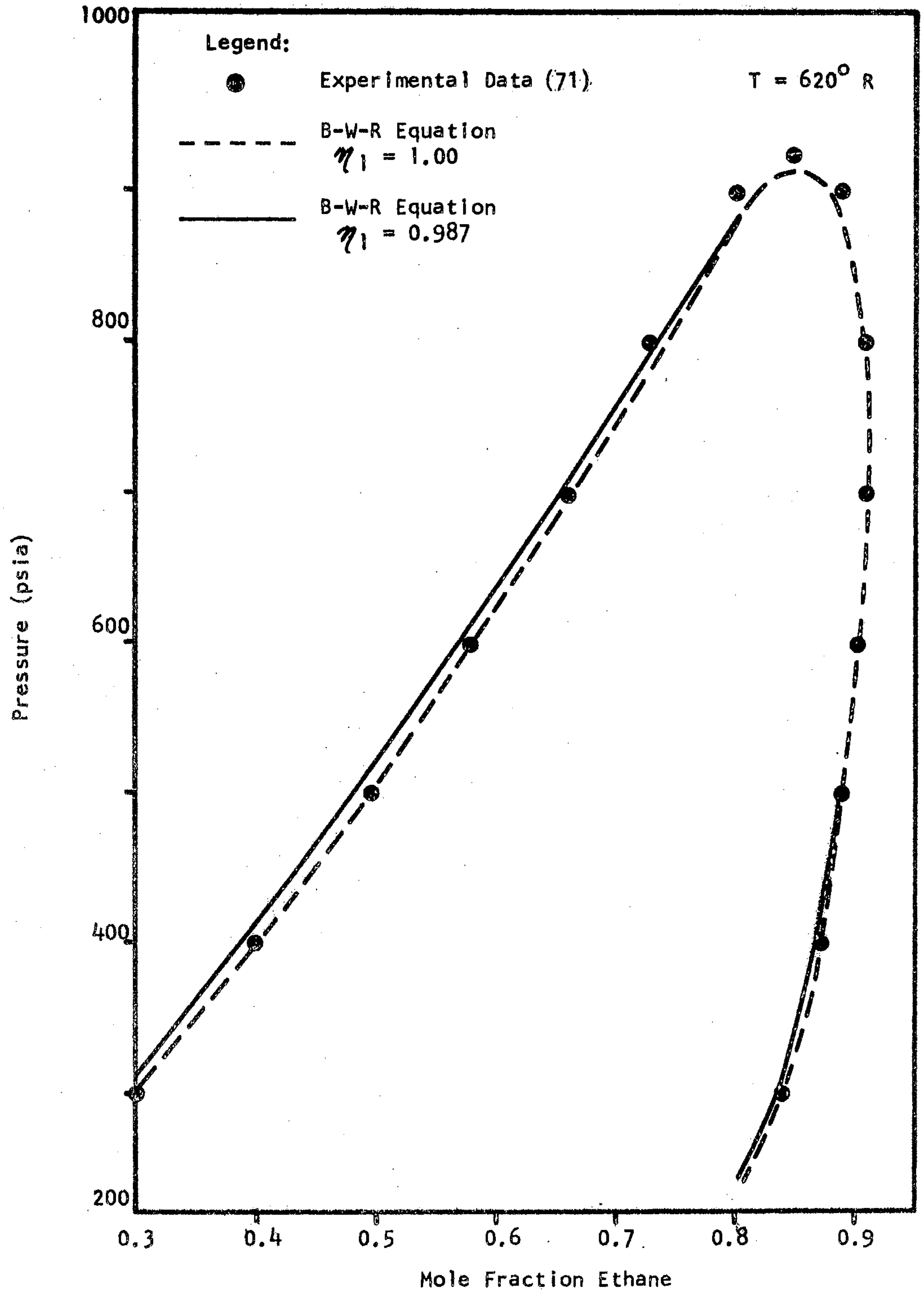

Figure 93. Pressure-Composition Diagram for the 620° R Isotherm for the Ethane/n-Pentane System

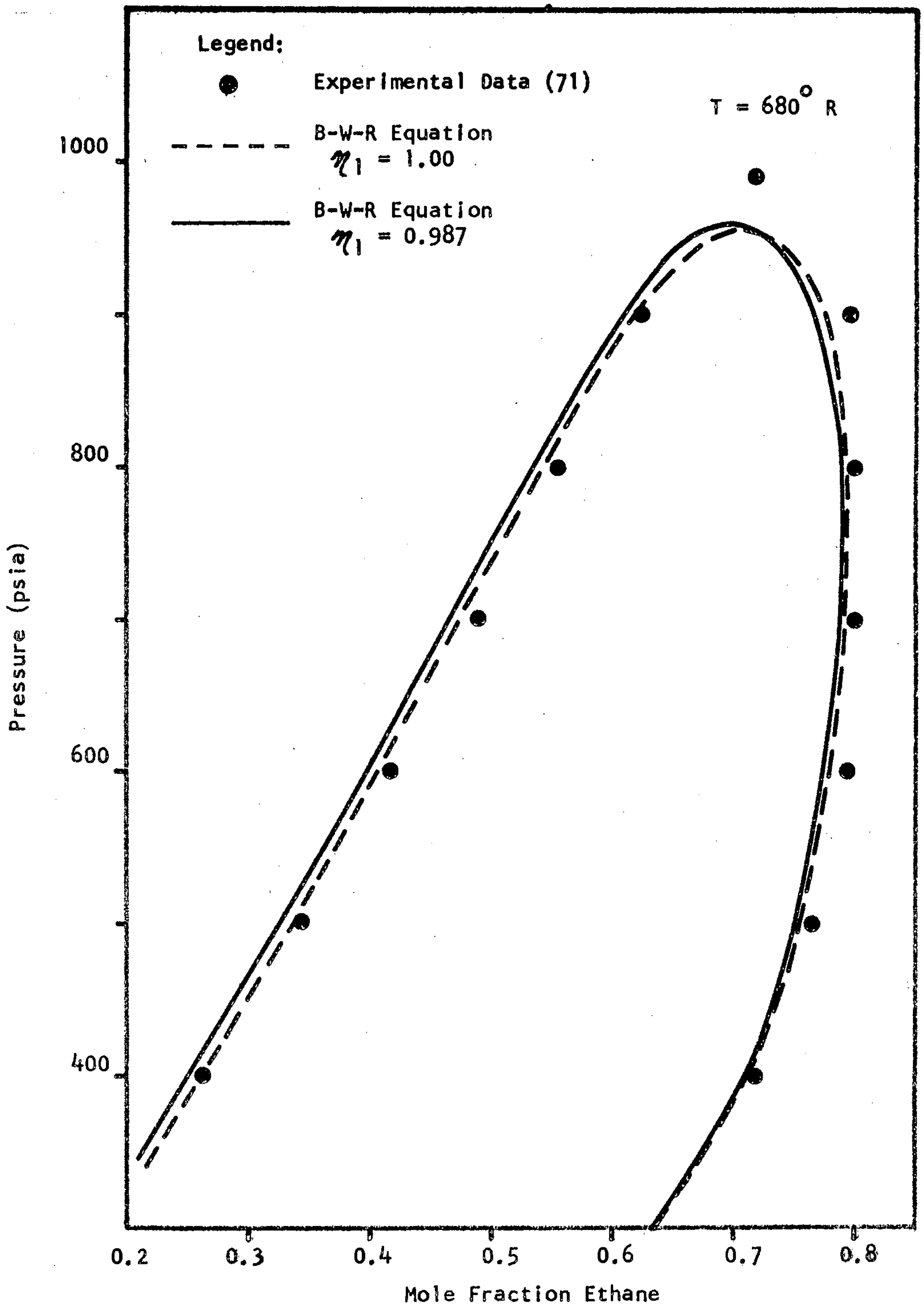

Figure 94. Pressure-Composition Diagram for the 680° R Isotherm for the Ethane/n-Pentane System

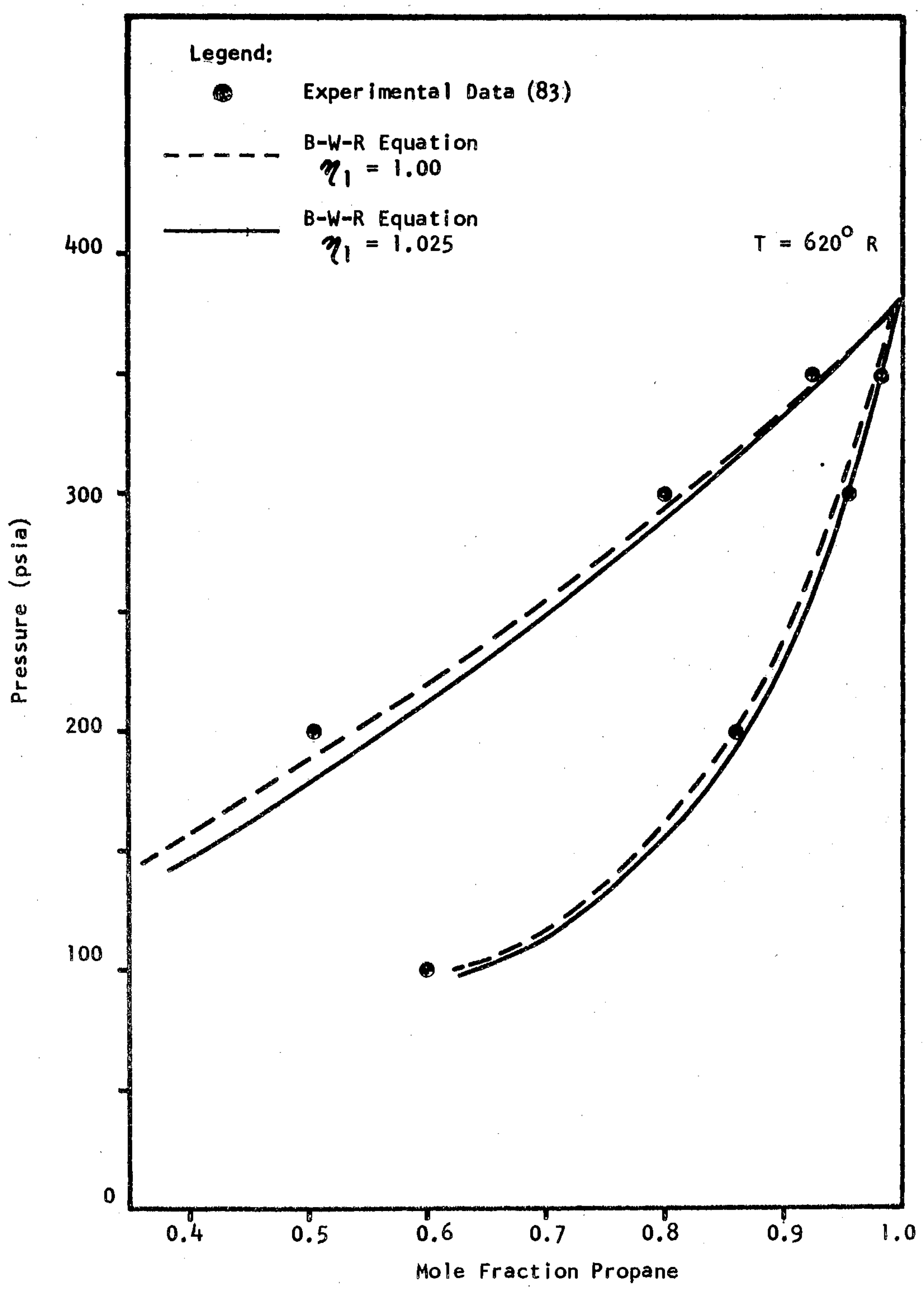

Figure 95. Pressure-Composition Diagram for the 620° R Isotherm for the Propane/n-Pentane System

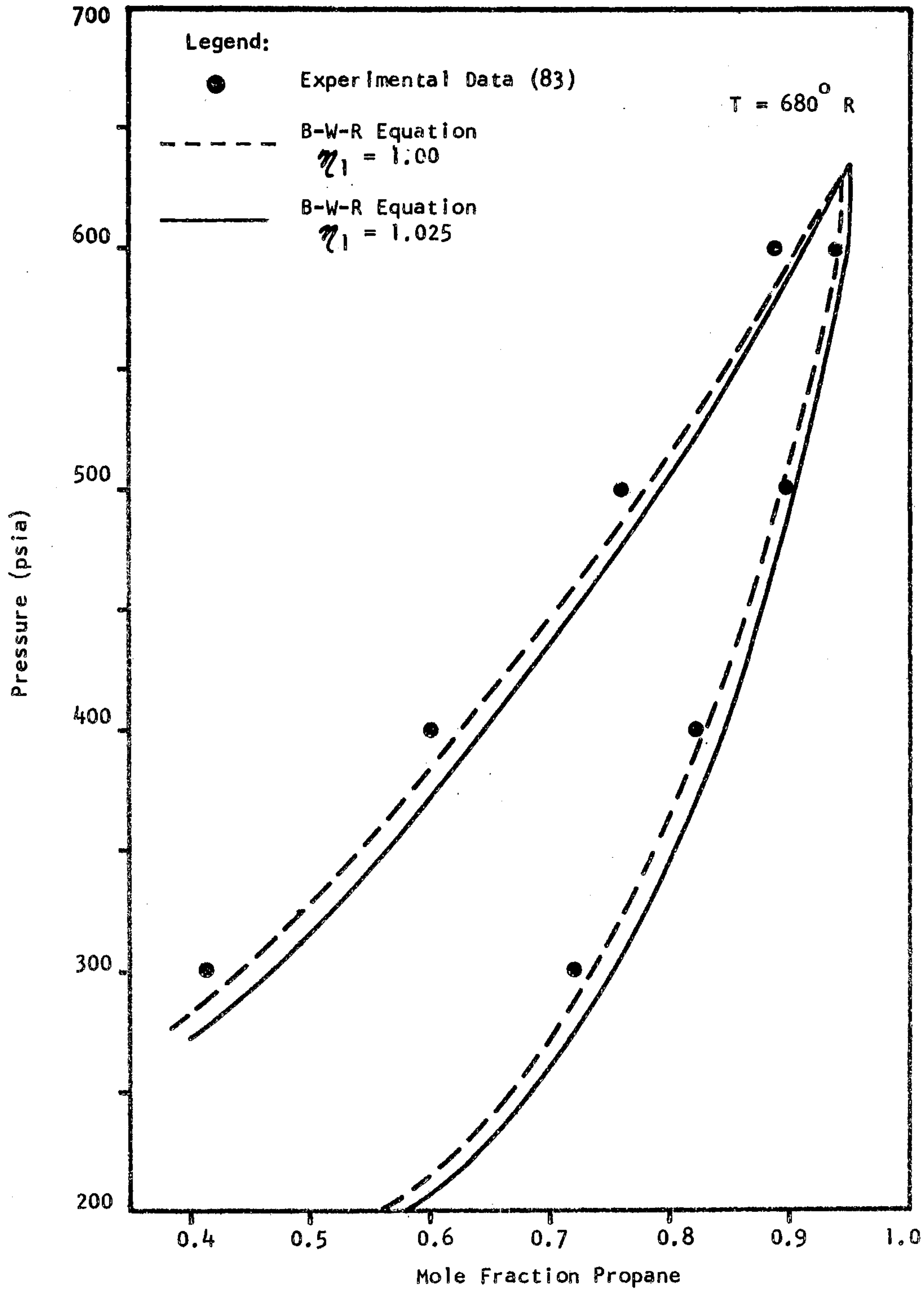

Figure 96. Pressure-Composition Diagram for the 680° R Isotherm for the Propane/n-Pentane System

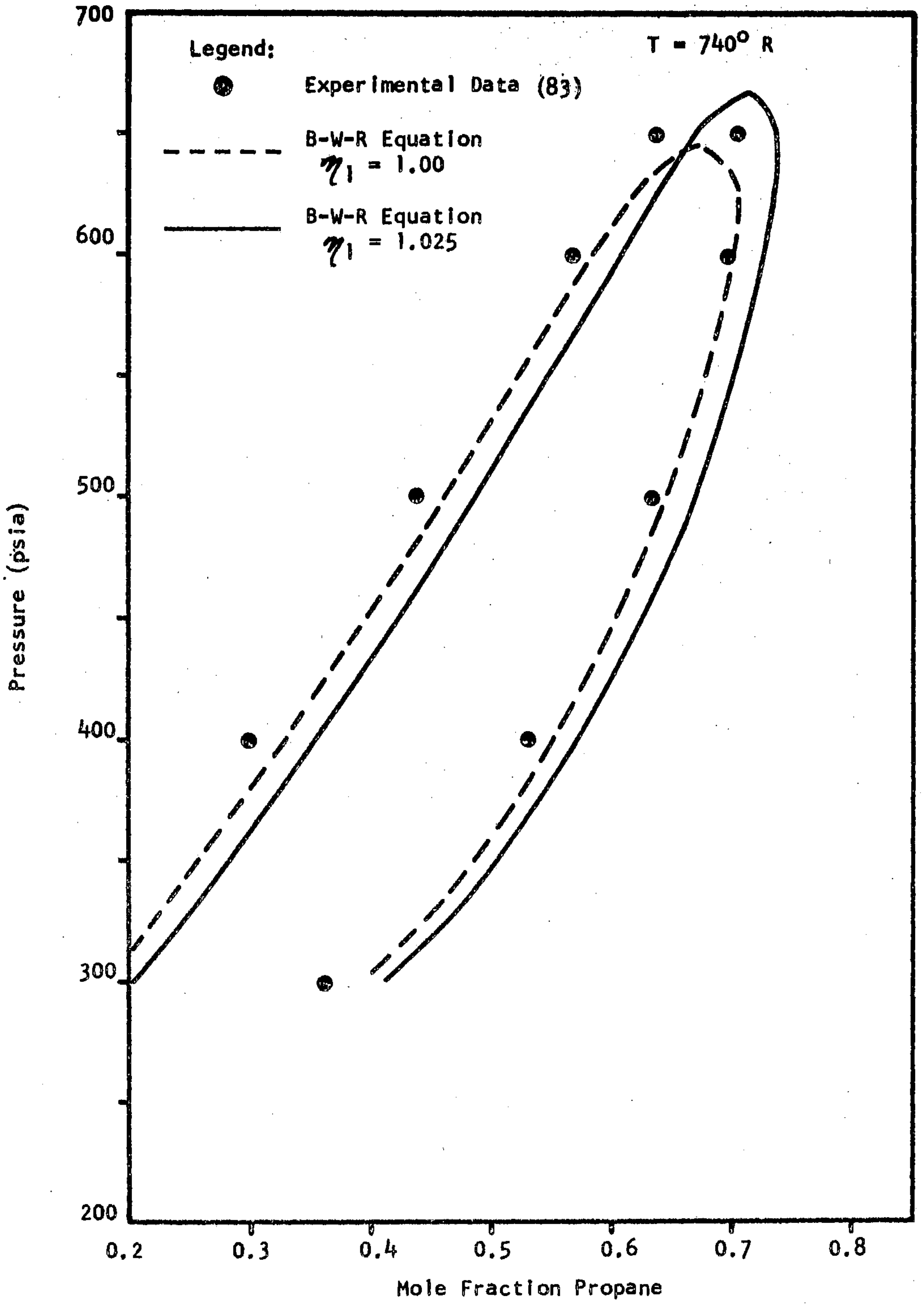

Figure 97. Pressure-Composition Diagram for the 740° R Isotherm for the Propane/n-Pentane System

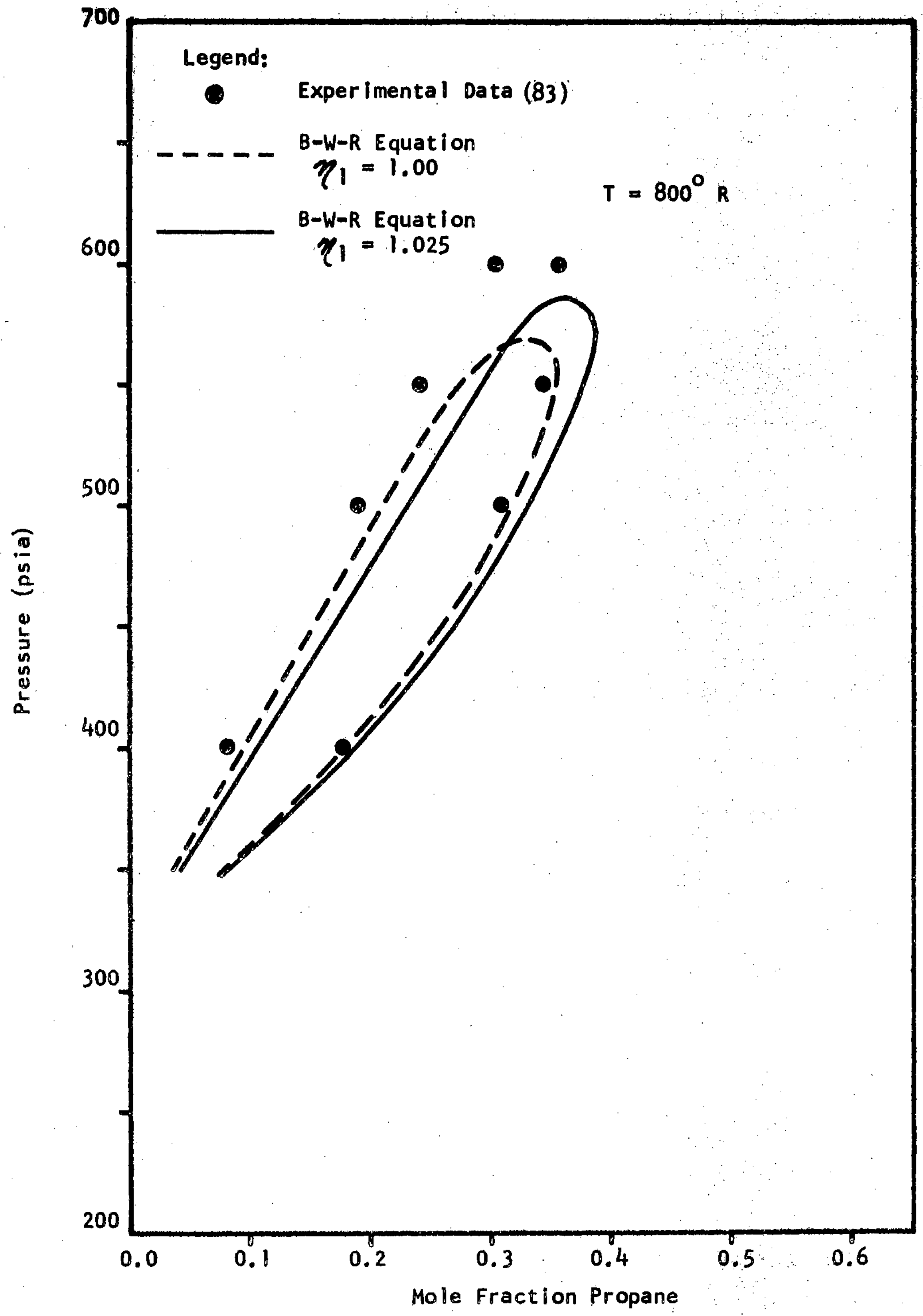

Figure 98. Pressure-Composition Diagram for the 800° R Isotherm for the Propane/n-Pentane System

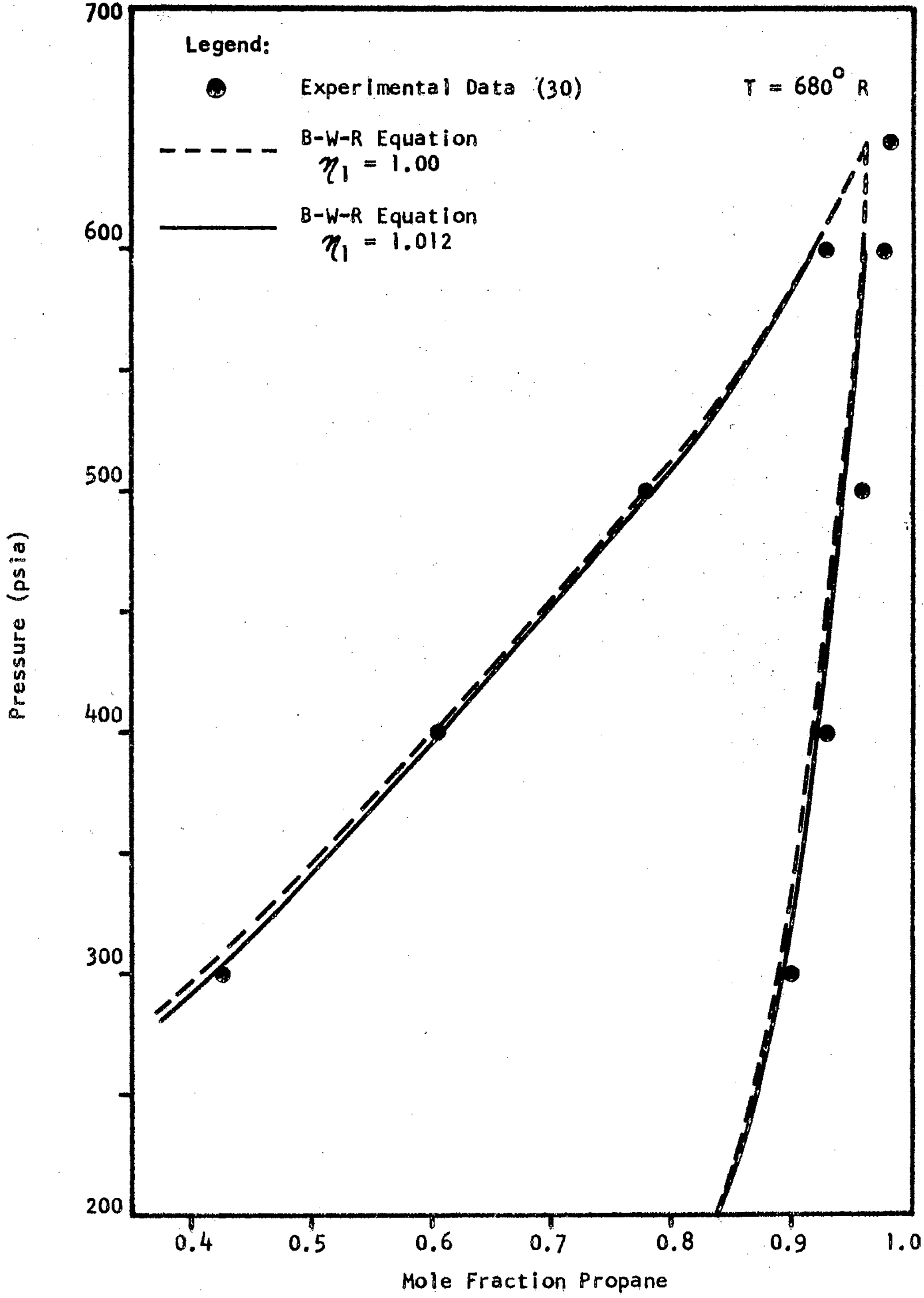

Figure 99. Pressure-Composition Diagram for the 680° R Isotherm for the Propane/Benzene System

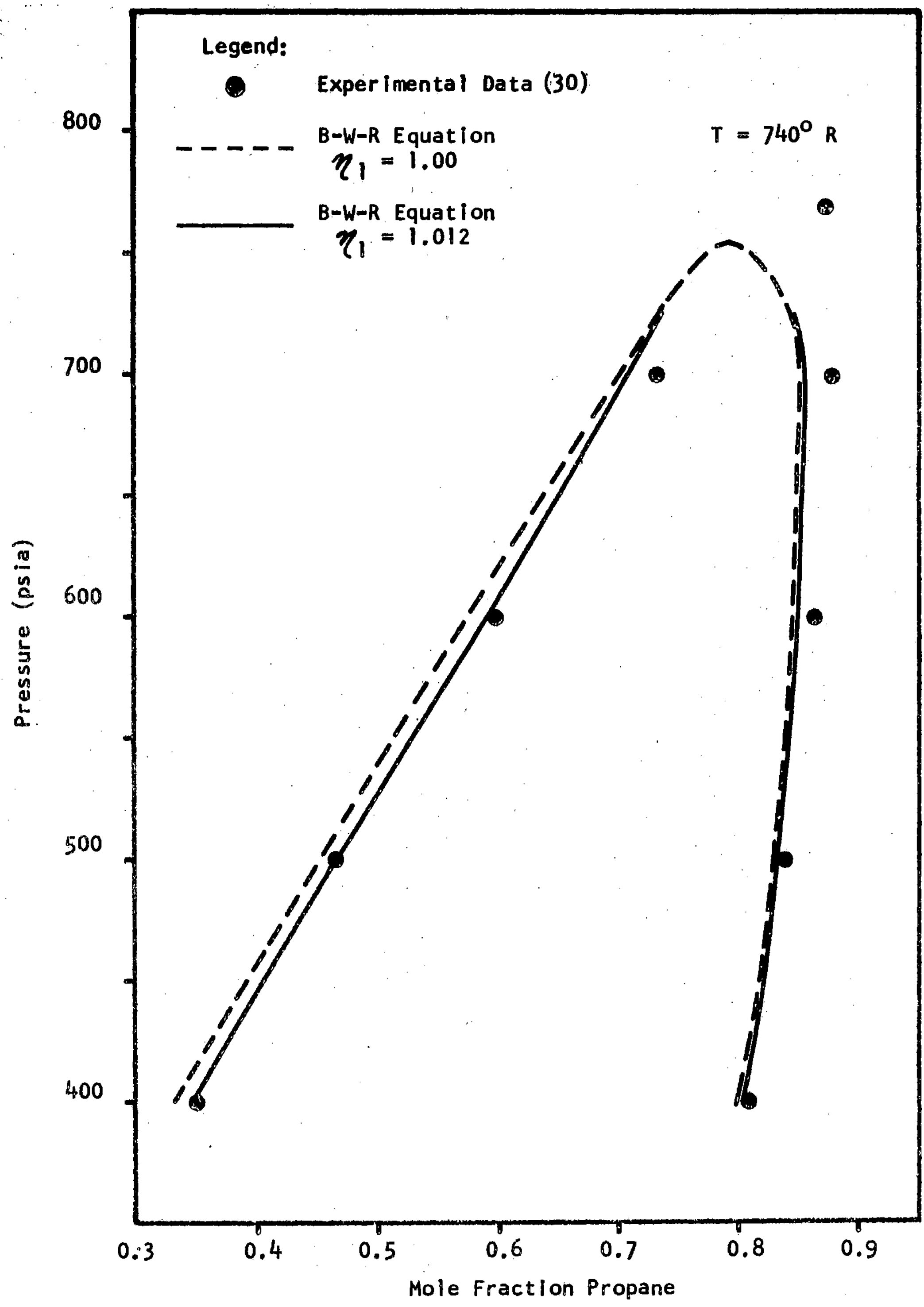

Figure 100. Pressure-Composition Diagram for the 740° R Isotherm for the Propane/Benzene System

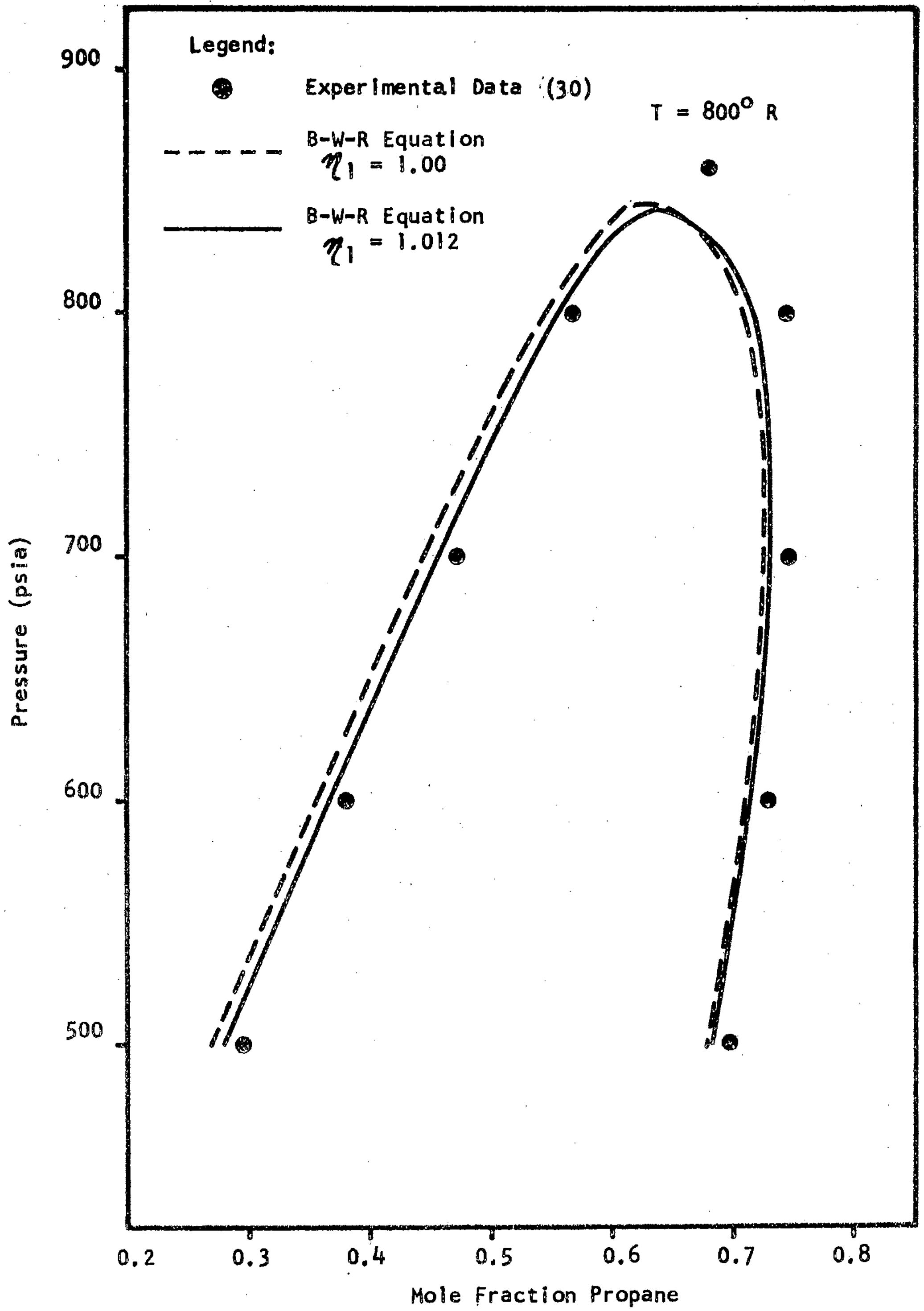

Figure 101. Pressure-Composition Diagram for the 800° R Isotherm for the Propane/Benzene System

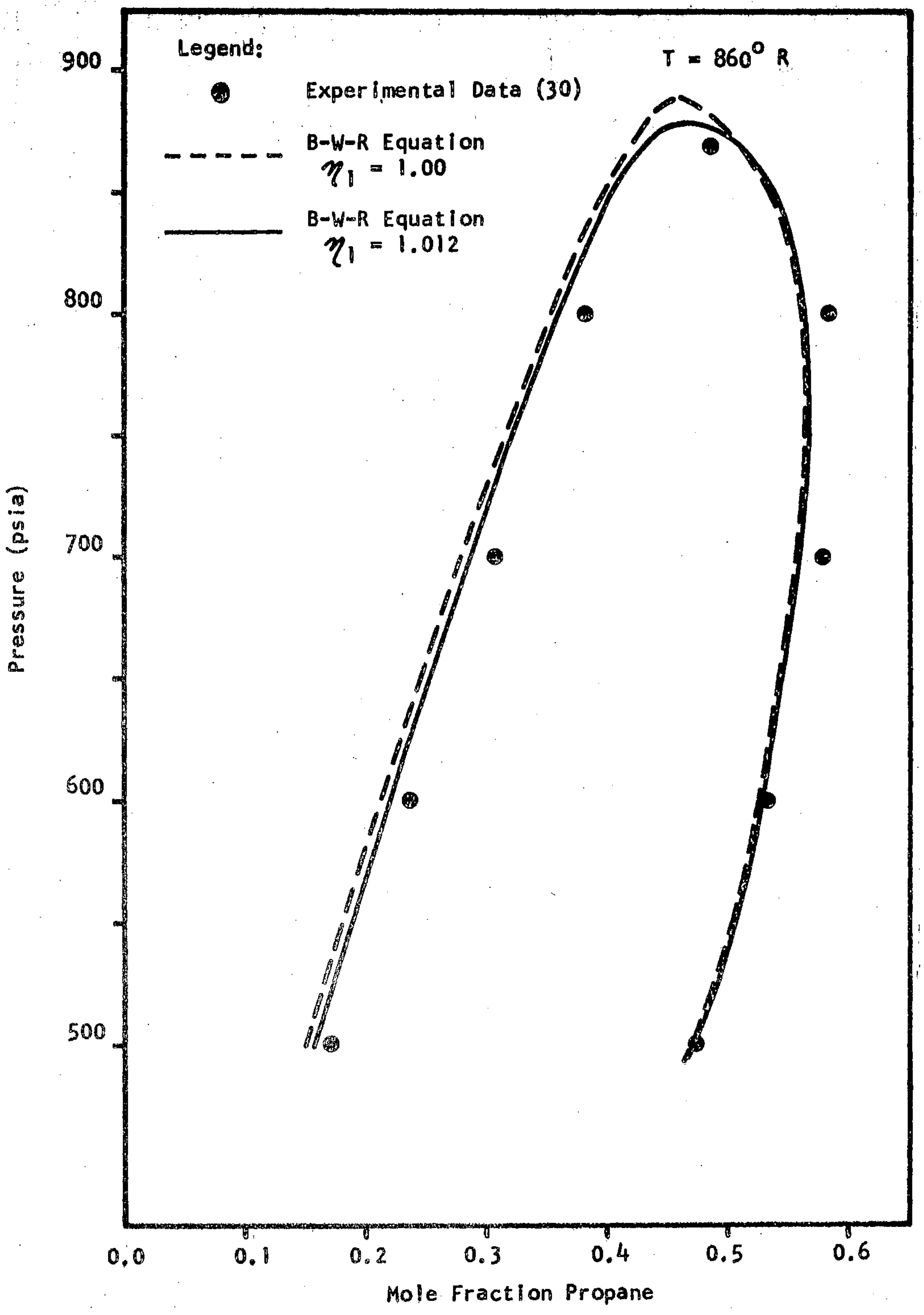

Figure 102. Pressure-Composition Diagram for the 860° R Isotherm for the Propane/Benzene System

# CHAPTER VIII

# CONCLUSIONS AND RECOMMENDATIONS

The purpose of this exploratory investigation was to integrate the thermodynamic criteria of the critical state of mixtures with a suitable equation of state to predict the critical properties of mixtures. The major conclusions drawn from each of the four primary objectives are presented along with recommendations for future study in the following sections.

The first objective, to review and investigate the fundamental thermodynamic criteria of the critical state, was achieved for both binary and ternary mixtures. The most useful approach in understanding the phenomenon of the critical state proved to be the identification of the critical state of a mixture as a unique point on the diffusion stability boundary. Using this approach, the critical state criteria for mixtures were defined in terms of simple derivatives of the pressure and molar Helmholtz free energy. These critical state derivatives were evaluated from a pressure explicit equation of state. However, the rapidly increasing complexity of the critical state criteria as the number of components in the mixture increases appears to limit the application of the equation of state approach to critical state predictions to quaternary or perhaps quinary mixtures. Future investigations into the thermodynamic theory of the critical state should be directed to finding simplications in the fundamental critical state criteria of quaternary and higher multicomponent mixtures. The eventual goal, if it were possible, would be a general procedure to calculate the critical state of an n-component mixture where n is on the order of 10.

The second objective, to select suitable equations of state and perform numerical calculations to predict the critical properties, was achieved by using both the Redlich-Kwong and the Benedict-Webb-Rubin equations of state on a variety of binary and ternary mixtures of interest. Analysis of the results of the critical state calculations showed that qualitative and semi-quantitative agreement with experimental data was obtained by using either the Redlich-Kwong or the B-W-R equation of state. In general, the average error levels in the predictions of the critical properties were comparable to those obtained from the best empirical correlations. The two-parameter Redlich-Kwong equation predicted the critical properties of binary mixtures as well as and often better than the eight-parameter B-W-R equation of state. The conclusion drawn from this result was that the ability of an equation of state to predict the critical properties of mixtures is directly related to the equation's ability to predict the corresponding critical properties of the pure components of the mixture. Thus, because of its simplicity and the fact that the Redlich-Kwong equation necessarily yields the exact critical temperature and pressure for any pure component, the Redlich-Kwong equation proved to be a much more satisfactory equation of state for critical property predictions than was first suspected.

The second major observation arising from the analysis of the calculation results was that both the Redlich-Kwong and the B-W-R equations of state predicted the $P_c$-$T_c$ relationship much more accurately than either the $T_c$-$x_2$ or $P_c$-$x_2$ relationships for binary mixtures. This result indicates that the mixing rules used extending the equations of state to mixtures do not accurately describe the mixture behavior. Future critical state investigations should be concerned with improving the mixing rules of existing equations of state or be limited to new or improved equations of state which combine the elements of simplicity and accuracy in pure component critical property predictions.

The third objective, to determine the need and methods for optimizing the binary interaction parameters of the mixing rules of the equations of state, was achieved for the binary systems used in the critical state calculations. The best representations of the critical properties were obtained by adjusting the value of the binary interaction parameters in the mixing rules of the constants a and $A_o$ of the Redlich-Kwong and B-W-R equations, respectively. The optimum value of the interaction parameter is characterized by a minimum in the sum of the squared deviations of the calculated from the experimental critical pressure-mole fraction relationship. Use of the optimum binary interaction parameters in the mixing rules of the Redlich-Kwong and B-W-R equations significantly reduced the average error levels in the predicted critical properties of binary mixtures. An analysis of the results using both equations of state showed that the difference in the value of the unoptimized and optimized binary interaction parameters increased as the difference between the molecular species of the pure components in the mixture increased.

The fourth objective, to investigate the use of the optimized binary interaction parameters in ternary mixture critical state calculations and in vapor-liquid equilibrium calculations in the retrograde region was suggested by the significant improvements obtained in the prediction of the critical properties of binary mixtures. Four binary systems were investigated with and without adjustment of the binary interaction parameters of the B-W-R equation of state. Only slight improvements in the accuracy of the liquid phase branch of the equilibium boundary were obtained using the optimum values of the binary interaction parameters. Thus, the values of the eight coefficients of the B-W-R equation and the range for which these coefficients are accurate are of much greater importance than the use of any optimized binary interaction parameters in VLE calculations.

The equation of state approach to the prediction of the critical states of mixtures offers several advantages over the empirical and semi-empirical correlation methods in use today. The general level of accuracy in the critical state predictions carried out in this investigation proved to be comparable to the best empirical correlations. However, the equation of state approach is not restricted to any particular class of mixture or equation of state. In addition, predictions of the critical pressure, volume, and composition at a specified critical temperature are obtained simultaneously rather than through separate correlations. Thus, the equation of state approach is more flexible in use and in possible modifications than are the strictly empirical correlations in use today. The major limitation of the equation of state approach is that derivations of the critical state relations in terms of an equation of state are lengthy even for ternary mixtures and the complexity of these equations increases very rapidly with the addition of each new component to the mixture. As a result, the equation of state approach in predicting critical states of mixtures ultimately appears to be limited to quaternary or, perhaps, quinary mixtures.

## LIST OF NOMENCLATURE

$A$ - Helmholtz free energy per mole

$A_o$ - Coefficient of the B-W-R equation of state

$a$ - Coefficient of either the R-K or B-W-R equation of state

$B_o$ - Coefficient of the B-W-R equation of state

$b$ - Coefficient of the B-W-R equation of state

$C_o$ - Coefficient of the B-W-R equation of state

$c$ - Coefficient of the B-W-R equation of state

$G$ - Gibbs free energy per mole

$M$ - Second critical state determinate for ternary mixtures

$N$ - Total number of components in a mixture

$n$ - Number of moles of a component

$P$ - Pressure

$R$ - Universal gas content

$T$ - Temperature

$U$ - First critical state determinate for ternary mixtures

$u$ - Chemical potential partial differential quantity

$V$ - Volume per mole

$x$ - Mole fraction of a component

### Greek Symbols

$\alpha$ - Coefficient of the B-W-R equation of state

$\eta$ - Binary interaction parameter of the B-W-R equation

$\gamma$ - Coefficient of the B-W-R equation of state

$\phi$ - Binary interaction parameter of the R-K equation of state

$\phi_1$ - Fugacity coefficient of component 1

$\theta$ - Binary interaction parameter of the R-K equation of state

$\rho$ - Density per mole

$\mu$ - Chemical potential

## Subscripts

c - Critical property

g - Vapor phase property

i - Component i property

j - Component j property

ij - i-j molecular interaction property

l - Liquid phase property

m - Mixture property

## Equation of State Abbreviations

| | |
|---|---|
| R-K | Redlich-Kwong equation of state |
| B-W-R | Benedict-Webb-Rubin equation of state |

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# APPENDIX A

## CRITCALC Computer Program

## CRITCALC Computer Program

The computer program developed for the prediction of the critical states of binary mixtures is designated by the name CRITCALC and was written in FORTRAN IV for use on the Oklahoma State University Computing Center's IBM 7040 digital computer. The CRITCALC program was written in modular form with each of the seven modules containing a basic sub-calculation. Figure 103 is a block diagram showing the inter-relationship between the modules. A description of the function of each of the seven modules is presented in the following sections.

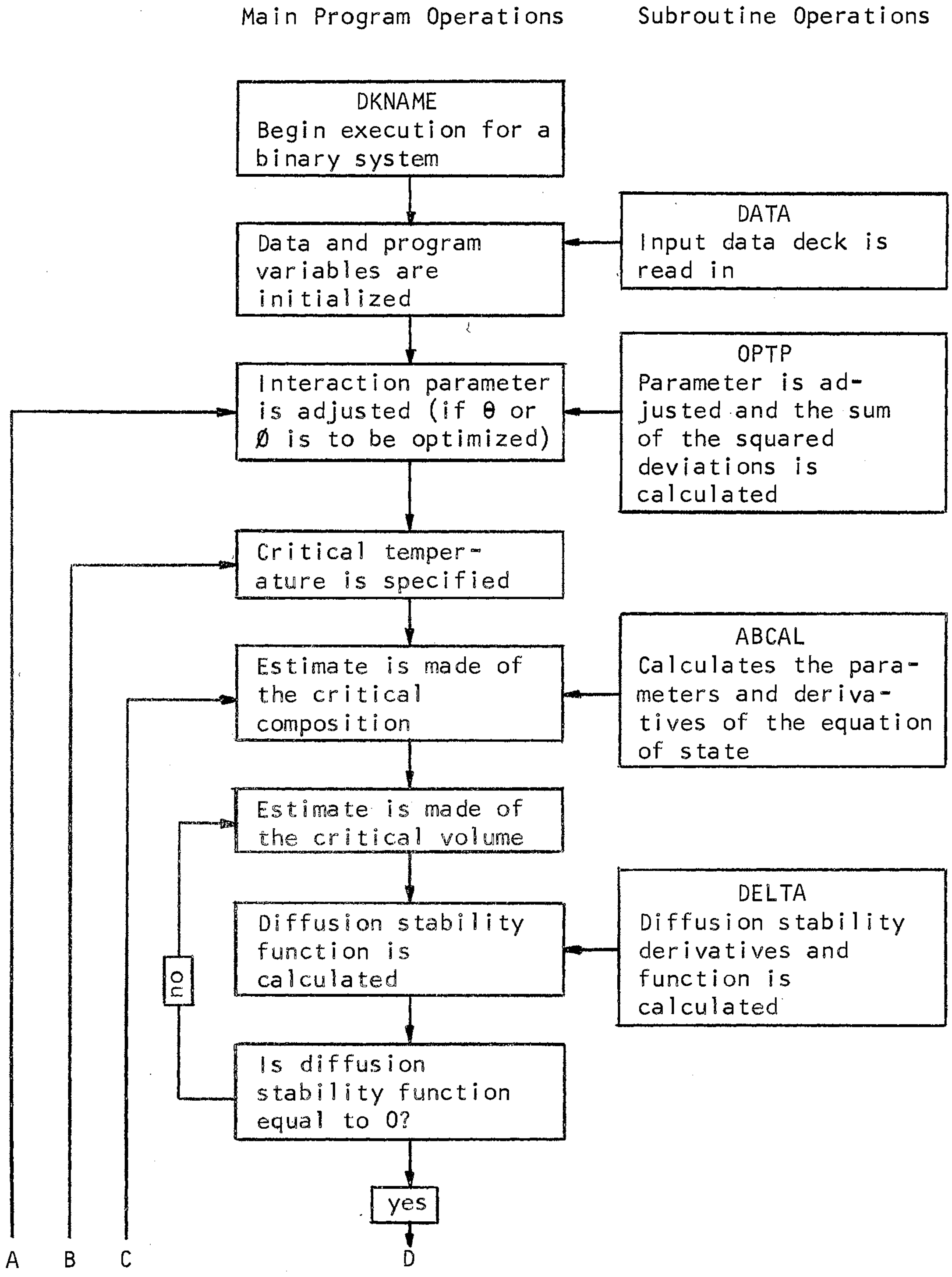
### Main Program

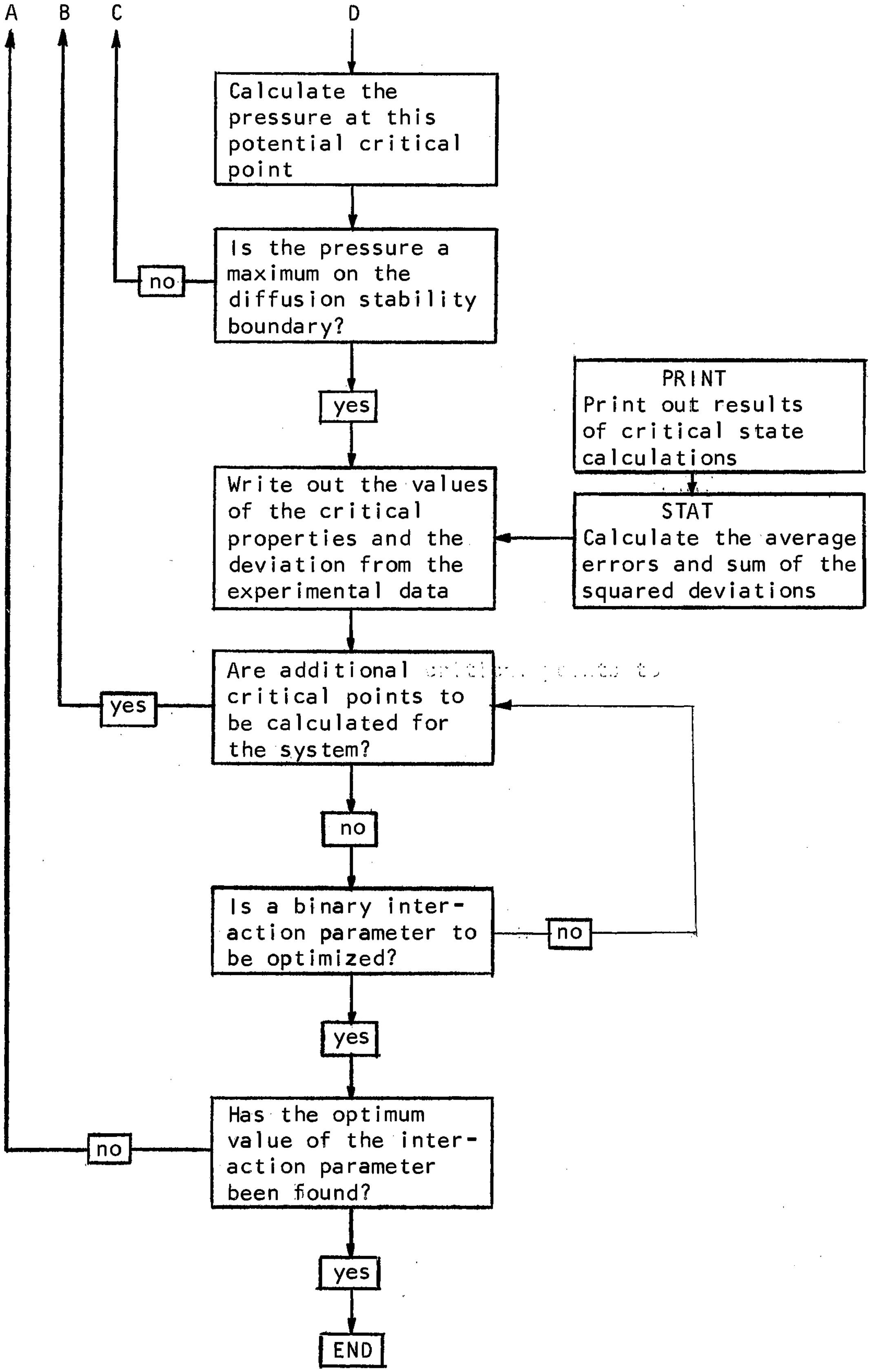
DKNAME is the executive program for the entire calculation. This module contains the search procedure used to determine the critical state of binary mixtures and is essentially independent of the equation of state chosen to evaluate the diffusion stability equation. The data input and output subroutines and the major calculational subroutines are called by this executive program at the appropriate time during the search procedure.

### Subroutine DATA

DATA is the data input subroutine. All input data required for the calculations are read in by this subroutine. DATA is called by the executive program DKNAME at the beginning of the calculations for each binary system.

Figure 103 CRITCALC Block Diagram




A
B
C
D
Calculate the pressure at this potential critical point
Is the pressure a maximum on the diffusion stability boundary?
no
yes
PRINT
Print out results of critical state calculations
STAT
Calculate the average errors and sum of the squared deviations
Write out the values of the critical properties and the deviation from the experimental data
Are additional critical points to be calculated for the system?
yes
no
Is a binary interaction parameter to be optimized?
no
yes
Has the optimum value of the interaction parameter been found?
no
yes
END

## Subroutine ABCAL

ABCAL is the subroutine that calculates the constants and derivatives of the constants of the equation of state with respect to the mole fraction of component 2 using the mixing rules of the equation of state. In this program, either the Redlich-Kwong or the B-W-R equation of state can be selected. ABCAL is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine DELTA

DELTA is the subroutine that calculates the diffusion stability boundary equation for a binary mixture evaluated in terms of an equation of state. In this program, either the Redlich-Kwong or the B-W-R equations of state can be selected to evaluate the diffusion stability boundary equation. DELTA is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine OPTP

OPTP is the subroutine that calculates the optimum values of the binary interaction parameters of the equation of state. In this program, either the Redlich-Kwong or the B-W-R equation of state can be selected. OPTP is called by the executive program DKNAME only if the optimization of the binary interaction parameters is to be carried out. Otherwise this subroutine is not required during the execution of the program.

### Subroutine PRINT

PRINT is the subroutine that prints out all the results of the critical state calculations and appropriate error or warning messages generated during the execution of the search procedure. PRINT is called by the executive program DKNAME after each critical state calculation at a specified critical temperature.

### Subroutine STAT

STAT is the subroutine that calculates the deviation of the calculated critical properties from the experimental values if experimental data is available. STAT is called by the executive program DKNAME after each set of critical state calculations for a given binary system.

### Program Specifications

A complete listing of the CRITCALC computer program is presented at the end of Appendix A. The input data requirements and format are discussed in the following sections. Each type of format is discussed in detail in any IBM Fortran Manual.

#### Input Data Cards

The input data cards required for the CRITCALC program are arranged in the following order:

CARD 1 "Problem Identification"

This card is used for the alphameric identification of the calculation set for a given binary system. Any short identifying remarks may be used.

READ: AB(18)
FORMAT: 18A4

### CARD 2 "Program Control Variables"

This card contains the five general control variables which control the operation of the program. Each variable and its allowable values are discussed below.

NEQN "Equation of State Variable"

NEQN = 1 The Redlich-Kwong equation of state is used.
NEQN = 2 The B-W-R equation of state is used.

NT "Critical State Calculation Variable"

NT = the number of critical points to be calculated for the given binary system.

NAD "Binary Interaction Parameter Optimization Variable"

NAD = 0 No optimization of the interaction parameters is to be carried out.
NAD = 1 Optimization of interaction parameter #1 is to be carried out. (Parameter #1 equals $\theta$ associated with the constant a in the R-K equation and $\eta_1$ associated with the constant $A_o$ in the B-W-R equation.)
NAD = 2 Optimization of interaction parameter #2 is to be carried out. (Parameter #2 equals $\phi$ associated with the constant b in the R-K equation and $\eta_2$ associated with the constant $B_o$ in the B-W-R equation.)
NAD = 3 Optimization of interaction parameter #3 is to be carried out. (Parameter #3 equals $\eta_3$ associated with the constant $C_o$ in the B-W-R equation.)
NAD = 4 Optimization of interaction parameter #4 is to be carried out. (Parameter #4 equals $\eta_4$ associated with the constant $\gamma$ in the B-W-R equation.)

NDEV "Statistical Control Variable"

NDEV = 0 No deviations in the calculated critical properties are to be calculated.
NDEV = 2 The deviations in the calculated critical pressure from the experimental values are to be calculated.

NDEV = 3 The deviations in the calculated critical pressure and mole fractions of the second component of the mixture are to be calculated.

NDEV = 4 The deviations in the calculated critical pressure, mole fractions, and volumes are to be calculated.

ERZ "Output Control Variable"

ERZ = 0.0 The final results of the critical state calculations are to be printed out.

ERZ = 1.0 The final results of the critical state calculations and the intermediate results of the binary interaction parameter optimization are to be carried out.

ERZ = 2.0 The final results and all intermediate calculation results during the search procedure are to be carried out.

```
READ:      NEQN, NT, NAD, NDEV, ERZ
FORMAT:    I2, I2, I2, I2, F10.3
```

**CARDS 3, 4** "Component Identification"

These two cards are used for the alphameric identification of the two components of the binary mixture. The component with the highest pure component critical temperature must be listed on the first of the two cards.

```
READ:      AB(18)
FORMAT:    18A4
```

**CARDS 5, 6** "Pure Component Critical Properties"

These two cards contain the critical temperature, pressure, and volume for each of the pure components of the mixture. The component with the highest critical temperature is always listed on the first of the two cards.

```
READ:      TC(i), PC(i), VC(i)
FORMAT:    F10.3, F10.3, F10.3
```

**CARDS 7-series** "Equation of State Parameters"

The number of cards and the information contained on each card depends on whether the Redlich-Kwong (NEQN = 1) or the B-W-R (NEQN = 2) equation of state is used.

NEQN = 1 Redlich-Kwong equation of state

**CARD 7** "Binary Interaction Parameters"

This card contains the two binary interaction parameter values associated with the constants $a_{12}$ and $b_{12}$ of the Redlich-Kwong equation, respectively.

READ: THETA(1), THETA(2)
FORMAT: F10.3, F10.3

NEQN = 2 B-W-R equation of state

**CARD 7a** "B-W-R Coefficients for Component 1"

This card contains the values of the four B-W-R coefficients $A_o$, $B_o$, $C_o$, and $\gamma$ for the first component.

READ: XX1(1), XX1(2), XX1(3), XX1(4)
FORMAT: E12.6, E12.6, E12.6, E12.6

**CARD 7b** "B-W-R Coefficients for Component 1"

This card contains the values of the four B-W-R coefficients a, b, c, and $\alpha$ for the first component.

READ: ZZ1(1), ZZ1(2), ZZ1(3), ZZ1(4)
FORMAT: E12.6, E12.6, E12.6, E12.6

**CARD 7c** "B-W-R Coefficients for Component 2"

This card contains the values of the four B-W-R coefficients $A_o$, $B_o$, $C_o$, and $\gamma$ for the second component.

READ: XX2(1), XX2(2), XX2(3), XX2(4)
FORMAT: E12.6, E12.6, E12.6, E12.6

**CARD 7d** "B-W-R Coefficients for Component 2"

This card contains the values of the four B-W-R coefficients a, b, c, and $\alpha$ for the second component.

READ: ZZ2(1), ZZ2(2), ZZ2(3), ZZ2(4)
FORMAT: E12.6, E12.6, E12.6, E12.6

**CARD 7e** "Binary Interaction Parameters"

This card contains the values of the binary interaction parameters associated with $A_{o_{12}}$, $B_{o_{12}}$, $C_{o_{12}}$, and $\gamma_{12}$ of the B-W-R equation of state.

READ: THETA(1), THETA(2), THETA(3), THETA(4)
FORMAT: F10.3, F10.3, F10.3, F10.3

**CARD 7f** "Ternary Interaction Parameters"

This card contains the values of the ternary interaction parameters associated with $a_{112}$, $b_{112}$, $c_{112}$, and $\alpha_{112}$ of the B-W-R equation of state.

READ: PHI(1), PHI(2), PHI(3), PHI(4)
FORMAT: F10.3, F10.3, F10.3, F10.3

**CARD 7g** "Ternary Interaction Parameters"

This card contains the values of the ternary interaction parameters associated with $a_{122}$, $b_{122}$, $c_{122}$, and $\alpha_{122}$ of the B-W-R equation of state.

READ: RHO(1), RHO(2), RHO(3), RHO(4)
FORMAT: F10.3, F10.3, F10.3, F10.3

**CARD 8** "Binary Mixture Critical Temperature Specification"

This card contains the NT (a positive integer) binary mixture critical temperatures that are specified in order to calculate the critical state.

READ: TT(i) where i = 1, 2, . . . NT
FORMAT: iF12.6

CARD 9 "Critical Pressure Correlation Parameters"

This card contains the five parameters used in the Sutton critical pressure correlation if experimental data has been analyzed. The parameters are:

| | |
|---|---|
| BPC1 | Critical pressure (bars) of component 1 |
| BPC2 | Critical pressure (bars) of component 2 |
| CA | Correlation parameter #1 |
| CB | Correlation parameter #2 |
| CC | Correlation parameter #3 |

The correlation is of the form:

$$PC = BPC1\ x_1^2 + BPC2\ x_2^2 + x_1 x_2 / \left[ CA + CB(x_1 - x_2) + CC(x_1 - x_2)^2 \right]$$

where

$x_i$ = mole fraction of component i

READ: BPC1, BPC2, CA, CB, CC
FORMAT: F10.3, F10.3, E10.4, E10.4, E10.4

## Program Output

Three types of output can be obtained from the CRITCALC program: final critical state results, intermediate calculation results, and error messages. Each type of output is discussed below.

### Final Results

The final results of the critical state calculations at specified critical temperatures are printed out by subroutine PRINT. The results for a typical calculation are shown in Figure 104.

### Intermediate Calculation Results

If ERZ = 2.0 in card 2 of the input data deck, then the intermediate results calculated during the course of the search procedure are printed out as well as the final results. This intermediate calculation feature of the program allows the search procedure to be followed in detail in case the calculation does not converge correctly. If the critical state calculation does not converge correctly, an error condition is encountered and the program automatically sets ERZ = 2.0 and prints out the intermediate results up to the error condition.

## Error Messages

When an error condition is encountered during the search procedure an appropriate error message is printed out indicating the area in which the search procedure failed to converge. In addition, a "caution" message is also printed out if the search procedure has converged to a point on the upper branch of the diffusion stability boundary. This condition would indicate an azeotropic mixture and the calculated critical point may be in error.

## Program Execution

Execution of the CRITCALC program was carried out on an IBM 7040 computer. The program proved to be extremely reliable and rarely failed to converge to the critical point for any of the systems investigated. The average execution time for a binary system for which five critical points were calculated was 70 seconds.

Figure 104 CRITCALC Calculation Results

```
CRITCALC     R-K EQN OF STATE     C3/BENZENE SYSTEM     (SUTTON OPT)

     COMPONENTS
        1   BENZENE
        2   PROPANE

                    PURE COMPONENT CRITICAL PROPERTIES

VARIABLE                      COMPONENT 1                    COMPONENT 2
TEMPERATURE                     1012.700                       665.680
PRESSURE                         714.000                       616.300
VOLUME                             4.217                         3.219

CRITICAL PROPERTY CALCULATION RESULTS WITH THE R-K EQUATION OF STATE


     MOLE FRACTIONS          Y(1) = 0.0219

               CRITICAL TEMPERATURE     679.600   DEG R
               CRITICAL PRESSURE        646.556   PSIA
               CRITICAL VOLUME            3.786   FT3/MOL

                  INTERACTION PARAMETERS

                     THETA   =   1.0000
                     PHI     =   1.0000


     DEVIATIONS FROM EXPERIMENTAL DATA

                  ABSOLUTE DEVIATION   PERCENTAGE  DEVIATION

       TEMPERATURE      0.000  DEG R     TEMPERATURE       0.00   PER CENT
       PRESSURE         9.252  PSIA      PRESSURE          1.45   PER CENT
```

```
$IBFTC DKNAME  DECK
C     CRITICAL STATE CALCULATIONS FOR BINARY MIXTURES USING THE
C        REDLICH-KWONG OR BENEDICT-WEBB-RUBIN EQUATIONS OF STATE
C
C             SEARCH FOR CRITICAL POINT AT A GIVEN CRITICAL TEMPERATURE
C
C        AUTHOR         ROBERT R SPEAR
C                       OKLAHOMA STATE UNIVERSITY
C                       AUGUST, 1968
C
C     SUBROUTINE OF THE MAIN PROGRAM
C        DATA      SUBROUTINE TO READ IN ALL INPUT DATA
C        OPTP      SUBROUTINE TO OPTIMIZE THE BINARY INTERACTION PARAMETERS
C        ABCAL     SUBROUTINE TO CALCULATE THE DERIVATIVES OF THE EQUATION OF
C                       STATE PARAMETERS
C        DELTA     SUBROUTINE TO CALCULATE THE CRITICAL STATE RELATIONS
C        PRINT     SUBROUTINE TO PRINT OUT THE CALCULATION RESULTS
C        STAT      SUBROUTINE TO CALCULATE THE DEVIATIONS OF THE CALCULATED
C                       FROM THE EXPERIMENTAL CRITICAL PROPERTIES
C
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     22(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     33),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
  200 FORMAT (26H1INTERMEDIATE CALCULATIONS,///)
  201 FORMAT (4H T =,F10.4,6H DEG R,//)
  202 FORMAT (/,5H NY =,I3,5X,7H Y(2) =,F8.5,/)
  203 FORMAT (10X,I3,7X,4H V =,F9.5,10X,8H DEL1 = ,E12.5)
  204 FORMAT (//,7X,26H VOLUME CONVERGENCE BEGINS,/)
  205 FORMAT (13X,I3,5X,4H V =,F9.5,5X,8H DEL1 = ,E12.5)
  206 FORMAT (//,25X,9H SOLUTION,5X,4H V =,F9.5,5X,4H P =,F10.3,/)
  207 FORMAT (/,8X,19H EXTREME Y(2) RANGE,/)
  208 FORMAT (12X,4H V =,F9.5,7X,8H DEL1 = ,E12.5)
  209 FORMAT (/,8X,7H Y(2) =,F9.5,21H IS GREATER THAN Y(C),/)
C
C
C     PRINCPAL VARIABLES OF THE MAIN PROGRAM
C        T         TEMPERATURE  (DEG R)
C        P         PRESSURE   (PSIA)
C        V         VOLUME   (FT3/IB-MOL)
C        R         UNIVERSAL GAS CONSTANT    (R = 10.7335)
C        Y(I)      MOLE FRACTION OF THE I-TH COMPONENT
C        TC(K)     CRITICAL TEMPERATURE OF PURE COMPONENT K
C        PC(K)     CRITICAL PRESSURE OF PURE COMPONENT K
C        VC(K)     CRITICAL VOLUME OF PURE COMPONENT K
C        VU        UPPER VOLUME LIMIT IN SEARCH FOR STABILITY BOUNDARY
C        VL        LOWER VOLUME LIMIT IN SEARCH FOR STABILITY BOUNDARY
C        DELV      VOLUME INCREMENT USED IN SEARCH PROCEDURE
C        DEL1      VALUE OF STABILITY EQUATION
C                       DEL1 = 0.0   ON THE STABILITY BOUNDARY
C        FLAG      ERROR MESSAGE VARIABLE
C        ERZ       INTERMEDIATE CALCULATION PRINT OUT VARIABLE
C                       ERZ = 0.0    NO INTERMEDIATE PRINT OUT
C                       ERZ = 1.0    PARTIAL PRINT OUT DURING OPTIMIZATION
C                       ERZ = 2.0    FULL INTERMEDIATE CALCULATION PRINT OUT
C
C
      NO=6
```

```
   65 CALL DATA
      LOX=0
      ERR=0.0
      WRT=ERZ
      VLOWZ=VLOW
      IF (NAD.EQ.0) GO TO 5
      NEND=0
      CALL OPTP
C
C     TEMPERATURE ITERATION BEGINS
C
    5 DO 99 K=1,NT
      YSIGN=0.0
      NLOOP=0
   57 T=TT(K)
      MSIGN=0
      RT=R*T
      ERZ=WRT
      FLAG=0.0
   10 NVL=0
      VLOW=VLOWZ
      YHIGH=1.0
      IF (ERZ.EQ.2.0) GO TO 40
C
C     INITIAL ESTIMATE OF Y(2) AT THE CRITICAL POINT
C
   41 NY=0
    7 NLOOP=NLOOP+1
      IF (NLOOP.EQ.75) GO TO 72
      PPC=0.0
      MLOOP=0
      YU=1.0
      IF (NVL.GT.0) GO TO 8
      YLOW=(T-TC(1))/(TC(2)-TC(1))
      IF (ABS(YLOW).GT.1.0) GO TO 80
      YLOWZ=YLOW+0.5*(1.0-YLOW)*YLOW
      IF (YLOWZ.GE.1.0) GO TO 15
      YLOW=YLOWZ
   15 YL=YLOW
      IF (YSIGN.GT.0.0) GO TO 62
    8 Y(2)=YL
      GO TO 33
   62 YLOWZ=YLOW-DELY*3.0*YSIGN
      IF (YLOWZ.LE.0.0) GO TO 63
      YLOW=YLOWZ
      YL=YLOW
      GO TO 8
   63 YLOW=YLOW/2.0
      GO TO 8
   80 IF (TC(1).GT.TC(2)) GO TO 81
      I=1
      J=2
      GO TO 82
   81 I=2
      J=1
   82 TCL=TC(I)
      TCH=TC(J)
      IF (T.LT.TCL) GO TO 83
      GO TO 85
   83 IF (I.EQ.2) GO TO 84
   86 YLOW=0.075
      GO TO 15
   84 YLOW=0.925
```

```
      GO TO 15
   85 IF (I.EQ.2) GO TO 86
      GO TO 84
C
C     MOLE FRACTION INTERATION BEGINS
C
   33 NY=NY+1
      IF (NY.GT.50) GO TO 72
      Y(1)=1.0-Y(2)
      IF (Y(1).GT.1.0) GO TO 73
      IF (Y(1).LT.0.0) GO TO 74
      IF (ERZ.EQ.2.0) GO TO 42
   43 CALL ABCAL
C
C     INITIAL ESTIMATE OF VOLUME AT THE CRITICAL POINT
C
      IF (NY.EQ.1) GO TO 34
      IF (NVL.GT.0) GO TO 34
      VLOW=V-DELV
   34 V=VLOW
   21 LOOP=0
C
C     VOLUME ITERATION BEGINS
C
   23 LOOP=LOOP+1
      IF (LOOP.GT.50) GO TO 70
      IF (V.GT.VHIGH) GO TO 14
      CALL DELTA
      IF (ERZ.EQ.2.0) GO TO 44
   45 IF (LOOP.GT.1) GO TO 24
      IF (DEL1.LT.0.0) GO TO 20
      VLOW=VLOW-1.5*DELV
      IF (VLOW.LT.0.0) GO TO 16
      GO TO 34
   16 NVL=NVL+1
      IF (NVL.EQ.15) GO TO 70
      VLOW=VLOWZ
      IF (YU.LT.1.0) GO TO 2
      YZ=YLOW
      YLOW=YLOW+0.20
      YL=YLOW
      GO TO 7
    2 YL=Y(2)
      YLOW=YL
      YZ=YLOW
      GO TO 3
   20 VL=V
      DL=DEL1
      V=V+DELV
      GO TO 23
C
C     VOLUME SEARCH BEGINS (NEWTONS METHOD)
C
   24 IF (ABS(DEL1).LT.0.01) GO TO 22
      IF (DEL1.GT.0.0) GO TO 25
      SLOPE=(DEL1-DL)/(V-VL)
      VV=V-DEL1/SLOPE
      IF (VV.LT.V) GO TO 35
      VL=V
      DL=DEL1
      IF ((VV-V).GT.(2.0*DELV)) GO TO 26
      IF ((VV-V).LT.0.00001) GO TO 31
      V=VV
```

```
      GO TO 23
   31 V=V+0.00002
      GO TO 23
   26 V=V+2.0*DELV
      GO TO 23
C
C     VOLUME CONVERGENCE BEGINS (INTERVAL HALVING METHOD)
C
   25 IF (ERZ.EQ.2.0) GO TO 46
   47 VU=V
      DU=DEL1
      KLOOP=0
   27 KLOOP=KLOOP+1
      IF (KLOOP.GT.50) GO TO 70
      V=(VU+VL)/2.0
      CALL DELTA
      IF (ERZ.EQ.2.0) GO TO 48
   49 IF (ABS(DEL1).LT.0.01) GO TO 22
      IF ((VU-VL).LE.0.00001) GO TO 22
      IF (DEL1.GT.0.0) GO TO 28
      VL=V
      GO TO 27
   28 VU=V
      GO TO 27
C
C     PRESSURE DETERMINATION AT THE VOLUME WHERE D = 0
C
   22 NVL=0
      IF (NEQN.EQ.2) GO TO 29
      P=RT/(V-X(2))-X(1)/(V*(V+X(2)))
      GO TO 30
   29 V2=V*V
      V3=V2*V
      V4=V2*V2
      T2=T*T
      CEXPON=Z(3)/EXP(X(4)/V2)
      P=RT/V*(1.0+X(2)/V+Z(2)/V2)-1.0/V2*(X(1)+Z(1)/V-Z(1)*Z(4)/V4+X(3)/
     1T2)+CEXPON/(T2*V3)*(1.0+X(4)/V2)
C
C     CHECK ON THE PRESSURE AS POSSIBLE CRITICAL POINT
C
   30 IF (ERZ.EQ.2.0) GO TO 50
   51 IF (P.LT.0.0) GO TO 13
      IF (MSIGN.EQ.1) GO TO 66
      IF (MSIGN.EQ.3) GO TO 78
      IF (MSIGN.EQ.4) GO TO 79
      IF (P.LT.PPC) GO TO 36
   13 IF (NY.EQ.1) GO TO 69
      IF (YHIGH.EQ.1.0) GO TO 59
      IF (YU.EQ.YHIGH) GO TO 79
      GO TO 59
   69 FIRSTP=P
   59 PPC=P
      PVC=V
      PY=Y(2)
      YLP=YL
      YL=Y(2)
      NVL=0
      IF (MSIGN.EQ.2) GO TO 68
      IF (YU.LT.1.0) GO TO 17
      YZ=Y(2)+DELY
      IF (YZ.LT.1.0) GO TO 9
      Y(2)=(1.0+Y(2))/2.0
```

```
      GO TO 39
   17 Y(2)=(YU+YL)/2.0
      GO TO 39
   79 MSIGN=3
      PPP=P
      PPV=V
      PPX=Y(2)
      YLP=Y(2)
      YUP=Y(2)
      Y(2)=Y(2)-0.001
      GO TO 33
   78 IF (P.GT.PPP) GO TO 77
      YL=YLP
      GO TO 1
   77 YU=YUP
    1 PPC=PPP
      PVC=PPV
      PY=PPX
      MSIGN=4
      GO TO 17
   66 IF (P.GT.PPC) GO TO 64
      MSIGN=0
      YL=PY
      YU=YUP
      GO TO 17
   64 YU=YL
      YUP=YU
      YL=YLP
      Y(2)=(YU+YL)/2.0
      V=PVC-DELV
      MSIGN=2
      MLOOP=MLOOP+1
      GO TO 39
   68 MSIGN=1
      YUP=YU
      Y(2)=YL-0.001
      V=PVC-DELV
      GO TO 33
C
C     CHECK ON POSSIBLE Y(2) GREATER THAN Y(2) AT THE CRITICAL POINT
C
   35 IF (ERZ.EQ.2.0) GO TO 52
   53 VU=V
      DU=DEL1
      MLOP=0
   38 MLOP=MLOP+1
      IF (MLOP.EQ.25) GO TO 11
      V=(VU+VL)/2.0
      IF ((VU-VL).LE.0.0001) GO TO 11
      IF (ERZ.EQ.2.0) GO TO 54
   55 CALL DELTA
      IF (DEL1.GT.0.0) GO TO 25
      SV=V
      SD=DEL1
      V=V+0.0001
      CALL DELTA
      IF (DEL1.LT.SD) GO TO 37
      VL=V
      DL=DEL1
      GO TO 38
   37 VU=V
      DU=DEL1
      GO TO 38
```

```
   11 YHIGH=Y(2)
      MLOOP=MLOOP+1
C
C     Y(2) ADJUSTMENT  -  Y(2) FOUND TO BE GREATER THAN AT THE CRITICAL POINT
C
   18 IF (ERZ.EQ.2.0) GO TO 56
   36 MLOOP=MLOOP+1
      IF (MLOOP.GT.50) GO TO 72
      IF (MLOOP.GT.1) GO TO 14
      IF (NY.EQ.1) GO TO 14
      IF (NVL.NE.0) GO TO 14
      MSIGN=1
      YU=Y(2)
      YUP=YU
      Y(2)=YL-0.001
      V=PVC-DELV
      GO TO 33
   14 IF (MSIGN.EQ.2) GO TO 67
      YU=Y(2)
      IF (NY.EQ.1) GO TO 19
      IF (NVL.EQ.0) GO TO 3
      YL=YZ
      V=VLOWZ
    3 Y(2)=(YU+YL)/2.0
      IF (NVL.GT.0) GO TO 39
    6 YL=PY
      Y(2)=(YU+YL)/2.0
      V=PVC
      GO TO 39
   67 YL=Y(2)
      GO TO 17
   19 YLOW=YLOW-DELY*2.5
      YL=YLOW
      Y(2)=YL
      NY=0
      GO TO 33
C
C     CHECK ON CONVERGENCE OF Y(2)
C
    9 Y(2)=YZ
   39 IF ((YU-YL).LT.0.0005) GO TO 12
      GO TO 33
C
C       CHECK ON POSSIBLE SOLUTION ON UPPER BRANCH OF THE V - Y(2) CURVE
C
   12 IF ((YHIGH-PY).GT.0.0001) GO TO 60
      IF (PPC.EQ.0.0) GO TO 75
      FLAG=8.0
      GO TO 61
C
C     INTERMEDIATE CALCULATION OUTPUT
C
   40 WRITE (NO,200)
      WRITE (NO,201) T
      GO TO 41
   42 WRITE (NO,202) NY,Y(2)
      GO TO 43
   44 WRITE (NO,203) LOOP,V,DEL1
      GO TO 45
   46 WRITE (NO,204)
      GO TO 47
   48 WRITE (NO,205) KLOOP,V,DEL1
      GO TO 49
```

```
   50 WRITE (NO,206) V,P
      GO TO 51
   52 WRITE (NO,207)
      GO TO 53
   54 WRITE (NO,208) V,DEL1
      GO TO 55
   56 WRITE (NO,209) Y(2)
      GO TO 36
C
C     ERROR MESSAGES
C
   70 FLAG=1.0
      GO TO 90
   72 FLAG=3.0
      GO TO 90
   73 FLAG=4.0
      GO TO 90
   74 FLAG=5.0
      GO TO 90
   75 FLAG=7.0
   90 ERR=1.0
      IF (ERZ.EQ.2.0) GO TO 61
      ERZ=2.0
      WRITE (NO,200)
      WRITE (NO,201) T
      GO TO 10
C
C     CRITICAL POINT SOLUTION AT THE SPECIFIED TEMPERATURE
C
   60 IF (ABS(PPC-FIRSTP).LT.0.0001) GO TO 58
      P=PPC
      V=PVC
      Y(2)=PY
      Y(1)=1.0-Y(2)
      IF (P.NE.0.0) GO TO 61
      GO TO 75
   58 YSIGN=YSIGN+1.0
      GO TO 57
   61 CALL PRINT
   99 CONTINUE
C
C     END OF TEMPERATURE ITERATION
C
      IF (NDEV.EQ.0) GO TO 65
      IF (ERR.EQ.1.0) GO TO 65
      CALL STAT
      IF (NAD.EQ.0) GO TO 65
      IF (NEND.EQ.1) GO TO 65
      CALL OPTP
      IF (FLAG.EQ.6.0) GO TO 4
      IF (FLAG.NE.10.0) GO TO 5
      NEND=1
      FLAG=0.0
      GO TO 5
    4 CALL PRINT
      GO TO 65
      END
$IBFTC DATAZ   DECK
      SUBROUTINE DATA
C     SUBROUTINE TO READ IN ALL THE INPUT DATA
C
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
```

```
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
  100 FORMAT (18A4)
  101 FORMAT (5I2,F10.3)
  103 FORMAT (3F10.3)
  104 FORMAT (2F12.3)
  105 FORMAT (6F12.6)
  106 FORMAT (4E12.6)
  107 FORMAT (4F10.3)
  108 FORMAT (2F10.3,3E10.4)
  200 FORMAT (2H1 ,18A4)
  201 FORMAT (//,5X,11H COMPONENTS)
  202 FORMAT (8X,I2,2X,18A4)
  203 FORMAT (//,13X,35H PURE COMPONENT CRITICAL PROPERTIES)
  204 FORMAT (/,3X,9H VARIABLE,9X,12H COMPONENT 1,9X,12H COMPONENT 2)
  205 FORMAT (2X,12H TEMPERATURE, 9X,F8.3,13X,F8.3)
  206 FORMAT (4X,7H VOLUME,12X,F8.3,13X,F8.3)
  207 FORMAT (3X,9H PRESSURE,11X,F8.3,13X,F8.3)
  208 FORMAT (2H1 ,//,20X,34H B-W-R EQUATION OF STATE CONSTANTS,///)
  209 FORMAT (25X,18H GROUP I CONSTANTS,//)
  210 FORMAT (10H COMPONENT,9X,3H A0,14X,3H B0,14X,3H C0,12X,6H GAMMA,//
     1)
  211 FORMAT (4X,2H 1,9X,E12.6,5X,E12.6,5X,E12.6,5X,E12.6,/)
  212 FORMAT (4X,2H 2,9X,E12.6,5X,E12.6,5X,E12.6,5X,E12.6,/)
  213 FORMAT (//,25X,19H GROUP II CONSTANTS,//)
  214 FORMAT (10H COMPONENT,9X,3H A ,14X,3H B ,14X,3H C ,12X,6H ALPHA,//
     1)
  215 FORMAT (///,5X,18H CALCULATION UNITS,//)
  217 FORMAT (10X,9H P = PSIA)
  216 FORMAT (10X,10H T = DEG R)
  218 FORMAT (10X,15H V = FT3/IB-MOL)
  219 FORMAT (10X,4H R =,F8.4,23H  PSIA*FT3/DEG R*IB-MOL)
  220 FORMAT (///,25X,23H INTERACTION PARAMETERS,//)
  221 FORMAT (12X,3H A0,7X,3H B0,7X,3H C0,5X,6H GAMMA,6X,2H A,8X,2H B,8X
     1,2H C,6X,6H ALPHA,/)
  222 FORMAT (6H THETA,4(5X,F5.3))
  223 FORMAT (6H PHI  ,40X,4(5X,F5.3))
  224 FORMAT (6H RHO  ,40X,4(5X,F5.3))
  225 FORMAT (2H1 ,//,20X,22H R-K EQUATION OF STATE)
  226 FORMAT (12X,2H A,7X,2H B,/)
C
C     PRINCIPAL VARIABLES OF THE PROGRAM
C        NAD       PROGRAM OPERATION CONTROL VARIABLE
C                       NAD = 0   NO OPTIMIZATION OF INTERACTION PARAMETERS
C                       NAD = K   OP IMIZATION OF INTERACTION PARAMETER K
C        NEQN      EQUATION OF STATE CONTROL VARIABLE
C                       NEQN = 1     REDLICH-KWONG EQUATION
C                       NEQN = 2     BENEDICT-WEBB-RUBIN EQUATION
C        NT        NUMBER OF CRITICAL POINTS TO BE CALCULATED
C        NDEV      ERROR AND STATISTICAL CALCULATION CONTROL VARIABLE
C                       NDEV = 0     NO ERROR CALCULATION
C                                    NO EXPTL CRITICAL PROPERTIES ARE REQUIRED
C                       NDEV = 2     ERROR CALCULATIONS ON CRITICAL PRESSURE
C                                    EXPTL PC MUST BE PROVIDED IN DATA
C                       NDEV = 3     ERROR CALCULATIONS ON PC AND VC
C                                    EXPTL PC AND VC MUST BE PROVIDED
C                       NDEV = 4     ERROR CALCULATIONS ON PC8 VC8 AND YC
C                                    EXPTL PC8 VC8 AND YC MUST BE PROVIDED
```

```
C         NOPTZ      CONTROL VARIABLE FOR EXPTL CRITICAL PRESSURE CURVE FIT
C                         NOPTZ = 1      REGULAR ORDER
C                         NOPTZ = 2      INVERSE ORDER
C         ERZ        INTERMEDIATE PRINT OUT CONTROL VARIABLE
C                    ERZ = 0.0   PRINT OUT OF CALCULATION RESULTS ONLY
C                    ERZ = 2.0   PRINT OUT OF INTERMEDIATE RESULTS
C
C      EQUATION OF STATE PARAMETERS
C         REDLICH-KWONG EQUATION
C           X(1)   = A (MIXTURE)
C           XX1(1)= A11
C           XX2(1)= A22
C           X(2)   = B (MIXTURE)
C           XX1(2)= B11
C           XX2(2)= B22
C
C         BENEDICT-WEBB-RUBIN EQUATION
C           X(1) =  A0 (MIXTURE)
C           X(2) =  B0 (MIXTURE)
C           X(3) =  C0 (MIXTURE)
C           X(4) =  GAMMA (MIXTURE)
C           Z(1) =  A   (MIXTURE)
C           Z(2) =  B   (MIXTURE)
C           Z(3) =  C   (MIXTURE)
C           Z(4) =  ALPHA  (MIXTURE)
C      BINARY INTERACTION PARAMETERS
C         REDLICH-KWONG EQUATION OF STATE
C         THETA(1)  PARAMETER A12
C         THETA(2)  PARAMETER B12
C
C         BENEDICT-WEBB-RUBIN EQUATION OF STATE
C          PRIMARY INTERACTION PARAMETERS
C           THETA(1)   PARAMETER A0-12
C           THETA(2)   NONE  --   PARAMETER B0-12 HAS THE LINEAR FORM
C           THETA(3)   PARAMETER C0-12
C           THETA(4)   PARAMETER GAMMA-12
C          SECONDARY INTERACTION PARAMETERS
C         PHI        (I,I,J) INTERACTION PARAMETERS
C         RHO        (I,J,J) INTERACTION PARAMETERS
C      SEARCH PROCEDURE VARIABLES
C         DELV       VOLUME INCREMENT USED IN SEARCH PROCEDURE
C         DELY       MOLE FRACTION INCREMENT USED IN SEARCH PROCEDURE
C
C
       IN=5
       NO=6
       NCP=2
       R=10.7335
       DELY=0.05
       DELV=0.25
C
C      PROGRAM IDENTIFICATION
       READ (IN,100) (AB(J),J=1,18)
       WRITE (NO,200) (AB(J),J=1,18)
C
C      PROGRAM CONTROL VARIABLES
       READ (IN,101) NEQN,NT,NAD,NDEV,NOPTZ,ERZ
       WRITE (NO,201)
C
C      COMPONENT IDENTIFICATION
       DO 99 I=1,2
       READ (IN,100) (AB(J),J=1,18)
    99 WRITE (NO,202) I,(AB(J),J=1,18)
```

```
      WRITE (NO,203)
      WRITE (NO,204)
C
C     PURE COMPONENT CRITICAL PROPERTIES
      DO 98 I=1,2
   98 READ (IN,103) TC(I),PC(I),VC(I)
      WRITE (NO,205) TC(1),TC(2)
      WRITE (NO,207) PC(1),PC(2)
      WRITE (NO,206) VC(1),VC(2)
      WRITE (NO,215)
      WRITE (NO,216)
      WRITE (NO,217)
      WRITE (NO,218)
      WRITE (NO,219) R
      IF (NEQN.EQ.1) GO TO 16
      NJ=4
      GO TO 15
   16 NJ=2
      GO TO 14
C
C     PURE COMPONENT PARAMETERS FOR THE B-W-R EQUATION OF STATE
   15 READ (IN,106) (XX1(J),J=1,NJ)
      READ (IN,106) (ZZ1(J),J=1,NJ)
      READ (IN,106) (XX2(J),J=1,NJ)
      READ (IN,106) (ZZ2(J),J=1,NJ)
C
C     BINARY INTERACTION PARAMETERS
   14 READ (IN,107) (THETA(J),J=1,NJ)
      IF (NEQN.EQ.1) GO TO 18
C
C     SECONDARY BINARY INTERACTION PARAMETERS FOR THE B-W-R EQUATION OF STATE
      READ (IN,107) (PHI(J),J=1,NJ)
      READ (IN,107) (RHO(J),J=1,NJ)
   17 WRITE (NO,208)
      WRITE (NO,209)
      WRITE (NO,210)
      WRITE (NO,211) (XX1(J),J=1,4)
      WRITE (NO,212) (XX2(J),J=1,4)
      WRITE (NO,213)
      WRITE (NO,214)
      WRITE (NO,211) (ZZ1(J),J=1,4)
      WRITE (NO,212) (ZZ2(J),J=1,4)
      GO TO 19
   18 WRITE (NO,225)
   19 WRITE (NO,220)
      IF (NEQN.EQ.1) GO TO 20
      WRITE (NO,221)
      GO TO 21
   20 WRITE (NO,226)
   21 WRITE (NO,222) (THETA(J),J=1,NJ)
      IF (NEQN.EQ.1) GO TO 22
      WRITE (NO,223) (PHI(J),J=1,NJ)
      WRITE (NO,224) (RHO(J),J=1,NJ)
C
C     SPECIFIED CRITICAL TEMPERATURES TO BE USED IN THE CALCULATIONS
   22 READ (IN,105) (TT(J),J=1,NT)
      DO 97 I=1,NT
   97 ETX(I)=TT(I)
      IF (NDEV.EQ.0) GO TO 30
C
C     CRITICAL PRESSURE CURVE FIT COEFFICENTS
C        NORMAL ORDER   COMPONENT WITH THE HIGHEST TC IS FIRST
C        INVERSE ORDER  COMPONENT WITH THE LOEST TC IS FIRST
```

```
      READ (IN,108) BPC1,BPC2,CA,CB,CC
   30 FACTH=2.00
      FACTL=0.25
   32 IF (VC(1).GT.VC(2)) GO TO 50
      I=2
      J=1
      GO TO 51
   50 I=1
      J=2
   51 VHIGH=VC(I)+FACTH*VC(I)
      VLOW=VC(J)-FACTL*VC(J)
      RETURN
      END
$IBFTC ABCALZ  DECK
      SUBROUTINE ABCAL
C     SUBROUTINE TO CALCULATE THE CONSTANTS FOR THE EQN OF STATE
C
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
  220 FORMAT (/,2X,16H B-W-R CONSTANTS)
  222 FORMAT (/,5X,8H GROUP I)
  226 FORMAT (/,5X,9H GROUP II)
  230 FORMAT (8X,5H A0 =,E12.5,3X,7H D1A0 =,E12.5,3X,7H D2A0 =,E12.5)
  231 FORMAT (8X,5H B0 =,E12.5,3X,7H D1B0 =,E12.5,3X,7H D2B0 =,E12.5)
  232 FORMAT (8X,5H C0 =,E12.5,3X,7H D1C0 =,E12.5,3X,7H D2C0 =,E12.5)
  233 FORMAT (8X,5H GM =,E12.5,3X,7H D1GM =,E12.5,3X,7H D2GM =,E12.5)
  234 FORMAT (8X,5H A  =,E12.5,3X,7H D1A  =,E12.5,3X,7H D2A  =,E12.5)
  235 FORMAT (8X,5H B  =,E12.5,3X,7H D1B  =,E12.5,3X,7H D2B  =,E12.5)
  236 FORMAT (8X,5H C  =,E12.5,3X,7H D1C  =,E12.5,3X,7H D2C  =,E12.5)
  237 FORMAT (8X,5H AL =,E12.5,3X,7H D1AL =,E12.5,3X,7H D2AL =,E12.5,/)
  240 FORMAT (/,2X,14H R-K CONSTANTS)
  241 FORMAT (5X,4H A =,E12.5,3X,6H D1A =,E12.5,3X,6H D2A =,E12.5)
  242 FORMAT (5X,4H B =,E12.5,3X,6H D1B =,E12.5,3X,6H D2B =,E12.5)
C
      NO=6
      Y1S=Y(1)*Y(1)
      Y2S=Y(2)*Y(2)
      IF (NEQN.EQ.1) GO TO 95
      EP=1.0/3.0
      Y2C=Y2S*Y(2)
      GO TO 96
C     REDLICH-KWONG EQATUION OF STATE
   95 TO5=T**0.5
      CON1=0.4278*R*R
      CON2=0.0865*R
      XX1(1)=CON1*TC(1)**2.5/(PC(1)*TO5)
      XX2(1)=CON1*TC(2)**2.5/(PC(2)*TO5)
      XX1(2)=CON2*TC(1)/PC(1)
      XX2(2)=CON2*TC(2)/PC(2)
   96 DO 99 I=1,NJ
      XX12=THETA(I)*SQRT(XX1(I)*XX2(I))
      QUAD=XX1(I)-2.0*XX12+XX2(I)
      SIM=XX12-XX1(I)
      X(I)=Y2S*QUAD+2.0*Y(2)*SIM+XX1(I)
      D1X(I)=2.0*Y(2)*QUAD+2.0*SIM
   99 D2X(I)=2.0*QUAD
```

```
      IF (NEQN.EQ.1) GO TO 97
C     BENEDICT-WEBB-RUBIN EQUATION OF STATE
      DO 98 I=1,4
      ZZ112=PHI(I)*(ZZ1(I)*ZZ1(I)*ZZ2(I))**EP
      ZZ122=RHO(I)*(ZZ1(I)*ZZ2(I)*ZZ2(I))**EP
      CUBE=ZZ2(I)-3.0*ZZ122+3.0*ZZ112-ZZ1(I)
      QUAD=ZZ122-2.0*ZZ112+ZZ1(I)
      SIM=ZZ112-ZZ1(I)
      Z(I)=Y2C*CUBE+3.0*Y2S*QUAD+3.0*Y(2)*SIM+ZZ1(I)
      D1Z(I)=3.0*Y2S*CUBE+6.0*Y(2)*QUAD+3.0*SIM
   98 D2Z(I)=6.0*Y(2)*CUBE+6.0*QUAD
      X(2)=Y(1)*XX1(2)+Y(2)*XX2(2)
      D1X(2)=XX2(2)-XX1(2)
      D2X(2)=0.0
C     INTERMEDIATE CALCULATION PRINT OUT
      IF (ERZ.LE.1.0) GO TO 50
      WRITE (NO,220)
      WRITE (NO,222)
      WRITE (NO,230) X(1),D1X(1),D2X(1)
      WRITE (NO,231) X(2),D1X(2),D2X(2)
      WRITE (NO,232) X(3),D1X(3),D2X(3)
      WRITE (NO,233) X(4),D1X(4),D2X(4)
      WRITE (NO,226)
      WRITE (NO,234) Z(1),D1Z(1),D2Z(1)
      WRITE (NO,235) Z(2),D1Z(2),D2Z(2)
      WRITE (NO,236) Z(3),D1Z(3),D2Z(3)
      WRITE (NO,237) Z(4),D1Z(4),D2Z(4)
      GO TO 50
   97 IF (ERZ.LE.1.0) GO TO 50
      WRITE (NO,240)
      WRITE (NO,241) X(1),D1X(1),D2X(1)
      WRITE (NO,242) X(2),D1X(2),D2X(2)
   50 RETURN
      END
$IBFTC DELTAZ  DECK
      SUBROUTINE DELTA
C     SUBROUTINE TO CALCULATE THE STABILITY BOUNDARY FOR A BINARY MIXTURE
C
      DOUBLE PRECISION ADD1,ADD2,ADD3,ADD4,ADD5,DPDY,SUM1,SUM2,SUM3,SUM4
     1,SUM5,DPDV,TERM1,TERM2,TERM3,TERM4,TERM5,TERM6,TERM7,TERM8,TERM9,D
     22FDY2,FAC1,FAC2,FAC3,FAC4,FAC5
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
      NO=6
      RT=R*T
      V2=V*V
      IF (NEQN.EQ.2) GO TO 50
C     REDLICH-KWONG CRITICAL STATE RELATIONS
      BRT=RT*X(2)
      BBRT=RT*D1X(2)
      BB2=D1X(2)*D1X(2)
      VMB=V-X(2)
      VMB2=VMB*VMB
      VPB=V+X(2)
      VPB2=VPB*VPB
      VPBV=1.0+X(2)/V
```

```
      TVPB=2.0*V+X(2)
      XLOG=ALOG(VPBV)
C     PRESSURE DERIVATIVES
      DPDV=(-1.0)*(RT/VMB2-X(1)*TVPB/(V2*VPB2))
      DPDY=BBRT/VMB2+1.0/(V*VPB)*(X(1)*D1X(2)/VPB-D1X(1))
C     HELMHOLTZ FREE ENERGY DERIVATIVE
      TERM1=BB2/VMB2+D2X(2)/VMB
      TERM2=XLOG/BRT*(D2X(1)-2.0*D1X(1)*D1X(2)/X(2)+2.0*X(1)*BB2/(X(2)*X
     1(2))-X(1)*D2X(2)/X(2))
      TERM3=1.0/(BRT*VPB)*(X(1)*D2X(2)+2.0*D1X(1)*D1X(2)-2.0*X(1)*BB2/X(
     12)-X(1)*BB2/VPB)
      TERM4=1.0/(Y(1)*Y(2))
      D2FDY2=RT*(TERM1-TERM2-TERM3+TERM4)
      GO TO 90
C
C     BENEDICT-WEBB-RUBIN CRITICAL STATE RELATIONS
   50 T2=T*T
      V3=V2*V
      V4=V3*V
      Y1Y2=Y(1)*Y(2)
      EXPON=1.0/EXP(X(4)/V2)
      CEXPON=Z(3)*EXPON/T2
      PCEXPO=D1Z(3)*EXPON/T2
C     PRESSURE DERIVATIVES
      ADD1=RT/V2*(D1X(2)+D1Z(2)/V)
      ADD2=1.0/V2*(D1X(1)+D1Z(1)/V+D1X(3)/T2)
      ADD3=1.0/(V2*V4)*(Z(1)*D1Z(4)+D1Z(1)*Z(4))
      ADD4=PCEXPO/V3*(1.0+X(4)/V2)
      ADD5=CEXPON*X(4)*D1X(4)/(V4*V3)
      DPDY=ADD1-ADD2+ADD3+ADD4-ADD5
      SUM1=RT/V2*(1.0+2.0*X(2)/V+3.0*Z(2)/V2)
      SUM2=1.0/V3*(2.0*X(1)+3.0*Z(1)/V+2.0*X(3)/T2)
      SUM3=6.0*Z(1)*Z(4)/(V3*V4)
      SUM4=3.0*CEXPON/V4*(1.0+X(4)/V2)
      SUM5=2.0*CEXPON*X(4)*X(4)/(V4*V4)
      DPDV=SUM1-SUM2+SUM3+SUM4-SUM5
      DPDV=(-1.0)*DPDV
C     HELMHOLTZ FREE ENERGY DERIVATIVES
      TERM1=RT/Y1Y2
      FAC1=1.0/V
      FAC2=RT*D2X(2)-D2X(1)-D2X(3)/T2
      TERM2=FAC1*FAC2
      FAC1=1.0/(2.0*V2)
      FAC2=D2Z(2)*RT-D2Z(1)
      TERM3=FAC1*FAC2
      FAC1=1.0/(5.0*V3*V2)
      FAC2=D2Z(1)*Z(4)
      FAC3=2.0*D1Z(1)*D1Z(4)
      FAC4=D2Z(4)*Z(1)
      TERM4=FAC1*(FAC2+FAC3+FAC4)
      FAC1=2.0*D1X(4)/(T2*X(4)*X(4))
      FAC2=D1Z(3)-Z(3)*D1X(4)/X(4)
      TERM5=FAC1*FAC2
      FAC1=1.0/(T2*X(4))
      FAC2=D2Z(3)-Z(3)*D2X(4)/X(4)
      TERM6=FAC1*FAC2
      FAC1=D2Z(3)*EXPON/T2
      FAC2=1.0/X(4)+1.0/(2.0*V2)
      TERM7=FAC1*FAC2
      FAC1=2.0*D1Z(3)*D1X(4)*EXPON/T2
      FAC2=1.0/(X(4)*V2)
      FAC3=1.0/(2.0*V4)
      FAC4=1.0/(X(4)*X(4))
```

```
      TERM8=FAC1*(FAC2+FAC3+FAC4)
      FAC1=Z(3)*D2X(4)*EXPON/T2
      FAC2=1.0/(X(4)*X(4))
      FAC3=1.0/(X(4)*V2)
      FAC4=1.0/(2.0*V4)
      TERM9=FAC1*(FAC2+FAC3+FAC4)
      FAC1=Z(3)*D1X(4)*D1X(4)*EXPON/T2
      FAC2=2.0/(X(4)*X(4)*V2)
      FAC3=1.0/(X(4)*V4)
      FAC4=1.0/(2.0*V4*V2)
      FAC5=2.0/(X(4)*X(4)*X(4))
      TERM10=FAC1*(FAC2+FAC3+FAC4+FAC5)
      D2FDY2=TERM1+TERM2+TERM3+TERM4-TERM5+TERM6-TERM7+TERM8+TERM9-TERM1
     10
C     CRITICAL STATE EQUATION FOR BINARY MIXTURES
   90 DEL1=DPDY*DPDY+DPDV*D2FDY2
      RETURN
      END
$IBFTC PRINTZ  DECK
      SUBROUTINE PRINT
C     SUBROUTINE TO PRINT OUT THE RESULTS AND PROGRAM ERRORS
C
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
  200 FORMAT (71H1CRITICAL PROPERTY CALCULATION RESULTS WITH THE B-W-R E
     1QUATION OF STATE)
  201 FORMAT (///,5X,15H MOLE FRACTIONS,5X,7H Y(1) =,F6.4)
  202 FORMAT (//,10X,21H CRITICAL TEMPERATURE,3X,F8.3,7H  DEG R)
  203 FORMAT (10X,18H CRITICAL PRESSURE,6X,F8.3,6H  PSIA)
  204 FORMAT (10X,16H CRITICAL VOLUME,8X,F8.3,9H  FT3/MOL)
  205 FORMAT (2H0,14X,8H THETA =,F6.4)
  206 FORMAT (16X,8H PHI   =,F6.4)
  207 FORMAT (////,5X,34H DEVIATIONS FROM EXPERIMENTAL DATA,/)
  208 FORMAT (7X,12H TEMPERATURE,8X,F12.3,7H  DEG R,11X,12H TEMPERATURE,
     13X,F7.2,10H  PER CENT)
  209 FORMAT (  7X, 9H PRESSURE,11X,F12.3,6H  PSIA,12X,9H PRESSURE,6X,F7
     1.2,10H  PER CENT)
  210 FORMAT (7X, 7H VOLUME,13X,F12.3,9H  FT3/MOL,9X,7H VOLUME, 8X,F7.2,
     110H  PER CENT)
  211 FORMAT (//,12X,23H INTERACTION PARAMETERS)
  212 FORMAT (2H0 ,26X,19H ABSOLUTE DEVIATION,6X,21H PERCENTAGE DEVIATIO
     1N,/)
  213 FORMAT (69H1CRITICAL PROPERTY CALCULATION RESULTS WITH THE R-K EQU
     1ATION OF STATE)
  214 FORMAT (/,15X,8H THETA =,F7.4)
  215 FORMAT (15X,8H PHI   =,F7.4)
  216 FORMAT (//,10X,3H A0,6X,3H B0,6X,3H C0,4X,6H GAMMA,5X,2H A,7X,2H B
     1,7X,2H C,5X,6H ALPHA)
  217 FORMAT (/,6H THETA,4(4X,F5.3))
  218 FORMAT (6H PHI  ,36X,4(4X,F5.3))
  219 FORMAT (6H RHO  ,36X,4(4X,F5.3))
  220 FORMAT (7X,14H MOLE FRACTION,6X,F13.4,17X,14H MOLE FRACTION, 1X,F7
     1.2,10H  PER CENT)
  221 FORMAT (/,15X,8H THETA =,F7.4,5X,14H OPTIMUM VALUE)
  222 FORMAT (15X,8H PHI   =,F7.4,5X,14H OPTIMUM VALUE)
  250 FORMAT (//,16H******ERROR*****)
```

```
  251 FORMAT (/,7X,24H VOLUME DID NOT CONVERGE)
  252 FORMAT (/,7X,39H ERROR IN CHECKING VALIDITY OF SOLUTION)
  253 FORMAT (/,7X,31H MOLE FRACTION DID NOT CONVERGE)
  254 FORMAT (/,7X,25H Y(1) IS GREATER THAN 1.0)
  255 FORMAT (/,7X,22H Y(1) IS LESS THAN 0.0)
  256 FORMAT (/,7X,45H OPTIMIZATION OF INTERACTION PARAMETER FAILED)
  257 FORMAT (/,7X,37H MAJOR ERROR IN CONVERGENCE PROCEDURE)
  258 FORMAT (/,7X,31H POSSIBLE UPPER BRANCH SOLUTION)
  259 FORMAT (//,18H *****CAUTION*****)
C
      NO=6
      IF (NAD.EQ.0) GO TO 20
      IF (ERZ.EQ.1.0) GO TO 20
      IF (LOX.EQ.1) GO TO 20
      IF (FLAG.GT.0.0) GO TO 60
      GO TO 40
   20 IF (NEQN.EQ.1) GO TO 10
      WRITE (NO,200)
      GO TO 11
   10 WRITE (NO,213)
   11 WRITE (NO,201) Y(1)
      IF (FLAG.EQ.8.0) GO TO 15
      IF (FLAG.GT.0.0) GO TO 60
C     CRITICAL STATE RESULTS
   15 WRITE (NO,202) T
      WRITE (NO,203) P
      WRITE (NO,204) V
      WRITE (NO,211)
      IF (NEQN.EQ.2) GO TO 41
      IF (NEND.EQ.1) GO TO 12
      WRITE (NO,214) THETA(1)
   14 WRITE (NO,215) THETA(2)
      GO TO 40
   12 IF (NAD.EQ.1) GO TO 13
      WRITE (NO,214) THETA(1)
      WRITE (NO,222) THETA(2)
      GO TO 40
   13 WRITE(NO,221) THETA(1)
      GO TO 14
   41 WRITE (NO,216)
      WRITE (NO,217) (THETA(I),I=1,4)
      WRITE (NO,218) (PHI(I),I=1,4)
      WRITE (NO,219) (RHO(I),I=1,4)
C     DEVIATIONS IN CRITICAL PROPERTIES CALCULATED
   40 IF (NDEV.EQ.0) GO TO 52
      SST(K)=T-ETX(K)
      ERRT(K)=ABS(SST(K)/ETX(K))*100.0
      IF (NDEV.LT.2) GO TO 51
      IF (NOPTZ.EQ.2) GO TO 89
      YTRM=Y(1)-Y(2)
      XTRM=CA+CB*YTRM+CC*YTRM*YTRM
      PP=BPC1*Y(1)*Y(1)+BPC2*Y(2)*Y(2)+Y(1)*Y(2)/XTRM
      GO TO 88
   89 YTRM=Y(2)-Y(1)
      XTRM=CA+CB*YTRM+CC*YTRM*YTRM
      PP=BPC2*Y(1)*Y(1)+BPC1*Y(2)*Y(2)+Y(1)*Y(2)/XTRM
   88 EPX(K)=PP*0.98692*14.696
      SSP(K)=P-EPX(K)
      ERRP(K)=ABS(SSP(K)/EPX(K))*100.0
   51 IF (NAD.EQ.0) GO TO 55
      IF (ERZ.EQ.1.0) GO TO 55
      IF (LOX.EQ.1) GO TO 55
   52 IF (FLAG.EQ.8.0) GO TO 67
```

```
      GO TO 50
   55 WRITE (NO,207)
      WRITE (NO,212)
      WRITE (NO,208) SST(K),ERRT(K)
      IF (NDEV.EQ.1) GO TO 52
      WRITE (NO,209) SSP(K),ERRP(K)
      IF (NDEV.EQ.2) GO TO 52
      WRITE (NO,220) SSY(K),ERRY(K)
      IF (NDEV.EQ.3) GO TO 52
      WRITE (NO,210) SSV(K),ERRV(K)
      GO TO 52
C     ERROR MESSAGES
   60 IF (FLAG.GT.1.0) GO TO 61
      WRITE (NO,250)
      WRITE (NO,251)
      GO TO 50
   61 IF (FLAG.GT.2.0) GO TO 62
      WRITE (NO,250)
      WRITE (NO,252)
      GO TO 50
   62 IF (FLAG.GT.3.0) GO TO 63
      WRITE (NO,250)
      WRITE (NO,253)
      GO TO 50
   63 IF (FLAG.GT.4.0) GO TO 64
      WRITE (NO,250)
      WRITE (NO,254)
      GO TO 50
   64 IF (FLAG.GT.5.0) GO TO 65
      WRITE (NO,250)
      WRITE (NO,255)
      GO TO 50
   65 IF (FLAG.GT.6.0) GO TO 66
      WRITE (NO,250)
      WRITE (NO,256)
      GO TO 50
   66 IF (FLAG.GT.7.0) GO TO 50
      WRITE (NO,250)
      WRITE (NO,257)
      GO TO 50
   67 WRITE (NO,259)
      WRITE (NO,258)
   50 RETURN
      END
$IBFTC STATZ   DECK
      SUBROUTINE STAT
C     SUBROUTINE TO CALCULATE DEVIATIONS FROM EXPERIMENTAL DATA
C
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
  200 FORMAT (2H1 ,////,30X,21H STATISTICAL ANALYSIS)
  202 FORMAT (//,21X,14H AVERAGE ERROR,4X,14H MAXIMUM ERROR,4X,25H SUM O
     1F SQUARED DEVIATION)
  203 FORMAT (23X,11H (PER CENT),6X,11H (PER CENT),//)
  204 FORMAT (6X,12H TEMPERATURE,6X,F6.1,11X,F6.1,17X,E12.5)
  205 FORMAT (6X,9H PRESSURE, 9X,F6.1,11X,F6.1,17X,E12.5)
```

```
  206 FORMAT (6X,7H VOLUME,11X,F6.1,11X,F6.1,17X,E12.5)
  207 FORMAT (6X,14H MOLE FRACTION,4X,F6.1,11X,F6.1,17X,E12.5)
  210 FORMAT (2H1 ,///,10X,21H STATISTICAL ANALYSIS)
C
      NO=6
      XNY=NT
      TMAX=0.0
      PMAX=0.0
      YMAX=0.0
      VMAX=0.0
      TSS=0.0
      PSS=0.0
      YSS=0.0
      VSS=0.0
      SUMT=0.0
      SUMP=0.0
      SUMY=0.0
      SUMV=0.0
      DO 99 I=1,NT
      SUMT=SUMT+ERRT(I)
      AVET=SUMT/XNY
      TSS=TSS+SST(I)*SST(I)
      TM=ERRT(I)
      IF (TM.LT.TMAX) GO TO 60
      TMAX=TM
   60 IF (NDEV.LT.2) GO TO 99
      SUMP=SUMP+ERRP(I)
      AVEP=SUMP/XNY
      PSS=PSS+SSP(I)*SSP(I)
      PM=ERRP(I)
      IF (PM.LT.PMAX) GO TO 99
      PMAX=PM
   99 CONTINUE
      IF (NAD.EQ.0) GO TO 55
      IF (ERZ.EQ.1.0) GO TO 55
      IF (LOX.EQ.1) GO TO 55
      GO TO 50
   55 WRITE (NO,210)
      WRITE (NO,202)
      WRITE (NO,203)
      WRITE (NO,204) AVET,TMAX,TSS
      IF (NDEV.LT.2) GO TO 50
      WRITE (NO,205) AVEP,PMAX,PSS
   50 RETURN
      END
$IBFTC OPTPZ   DECK
      SUBROUTINE OPTP
C
C     SUBROUTINE TO CALCULATE THE OPTIMUM INTERACTION PARAMETERS
C        CRITERION     MINIMUM IN THE SUM OF THE SQUARED DEVIATION OF THE
C                      CALCULATION FROM THE EXPERIMENTAL CRITICAL PRESSURE
C
C
      DIMENSION STHETA(50),SPSS(50)
      DIMENSION AB(20),Y(2),TC(2),PC(2),VC(2),ETX(30),EPX(30),EVX(30),XX
     11(4),XX2(4),ZZ1(4),ZZ2(4),THETA(4),PHI(4),RHO(4),D1X(4),D2X(4),D1Z
     2(4),D2Z(4),X(4),Z(4),TT(30),SSP(30),SST(30),SSV(30),EYX(30),SSY(30
     3),ERRT(30),ERRP(30),ERRY(30),ERRV(30)
      COMMON K,LZ,LOX,NJ,NT,NAD,NCP,NDEV,NEND,NEQN,NOTE,ERZ,ERR,FLAG,R,T
     1,P,V,Y,TC,PC,VC,THETA,PHI,RHO,VLOW,VHIGH,DELV,DELY,DEL1,ETX,EPX,EV
     2X,SST,SSP,SSV,X,Z,XX1,XX2,ZZ1,ZZ2,D1X,D1Z,D2X,D2Z,ABC,XYZ,TT,EYX,S
     3SY,PSS,YSS,ERRT,ERRP,ERRY,ERRV,CA,CB,CC,BPC1,BPC2,NOPTZ,NEXT,AEXT
C
```

```
  200 FORMAT (//////////,39H OPTIMIZATION OF INTERACTION PARAMETERS)
  201 FORMAT (/,7X,I3,7H THETA(,I2,3H) =,F7.5,5X,26H PRESSURE SUM OF SQU
     1ARES =,E12.5)
  202 FORMAT (//,15X,8H PARMH =,F7.5,3X,7H PSSH =,E12.5,5X,8H PARML =,F7
     1.5,3X,7H PSSL =,E12.5)
  203 FORMAT (//,20X,5H KOT=,I2,2X,8H HIPARM=,F6.3,4X,8H PTHETA=,F6.3,4X
     1,6H PSSP=,E12.5,4X,7H PPSSP=,E12.5)
C
C       SUBROUTINE VARIABLES
C          THETA(K)      THE BINARY INTERACTION PARAMETER TO BE OPTIMIZED
C          PSS        SUM OF SQUARED DEVIATION IN THE CALC AND EXPTL PC
C          DEL        MAJOR INCREMENT IN ADJUSTING THE INTERACTION PARAMETER
C          SDEL       SUB-INCREMENT IN ADJUSTING THE INTERACTION PARAMETER
C          PARMH      UPPER LIMIT OF THE PARAMETER DURING THE SEARCH PROCEDURE
C          PARML      LOWER LIMIT OF THE PARAMETER DURING THE SEARCH PROCEDURE
C          PSSH       UPPER LIMIT OF THE PC SUM OF SQUARES
C          PSSL       LOWER LIMIT OF THE PC SUM OF SQUARES
C
C
      IN=5
      NO=6
    1 LOX=LOX+1
      LNX=LOX-1
      IF (LOX.EQ.50) GO TO 70
      IF (ERZ.GT.0.0) GO TO 80
    5 IF (LOX.GT.1) GO TO 20
      KOT=0
      PARML=0.0
      DEL=0.050
      SDEL=0.002
C     DETERMINATION OF PARAMETER TO BE OPTIMIZED
      GO TO (71,72,73,74),NAD
   71 KK=1
      GO TO 10
   72 KK=2
      GO TO 10
   73 KK=3
      GO TO 10
   74 KK=4
   10 PARMH=THETA(KK)
      HIPARM=PARMH
      GO TO 65
   20 STHETA(LNX)=THETA(KK)
      SPSS(LNX)=PSS
      IF (LOX.GT.2) GO TO 30
      PSSH=PSS
   21 THETA(KK)=THETA(KK)-DEL
      PSSP=PSS
      GO TO 65
   30 IF (PSS.GT.PSSP) GO TO 40
      IF (KOT.EQ.1) GO TO 34
      IF (KOT.EQ.2) GO TO 33
      PTHETA=PARMH
      PPSSP=PSSH
      PARMH=THETA(KK)
      PSSH=PSS
      IF (PARML.EQ.0.0) GO TO 21
      KOT=1
   31 THETA(KK)=PARMH+SDEL
      PSSP=PSSH
      GO TO 65
   55 THETA(KK)=(PARMH+PARML)/2.0
      PSSP=PSSH
```

```
      GO TO 65
   40 IF (KOT.EQ.1) GO TO 37
      IF (KOT.EQ.2) GO TO 45
      IF (KOT.EQ.3) GO TO 41
      KOT=2
      ZPARM=THETA(KK)
      ZPSS=PSS
      GO TO 31
   33 IF (PARMH.EQ.HIPARM) GO TO 11
   34 PARML=PARMH
      PSSL=PSSH
      SMX=PARML+DEL
      IF (ABS(SMX-PTHETA).GE.0.001) GO TO 12
   35 PARMH=PTHETA
      PSSH=PPSSP
   37 KOT=0
      GO TO 55
   11 PARML=PARMH
      PSSL=PSSH
      HIPARM=PARMH+4.0*DEL
      PARMH=PARML+DEL
   12 THETA(KK)=PARML+DEL
      IF (THETA(KK).GE.2.50) GO TO 70
      KOT=3
      GO TO 65
   41 PARMH=THETA(KK)
      PSSH=PSS
      KOT=0
      GO TO 55
   45 PARML=ZPARM
      PSSL=ZPSS
      KOT=0
      GO TO 55
   80 IF (LOX.EQ.1) GO TO 5
      WRITE (NO,200)
      WRITE (NO,201) LOX,KK,THETA(KK),PSS
      GO TO 5
   70 FLAG=6.0
      GO TO 95
   65 IF ((PARMH-PARML).GE.0.005) GO TO 90
      LOX=1
      FLAG=10.0
      THETA(KK)=(PARMH+PARML)/2.0
   90 IF (ERZ.EQ.0.0) GO TO 95
      WRITE (NO,202) PARMH,PSSH,PARML,PSSL
      WRITE (NO,203) KOT,HIPARM,PTHETA,PSSP,PPSSP
      IF (LOX.EQ.1) GO TO 95
      MDX=0
      DO 99 JJ=1,LNX
      IF (THETA(KK).NE.STHETA(JJ)) GO TO 99
      PSS=SPSS(JJ)
      MDX=1
   99 CONTINUE
      IF (MDX.EQ.1) GO TO  1
   95 RETURN
      END
CRITCALC      B-W-R EQN OF STATE       C1/C2 SYSTEM
 2 5 1 2   1.0
ETHANE
METHANE
550.01    709.82    2.416
343.13    669.70    1.593
+.156707E+05+.100554E+01+.219427E+10+.302790E+01
```

```
+.208502E+05+.285393E+01+.641314E+10+.100044E+01
+.699525E+04+.682401E+00+.275763E+09+.153961E+01
+.298412E+04+.867325E+00+.498106E+09+.511172E+00
1.00        1.00        1.00        1.00
1.00        1.00        1.00        1.00
1.00        1.00        1.00        1.00
367.63     428.3        473.6       509.1       543.6
48.8      46.4      +.5689E-02+.1201E-02+.2117E-03
CRITCALC      R-K EQN OF STATE      C1/C3 SYSTEM    (SUTTON OPT)
 1 7 0 2   0.0
PROPANE
METHANE
665.68    616.3     3.219
343.13    669.70    1.593
0.90        1.00
654.3       641.6       624.1       604.6       582.6       556.1
520.1
42.6      46.4      +.3876E-02+.2541E-02+.2257E-03
```

# APPENDIX B

# TERNCALC COMPUTER PROGRAM

## TERNCALC Computer Program

The computer program developed for the prediction of the critical states of ternary mixtures is designated by the name TERNCALC and was written in FORTRAN IV for use on the Oklahoma State University Computing Center's IBM 7040 digital computer. The TERNCALC program was written in modular form with each of the six modules containing a basic subcalculation or function of the program. Figure 105 is a block diagram showing the inter-relationship between the modules. A description of the function of each of the modules is presented in the following sections.

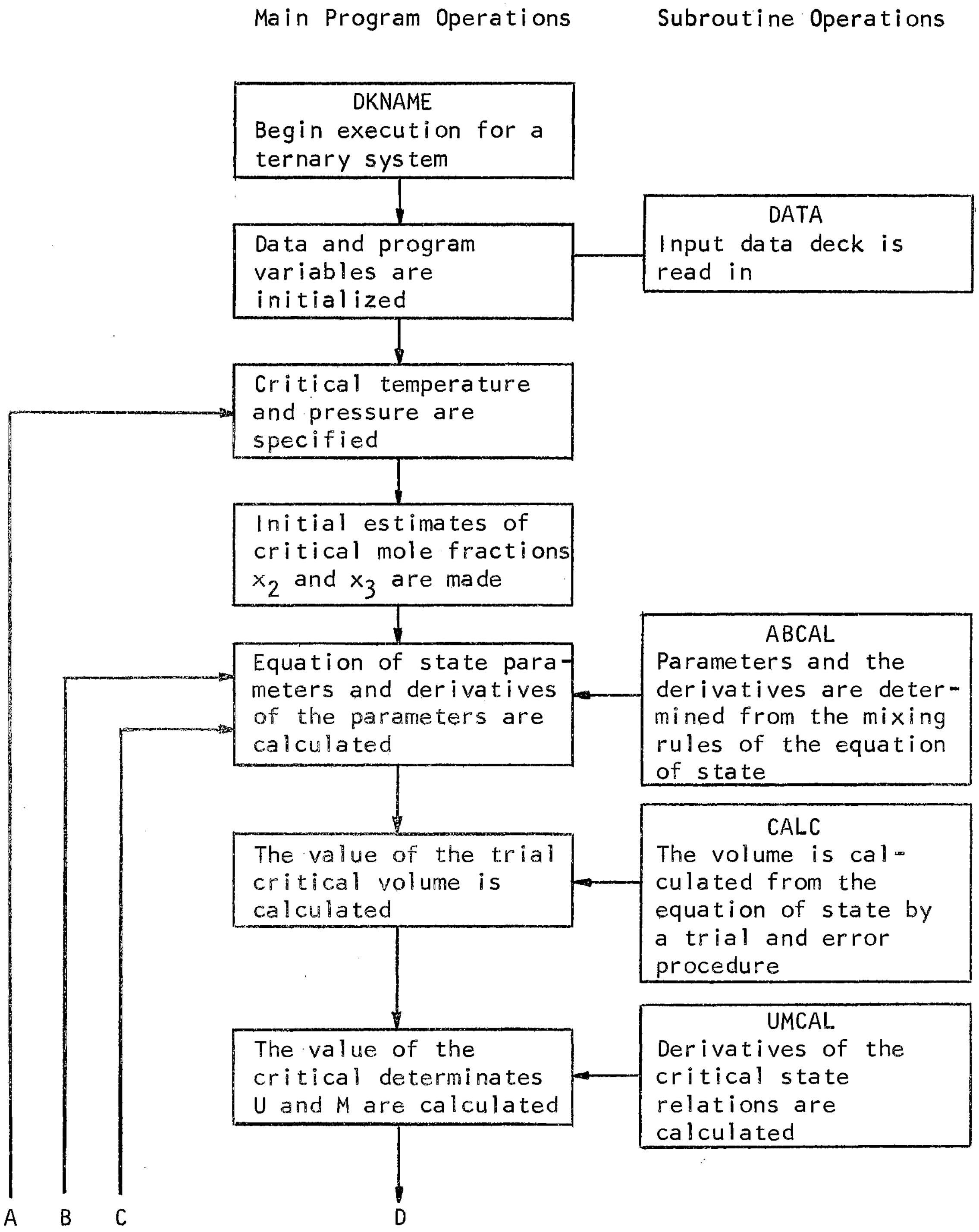
### Main Program

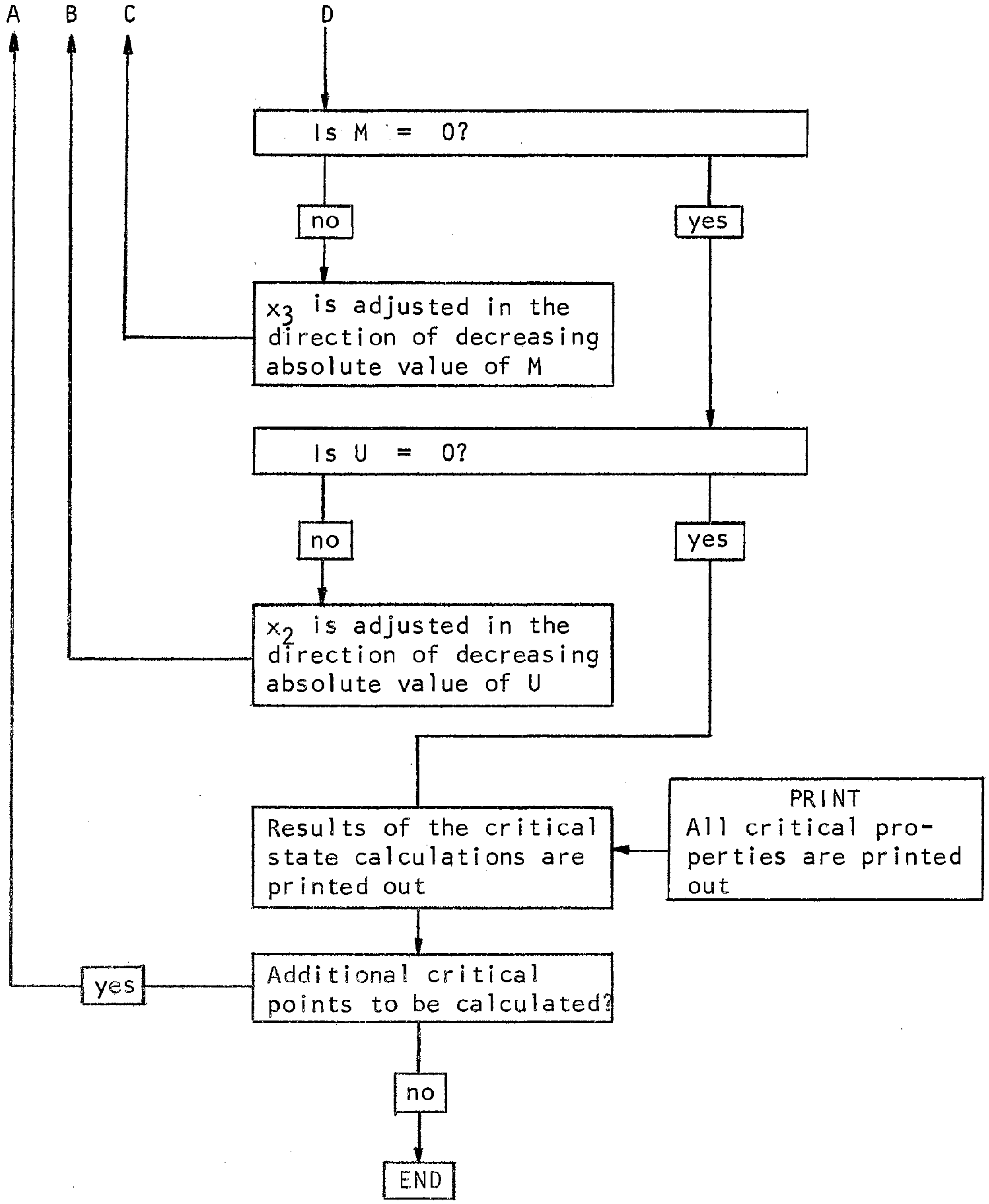
DKNAME is the executive program for the entire calculation. This module contains the search procedure used to determine the critical state of ternary mixtures. The program was written and developed for the Redlich-Kwong equation of state. The data input and output subroutines and the major calculational subroutines are called by this executive program at the appropriate time during the search procedure.

### Subroutine DATA

DATA is the data input subroutine. All input data required for the calculations are read in by this subroutine. DATA is called by the executive program DKNAME at the beginning of the calculations for each ternary system.

Figure 105 TERNCALC Block Diagram




A
B
C
D
Is M = 0?
no
yes
$x_3$ is adjusted in the direction of decreasing absolute value of M
Is U = 0?
no
yes
$x_2$ is adjusted in the direction of decreasing absolute value of U
Results of the critical state calculations are printed out
PRINT All critical properties are printed out
Additional critical points to be calculated?
yes
no
END

## Subroutine ABCAL

ABCAL is the subroutine that calculates the constants and derivatives of the constants of the equation of state with respect to the mole fractions of the second and third components using the modified mixing rules of the Redlich-Kwong equation of state. ABCAL is called by the executive program DKNAME during the mole fraction iterations of the search procedure.

## Subroutine CALC

CALC is the subroutine that calculates the molar volume of the ternary mixture from the Redlich-Kwong equation of state at a specified temperature, pressure, and composition. An interval-halving trial and error search procedure is used to obtain values for the molar volume required in the critical state derivatives. CALC is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine UMCAL

UMCAL is the subroutine that calculates the values of the various critical state derivatives in terms of the Redlich-Kwong equation of state. These values are substituted into the equations for the U and M matrices to obtain values for the critical state equations used in the iterative search procedure. UMCAL is called by subroutine CALC after determining the molar volume.

## Subroutine PRINT

PRINT is the subroutine that prints out all the results of the critical state calculations and appropriate error messages generated during the execution of the search procedure. PRINT is called by the executive program DKNAME after each critical state calculation at a specified critical temperature and pressure.

## Input Data Cards

The input data cards required for the TERNCALC program are arranged in the following order:

CARD 1 "Problem Identification"

This card is used for the alphameric identification of the calculation set for a given ternary system. Any short identifying remarks may be used.

READ: AB(18)
FORMAT: 18A4

CARD 2 "Program Control Variables"

This card contains the two general control variables required in the operation of the program. Each variable is described below.

NT "Critical State Calculation Variable"

NT = the number of critical isotherms to be investigated for a given ternary system

ERZ "Output Control Variable"

ERZ = 0.0 The final results of the critical state calculations are to be printed out.
ERZ = 2.0 The final results and all intermediate results calculated during the course of the search procedure are to be printed out.

```
READ:    NT, ERZ
FORMAT:  I3, F10.3
```

**CARD 3** "Critical Isobar Variable"

This card contains the number of critical isobars associated with each of the critical isotherms to be investigated. The variable NP(I) represents the number of critical isobars to be investigated at the critical isotherm TT(I) specified in card 4. Thus, NP(I) is a positive integer ranging from 1 to 20.

```
READ:    (NP(I), I=1, NT)
FORMAT:  24I3
```

**CARDS 4i** "Critical Isotherm Specifications"

These cards contain the values of the NT critical isotherms to be used in the critical state calculations. TT(I) is the value of the critical isotherm in degrees Rankine.

```
READ:    (TT(I), I=1,NT)
FORMAT:  6F12.3
```

**CARDS 5i** "Critical Isobars and Initial Estimates"

This series of cards, one card for each T,P set, contains the values of the critical isobars in psia units, PP(I,J), and the initial estimates of the critical mole fractions of components 2 and 3, Y2S(I,J) and Y3S(I,J).

```
READ:    PP(I,J), Y2S(I,J), Y3S(I,J)
FORMAT:  3F12.3
```

**CARD 6** "Ternary System Identification"

This card contains an alphameric identification of the ternary mixture system. Any short identifying remarks can be used but it is most useful to identify the three components of the system by name or symbol.

```
READ:     (ABB(I), I = 1,10)
FORMAT:   10A4
```

**CARD 7i** "Mixture Component Identification"

These three cards contain an alphameric identification of the ternary mixture components, one component per card.

```
READ:     (AB(I), I = 1,18)
FORMAT:   18A4
```

**CARD 8i** "Pure Component Critical Properties"

These three cards contain the pure component critical temperature and pressure, variables TC(I) and PC(I), one set per card. The units of TC(I) must be $^{o}R$ and the units of PC(I) must be psia.

```
READ:     TC(I), PC(I)
FORMAT:   2F10.3
```

**CARD 9i** "Binary Interaction Parameters"

These two cards contain the values of the binary interaction parameters to be used in the mixing rules of the Redlich-Kwong equation of state. The first card contains the parameters associated with the constant a: $\theta_{12}$, $\theta_{13}$, and $\theta_{23}$. The second card contains the parameters associated with the constant b: $\phi_{12}$, $\phi_{13}$, and $\phi_{23}$.

```
READ:     X12(I), X13(I), X23(I)
FORMAT:   3F12.3
```

## Program Output

Three types of output can be obtained from the TERNCALC program: final critical state results, intermediate calculation results indicating the path taken by the search procedure, and error messages. Each type of output is discussed below.

### Final Results

The final results of the critical state calculations at specified critical temperature-pressure sets are printed out by subroutine PRINT. The results of a typical calculation are shown in Figure 106.

### Intermediate Calculation Results

If ERZ = 2.0 in card 2 of the input data deck, then the intermediate results calculated during the course of the search procedure are printed out along with the final critical state results. This intermediate calculation feature of the program allows the search procedure to be followed in detail in case the calculation does not appear to be converging correctly.

### Error Messages

When an error condition is encountered during the search procedure an appropriate error message is printed out indicating the area in which the search procedure failed to converge. The calculation is then terminated at this point.

## Program Execution

Execution of the TERNCALC program was carried out on an IBM 7040 computer. The program proved to be less reliable than the CRITCALC program since the convergence procedure proved to be rather dependent on the initial estimates of the critical composition. The average execution time for one critical point calculation was 20 to 30 seconds.

Figure 106 TERNCALC Calculation Results

```
SYSTEM  -  C1/C2/NC5


     CRITICAL POINT PROPERTIES


        T  =   569.690  DEG R
        P  =  2000.000  PSIA
        V  =   1.67130  FT3/IB-MOL

                  CRITICAL COMPOSITION


                     Y(1)  =  0.6647
                     Y(2)  =  0.2039
                     Y(3)  =  0.1314

                              INTERACTION PARAMETERS


                                  A12  =  1.0000     B12  =  1.0000
                                  A12  =  1.0000     B13  =  1.0000
                                  A23  =  1.0000     B23  =  1.0000



                                 MATRIX DATA

                                    DU  =  -0.58764E-02
                                    DM  =   0.51952E-02
```

```
$IBFTC DKNAME  DECK
C
C     CRITICAL POINT CALCULATIONS FOR TERNARY MIXTURES
C        AUTOMATIC SEARCH PROGRAM USING THE EQUATION OF STATE APPROACH
C             REDLICH-KWONG EQUATION OF STATE
C
C                  CRITICAL COMPOSITIONS CALCULATED FROM SPECIFIED SETS OF
C                  TEMPERATURE AND PRESSURE DATA
C
C     SUBROUTINES OF THE MAIN PROGRAM
C        DATA      SUBROUTINE TO READ IN THE INPUT DATA
C        CALC      SUBROUTINE TO CALCULATE THE U AND M MATRICES
C        UMCAL     SUBROUTINE TO CALCULATE THE CRITICAL STATE RELATIONS
C        ABCAL     SUBROUTINE TO CALCULATE THE REDLICH-KWONG PARAMETERS
C        PRINT     SUBROUTINE TO PRINT OUT THE RESULTS
C
C
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
  200 FORMAT (26H1INTERMEDIATE CALCULATIONS,//)
  201 FORMAT (2X,4H T =,F10.3,4X,4H P =,F10.3,/)
  202 FORMAT (//,4X,23H SEARCH FOR Y(3) BEGINS,10X,7H Y(2) =,F8.5,/)
  203 FORMAT (7X,I3,4X,7H Y(3) =,F9.5,4X,5H DM =,F12.4,7X,5H DU =,F12.4)
  204 FORMAT (//,6X,39H INTERVAL FOR Y(3) HAS BEEN ESTABLISHED,/)
  205 FORMAT (10X,I3,4X,7H Y(3) =,F9.5,4X,5H DM =,F12.4,7X,5H DU =,F12.4
     1)
  206 FORMAT (///,8X,16H SEARCH FOR Y(2),/)
  207 FORMAT (11X,I3,4X,7H Y(2) =,F9.5,4X,5H DU =,F12.4)
  208 FORMAT (///,10X,39H INTERVAL FOR Y(2) HAS BEEN ESTABLISHED,/)
C
C
C     VARIABLES
C        NT      NUMBER OF CRITICAL ISOTHERMS TO BE INVESTIGATED
C        NP(I)   NUMBER OF CRITICAL ISOBARS FOR THE ITH CRITICAL ISOTHERM
C        Y(I)    MOLE FRACTION OF COMPONENT I OF THE MIXTURE
C        DELY2   COMPOSITION INCREMENT FOR COMPONENT 2
C        DELY3   COMPOSITION INCREMENT FOR COMPONENT 3
C        DU      CALCULATED VALUE OF MATRIX  U
C        DM      CALCULATED VALUE OF MATRIX  M
C        ERZ     CONTROL VARIABLE FOR INTERMEDIATE PRINT OUT
C                      ERZ = 0.0      NO PRINT OUT OF INTERMEDIATE CALCULATIONS
C                      ERZ = 2.0      FULL PRINT OUT OF CALCULATIONS
C
      NO=6
      R=10.7335
   65 CALL DATA
C
C     CRITICAL TEMPERATURE CALCULATION LOOP
C
      DO 99 I=1,NT
      T=TT(I)
      NPP=NP(I)
C
C     CRITICAL PRESSURE CALCULATION LOOP
C
      DO 98 J=1,NPP
      P=PP(I,J)
      IF (ERZ.EQ.2.0) GO TO 50
   51 NLOOP=0
      MLOOP=0
      NN=0
```

```
      FLAG=0.0
      Y2H=1.0
      Y2L=0.0
      DELY3=0.010
      DELY2=0.01
      Y(2)=Y2S(I,J)-DELY2/2.0
      Y(3)=Y3S(I,J)-DELY3/2.0
   29 Y(1)=1.0-Y(2)-Y(3)
      DO 97 K=1,2
      IF (Y(K+1).GT.0.15) GO TO 97
      IF (K.EQ.1) GO TO 6
      DELY3=Y(3)/5.1
      GO TO 97
    6 DELY2=Y(2)/5.1
   97 CONTINUE
    4 LOOP=0
      KLOOP=0
      MM=0
C
C     SEARCH BEGINS AT CONSTANT Y(2) FOR Y(3) WHERE DM = 0
C
    5 LOOP=LOOP+1
      IF (LOOP.EQ.75) GO TO 71
      Y(1)=1.0-Y(2)-Y(3)
      INDX=1
      GO TO 7
    8 CALL CALC
      IF (LOOP.EQ.1) GO TO 13
      IF (ERZ.EQ.2.0) GO TO 54
   55 IF (ABS(DM).LE.0.01) GO TO 30
      IF (ABS(DM).GT.PDM) GO TO 24
      IF (DM.GT.0.0) GO TO 10
   26 IF (MSIGN.EQ.1) GO TO 20
   12 MSIGN=0
      XLIM=Y(3)
      GO TO 14
   10 IF (MSIGN.EQ.0) GO TO 21
   11 MSIGN=1
      YLIM=Y(3)
   14 Y(3)=Y(3)+XY3*DELY3
      GO TO 5
C
   24 IF (MSIGN.EQ.0) GO TO 25
      IF (DM.LT.0.0) GO TO 26
      GO TO 27
   25 IF (DM.GT.0.0) GO TO 10
   27 MM=MM+1
      XY3=(-1.0)*XY3
      IF (MM.EQ.2) GO TO 78
      Y(3)=PY3
      LOOP=1
      GO TO 5
C
   13 IF (ERZ.EQ.2.0) GO TO 52
   53 IF (ABS(DM).LE.0.01) GO TO 30
      IF (DU.GT.0.0) GO TO 28
   16 PDM=ABS(DM)
      PY3=Y(3)
      Y(3)=Y(3)+0.002
      Y(1)=1.0-Y(2)-Y(3)
      CALL CALC
      IF (DM.GT.PDM) GO TO 1
      XY3=-1.0
```

```
      GO TO 15
    1 XY3=+1.0
   15 IF (DM.LT.0.0) GO TO 12
      XY3=-1.0
      GO TO 11
C
C
   28 NN=NN+1
      IF (NN.GE.2) GO TO 16
      Y(2)=Y(2)-DELY2/2.0
      GO TO 29
C
   20 XLIM=Y(3)
      GO TO 22
   21 YLIM=Y(3)
   22 IF (ERZ.EQ.2.0) GO TO 56
   57 KLOOP=KLOOP+1
      IF (KLOOP.EQ.25) GO TO 72
      IF (ERZ.EQ.2.0) GO TO 58
   59 IF (ABS(YLIM-XLIM).LE.0.0001) GO TO 30
      IF (ABS(DM).LE.0.01) GO TO 30
      Y(3)=(YLIM+XLIM)/2.0
      Y(1)=1.0-Y(2)-Y(3)
      INDX=2
      GO TO 7
    9 CALL CALC
      IF (DM.GT.0.0) GO TO 23
      XLIM=Y(3)
      GO TO 57
   23 YLIM=Y(3)
      GO TO 57
    7 KG=0
      KL=0
      DO 96 K=1,3
      IF (Y(K).GT.1.0) GO TO 2
      IF (Y(K).LT.0.0) GO TO 3
      GO TO 96
    2 KG=K
      GO TO 96
    3 KL=K
   96 CONTINUE
      IF (KG.GT.0) GO TO 75
      IF (KL.GT.0) GO TO 76
      IF (INDX.EQ.1) GO TO 8
      GO TO 9
C
C     ADJUSTMENT OF Y(2) IF DU IS NOT EQUAL TO 0
C
   30 IF (NLOOP.GT.0) GO TO 40
      IF (ERZ.EQ.2.0) GO TO 60
   61 IF (MLOOP.EQ.20) GO TO 73
      MLOOP=MLOOP+1
      IF (ABS(DU).LE.0.01) GO TO 45
      IF (MLOOP.EQ.1) GO TO 31
      IF (DU.GT.0.0) GO TO 32
      IF (NSIGN.EQ.1) GO TO 33
   34 NSIGN=0
      Y2L=Y(2)
      Y(2)=Y(2)+DELY2/2.0
      GO TO 39
   32 IF (NSIGN.EQ.0) GO TO 35
   36 NSIGN=1
      Y2H=Y(2)
```

```
      Y(2)=Y(2)-DELY2/2.0
      GO TO 39
   31 IF (DU.GT.0.0) GO TO 36
      GO TO 34
   38 Y(2)=(Y2H+Y2L)/2.0
   39 DELY3=0.8*DELY3
      GO TO 4
   33 Y2L=Y(2)
      GO TO 40
   35 Y2H=Y(2)
   40 IF (ERZ.EQ.2.0) GO TO 62
   63 NLOOP=NLOOP+1
      IF (NLOOP.EQ.1) GO TO 38
      IF (NLOOP.EQ.25) GO TO 74
      IF ((Y2H-Y2L).LE.0.0001) GO TO 45
      IF (ABS(DU).LE.0.01) GO TO 45
      IF (DU.GT.0.0) GO TO 41
      Y2L=Y(2)
      GO TO 42
   41 Y2H=Y(2)
   42 Y(2)=(Y2H+Y2L)/2.0
      GO TO 39
C
C     INTERMEDIATE PRINT OUT
C
   50 WRITE (NO,200)
      WRITE (NO,201) T,P
      GO TO 51
   52 WRITE (NO,202) Y(2)
      WRITE (NO,203) LOOP,Y(3),DM,DU
      GO TO 53
   54 WRITE (NO,203) LOOP,Y(3),DM,DU
      GO TO 55
   56 WRITE (NO,204)
      GO TO 57
   58 WRITE (NO,205) KLOOP,Y(3),DM,DU
      GO TO 59
   60 WRITE (NO,206)
      WRITE (NO,207) MLOOP,Y(2),DU
      GO TO 61
   62 WRITE (NO,208)
      WRITE (NO,207) NLOOP,Y(2),DU
      GO TO 63
C
C     ERROR MESSAGES
C
   71 FLAG=1.0
      GO TO 90
   72 FLAG=2.0
      GO TO 90
   73 FLAG=3.0
      GO TO 90
   74 FLAG=4.0
      GO TO 90
   75 FLAG=5.0
      GO TO 90
   76 FLAG=6.0
      GO TO 90
   78 FLAG=7.0
      GO TO 90
C
C     PRINT OUT OF CALCULATED RESULTS
C
```

```
   45 CALL CALC
   90 CALL PRINT
   98 CONTINUE
   99 CONTINUE
      GO TO 65
      END
$IBFTC CALCZ   DECK
      SUBROUTINE CALC
C     SUBROUTINE TO CALCULATE THE U AND M MATRICES
C
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
  500 FORMAT (///,25H VOLUME CONVERGENCE ERROR)
C
C     VARIABLES
C        T           TEMPERATURE
C        V           VOLUME
C        Y(I)        MOLE FRACTION OF THE ITH COMPONENT
C        X(I)        REDLICH-KWONG EQUATION OF STATE PARAMETERS
C                          I = 1   CONSTANT  A
C                          I = 2   CONSTANT  B
C
      NO=6
      RT=R*T
      Y(1)=1.0-Y(2)-Y(3)
      CALL ABCAL
      K=0
C
C     VOLUME CALCULATION FROM THE REDLICH-KWONG EQUATION OF STATE
C        INTERVAL HALVING TRIAL AND ERROR PROCEDURE
C
      ZL=X(2)*P/RT
      BP=ZL
      ZU=ZL+3.0
    1 ZAVG=(ZU+ZL)/2.0
      K=K+1
      IF (K.GT.100) GO TO 70
      H=BP/ZAVG
      AOB=X(1)/(X(2)*RT)
      ZCAL=1.0/(1.0-H)-(AOB*H/(1.0+H))
      IF (ABS(ZAVG-ZCAL).LE.0.00001) GO TO 3
      IF (ZAVG.GT.ZCAL) GO TO 4
      ZL=ZAVG
      GO TO 1
    4 ZU=ZAVG
      GO TO 1
   70 WRITE (NO,500)
      CALL EXIT
    3 V=ZCAL*RT/P
      CALL UMCAL
      RETURN
      END
$IBFTC ABCALZ  DECK
      SUBROUTINE ABCAL
C     SUBROUTINE TO CALCULATE THE DERIVATIVES OF THE CONSTANTS FOR THE R-K EQN
C
      DIMENSION XX1(3),XX2(3),XX3(3)
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
```

```
C
C     VARIABLES
C        SUBSCRIPTS
C            I = 1   CONSTANT  A  OF THE REDLICH-KWONG EQUATION OF STATE
C            I = 2   CONSTANT  B  OF THE REDLICH-KWONG EQUATION OF STATE
C
C        X(I)      MIXTURE PARAMETERS  (A  OR  B)
C        XX1(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 1
C        XX2(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 2
C        XX3(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 3
C        XX12      BINARY CONSTANT (A12 OR B12) FOR COMPONENT 1-2 INTERACTION
C        XX13      BINARY CONSTANT (A13 OR B13) FOR COMPONENT 1-3 INTERACTION
C        XX23      BINARY CONSTANT (233 OR B23) FOR COMPONENT 2-3 INTERACTION
C        D1X2(I)   FIRST DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2
C        D1X3(I)   FIRST DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 3
C        D2X2(I)   SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2
C        D2X3(I)   SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 3
C        D2X23(I)  SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2 AND 3
C
      NO=6
      T05=T**0.5
      CON1=0.4278*R*R
      CON2=0.0865*R
      XX1(1)=CON1*TC(1)**2.5/(PC(1)*T05)
      XX2(1)=CON1*TC(2)**2.5/(PC(2)*T05)
      XX3(1)=CON1*TC(3)**2.5/(PC(3)*T05)
      XX1(2)=CON2*TC(1)/PC(1)
      XX2(2)=CON2*TC(2)/PC(2)
      XX3(2)=CON2*TC(3)/PC(3)
      DO 99 I=1,2
      XX12=X12(I)*SQRT(XX1(I)*XX2(I))
      XX13=X13(I)*SQRT(XX1(I)*XX3(I))
      XX23=X23(I)*SQRT(XX2(I)*XX3(I))
      XTERM1=XX1(I)-XX12+XX23-XX13
      XTERM2=XX1(I)-2.0*XX12+XX2(I)
      XTERM3=XX1(I)+XX3(I)-2.0*XX13
      X(I)=Y(3)*Y(3)*XTERM3+2.0*Y(2)*Y(3)*XTERM1+Y(2)*Y(2)*XTERM2+2.0*Y(
     13)*(XX13-XX1(I))+2.0*Y(2)*(XX12-XX1(I))+XX1(I)
      D1X2(I)=2.0*Y(3)*XTERM1+2.0*Y(2)*XTERM2+2.0*(XX12-XX1(I))
      D1X3(I)=2.0*Y(2)*XTERM1+2.0*Y(3)*XTERM3+2.0*(XX13-XX1(I))
      D2X2(I)=2.0*XTERM2
      D2X3(I)=2.0*XTERM3
   99 D2X23(I)=2.0*XTERM1
      RETURN
      END
$IBFTC UMCALZ  DECK
      SUBROUTINE UMCAL
C     SUBROUTINE TO CALCULATE U AND M FOR TERNARY MIXTURES
C
      DOUBLE PRECISION FAC1,FAC2,FAC3,FAC4,FAC5,FAC6,FAC7,FAC8,TM1,TM2,T
     1M3,TM4,TM5,TM6,TM7,TM8,TM9,TM10,TM11,P1V,P2V,P1X2,P1X3,P2X22,P2X23
     2,P2X3V,P2X2V,P2X33,F2X22,F2X33,F2X23,F3X222,F3X223,F3X233,F3X333,G
     32X22,G2X23,G2X33,G3X222,G3X223,G3X233,G3X333
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
C
C     PRESSURE DERIVATIVES FOR THE R-K EQUATION OF STATE
C
C
C     VARIABLES
C        R         UNIVERSAL GAS CONSTANT
```

```
C        P         PRESSURE
C        V         VOLUME
C        Y(I)      MOLE FRACTION OF THE ITH COMPONENT
C
C        REDLICH-KWONG PARAMETERS AND DERIVATIVES
C        SUBSCRIPTS
C            I = 1   CONSTANT  A  OF THE REDLICH-KWONG EQUATION OF STATE
C            I = 2   CONSTANT  B  OF THE REDLICH-KWONG EQUATION OF STATE
C        X(I)      MIXTURE PARAMETERS  (A  OR  B)
C        XX1(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 1
C        XX2(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 2
C        XX3(I)    COMPONENT CONSTANTS (A OR B) FOR COMPONENT 3
C        XX12      BINARY CONSTANT (A12 OR B12) FOR COMPONENT 1-2 INTERACTION
C        XX13      BINARY CONSTANT (A13 OR B13) FOR COMPONENT 1-3 INTERACTION
C        XX23      BINARY CONSTANT (233 OR B23) FOR COMPONENT 2-3 INTERACTION
C        D1X2(I)   FIRST DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2
C        D1X3(I)   FIRST DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 3
C        D2X2(I)   SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2
C        D2X3(I)   SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 3
C        D2X23(I)  SECOND DERIVATIVE OF A OR B WITH RESPECT TO COMPONENT 2 AND 3
C
C
      NO=6
      RT=R*T
      RY1=1.0/Y(1)
      RY2=1.0/Y(2)
      RY3=1.0/Y(3)
      B2=X(2)*X(2)
      B3=B2*X(2)
      V2=V*V
      V3=V2*V
      VMB=V-X(2)
      VMB2=VMB*VMB
      VMB3=VMB2*VMB
      VPB=V+X(2)
      VPB2=VPB*VPB
      VPB3=VPB2*VPB
      BRT=X(2)*RT
      RBV=1.0/(BRT*VPB)
      TVPB=2.0*V+X(2)
      XLOG=ALOG(1.0+X(2)/V)/BRT
      SBB2=D1X2(2)*D1X2(2)
      SBB3=D1X3(2)*D1X3(2)
      CBB2=SBB2*D1X2(2)
      CBB3=SBB3*D1X3(2)
      DAB22=D1X2(1)*D1X2(2)
      DAB33=D1X3(1)*D1X3(2)
      DBB23=D1X2(2)*D1X3(2)
      DAB23=D1X2(1)*D1X3(2)
      DAB32=D1X3(1)*D1X2(2)
C
C     PRESSURE DERIVATIVES
C
      TM1=(-1.0)*RT/VMB2
      TM2=X(1)*TVPB/(V2*VPB2)
      P1V=TM1+TM2
C
      SP1V=P1V*P1V
      CP1V=P1V*P1V*P1V
C
      TM1=2.0*RT/VMB3
      TM2=2.0*X(1)/(V2*VPB2)
      TM3=2.0*X(1)*TVPB*TVPB/(V3*VPB3)
```

```
      P2V=TM1+TM2-TM3
C
      TM1=RT*D1X2(2)/VMB2
      TM2=X(1)*D1X2(2)/(V*VPB2)
      TM3=D1X2(1)/(V*VPB)
      P1X2=TM1+TM2-TM3
C
      TM1=RT*D1X3(2)/VMB2
      TM2=X(1)*D1X3(2)/(V*VPB2)
      TM3=D1X3(1)/(V*VPB)
      P1X3=TM1+TM2-TM3
C
      FAC1=RT/VMB2
      FAC2=D2X2(2)+2.0*SBB2/VMB
      TM1=FAC1*FAC2
      FAC3=1.0/(V*VPB2)
      FAC4=2.0*DAB22-2.0*X(1)*SBB2/VPB+X(1)*D2X2(2)-D2X2(1)*VPB
      TM2=FAC3*FAC4
      P2X22=TM1+TM2
C
      FAC1=RT/VMB2
      FAC2=D2X23(2)+2.0*DBB23/VMB
      TM1=FAC1*FAC2
      TM2=D2X23(1)/(V*VPB)
      TM3=(DAB23+DAB32+X(1)*D2X23(2))/(V*VPB2)
      TM4=2.0*X(1)*DBB23/(V*VPB3)
      P2X23=TM1-TM2+TM3-TM4
C
      FAC1=RT/VMB2
      FAC2=D2X3(2)+2.0*SBB3/VMB
      TM1=FAC1*FAC2
      FAC3=1.0/(V*VPB2)
      FAC4=2.0*DAB33-2.0*X(1)*SBB3/VPB+X(1)*D2X3(2)-D2X3(1)*VPB
      TM2=FAC3*FAC4
      P2X33=TM1+TM2
C
      TM1=D1X2(1)*TVPB/(V2*VPB2)
      TM2=X(1)*D1X2(2)/(V2*VPB2)
      TM3=2.0*X(1)*D1X2(2)/(V*VPB3)
      TM4=2.0*RT*D1X2(2)/VMB3
      P2X2V=TM1-TM2-TM3-TM4
C
      TM1=D1X3(1)*TVPB/(V2*VPB2)
      TM2=X(1)*D1X3(2)/(V2*VPB2)
      TM3=2.0*X(1)*D1X3(2)/(V*VPB3)
      TM4=2.0*RT*D1X3(2)/VMB3
      P2X3V=TM1-TM2-TM3-TM4
C
C     HELMHOLTZ FREE ENERGY DERIVATIVES FOR THE R-K EQUATION OF STATE
C
C
      TM1=SBB2/VMB2+D2X2(2)/VMB
      FAC1=D2X2(1)-2.0*DAB22/X(2)+2.0*X(1)*SBB2/B2-X(1)*D2X2(2)/X(2)
      TM2=XLOG*FAC1
      FAC2=X(1)*D2X2(2)+2.0*DAB22-2.0*X(1)*SBB2/X(2)-X(1)*SBB2/VPB
      TM3=FAC2*RBV
      F2X22=RT*(TM1-TM2-TM3+RY2+RY1)
C
      TM1=SBB3/VMB2+D2X3(2)/VMB
      FAC1=D2X3(1)-2.0*DAB33/X(2)+2.0*X(1)*SBB3/B2-X(1)*D2X3(2)/X(2)
      TM2=XLOG*FAC1
      FAC2=X(1)*D2X3(2)+2.0*DAB33-2.0*X(1)*SBB3/X(2)-X(1)*SBB3/VPB
      TM3=FAC2*RBV
```

```
      F2X33=RT*(TM1-TM2-TM3+RY3+RY1)
C
      TM1=D2X23(2)/VMB+DBB23/VMB2
      FAC1=D2X23(1)-DAB23/X(2)-DAB32/X(2)-X(1)*D2X23(2)/X(2)+2.0*X(1)*DB
     1B23/B2
      TM2=XLOG*FAC1
      FAC2=DAB23-2.0*X(1)*DBB23/X(2)+DAB32+X(1)*D2X23(2)-X(1)*DBB23/VPB
      TM3=FAC2*RBV
      F2X23=RT*(TM1-TM2-TM3+RY1)
C
      TM1=3.0*D1X2(2)*D2X2(2)/VMB2+2.0*CBB2/VMB3
      FAC1=3.0/X(2)*XLOG
      FAC3=DAB22+X(1)*D2X2(2)-X(1)*SBB2/X(2)
      FAC2=D2X2(1)*D1X2(2)+D1X2(1)*D2X2(2)-2.0*D1X2(2)/X(2)*FAC3
      TM2=FAC1*FAC2
      FAC4=3.0*(D2X2(1)*D1X2(2)+D1X2(1)*D2X2(2))-6.0*D1X2(2)/X(2)*FAC3-3
     1.0*D1X2(2)/VPB*FAC3+2.0*X(1)*CBB2/VPB2
      TM3=FAC4*RBV
      F3X222=RT*(TM1+TM2-TM3+RY1*RY1-RY2*RY2)
C
      TM1=3.0*D1X3(2)*D2X3(2)/VMB2+2.0*CBB3/VMB3
      FAC1=3.0*X(2)*XLOG
      FAC3=DAB33+X(1)*D2X3(2)-X(1)*SBB3/X(2)
      FAC2=D2X3(1)*D1X3(2)+D1X3(1)*D2X3(2)-2.0*D1X3(2)/X(2)*FAC3
      TM2=FAC1*FAC2
      FAC4=3.0*(D2X3(1)*D1X3(2)+D1X3(1)*D2X3(2))-6.0*D1X3(2)/X(2)*FAC3-3
     1.0*D1X3(2)/VPB*FAC3+2.0*X(1)*CBB3/VPB2
      TM3=RBV*FAC4
      F3X333=RT*(TM1+TM2-TM3+RY1*RY1-RY3*RY3)
C
      TM1=(2.0*D1X2(2)*D2X23(2)+D2X2(2)*D1X3(2))/VMB2
      TM2=2.0*SBB2*D1X3(2)/VMB3
      FAC1=2.0*(D2X23(1)*D1X2(2)+D1X2(1)*D2X23(2))
      FAC2=D1X3(1)*D2X2(2)+D2X2(1)*D1X3(2)
      TM3=XLOG/X(2)*(FAC1+FAC2)
      FAC3=2.0*D1X2(1)*D1X2(2)*D1X3(2)+D1X3(1)*SBB2+2.0*X(1)*D1X2(2)*D2X
     123(2)+X(1)*D2X2(2)*D1X3(2)
      FAC4=6.0*X(1)*SBB2*D1X3(2)
      TM4=XLOG/B2*(FAC4/X(2)-2.0*FAC3)
      TM5=RBV*(FAC2+FAC1-2.0/X(2)*FAC3+FAC4/B2-1.0/VPB*FAC3+FAC4/(2.0*X(
     12)*VPB)+FAC4/(3.0*VPB2))
      F3X223=RT*(TM1+TM2+TM3+TM4-TM5+RY1*RY1)
C
      TM1=(2.0*D1X3(2)*D2X23(2)+D2X3(2)*D1X2(2))/VMB2
      TM2=2.0*SBB3*D1X2(2)/VMB3
      FAC1=2.0*(D2X23(1)*D1X3(2)+D1X3(1)*D2X23(2))
      FAC2=D1X2(1)*D2X3(2)+D2X3(1)*D1X2(2)
      TM3=XLOG/X(2)*(FAC1+FAC2)
      FAC3=2.0*D1X3(1)*D1X2(2)*D1X3(2)+D1X2(1)*SBB3+2.0*X(1)*D1X3(2)*D2X
     123(2)+X(1)*D1X2(2)*D2X3(2)
      FAC4=6.0*X(1)*D1X2(2)*SBB3
      TM4=XLOG/B2*(FAC4/X(2)-2.0*FAC3)
      TM5=RBV*(FAC2+FAC1-2.0/X(2)*FAC3+FAC4/B2-1.0/VPB*FAC3+FAC4/(2.0*X(
     12)*VPB)+FAC4/(3.0*VPB2))
      F3X233=RT*(TM1+TM2+TM3+TM4-TM5+RY1*RY1)
C
C     GIBBS FREE ENERGY DERIVATIVES
C
C

      G2X22=F2X22+P1X2*P1X2/P1V
      G2X23=F2X23+P1X2*P1X3/P1V
      G2X33=F2X33+P1X3*P1X3/P1V
C
```

```
      G3X222=F3X222+3.0*P1X2*P2X22/P1V-3.0*P1X2*P1X2*P2X2V/SP1V+P1X2*P1X
     12*P1X2*P2V/CP1V
      G3X223=F3X223+(2.0*P1X2*P2X23 +P1X3*P2X22)/P1V-(2.0*P1X2*P1X3*P2X2
     1V)/SP1V+(P1X2*P1X2*P1X3*P2V)/CP1V-P1X2*P1X2*P2X3V/SP1V
      G3X233=F3X233+(2.0*P1X3*P2X23+P1X2*P2X33)/P1V-(2.0*P1X3*P1X2*P2X3V
     1)/SP1V+(P1X3*P1X3*P1X2*P2V)/CP1V-P1X3*P1X3*P2X2V/SP1V
      G3X333=F3X333+3.0*P1X3*P2X33/P1V-3.0*P1X3*P1X3*P2X3V/SP1V+P1X3*P1X
     13*P1X3*P2V/CP1V
C
C     U AND M MATRIX DETERMINATION
C
C
      DU=G2X22*G2X33-G2X23*G2X23
      FAC1=G2X33*G2X33*G3X222
      FAC2=G2X23*(3.0*G2X33*G3X223+G2X22*G3X333)
      FAC3=G3X233*(G2X22*G2X33+2.0*G2X23*G2X23)
      DM=FAC1-FAC2+FAC3
      DU=DU/0.1E+09
      DM=DM/0.1E+14
      RETURN
      END
$IBFTC PRINZ   DECK
      SUBROUTINE PRINT
C     SUBROUTINE TO PRINT OUT RESULTS
C
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
C
  200 FORMAT (3X,26H CRITICAL POINT PROPERTIES,//)
  201 FORMAT (7X,4H T =,F10.3,6H DEG R)
  202 FORMAT (7X,4H P =,F10.3,5H PSIA)
  203 FORMAT (7X,4H V =,F10.5,11H FT3/IB-MOL,//)
  204 FORMAT (12X,7H Y(1) =,F8.4)
  205 FORMAT (12X,7H Y(2) =,F8.4)
  206 FORMAT (12X,7H Y(3) =,F8.4,///)
  207 FORMAT (17X,12H MATRIX DATA,/)
  208 FORMAT (21X,5H DU =,E12.5)
  209 FORMAT (21X,5H DM =,E12.5)
  300 FORMAT (2H1 ,//,11H SYSTEM -   ,10A4,///)
  301 FORMAT (10X,21H CRITICAL COMPOSITION,/)
  302 FORMAT (15X,23H INTERACTION PARAMETERS,/)
  303 FORMAT (19X,6H A12 =,F8.4,4X,6H B12 =,F8.4)
  304 FORMAT (19X,6H A13 =,F8.4,4X,6H B13 =,F8.4)
  305 FORMAT (19X,6H A23 =,F8.4,4X,6H B23 =,F8.4,/////)
  500 FORMAT (///,25H ERROR***** LOOP EXCEEDED)
  501 FORMAT (///,25H ERROR*****KLOOP EXCEEDED)
  502 FORMAT (///,25H ERROR*****MLOOP EXCEEDED)
  503 FORMAT (///,25H ERROR*****NLOOP EXCEEDED)
  504 FORMAT (///,14H ERROR***** Y(,I2,8H) .GT. 1)
  505 FORMAT (///,14H ERROR***** Y(,I2,8H) .LT. 0)
  506 FORMAT (///,39H ERROR***** INITIAL Y(3) SEARCH INVALID)
C
      NO=6
      WRITE (NO,300) (ABB(J),J=1,10)
      WRITE (NO,200)
      WRITE (NO,201) T
      WRITE (NO,202) P
      IF (FLAG.NE.0.0) GO TO 70
      WRITE (NO,203) V
      WRITE (NO,301)
      WRITE (NO,204) Y(1)
```

```
      WRITE (NO,205) Y(2)
      WRITE (NO,206) Y(3)
      WRITE (NO,302)
      WRITE (NO,303) X12(1),X12(2)
      WRITE (NO,304) X13(1),X13(2)
      WRITE (NO,305) X23(1),X23(2)
      WRITE (NO,207)
      WRITE (NO,208) DU
      WRITE (NO,209) DM
      GO TO 99
C
C     ERROR MESSAGES
   70 IF (FLAG.GT.1.0) GO TO 72
      WRITE (NO,500)
      GO TO 99
   72 IF (FLAG.GT.2.0) GO TO 73
      WRITE (NO,501)
      GO TO 99
   73 IF (FLAG.GT.3.0) GO TO 74
      WRITE (NO,502)
      GO TO 99
   74 IF (FLAG.GT.4.0) GO TO 75
      WRITE (NO,503)
      GO TO 99
   75 IF (FLAG.GT.5.0) GO TO 76
      WRITE (NO,504) KG
      GO TO 99
   76 IF (FLAG.GT.6.0) GO TO 78
      WRITE (NO,505) KL
      GO TO 99
   78 WRITE (NO,506)
   99 CONTINUE
      END
$IBFTC DATAZ   DECK
      SUBROUTINE DATA
C     SUBROUTINE TO READ IN THE DATA
C
      DIMENSION AB(20)
      COMMON NT,NP(20),TT(20),PP(20,20),Y2S(20,20),Y3S(20,20),X12(2),X13
     1(2),X23(2),PC(3),TC(3),VC(3),R,T,V,P,Y(3),X(2),D1X2(2),D1X3(2),D2X
     22(2),D2X3(2),D2X23(2),DU,DM,ERZ,FLAG,ABB(10),KG,KL
C
  100 FORMAT (18A4)
  101 FORMAT (I3,F12.3)
  102 FORMAT (4F12.3)
  103 FORMAT (2F10.3)
  104 FORMAT (3F12.3)
  105 FORMAT (6F12.3)
  106 FORMAT (24I3)
  107 FORMAT (10A4)
  200 FORMAT (2H1 ,18A4)
  205 FORMAT (I3,5X,18A4)
  210 FORMAT (//,11H COMPONENTS,/)
  220 FORMAT(//,10X,35H PURE COMPONENT CRITICAL PROPERTIES,/)
  221 FORMAT (10H  VARIABLE,10X,12H COMPONENT 1,10X,12H COMPONENT 2,10X,
     112H COMPONENT 3)
  222 FORMAT (12H TEMPERATURE,9X,F8.3,13X,F8.3,13X,F8.3)
  223 FORMAT (10H  PRESSURE,11X,F8.3,13X,F8.3,13X,F8.3,//)
  225 FORMAT (5X,23H INTERACTION PARAMETERS,/)
  226 FORMAT (12X,2H A,9X,2H B)
  227 FORMAT (2X,4H X12,3X,F6.3,5X,F6.3)
  228 FORMAT (2X,4H X13,3X,F6.3,5X,F6.3)
  229 FORMAT (2X,4H X23,3X,F6.3,5X,F6.3)
```

```
C
C      CALCULATIONAL UNITS
C        PRESSURE       P     PSIA
C        TEMPERATURE    T     DEG R
C        VOLUME         V     FT3/IB-MOL
C        GAS CONSTANT   R = 10.7335 (PSIA)(FT3)/(IB-MOL)(DEG R)
C
      IN=5
      NO=6
C
C     PROGRAM IDENTIFICATION
      READ (IN,100) (AB(J),J=1,18)
      WRITE (NO,200) (AB(J),J=1,18)
C
C     NUMBER OF CRITICAL ISOTHERMS TO BE INVESTIGATED
      READ (IN,101) NT,ERZ
C
C     NUMBER OF CRITICAL ISOBARS ASSOCIATED WITH EACH CRITICAL ISOTHERM
      READ (IN,106) (NP(I),I=1,NT)
C
C     VALUES OF THE CRITICAL ISOTHERMS TO BE INVESTIAGED
      READ (IN,105) (TT(I),I=1,NT)
      DO 97 I=1,NT
      NPP=NP(I)
C
C     VALUES OF THE CRITICAL ISOBARS AND INITIAL ESTIMATES OF THE COMPOSITION
      DO 96 J=1,NPP
   96 READ (IN,104) PP(I,J),Y2S(I,J),Y3S(I,J)
   97 CONTINUE
C
C     TERNARY SYSTEM IDENTIFICATION
      READ (IN,107) (ABB(J),J=1,10)
      WRITE (NO,210)
C
C     MIXTURE COMPONENTS IDENTIFICATION
      DO 98 I=1,3
      READ (IN,100) (AB(J),J=1,18)
   98 WRITE (NO,205) I,(AB(J),J=1,18)
C
C     PURE COMPONENT CRITICAL PROPERTIES
      DO 99 I=1,3
   99 READ (IN,103) TC(I),PC(I)
      WRITE (NO,220)
      WRITE (NO,221)
      WRITE (NO,222) TC(1),TC(2),TC(3)
      WRITE (NO,223) PC(1),PC(2),PC(3)
C
C     BINARY INTERACTION PARAMETERS
      DO 92 I=1,2
   92 READ (IN,104) X12(I),X13(I),X23(I)
      WRITE (NO,225)
      WRITE (NO,226)
      WRITE (NO,227) X12(1),X12(2)
      WRITE (NO,228) X13(1),X13(2)
      WRITE (NO,229) X23(1),X23(2)
      RETURN
      END
C1/C3/NC4 TERNARY SYSTEM      R-K EQN OF STATE
  2  0.0
  5  5
599.69      619.69
1400.0      0.33        0.120
1500.0      0.250       0.170
```

```
1600.0          0.170           0.220
1700.0          0.100           0.250
1800.0          0.05            0.260
1400.0          0.300           0.150
1500.0          0.200           0.220
1600.0          0.13            0.260
1700.0          0.06            0.270
1800.0          0.03            0.29
C1/C3/NC4
METHANE
PROPANE
N-BUTANE
343.13          673.1
665.68          616.3
765.31          550.66
1.00            1.00            1.00
1.00            1.00            1.00
```

# APPENDIX C

# VLECALC COMPUTER PROGRAM

## VLECALC Computer Program

The VLECALC computer program was developed for the prediction of vapor-liquid equilibrium points of binary mixtures and was written in FORTRAN IV for use on the Oklahoma State University Computing Center's IBM 7040 digital computer. The VLECALC program was written in modular form with each of the ten modules containing a basic sub-calculation or function of the program. Figure 107 is a block diagram showing the inter-relationship between the modules. A description of the function of each module is presented in the following sections.

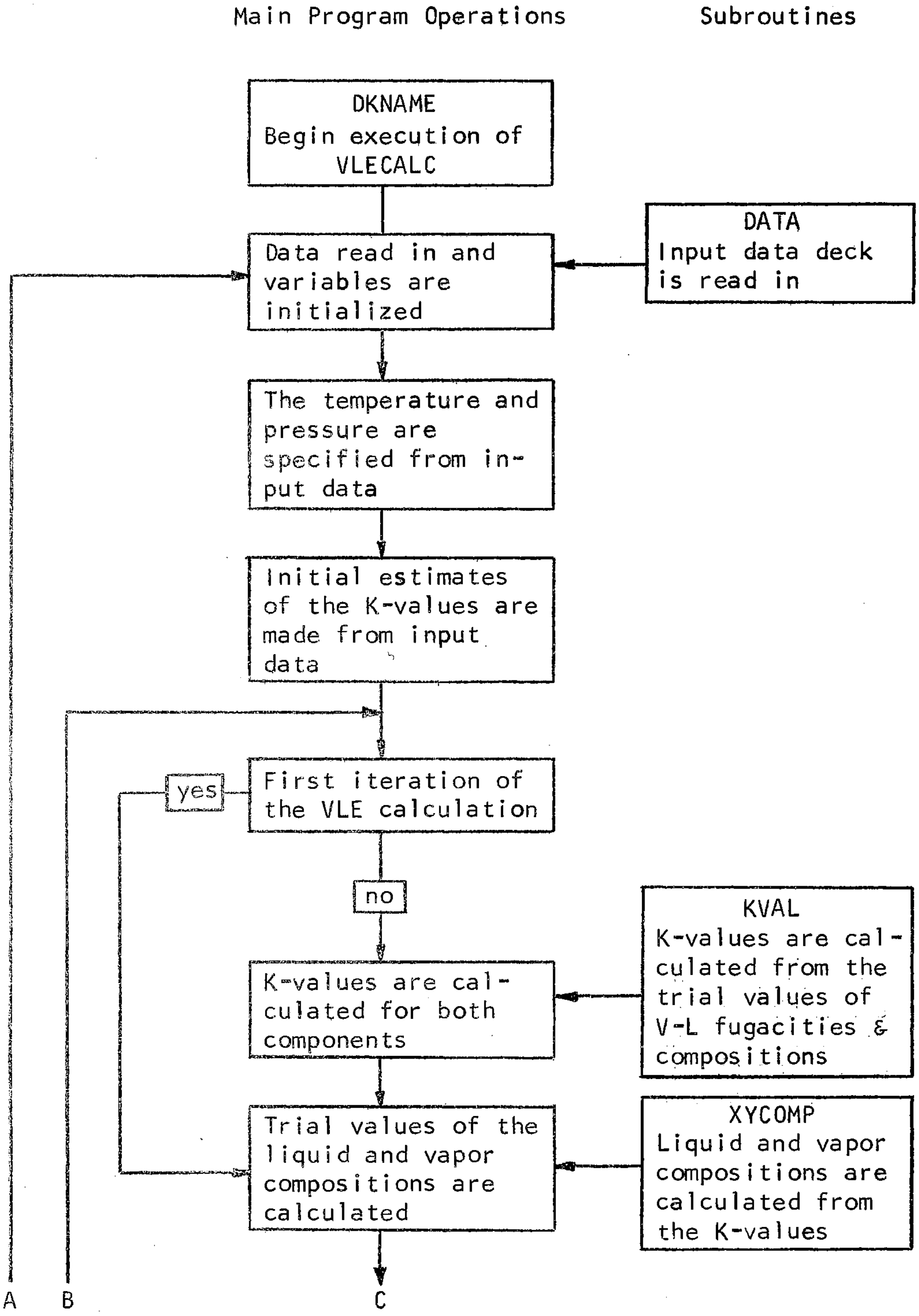
### Main Program

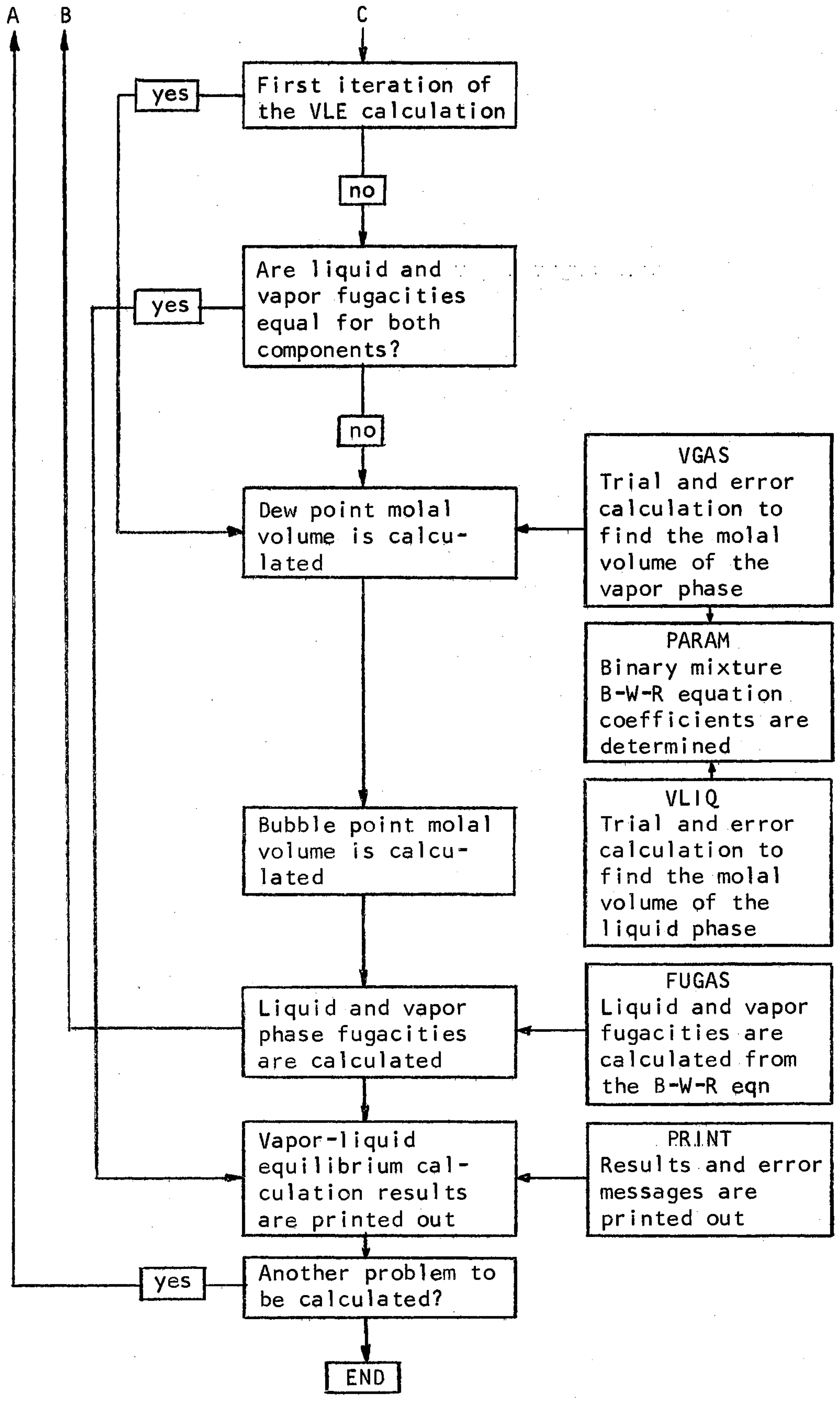
DKNAME is the executive program for the entire calculation. This module contains the search procedure used to determine the vapor-liquid equilibrium points of binary mixtures. The program was written and developed for the B-W-R equation of state. The data input and output subroutines and the major calculation subroutines are called by this executive program at the appropriate time during the search procedure.

### Subroutine DATA

DATA is the data input subroutine. All input data required for the calculations are read in by this subroutine. DATA is called by the executive program DKNAME at the beginning of the calculations for each binary system.

Figure 107 VLECALC Block Diagram




A
B
C
First iteration of the VLE calculation
yes
no
Are liquid and vapor fugacities equal for both components?
yes
no
Dew point molal volume is calculated
VGAS
Trial and error calculation to find the molal volume of the vapor phase
PARAM
Binary mixture B-W-R equation coefficients are determined
Bubble point molal volume is calculated
VLIQ
Trial and error calculation to find the molal volume of the liquid phase
Liquid and vapor phase fugacities are calculated
FUGAS
Liquid and vapor fugacities are calculated from the B-W-R eqn
Vapor-liquid equilibrium calculation results are printed out
PRINT
Results and error messages are printed out
Another problem to be calculated?
yes
END

## Subroutine KVAL

KVAL is the subroutine that calculates the equilibrium ratios for both components from the calculated vapor and liquid fugacities and the mole fractions of both components in the vapor and liquid phases. This subroutine is independent of the equation of state used in the other subroutines of the calculation. KVAL is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine XYCOMP

XYCOMP is the subroutine that calculates the vapor and liquid phase compositions from the calculated equilibrium ratios. This subroutine is independent of the equation of state used in the other subroutines of the calculation. XYCOMP is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine VGAS

VGAS is the subroutine that calculates the dew point molal volume. A trial and error procedure is used to determine the volume at the specified temperature, pressure, and composition using the B-W-R equation of state. VGAS is called by the executive program DKNAME during the iterations of the search procedure.

## Subroutine VLIQ

VLIQ is the subroutine that calculates the bubble point molal volume. A trial and error procedure is used to determine the volume at the specified temperature, pressure, and composition using the B-W-R equation of state. VLIQ is called by the executive program DKNAME during the iterations of the search procedure.

### Subroutine PARAM

PARAM is the subroutine that calculates the binary mixture coefficients of the B-W-R equation of state using the mixing rules derived for binary mixtures. Provisions have been made for adjusting the values of the binary interaction parameters. PARAM is called by subroutines VGAS and VLIQ during the iterations of the search procedure.

### Subroutine FUGAS

FUGAS is the subroutine that calculates the vapor and liquid phase fugacities derived from the B-W-R equation of state. FUGAS is called by subroutines VGAS and VLIQ during the iterations of the search procedure.

### Subroutine CONST

CONST is the subroutine that contains the values of the coefficients of the B-W-R equation of state for twelve pure components: methane, ethylene, ethane, propylene, propane, i-butane, i-butylene, n-butane, i-pentane, n-pentane, n-hexane, and n-heptane. CONST is called by the data input subroutine DATA at the beginning of the calculations for a binary system.

## Subroutine PRINT

PRINT is the subroutine that prints out all the results of the vapor-liquid equilibrium calculations and appropriate error messages generated during the execution of the search procedure. PRINT is called by the executive program DKNAME after each completed calculation.

## Input Data Cards

The input data cards required for the VLECALC program are arranged in the following order:

CARD 1 "Problem Identification"

This card is used for the alphameric identification of the calculation set for a given binary system. Any short identifying remarks may be used.

READ: AB(18)
FORMAT: 18A4

CARD 2 "Program Control Variables"

This card contains the three general control variables required to guide the operation of the program. Each variable is described below.

NCP "Number of Components Variable"

NCP = 2 for a binary mixture system

NDP "Number of Data Points Variable"

NDP = number of vapor-liquid equilibrium points to be calculated for this binary system

ERZ "Output Control Variable"

ERZ = 0.0 The final results of the vapor-liquid equilibrium calculations are to be printed out.

ERZ = 2.0 The final results and all intermediate results calculated during the course of the search procedure are to be printed out.

READ: NCP, NDP, ERZ
FORMAT: I3, I3, F10.3

### CARD 3 "Component Number and Identification"

This card contains the component number (#1 or #2) and an alphameric identification of the component. Any short identifying remark may be used as the component identification.

READ: NOC(I), (AB(J), J=1,18)
FORMAT: I3, 18A4

### CARD 4 "Interaction Parameters for Binary Mixtures"

This card contains the values of the interaction parameters to be used in the mixing rules of the B-W-R equation of state. These interaction parameters are associated with the binary mixture parameters $X_{12}$, $X_{112}$, and $X_{122}$ where X can equal $A_o$, $B_o$, $C_o$, and $\gamma$. In most cases the values of $X_{112}$, and $X_{122}$ are set equal to 1.0.

READ: TX12(I), TZ112(I), TZ122(I)
FORMAT: F10.3, F10.3, F10.3

### CARD 5 "VLE Calculation Data Variables"

This card contains the specified temperature and pressure sets and initial estimates of the equilibrium ratios and the bubble point density used in the first iteration of the program. The units on temperature, pressure, and density are degrees Rankine, psia, and lb-mol/ft$^3$, respectively.

READ: TT(I), PP(I), EKI(I,1), EKI(I,2), SIGMA(I)
FORMAT: F10.3, F10.3, F10.3, F10.3, F10.3

## Program Output

Three types of output can be obtained from the VLECALC program: final results of the vapor-liquid equilibrium calculations, intermediate calculation results indicating the path taken by the search procedure, and error messages. Each type of output is discussed below.

### Final Results

The final results of the vapor-liquid equilibrium calculations at specified temperature-pressure sets are printed out by subroutine PRINT. The results of a typical calculation are shown in Figure 108.

### Intermediate Calculation Results

If ERZ = 2.0 in card 2 of the input data deck, then the intermediate results calculated during the course of the search procedure are printed out along with the final vapor-liquid equilibrium calculation results. This intermediate calculation feature of the program allows the search procedure to be studied in detail in case the calculation does not appear to be converging correctly.

### Error Messages

When an error condition is encountered during the search procedure an appropriate error message is printed out indicating the area in which the search procedure failed to converge. The calculation is then terminated at this point.

## Program Execution

Execution of the VLECALC program was carried out on an IBM 7040 computer. The program proved to be reliable and rarely failed to converge to the correct solution when reasonable estimates of the bubble point density were specified in the input data. The average execution time for a binary system with ten vapor-liquid equilibrium points to be calculated was 2/3 minutes.

Figure 108 VLECALC Calculation Results

```
VLE CALCULATIONS          C3/N-PENTANE SYSTEM          B-W-R EQN OF STATE

     SYSTEM COMPONENTS

        1      PROPANE
        2      N-PENTANE

     INTERACTION PARAMETERS

                         A0            B0            C0           GAMMA

        X12            1.000         1.000         1.000         1.000


B-W-R VAPOR-LIQUID EQUILIBRIUM CALCULATION

                                            T  =  619.690  DEG R
                                            P  =  100.000  PSIA

     VAPOR PHASE                                 LIQUID PHASE

         VOLUME                                      VOLUME

            V  =  57.83056                              V  =  1.95349

         COMPOSITION                                 COMPOSITION

            Y(1)  =  0.622153                           X(1)  =  0.212476
            Y(2)  =  0.377847                           X(2)  =  0.787524

         FUGACITIES                                  FUGACITIES

            F(1)  =  0.58287E 02                        F(1)  =  0.58288E 02
            F(2)  =  0.30417E 02                        F(2)  =  0.30416E 02

                              EQUILIBRIUM RATIOS

                              K(1)  =  2.928109
                              K(2)  =  0.479791
```

```
$IBFTC DKNAME  DECK
C     MAIN PROGRAM
C     PROGRAM TO CALCULATE THE EQUILIBRIUM COMPOSTION OF COEXISTING PHASES
C     USING THE BENEDICT-WEBB-RUBIN EQUATION OF STATE
C
C
C          AUTHOR                ROBERT R SPEAR
C          DATE                  APRIL, 1968
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C
  200 FORMAT (60H1 EQUILIBRIUM COMPOSITION CALCULATION --  B-W-R EQN OF
     1STATE,//)
  201 FORMAT (2X,4H T =,F10.3,6H DEG R,7X,4H P =,F12.3,5H PSIA,///)
  202 FORMAT (3X,12H ITERATION =,I3,/)
  203 FORMAT (5X,7H K(1) =,F10.5,4X,7H Y(1) =,F10.5,4X,7H X(1) =,F10.5,4
     1X,5H FV =,E12.5,4X,5H FL =,E12.5)
  204 FORMAT (5X,7H K(2) =,F10.5,4X,7H Y(2) =,F10.5,4X,7H X(2) =,F10.5,4
     1X,5H FV =,E12.5,4X,5H FL =,E12.5)
  205 FORMAT (5X,7H K(3) =,F10.5,4X,7H Y(3) =,F10.5,4X,7H X(3) =,F10.5,4
     1X,5H FV =,E12.5,4X,5H FL =,E12.5)
C
C
C     SUBROUTINES
C        KVAL      CALCULATES THE EQUILIBRIUM RATIO
C        XYCOMP    CALCULATES THE LIQUID AND VAPOR COMPOSITIONS
C        PARAM     CALCULATES THE MIXTURE PARAMETERS FOR THE B-W-R EQN
C        FUGAS     CALCULATES THE LIQUID AND VAPOR FUGACITIES
C        VGAS      CALCULATES THE DEW POINT MOLAL VOLUME
C        VLIQ      CALCULATES THE BUBBLE POINT MOLAL VOLUME
C        PRINT     PRINTS OUT THE CALCULATION RESULTS
C        DATA      READS IN THE INPUT DATA FOR THE CALCULATIONS
C        CONST     PROVIDES VALUES OF THE B-W-R EQN CONSTANTS
C
C     VARIABLES IN THE MAIN PROGRAM
C        Y(I,J)    VAPOR OR LIQUID COMPOSITION OF COMPONENT J
C                       I = 1    VAPOR PHASE
C                       I = 2    LIQUID PHASE
C        F(I,J)    VAPOR OR LIQUID FUGACITY OF COMPONENT J
C        EK(K)     EQUILIBRIUM RATIO OF COMPONENT  K
C        FLAG = 0.0     CALCULATION IS PROCEEDING NORMALLY
C        FLAG = 3.0     CALCULATION HAS NOT CONVERGED IN 35 PASSES
C        FLAG = 10.0    CALCULATION HAS CONVERGENCED TO THE FINAL ANSWER
C        ERZ       CONTROL VARIABLES FOR INTERMEDIATE PRINT OUT
C           ERZ = 0.0          NO INTERMEDIATE PRINT OUT
C           ERZ = 2.0          TOTAL INTERMEDIATE PRINT OUT
C
C
      NO=6
      R=10.7185
      POW=1.0/3.0
   65 CALL DATA
      DO 99 I=1,NDP
      II=I
      T=TT(I)
      P=PP(I)
      RT=R*T
      PRT=P/RT
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      T2=T*T
      IF (NCP.EQ.2) GO TO 30
      Y(2,1)=YY(I)
   30 DO 98 J=1,NCP
   98 EK(J)=EKI(I,J)
      DO 97 N=1,2
      DO 96 M=1,3
   96 F(N,M)=0.0
   97 CONTINUE
      IF (ERZ.EQ.2.0) GO TO 40
   41 NC=0
      FLAG=0.0
   50 NC=NC+1
      IF (NC.EQ.35) GO TO 70
      IF (NC.EQ.1) GO TO 20
      CALL KVAL
   20 CALL XYCOMP
      IF (ERZ.EQ.2.0) GO TO 42
   43 IF (FLAG.EQ.6.0) GO TO 90
      IF (FLAG.EQ.7.0) GO TO 90
      IF (NC.EQ.1) GO TO 21
      KT=0
      DO 95 J=1,NCP
      ZXX=0.001*F(1,J)
      IF (ABS(F(1,J)-F(2,J)).GT.ZXX) GO TO 95
      KT=KT+1
   95 CONTINUE
      IF (KT.LT.NCP) GO TO 21
      FLAG=10.0
      GO TO 90
   21 CALL VGAS
      IF (FLAG.EQ.1.0) GO TO 90
      IF (FLAG.EQ.4.0) GO TO 90
      CALL VLIQ
      IF (FLAG.EQ.2.0) GO TO 90
      IF (FLAG.EQ.5.0) GO TO 90
      GO TO 50
   40 WRITE (NO,200)
      WRITE (NO,201) T,P
      GO TO 41
   42 WRITE (NO,202) NC
      WRITE (NO,203) EK(1),Y(1,1),Y(2,1),F(1,1),F(2,1)
      WRITE (NO,204) EK(2),Y(1,2),Y(2,2),F(1,2),F(2,2)
      IF (NCP.EQ.2) GO TO 43
      WRITE (NO,205) EK(3),Y(1,3),Y(2,3),F(1,3),F(2,3)
      GO TO 43
   70 FLAG=3.0
   90 CALL PRINT
   99 CONTINUE
      GO TO 65
      END
$IBFTC XYCOMZ  DECK
      SUBROUTINE XYCOMP
C     SUBROUTINE TO CALCULATE THE LIQUID AND VAPOR COMPOSITIONS
C
      DIMENSION PY(2,3)
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C     VARIABLES
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C
C        NCP        NUMBER OF COMPONENTS IN THE MIXTURE
C        EK(K)      EQUILIBRIUM RATIO FOR COMPONENT  K
C        Y(I,J)     VAPOR OR LIQUID COMPOSITION
C                             I = 1    VAPOR PHASE
C                             I = 2    LIQUID PHASE
C
C
      NO=6
      NOTE=0
      KT=0
      IF (NC.GT.1) GO TO 20
      Y(2,2)=0.0
      Y(2,3)=0.0
      IF (NCP.EQ.3) GO TO 20
      Y(2,1)=0.0
   20 DO 97 J=1,NCP
   97 PY(2,J)=Y(2,J)
      IF (NCP.EQ.3) GO TO 50
      Y(2,1)=(1.0-EK(2))/(EK(1)-EK(2))
      Y(2,2)=1.0-Y(2,1)
      GO TO 55
   50 Y(2,2)=(1.0-EK(3)+Y(2,1)*(EK(3)-EK(1)))/(EK(2)-EK(3))
      Y(2,3)=1.0-Y(2,1)-Y(2,2)
   55 DO 96 K=1,NCP
      IF (Y(2,K).GT.1.0) GO TO 10
      IF (Y(2,K).LT.0.0) GO TO 10
      GO TO 96
   10 NOTE=1
   96 CONTINUE
      IF (NOTE.EQ.0) GO TO 52
      FLAG=6.0
      GO TO 99
   52 DO 95 K=1,NCP
      Y(1,K)=EK(K)*Y(2,K)
      IF (Y(1,K).GT.1.0) GO TO 11
      IF (Y(1,K).LT.0.0) GO TO 11
      GO TO 95
   11 NOTE=2
   95 CONTINUE
      IF (NOTE.EQ.0) GO TO 99
      IF (NOTE.EQ.1) GO TO 99
      FLAG=7.0
   99 RETURN
      END
$IBFTC VGASZ   DECK
      SUBROUTINE VGAS
C     SUBROUTINE TO CALCULATE THE DEW POINT MOLAL VOLUME
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C
  200 FORMAT (///,9X,35H DEW POINT MOLAL VOLUME CALCULATION,/)
  201 FORMAT (37X,11H CALCULATED,5X,9H PRESSURE)
  202 FORMAT (22X,8H DENSITY,8X,9H PRESSURE,5X,11H DIFFERENCE,/)
  203 FORMAT (13X,I3,4X,E12.5,3X,F12.3,5X,F12.3)
  204 FORMAT (/,20X,5H DG =,F10.5)
C
C     VARIABLES
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C
C         INDX = 1   VAPOR PHASE
C         S          TRIAL VALUE OF THE DENSITY
C         SV         DEW POINT DENSITY
C         PC         CALCULATED PRESSURE
C         P          PRESSURE SPECIFIED IN DATA
C
      NO=6
      INDX=1
      CALL PARAM
      IF (ERZ.EQ.2.0) GO TO 40
   41 LOOP=0
      PS=0.0
      PC=0.0
    5 LOOP=LOOP+1
      IF (LOOP.EQ.25) GO TO 70
      IF (LOOP.GT.2) GO TO 10
      IF (LOOP.EQ.2) GO TO 11
      ZZ=0.700
      GO TO 12
   11 ZZ=0.389
      PS=S
   12 S=PRT/ZZ
      GO TO 13
   10 PPS=PS
      PS=S
      S=PS+(PS-PPS)*(P-PC)/(PC-PPC)
   13 PPC=PC
      GS2=(-1.0)*X(4)*S*S
      EGS=EXP(GS2)
      S3=S*S*S
      PTRM1=Z(3)/T2*(1.0-GS2)*EGS+Z(1)*Z(4)*S3-Z(1)+Z(2)*RT
      PTRM2=X(2)*RT-X(1)-X(3)/T2
      PC=S*(((PTRM1*S+PTRM2)*S)+RT)
      DP=PC-P
      IF (ERZ.EQ.2.0) GO TO 42
   43 IF (ABS(S-PS).LE.0.00001) GO TO 50
      GO TO 5
   40 WRITE (NO,200)
      WRITE (NO,201)
      WRITE (NO,202)
      GO TO 41
   42 WRITE (NO,203) LOOP,S,PC,DP
      GO TO 43
   70 FLAG=1.0
      GO TO 99
   71 FLAG=4.0
      GO TO 99
   50 IF (S.LT.0.0) GO TO 71
      SV=S
      IF (ERZ.EQ.0.0) GO TO 51
      WRITE (NO,204) S
   51 CALL FUGAS
   99 RETURN
      END
$IBFTC VLIQZ   DECK
      SUBROUTINE VLIQ
C     SUBROUTINE TO CALCULATE THE BUBBLE POINT MOLAL VOLUME
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
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     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C
 200 FORMAT (///,12X,38H BUBBLE POINT MOLAL VOLUME CALCULATION,/)
 201 FORMAT (40X,11H CALCULATED,5X,9H PRESSURE)
 202 FORMAT (25X,8H DENSITY,8X,9H PRESSURE,5X,11H DIFFERENCE,/)
 203 FORMAT (16X,I3,4X,E12.5,5X,F12.3,5X,F12.3)
 204 FORMAT (/,23X,5H DL =,F10.5)
C
C     VARIABLES
C
C         INDX = 2  LIQUID PHASE
C         S         TRIAL VALUE OF THE DENSITY
C         SL        BUBBLE POINT DENSITY
C         PC        CALCULATED PRESSURE
C         P         PRESSURE SPECIFIED IN DATA
C
      NO=6
      NOTE=0
      INDX=2
      CALL PARAM
      IF (ERZ.EQ.2.0) GO TO 40
  41  LOOP=1
      PC=0.0
      IF (NC.GT.1) GO TO 13
      S=SIGMA(II)
      PS=0.0
      GO TO 13
   5  LOOP=LOOP+1
      IF (LOOP.EQ.25) GO TO 70
      XLOOP=LOOP
      XLOOP=1.0+XLOOP/5.0
      IF (LOOP.EQ.2) GO TO 13
      PPS=PS
      PS=S
      S=S-DSP*DP
  16  IF (ABS(PS-S).LT.0.25) GO TO 13
      IF (S.LT.PS) GO TO 15
      S=PS+0.25/XLOOP
      GO TO 13
  15  S=PS-0.25/XLOOP
  13  PPC=PC
  14  GS2=(-1.0)*X(4)*S*S
      EGS=EXP(GS2)
      S3=S*S*S
      PTRM1=Z(3)/T2*(1.0-GS2)*EGS+Z(1)*Z(4)*S3-Z(1)+Z(2)*RT
      PTRM2=X(2)*RT-X(1)-X(3)/T2
      PC=S*(((PTRM1*S+PTRM2)*S)+RT)
      DP=PC-P
      IF (LOOP.EQ.1) GO TO 30
      DSP=(S-PS)/(PC-PPC)
      IF (ERZ.EQ.2.0) GO TO 42
  43  IF (ABS(S-PS).LE.0.00001) GO TO 50
      GO TO 5
  30  PS=S
      IF (NC.GT.2) GO TO 31
      S=1.10*S
      GO TO 5
  31  S=1.01*S
      GO TO 5
  40  WRITE (NO,200)
      WRITE (NO,201)
      WRITE (NO,202)
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      GO TO 41
   42 WRITE (NO,203) LOOP,S,PC,DP
      GO TO 43
   70 FLAG=2.0
      GO TO 99
   71 FLAG=5.0
      GO TO 99
   50 IF (S.LT.0.0) GO TO 71
      SL=S
      IF (ERZ.EQ.0.0) GO TO 51
      WRITE (NO,204) SL
   51 CALL FUGAS
   99 RETURN
      END
$IBFTC PARAMZ  DECK
      SUBROUTINE PARAM
C     SUBROUTINE TO CALCULATE THE MIXTURE PARAMETERS FOR THE B-W-R EQN
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),CG2,EGS
C
C     VARIABLES
C
C         Y(I,J)     VAPOR OF LIQUID PHASE COMPOSITION
C         X(I)       GROUP I B-W-R CONSTANT FOR THE MIXTURE
C                         I = 1      AO
C                         I = 2      BO
C                         I = 3      CO
C                         I = 4      GAMMA
C         Z(I)       BROUP II B-W-R CONSTANT FOR THE MIXTURE
C                         I = 1      A
C                         I = 2      B
C                         I = 3      C
C                         I = 4      ALPHA
C         XK(I,J)    PURE COMPONENT GROUP 2 B-W-R CONSTANT
C                         I = CONSTANT NUMBER
C                         J = COMPONENT NUMBER
C         ZK(I,J)    PURE COMPONENT GROUP II B-W-R CONSTANT
C                         I = CONSTANT NUMBER
C                         J = COMPONENT NUMBER
C
      NO=6
      Y1S=Y(INDX,1)*Y(INDX,1)
      Y2S=Y(INDX,2)*Y(INDX,2)
      IF (NCP.EQ.2) GO TO 10
      Y3S=Y(INDX,3)*Y(INDX,3)
   10 Y12=Y(INDX,1)*Y(INDX,2)
      IF (NCP.EQ.2) GO TO 11
      Y13=Y(INDX,1)*Y(INDX,3)
      Y23=Y(INDX,2)*Y(INDX,3)
   11 Y1C=Y1S*Y(INDX,1)
      Y2C=Y2S*Y(INDX,2)
      IF (NCP.EQ.2) GO TO 12
      Y3C=Y3S*Y(INDX,3)
   12 DO 95 I=1,4
      IF (I.EQ.2) GO TO 95
      XXX(I,1)=TX12(I)*SQRT(XK(I,1)*XK(I,2))
      X12=XXX(I,1)
      IF (NCP.EQ.2) GO TO 13
      XXX(I,2)=TX13(I)*SQRT(XK(I,1)*XK(I,3))
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      X13=XXX(I,2)
      XXX(I,3)=TX23(I)*SQRT(XK(I,2)*XK(I,3))
      X23=XXX(I,3)
   13 X(I)=Y1S*XK(I,1)+2.0*Y12*X12+Y2S*XK(I,2)
      IF (NCP.EQ.2) GO TO 95
      X(I)=X(I)+2.0*Y13*X13+2.0*Y23*X23+Y3S*XK(I,3)
   95 CONTINUE
      X(2)=Y(INDX,1)*XK(2,1)+Y(INDX,2)*XK(2,2)
      IF (NCP.EQ.2) GO TO 14
      X(2)=X(2)+Y(INDX,3)*XK(2,3)
   14 DO 96 I=1,4
      Z112=TZ112(I)*(ZK(I,1)*ZK(I,1)*ZK(I,2))**POW
      Z122=TZ122(I)*(ZK(I,1)*ZK(I,2)*ZK(I,2))**POW
      IF (NCP.EQ.2) GO TO 15
      Z113=TZ113(I)*(ZK(I,1)*ZK(I,1)*ZK(I,3))**POW
      Z133=TZ113(I)*(ZK(I,1)*ZK(I,3)*ZK(I,3))**POW
      Z223=TZ223(I)*(ZK(I,2)*ZK(I,2)*ZK(I,3))**POW
      Z233=TZ233(I)*(ZK(I,2)*ZK(I,3)*ZK(I,3))**POW
      Z123=TZ123(I)*(ZK(I,1)*ZK(I,2)*ZK(I,3))**POW
   15 Z(I)=Y1C*ZK(I,1)+3.0*Y1S*Y(INDX,2)*Z112+3.0*Y(INDX,1)*Y2S*Z122+Y2C
     1*ZK(I,2)
      IF (NCP.EQ.2) GO TO 96
      Z(I)=Z(I)+3.0*Y1S*Y(INDX,3)*Z113+6.0*Y(INDX,1)*Y(INDX,2)*Y(INDX,3)
     1*Z123+3.0*Y(INDX,1)*Y3S*Z133+3.0*Y2S*Y(INDX,3)*Z223+3.0*Y(INDX,2)*
     2Y3S*Z233+Y3C*ZK(I,3)
   96 CONTINUE
      RETURN
      END
$IBFTC FUGASZ  DECK
      SUBROUTINE FUGAS
C     SUBROUTINE TO CALCULATE THE LIQUID OR VAPOR FUGACITIES
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C
C
C     VARIABLES
C         INDX        PHASE IDENTIFICATION VARIABLE
C                         INDX = 1       VAPOR PHASE
C                         INDX = 2       LIQUID PHASE
C         SL          BUBBLE POINT DENSITY
C         SV          DEW POINT DENSITY
C         F(I,J)      VAPOR OR LIQUID PHASE FUGACITY OF COMPONENT  J
C                           I = 1     VAPOR PHASE
C                           I = 2     LIQUID PHASE
C
C
      NO=6
      IF (INDX.EQ.1) GO TO 10
      S=SL
      XYZ(2)=1.0/SL
      GO TO 11
   10 S=SV
      XYZ(1)=1.0/SV
   11 PGS=(-1.0)/GS2*(1.0-EGS)
      XT1=PGS-0.5*EGS
      XT2=PGS-EGS+GS2*EGS*0.5
      S3=S*S*S
      DO 99 K=1,NCP
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      IF (K.EQ.1) GO TO 16
      IF (K.EQ.2) GO TO 15
      ATM=Y(INDX,3)*XK(1,3)+Y(INDX,1)*XXX(1,1)+Y(INDX,2)*XXX(1,3)
      CTM=Y(INDX,3)*XK(3,3)+Y(INDX,1)*XXX(3,1)+Y(INDX,2)*XXX(3,3)
      GO TO 20
   15 ATM=Y(INDX,2)*XK(1,2)+Y(INDX,1)*XXX(1,1)
      CTM=Y(INDX,2)*XK(3,2)+Y(INDX,1)*XXX(3,1)
      IF (NCP.EQ.2) GO TO 20
      ATM=ATM+Y(INDX,3)*XXX(1,3)
      CTM=CTM+Y(INDX,3)*XXX(3,3)
      GO TO 20
   16 ATM=Y(INDX,1)*XK(1,1)+Y(INDX,2)*XXX(1,1)
      CTM=Y(INDX,1)*XK(3,1)+Y(INDX,2)*XXX(3,1)
      IF (NCP.EQ.3) GO TO 20
      ATM=ATM+Y(INDX,3)*XXX(1,2)
      CTM=CTM+Y(INDX,3)*XXX(3,2)
   20 XT3=3.0/T2*(Z(3)*Z(3)*ZK(3,K))**POW
      XT4=2.0/T2*Z(3)*SQRT(XK(4,K)/X(4))
      FTRM1=RT*(X(2)+XK(2,K))-2.0*(ATM+CTM/T2)
      FTRM2=RT*(Z(2)*Z(2)*ZK(2,K))**POW-(Z(1)*Z(1)*ZK(1,K))**POW
      FTRM3=Z(1)*(Z(4)*Z(4)*ZK(4,K))**POW+Z(4)*(Z(1)*Z(1)*ZK(1,K))**POW
      FTRM4=XT1*XT3
      FTRM5=XT2*XT4
      FAC=FTRM1+S*(1.5*FTRM2+FTRM4-FTRM5+0.6*FTRM3*S3)
      F(INDX,K)=RT*S*EXP(S/RT*FAC)*Y(INDX,K)
   99 CONTINUE
      RETURN
      END
$IBFTC KVALZ   DECK
      SUBROUTINE KVAL
C     SUBROUTINE TO CALCULATE THE EQUILIBRIUM RATIOS
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
C     VARIABLES
C
C        EK(K)      EQUILIBRIUM RATIO FOR COMPONENT  K
C
      NO=6
      DO 95 K=1,NCP
   95 EK(K)=(F(2,K)*Y(1,K))/(F(1,K)*Y(2,K))
   99 RETURN
      END
$IBFTC PRINTZ  DECK
      SUBROUTINE PRINT
C     SUBROUTINE TO PRINT OUT THE RESULTS OF THE CALCULATIONS
C
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
  200 FORMAT (2H1 ,//,43H B-W-R VAPOR-LIQUID EQUILIBRIUM CALCULATION,///
     1)
  201 FORMAT (35X,4H T =,F10.3,6H DEG R)
  202 FORMAT (35X,4H P =,F10.3,5H PSIA,///)
  203 FORMAT (4X,12H VAPOR PHASE,41X,13H LIQUID PHASE,//)
  204 FORMAT (9X,12H COMPOSITION,42X,12H COMPOSITION,/)
```

```
  205 FORMAT (12X,7H Y(1) =,F10.6,37X,7H X(1) =,F10.6)
  206 FORMAT (12X,7H Y(2) =,F10.6,37X,7H X(2) =,F10.6)
  207 FORMAT (12X,7H Y(3) =,F10.6,37X,7H X(3) =,F10.6)
  208 FORMAT (//,9X,11H FUGACITIES,43X,11H FUGACITIES,/)
  209 FORMAT (12X,7H F(1) =,E12.5,34X,7H F(1) =,E12.5)
  210 FORMAT (12X,7H F(2) =,E12.5,34X,7H F(2) =,E12.5)
  211 FORMAT (12X,7H F(3) =,E12.5,34X,7H F(3) =,E12.5)
  212 FORMAT (///,35X,19H EQUILIBRIUM RATIOS,/)
  213 FORMAT (39X,7H K(1) =,F10.6)
  214 FORMAT (39X,7H K(2) =,F10.6)
  215 FORMAT (39X,7H K(3) =,F10.6)
  216 FORMAT (9X,7H VOLUME,47X,7H VOLUME,/)
  217 FORMAT (12X,4H V =,F10.5,40X,4H V =,F10.5,//)
  500 FORMAT (///,10X,11H ERROR*****,//)
  501 FORMAT (15X,34H DEW POINT VOLUME DID NOT CONVERGE)
  502 FORMAT (15X,37H BUBBLE POINT VOLUME DID NOT CONVERGE)
  503 FORMAT (15X,27H TOTAL ITERATIONS EXCEED 25)
  504 FORMAT (15X,36H DEW POINT DENSITY IS LESS THAN ZERO)
  505 FORMAT (15X,39H BUBBLE POINT DENSITY IS LESS THAN ZERO)
  506 FORMAT (15X,27H INVALID LIQUID COMPOSITION)
  507 FORMAT (15X,26H INVLAID VAPOR COMPOSITION)
C
C
      NO=6
      WRITE (NO,200)
      WRITE (NO,201) T
      WRITE (NO,202) P
      IF (FLAG.NE.10.0) GO TO 70
      WRITE (NO,203)
      WRITE (NO,216)
      WRITE (NO,217) XYZ(1),XYZ(2)
      WRITE (NO,204)
      WRITE (NO,205) Y(1,1),Y(2,1)
      WRITE (NO,206) Y(1,2),Y(2,2)
      IF (NCP.EQ.2) GO TO 10
      WRITE (NO,207) Y(1,3),Y(2,3)
   10 WRITE (NO,208)
      WRITE (NO,209) F(1,1),F(2,1)
      WRITE (NO,210) F(1,2),F(2,2)
      IF (NCP.EQ.2) GO TO 11
      WRITE (NO,211) F(1,3),F(2,3)
   11 WRITE (NO,212)
      WRITE (NO,213) EK(1)
      WRITE (NO,214) EK(2)
      IF (NCP.EQ.2) GO TO 90
      WRITE (NO,215) EK(3)
      GO TO 90
   70 IF (FLAG.GT.1.0) GO TO 71
      WRITE (NO,500)
      WRITE (NO,501)
      GO TO 90
   71 IF (FLAG.GT.2.0) GO TO 72
      WRITE (NO,500)
      WRITE (NO,502)
   72 IF (FLAG.GT.3.0) GO TO 73
      WRITE (NO,500)
      WRITE (NO,503)
      GO TO 90
   73 IF (FLAG.GT.4.0) GO TO 74
      WRITE (NO,500)
      WRITE (NO,504)
      GO TO 90
   74 IF (FLAG.GT.5.0) GO TO 75
```

```
      WRITE (NO,500)
      WRITE (NO,505)
      GO TO 90
   75 IF (FLAG.GT.6.0) GO TO 76
      WRITE (NO,500)
      WRITE (NO,506)
      GO TO 90
   76 WRITE (NO,500)
      WRITE (NO,507)
   90 RETURN
      END
$IBFTC DATAZ   DECK
      SUBROUTINE DATA
C     SUBROUTINE TO READ IN THE DATA
C
      DIMENSION AB(20)
      COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
     1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
     2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
     3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
     4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
  100 FORMAT (20A4)
  101 FORMAT (2I3,F10.3)
  102 FORMAT (3F10.3)
  103 FORMAT (7F10.3)
  104 FORMAT (5F10.3)
  105 FORMAT (7F10.3)
  106 FORMAT (I3,18A4)
  200 FORMAT (2H1 ,//,2X,20A4,//)
  201 FORMAT (4X,18H SYSTEM COMPONENTS,/)
  202 FORMAT (7X,I2,2X,10A4)
  203 FORMAT (///,4X,23H INTERACTION PARAMETERS,//)
  204 FORMAT (20X,3H A0,7X,3H B0,7X,3H C0,5X,6H GAMMA,11X,2H A,8X,2H B,8
     1X,2H C,6X,6H ALPHA,/)
  205 FORMAT (9X,4H X12,5X,F6.3,3(4X,F6.3))
  206 FORMAT (9X,5H Z112,48X,F6.3,3(4X,F6.3))
  207 FORMAT (9X,5H Z122,48X,F6.3,3(4X,F6.3))
  208 FORMAT (9X,4H X13,5X,F6.3,3(4X,F6.3))
  209 FORMAT (9X,4H X23,5X,F6.3,3(4X,F6.3))
  210 FORMAT (9X,5H Z113,48X,F6.3,3(4X,F6.3))
  211 FORMAT (9X,5H Z133,48X,F6.3,3(4X,F6.3))
  212 FORMAT (9X,5H Z223,48X,F6.3,3(4X,F6.3))
  213 FORMAT (9X,5H Z233,48X,F6.3,3(4X,F6.3))
  214 FORMAT (9X,5H Z123,48X,F6.3,3(4X,F6.3))
C
C     VARIABLES
C        NCP        NUMBER OF COMPONENTS IN THE MIXTURE
C        NDP        NUMBER OF DATA POINTS TO BE CALCULATED
C        ERZ        INTERMEDIATE CALCULATION VARIABLE
C              ERZ=0.0    NO INTERMEDIATE PRINT OUT OF CALCULATIONS
C              ERZ=2.0       INTERMEDIATE PRINT OUT OF CALCULATIONS
C        NOC(I)     COMPONENT REFERENCE NUMBER
C        TT(I)      TEMPERATURE SPECIFIED IN CALCULATION  I
C        PP(I)      PRESSURE SPECIFIED IN CALCULATION  I
C        EKI(I,J)   INITIAL ESTIMATE OF THE EQUILIBRIUM RATIO FOR COMPONENT J IN
C                   DATA CASE  I
C        SIGMA(I)   INITIAL ESTIMATE OF THE BUBBLE POINT DENSITY
C
C
      IN=5
      NO=6
C
```

```
C       PROGRAM IDENTIFICATION
        READ (IN,100) (AB(J),J=1,20)
        WRITE (NO,200) (AB(J),J=1,20)
C
C       PROGRAM CONTROL VARIABLES
        READ (IN,101) NCP,NDP,ERZ
        WRITE (NO,201)
C
C       COMPONENT NUMBER AND IDENTIFICATION
        DO 99 I=1,NCP
        READ (IN,106) NOC(I),(AB(J),J=1,18)
   99   WRITE (NO,202) I,(AB(J),J=1,10)
        WRITE (NO,203)
        WRITE (NO,204)
        IF (NCP.EQ.3) GO TO 10
C
C       INTERACTION PARAMETERS FOR BINARY MIXTURES
        DO 98 I=1,4
   98   READ (IN,102) TX12(I),TZ112(I),TZ122(I)
        WRITE (NO,205) (TX12(I),I=1,4)
        WRITE (NO,206) (TZ112(I),I=1,4)
        WRITE (NO,207) (TZ122(I),I=1,4)
        GO TO 50
C
C       INTERACTION PARAMETERS FOR TERNARY MIXTURES
   10   DO 97 I=1,4
   97   READ (IN,102) TX12(I),TX13(I),TX23(I)
        WRITE (NO,205) (TX12(I),I=1,4)
        WRITE (NO,208) (TX13(I),I=1,4)
        WRITE (NO,209) (TX23(I),I=1,4)
        DO 96 I=1,4
   96   READ (IN,103) TZ112(I),TZ122(I),TZ113(I),TZ133(I),TZ223(I),TZ233(I
       1),TZ123(I)
        WRITE (NO,206) (TZ112(I),I=1,4)
        WRITE (NO,207) (TZ122(I),I=1,4)
        WRITE (NO,210) (TZ113(I),I=1,4)
        WRITE (NO,211) (TZ133(I),I=1,4)
        WRITE (NO,212) (TZ223(I),I=1,4)
        WRITE (NO,213) (TZ233(I),I=1,4)
        WRITE (NO,214) (TZ123(I),I=1,4)
        IF (NCP.EQ.3) GO TO 11
C
C       DATA FOR V-L E CALCULATION
   50   DO 95 I=1,NDP
   95   READ (IN,104) TT(I),PP(I),EKI(I,1),EKI(I,2),SIGMA(I)
        GO TO 51
   11   DO 94 I=1,NDP
   94   READ (IN,105) TT(I),PP(I),YY(I),EKI(I,1),EKI(I,2),EKI(I,3),SIGMA(I
       1)
   51   CALL CONST
        RETURN
        END
$IBFTC CONSTZ  DECK
        SUBROUTINE CONST
C       SUBROUTINE TO PROVIDE VALUES OF THE B-W-R EQN CONSTANTS
C
        COMMON NDP,NC,NCP,INDX,II,LOX,KOX,NOC(25),R,P,T,T2,RT,POW,SV,SL,PR
       1T,ERZ,FLAG,TT(90),PP(90),YY(90),SIGMA(90),DSPI(90),ABC(90),XYZ(90)
       2,EK(3),TX12(4),TX13(4),TX23(4),X(4),Z(4),TZ112(4),TZ122(4),TZ113(4
       3),TZ133(4),TZ223(4),TZ233(4),TZ123(4),Y(2,3),F(2,3),EKI(90,3),XK(4
       4,3),ZK(4,3),XXX(4,4),YYY(5,5),GS2,EGS
C
        NO=6
```

```
      DO 99 J=1,NCP
      NCO=NOC(J)
      GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13),NCO
C     METHANE
    1 XK(1,J)=+.699525E+04
      XK(2,J)=+.682401E+00
      XK(3,J)=+.275763E+09
      XK(4,J)=+.153961E+01
      ZK(1,J)=+.298412E+04
      ZK(2,J)=+.867325E+00
      ZK(3,J)=+.498106E+09
      ZK(4,J)=+.511172E+00
      GO TO 99
C     ETHYLENE
    2 XK(1,J)=+.125936E+05
      XK(2,J)=+.891980E+00
      XK(3,J)=+.160228E+10
      XK(4,J)=+.236844E+01
      ZK(1,J)=+.156455E+05
      ZK(2,J)=+.220678E+01
      ZK(3,J)=+.413360E+10
      ZK(4,J)=+.731661E+00
      GO TO 99
C     ETHANE
    3 XK(1,J)=+.156707E+05
      XK(2,J)=+.100554E+01
      XK(3,J)=+.219427E+10
      XK(4,J)=+.302790E+01
      ZK(1,J)=+.208502E+05
      ZK(2,J)=+.285393E+01
      ZK(3,J)=+.641314E+10
      ZK(4,J)=+.100044E+01
      GO TO 99
C     PROPYLENE
    4 XK(1,J)=+.230492E+05
      XK(2,J)=+.136263E+01
      XK(3,J)=+.536597E+10
      XK(4,J)=+.469325E+01
      ZK(1,J)=+.467586E+05
      ZK(2,J)=+.479997E+01
      ZK(3,J)=+.200830E+11
      ZK(4,J)=+.187312E+01
      GO TO 99
C     PROPANE
    5 XK(1,J)=+.259154E+05
      XK(2,J)=+.155884E+01
      XK(3,J)=+.620993E+10
      XK(4,J)=+.564524E+01
      ZK(1,J)=+.572480E+05
      ZK(2,J)=+.577355E+01
      ZK(3,J)=+.252478E+11
      ZK(4,J)=+.249577E+01
      GO TO 99
C     I-BUTANE
    6 XK(1,J)=+.385874E+05
      XK(2,J)=+.220329E+01
      XK(3,J)=+.103847E+11
      XK(4,J)=+.872447E+01
      ZK(1,J)=+.117047E+06
      ZK(2,J)=+.108890E+02
      ZK(3,J)=+.559777E+11
      ZK(4,J)=+.441496E+01
      GO TO 99
```

```
C     I-BUTYLENE
    7 XK(1,J)=+.337629E+05
      XK(2,J)=+.185858E+01
      XK(3,J)=+.113296E+11
      XK(4,J)=+.759401E+01
      ZK(1,J)=+.102251E+06
      ZK(2,J)=+.893375E+01
      ZK(3,J)=+.538072E+11
      ZK(4,J)=+.374417E+01
      GO TO 99
C     N-BUTANE
    8 XK(1,J)=+.380296E+05
      XK(2,J)=+.199211E+01
      XK(3,J)=+.121305E+11
      XK(4,J)=+.872447E+01
      ZK(1,J)=+.113705E+06
      ZK(2,J)=+.102636E+02
      ZK(3,J)=+.619256E+11
      ZK(4,J)=+.452693E+01
      GO TO 99
C     I-PENTANE
    9 XK(1,J)=+.482536E+04
      XK(2,J)=+.256386E+01
      XK(3,J)=+.213367E+11
      XK(4,J)=+.118807E+02
      ZK(1,J)=+.226902E+06
      ZK(2,J)=+.171441E+02
      ZK(3,J)=+.136025E+12
      ZK(4,J)=+.698777E+01
      GO TO 99
C     N-PENTANE
   10 XK(1,J)=+.459288E+05
      XK(2,J)=+.251096E+01
      XK(3,J)=+.259172E+11
      XK(4,J)=+.121886E+02
      ZK(1,J)=+.246148E+06
      ZK(2,J)=+.171441E+02
      ZK(3,J)=+.161306E+12
      ZK(4,J)=+.743992E+01
      GO TO 99
C     N-HEXANE
   11 XK(1,J)=+.544340E+04
      XK(2,J)=+.284835E+01
      XK(3,J)=+.405562E+11
      XK(4,J)=+.171115E+02
      ZK(1,J)=+.429901E+06
      ZK(2,J)=+.280032E+02
      ZK(3,J)=+.296077E+12
      ZK(4,J)=+.115539E+02
      GO TO 99
C     N-HEPTANE
   12 XK(1,J)=+.660706E+05
      XK(2,J)=+.318782E+01
      XK(3,J)=+.579840E+11
      XK(4,J)=+.230942E+02
      ZK(1,J)=+.626106E+06
      ZK(2,J)=+.389917E+02
      ZK(3,J)=+.483427E+12
      ZK(4,J)=+.179056E+02
      GO TO 99
C     BENZENE
   13 XK(1,J)=+.245485E+05
      XK(2,J)=+.805756E+00
```

```
      XK(3,J)=+.419076E+11
      XK(4,J)=+.751845E+01
      ZK(1,J)=+.336469E+06
      ZK(2,J)=+.196634E+02
      ZK(3,J)=+.230248E+12
      ZK(4,J)=+.287773E+01
   99 CONTINUE
      RETURN
      END
VLE CALCULATIONS         C2/NC5 SYSTEM             B-W-R EQN OF STATE
  2 54    0.0
  3  ETHANE
 10  N-PENTANE
0.987       1.00        1.00
1.00        1.00        1.00
1.00        1.00        1.00
1.00        1.00        1.00
499.69      100.0       3.290       0.0698      0.670
499.69      150.0       2.238       0.0600      0.670
499.69      200.0       1.725       0.0546      0.700
499.69      250.0       1.416       0.0531      0.750
499.69      300.0       1.216       0.0533      0.800
499.69      350.0       1.078       0.0523      0.800
499.69      360.0       1.050       0.0518      0.800
499.69      370.0       1.030       0.0513      0.800
559.69      100.0       5.560       0.1830      0.570
559.69      200.0       2.854       0.1274      0.600
559.69      300.0       1.967       0.1169      0.670
559.69      400.0       1.535       0.1195      0.670
559.69      500.0       1.296       0.1290      0.670
559.69      600.0       1.150       0.1456      0.680
559.69      700.0       1.062       0.2011      0.600
559.69      725.0       1.040       0.2500      0.600
559.69      735.0       1.030       0.5000      0.600
559.69      750.0       1.010       0.9000      0.500
619.69      200.0       4.050       0.2849      0.550
619.69      300.0       2.814       0.2293      0.570
619.69      400.0       2.185       0.2127      0.570
619.69      500.0       1.803       0.2150      0.570
619.69      600.0       1.556       0.2307      0.580
619.69      700.0       1.382       0.2657      0.600
619.69      800.0       1.247       0.3327      0.600
619.69      900.0       1.110       0.5538      0.510
619.69      910.0       1.075       0.7500      0.505
619.69      915.0       1.050       0.9500      0.505
679.69      200.0       5.090       0.5722      0.480
679.69      300.0       3.540       0.4439      0.500
679.69      400.0       2.733       0.3815      0.500
679.69      500.0       2.234       0.3560      0.500
679.69      600.0       1.895       0.3548      0.500
679.69      700.0       1.630       0.3907      0.500
679.69      800.0       1.440       0.4469      0.500
679.69      900.0       1.277       0.5401      0.490
679.69      950.0       1.175       0.7000      0.490
679.69      975.0       1.075       0.8850      0.420
729.69      200.0       5.730       0.9600      0.425
729.69      300.0       3.970       0.7346      0.420
729.69      400.0       3.030       0.6254      0.430
729.69      500.0       2.459       0.5893      0.430
729.69      600.0       2.067       0.5464      0.450
729.69      700.0       1.782       0.5922      0.450
729.69      800.0       1.546       0.6379      0.460
729.69      900.0       1.306       0.7288      0.425
```

| | | | | |
|---|---|---|---|---|
| 729.69 | 925.0 | 1.200 | 0.8500 | 0.425 |
| 729.69 | 935.0 | 1.100 | 0.6250 | 0.425 |
| 789.69 | 400.0 | 2.825 | 0.9138 | 0.350 |
| 789.69 | 500.0 | 2.522 | 0.8186 | 0.333 |
| 789.69 | 600.0 | 2.054 | 0.7983 | 0.325 |
| 789.69 | 700.0 | 1.516 | 0.8532 | 0.300 |
| 789.69 | 725.0 | 1.250 | 0.9000 | 0.300 |
| 789.69 | 735.0 | 1.100 | 0.9500 | 0.300 |

# VITA

Robert Ray Spear

Candidate for the Degree of

Docter of Philosophy

Thesis: AN EQUATION OF STATE APPROACH TO THE PREDICTION OF CRITICAL STATES OF MIXTURES

Major Field: Chemical Engineering

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Education: Attended elementary and high school in Pueblo, Colorado and graduated from Central High School in June, 1960; graduated from Pueblo Junior College in June, 1962; received a Bachelor of Science degree in chemical engineering from the University of Colorado in June, 1964; received a Master of Science degree in chemical engineering from Oklahoma State University in May, 1966; completed requirements for Doctor of Philosophy in chemical engineering from Oklahoma State University in August, 1969. Membership in scholarly or professional societies included Phi Theta Kappa, A.I.Ch.E., and Omega Chi Epsilon.

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