A STUDY OF MODIFICATIONS TO THE BENEDICT-WEBB-RUBIN EQUATION OF STATE - EXTENSION TO LOW TEMPERATURES AND APPLICATIONS TO BINARY MIXTURES

By

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A STUDY OF MODIFICATIONS TO THE BENEDICT-WEBB-RUBIN EQUATION OF STATE - EXTENSION TO LOW TEMPERATURES AND APPLICATIONS TO BINARY MIXTURES

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PREFACE

A study of several promising modifications to the Benedict-Webb-Rubin equation of state was made. The equation was modified to improve predicted saturated phase properties of methane at low temperatures. Experimental vapor pressures and saturated liquid densities were used to calculate two BWR parameters, simultaneously, as linear functions of reciprocal temperature. Also, two parameters were simultaneously determined as functions of reciprocal temperature based only on experimental vapor pressures.

BWR parameters giving exact fit to critical point conditions were determined from volumetric properties for the pure components methane and hydrogen sulfide. Finally, pure component BWR parameters determined in this study were used with a modified mixing rule for the parameter A_o to make vapor-liquid equilibria calculations for methane-hydrogen sulfide mixtures.

I wish to express my thanks and appreciation to my adviser, Dr. R. L. Robinson, Jr., for his guidance and encouragement throughout the course of this study. I am indebted to Mr. Charles J. Mundis for his aid in certain areas of this investigation and to all fellow graduate students from whom I received assistance. Finally, I am deeply grateful to my parents for their constant encouragement during my work.

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CHAPTER I

INTRODUCTION

A very general method for calculating the thermodynamic properties of pure components and their mixtures is by means of equations of state. The equation of state is an analytic expression that relates pressure, temperature, molar volume, and composition. Since thermodynamic properties are functions of state, an equation of state represents an analytic tool from which these properties may be derived. Many equations of state have been proposed, but of the most widely used equations, none can reproduce experimental data over a wide range of pressure and temperature as well as the Benedict-Webb-Rubin (BWR) equation.

The BWR equation of state is an empirical equation, specifically formulated to describe the volumetric and phase behavior of hydrocarbons and their mixtures for reduced temperatures exceeding 0.6. The equation has proven to be accurate at densities up to twice the critical density.

Low temperature applications of the BWR equation have been a subject of much concern. The original equation is limited to temperatures above about 0.6 of the critical temperature. Below reduced temperatures of 0.6, predicted vapor pressures deviate considerably from experimental values. However, the equation can be improved by adjusting one or more of the coefficients with temperature.

Another shortcoming of the BWR equation that has attracted much interest is its inability to accurately predict vapor-liquid equilibria for mixtures containing wide boiling range hydrocarbons or mixtures of hydrocarbons and non-hydrocarbons. To improve equilibrium calculations for mixtures, an empirical interaction constant can be introduced into the mixing rule of the parameter A_o.

One purpose of this investigation was to develop BWR parameters such that the equation could be extrapolated to low temperatures without introducing serious error. Another goal was to develop a technique for determining BWR parameters that can be used to accurately predict p-v-T properties and also fit the critical point. The final objective of this study was to apply improved pure component parameters to mixtures in order to test the mixture rules and to improve them if necessary.

The particular system chosen for test applications was the methane-hydrogen sulfide system. The methane-hydrogen sulfide system presents a rigorous test since molecules of the two compounds are not alike. Also, methane-hydrogen sulfide mixtures occur in many industrial processes.

CHAPTER II

REVIEW OF PREVIOUS WORK

Since its development, the Benedict-Webb-Rubin equation (4, 5) has been the object of some very extensive studies. A complete review of all previous work would be too lengthy to present here. Therefore, only a few selected references to reviews of studies done on the BWR equation will be given.

The equation was originally developed to represent thermodynamic properties of light hydrocarbons and their mixtures. The authors recommended the equation for use at reduced temperatures greater than 0.6 and reduced densities less than 2.0. However, the equation has since been applied to a wider range of pure components and mixtures. Properties of some non-hydrocarbons and mixtures of hydrocarbons and non-hydrocarbons have been calculated with the BWR equation. Also, the equation has been used to calculate properties for mixtures containing hydrocarbons as heavy as $C_{22}H_{46}$ (26). Comprehensive reviews of applications and extensions of the BWR equation are presented by Barner and Adler (2), Ellington (14), and Starling (27). Cooper and Goldfrank (9) recently compiled BWR coefficients for thirty-eight compounds and gave reference to their origin.

In order to improve the BWR equation at low temperatures, previous investigators have adjusted a single parameter with temperature. Most workers chose to adjust C_o (3, 6, 7, 18, 28, 32) while some modified γ

(3, 21, 25). Simultaneously using both p-v-T and enthalpy data for methane, Cox (10) modified C_o and 'a' to be linear functions of reciprocal temperature.

Stotler and Benedict (28) suggested modification of the mixing rule of A_o to improve vapor-liquid equilibria calculations for binary mixtures. Several investigators (17, 30, 31) have since applied an empirical interaction coefficient to the mixing rule of A_o for various mixtures, especially those containing non-hydrocarbons.

CHAPTER III

PRELIMINARY INVESTIGATIONS

Several preliminary studies were made in an attempt to determine which of the eight BWR parameters had the greatest effect on various properties. The effects of each parameter on pressure, liquid and vapor fugacity, and vapor pressure of methane were investigated. These investigations helped to provide a basis for modification of the BWR equation.

Sensitivity of Pressure to Each BWR Parameter

The effect of each parameter on the predicted pressure was determined for reduced densities in the range of 0.4 to 3.0 and reduced temperatures from 0.6 to 3.0. The measure of sensitivity used was the change in pressure per one per cent change in the parameter being considered, expressed as

$$\text{pressure sensitivity} = k_i \left(\frac{\partial p}{\partial k_i} \right)_{T,\rho}$$

where k_i is the parameter being considered; P, pressure; T, temperature; and ρ is the density. Expressions for $(\partial P/\partial k_i)_{T,\rho}$ were derived from the Benedict-Webb-Rubin equation (4), given as

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

$$+ a\alpha\rho^6 + (\frac{c\rho^3}{T^2})(1 + \gamma\rho^2) \exp(-\gamma\rho^2) \qquad (3\text{-}1)$$

where R is the gas constant and B_o, A_o, C_o, b, a, α , c, and γ are the "BWR constants". The resulting equations for sensitivities are

$$B_o\left(\frac{\partial P}{\partial B_o}\right) = B_o RT\rho^2 \qquad (3\text{-}2)$$

$$A_o\left(\frac{\partial P}{\partial A_o}\right) = -A_o\rho^2 \qquad (3\text{-}3)$$

$$C_o\left(\frac{\partial P}{\partial C_o}\right) = -\frac{C_o\rho^2}{T^2} \qquad (3\text{-}4)$$

$$b\left(\frac{\partial P}{\partial b}\right) = bRT\rho^3 \qquad (3\text{-}5)$$

$$a\left(\frac{\partial P}{\partial a}\right) = a(-\rho^3 + \alpha\rho^6) \qquad (3\text{-}6)$$

$$\alpha\left(\frac{\partial P}{\partial \alpha}\right) = a\alpha\rho^6 \qquad (3\text{-}7)$$

$$c\left(\frac{\partial P}{\partial c}\right) = \left(\frac{c\rho^3}{T^2}\right)(1 + \gamma\rho^2)\ \exp\ (-\gamma\rho^2) \qquad (3\text{-}8)$$

$$\gamma\left(\frac{\partial P}{\partial \gamma}\right) = -\left(\frac{\gamma^2 c\rho^7}{T^2}\right)\exp\ (-\gamma\rho^2) \qquad (3\text{-}9)$$

In order to determine which of the parameters had the greatest effect, A_o was used as a basis for comparison. That is, the ratio of the pressure sensitivity to k_i to the sensitivity to A_o was calculated. As a reference to the absolute sensitivity of pressure to each parameter, a plot of the absolute sensitivity of pressure to A_o is shown in Figure 1. The general form of the relative sensitivity is

$$\frac{k_i\left(\frac{\partial P}{\partial k_i}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{k_i}{A_o}\left(\frac{\partial A_o}{\partial k_i}\right)$$

The above ratio can be described as the per cent change in A_o required to compensate for a one per cent change in k_i to keep the calculated pressure unchanged. The equations used to calculate relative sensitivities are

$$\frac{B_o\left(\frac{\partial P}{\partial B_o}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = -\frac{B_oRT}{A_o} \tag{3-10}$$

$$\frac{A_o\left(\frac{\partial P}{\partial A_o}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = 1 \tag{3-11}$$

$$\frac{C_o\left(\frac{\partial P}{\partial C_o}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{C_o}{A_oT^2} \tag{3-12}$$

$$\frac{b\left(\frac{\partial P}{\partial b}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{-bRT\rho}{A_o} \tag{3-13}$$

$$\frac{a\left(\frac{\partial P}{\partial a}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{a\rho}{A_o}\,(1-\alpha\rho^3) \tag{3-14}$$

$$\frac{\alpha\left(\frac{\partial P}{\partial \alpha}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = -\frac{a\alpha\rho^4}{A_o} \tag{3-15}$$

$$\frac{c\left(\frac{\partial P}{\partial c}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{c\rho+c\gamma\rho^3}{A_oT^2\exp(\gamma\rho^2)} \tag{3-16}$$

$$\frac{\gamma\left(\frac{\partial P}{\partial \gamma}\right)}{A_o\left(\frac{\partial P}{\partial A_o}\right)} = \frac{\gamma^2 c \rho^5}{A_o T^2 \exp(\gamma\rho^2)} \tag{3-17}$$

The results of the relative pressure sensitivities are shown in Figures 2-8. Comparisons of these figures show which parameters have the greatest effect on pressure. Over the range of reduced temperatures and reduced densities studied, the parameters A_o, b, and α proved to be the most significant. Figure 9 shows the regions in which each of these parameters had the greatest effect on pressure.

This preliminary investigation of effects on pressure indicated that A_o, b, and α may be best suited for modification to predict pressures since the equation is most sensitive to changes in these parameters. However, Benedict (4) stated that the equation is not suitable for use at densities above twice the critical density. In the range of densities less than twice the critical, only A_o and b are most significant, with A_o being most important over most of this region.

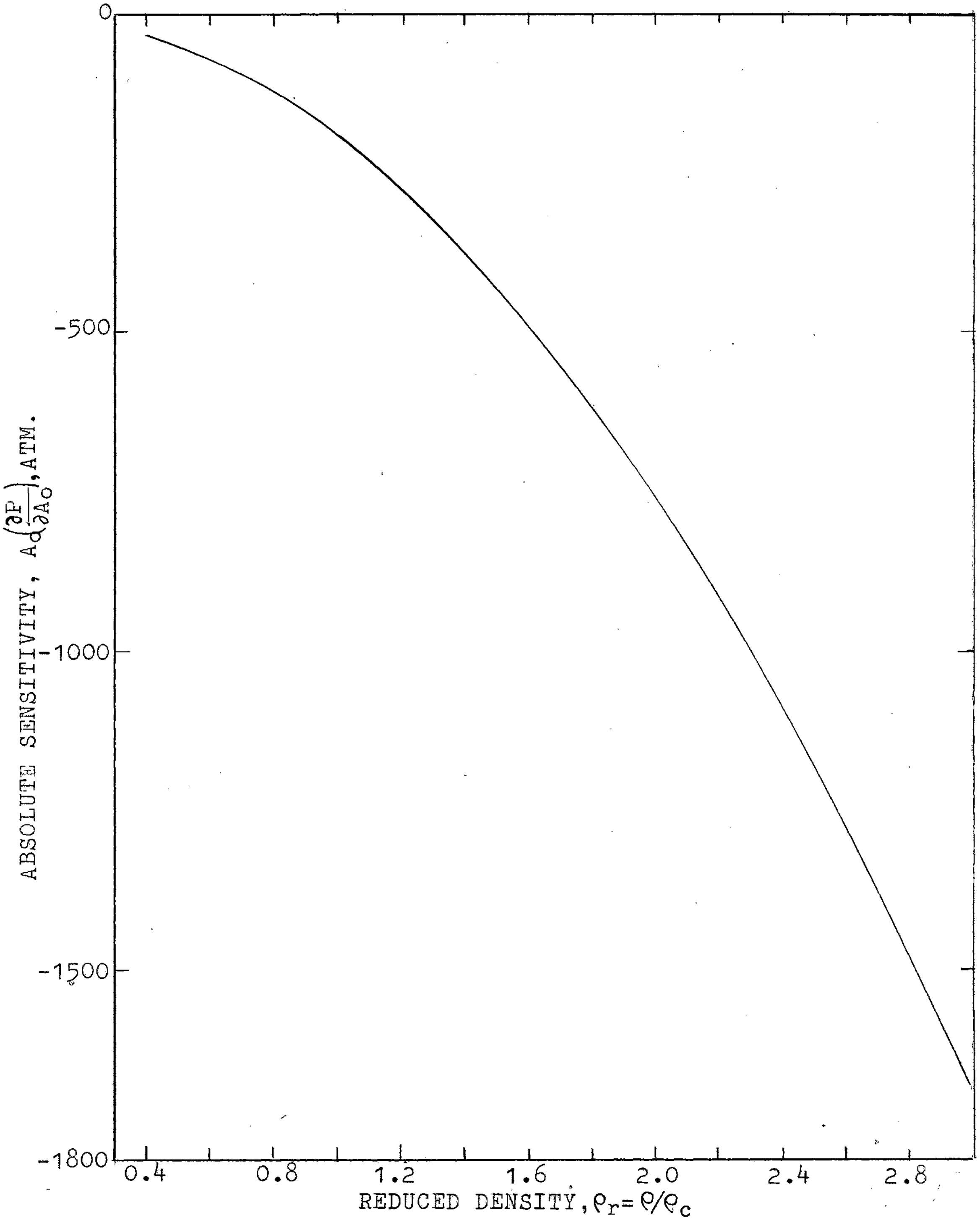


Figure 1. Absolute Sensitivity Of Pressure To A_o

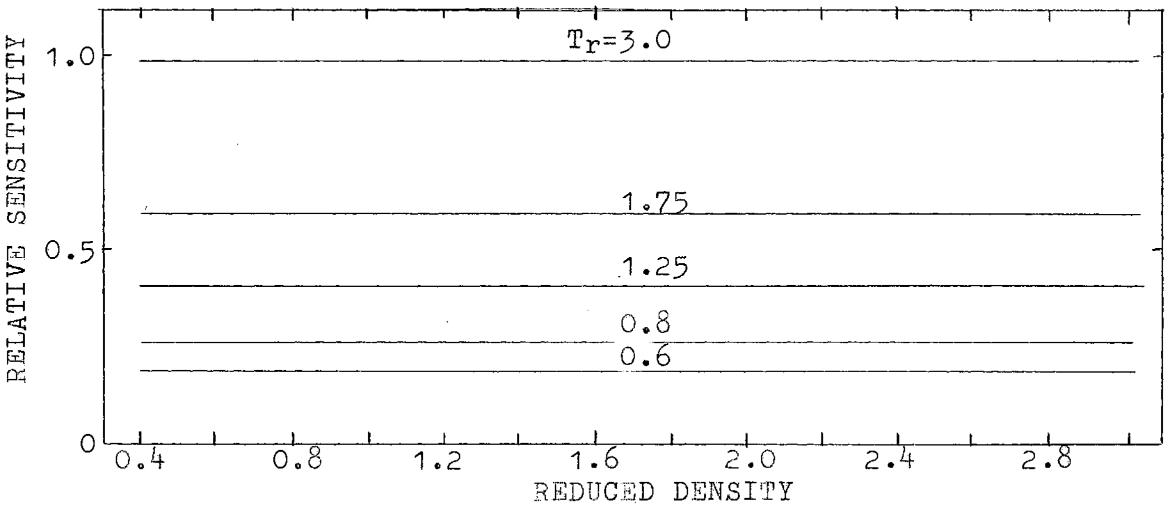


Figure 2. Relative Sensitivity Of Pressure To B_o

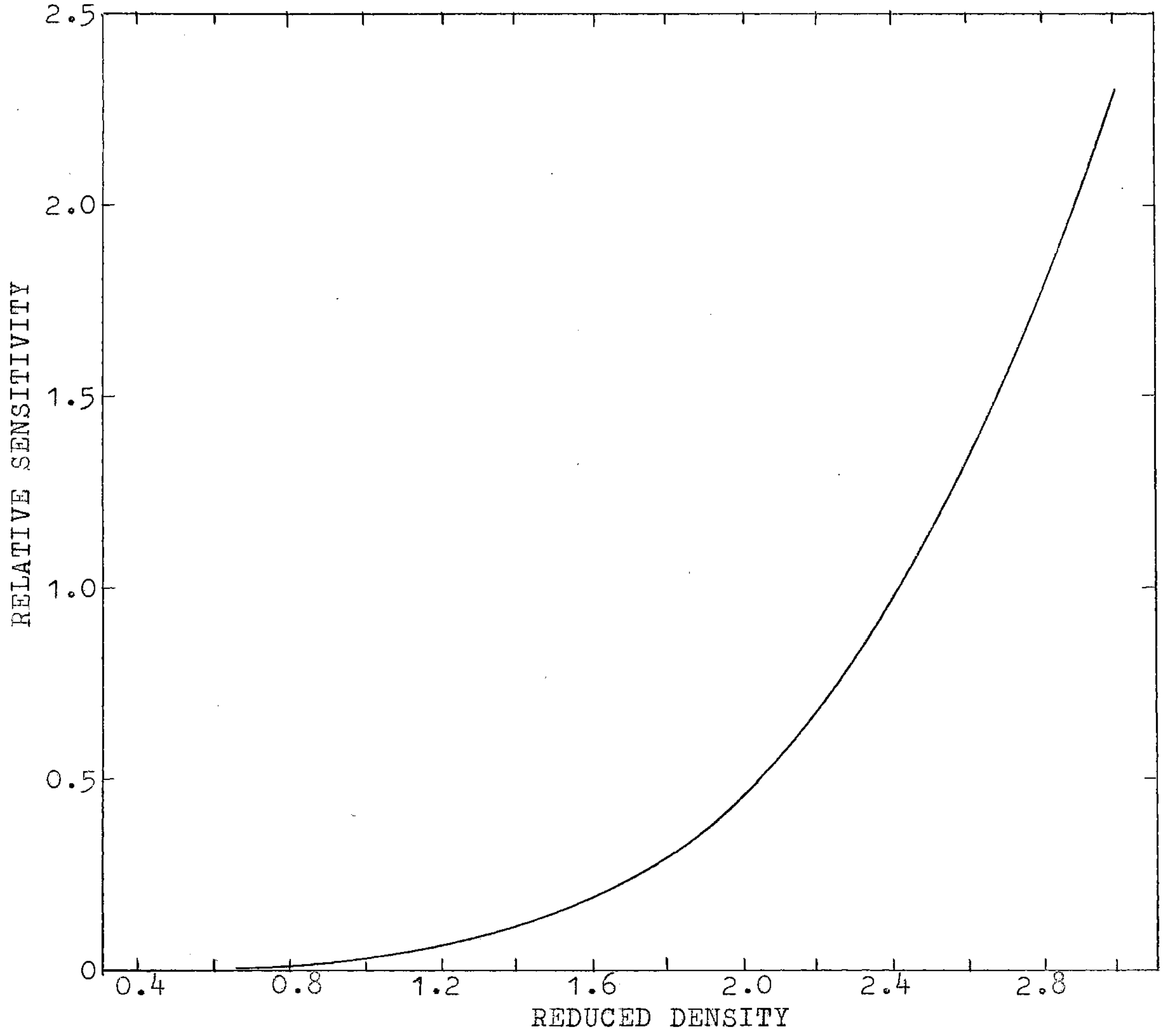


Figure 3. Relative Sensitivity Of Pressure To α

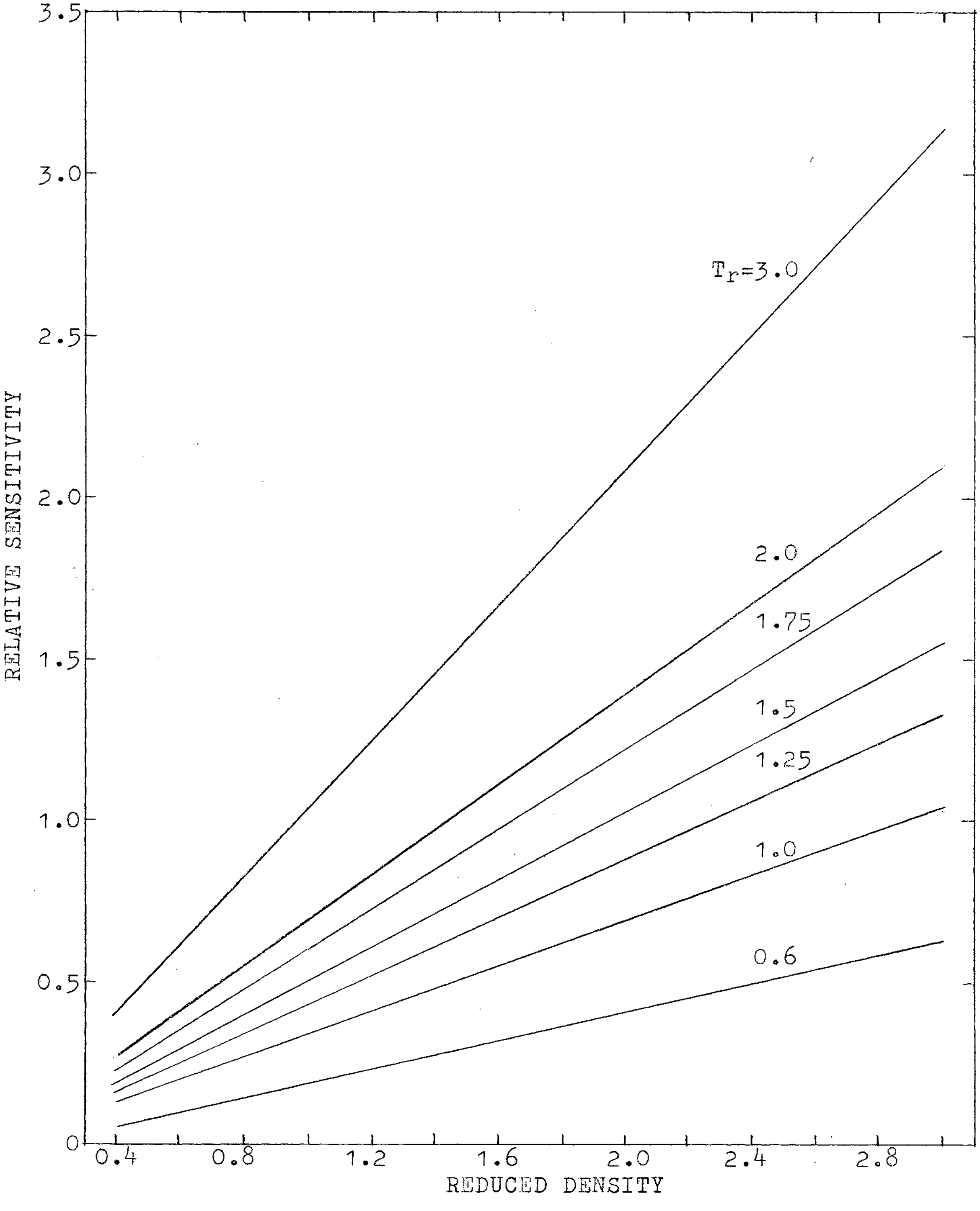


Figure 4. Relative Sensitivity Of Pressure To b

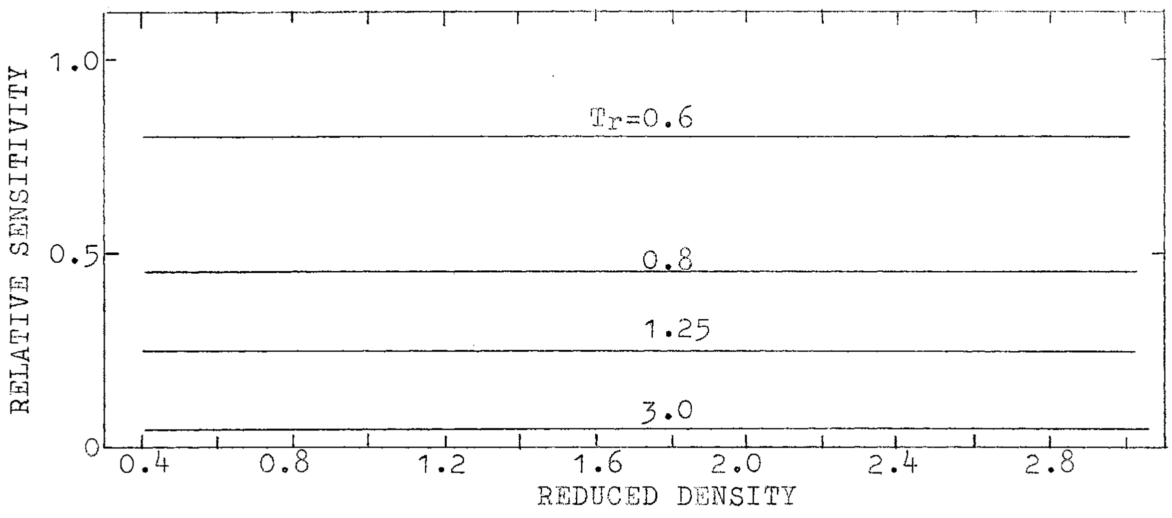


Figure 5. Relative Sensitivity Of Pressure To C_o

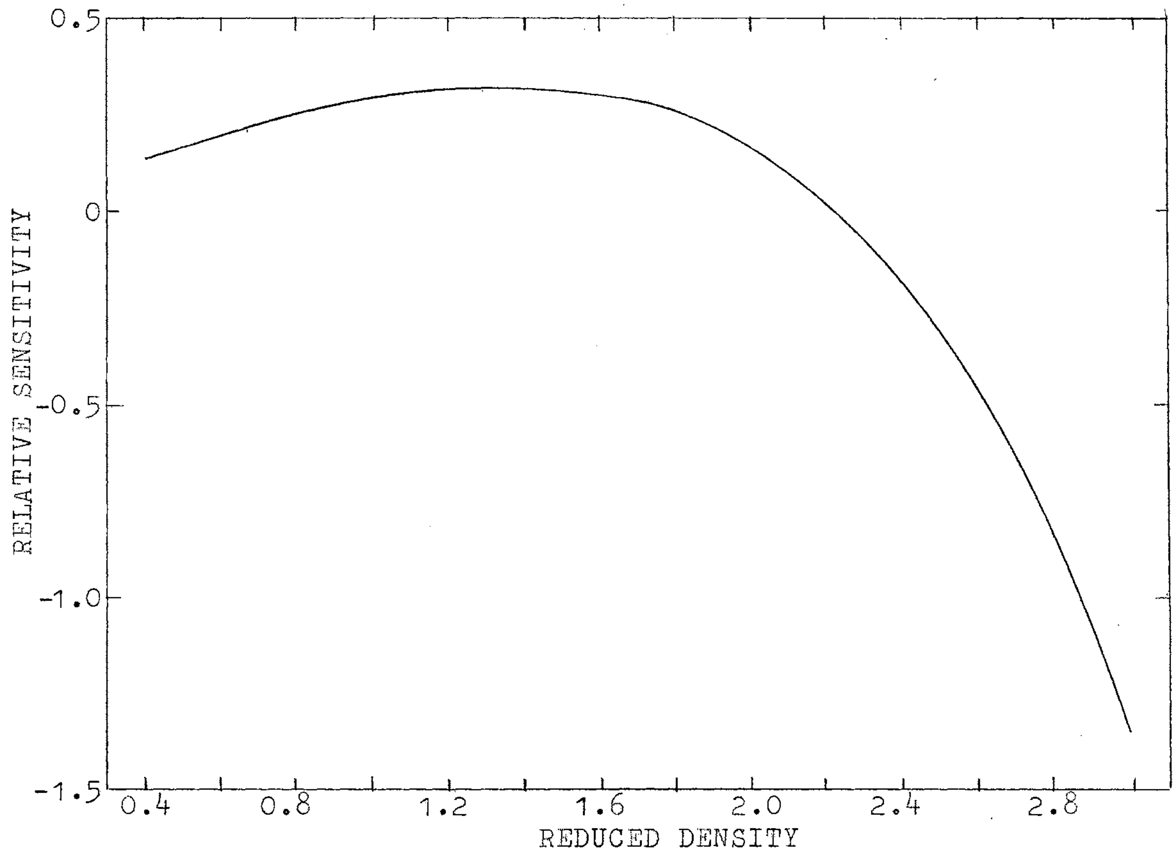


Figure 6. Relative Sensitivity Of Pressure To 'a'

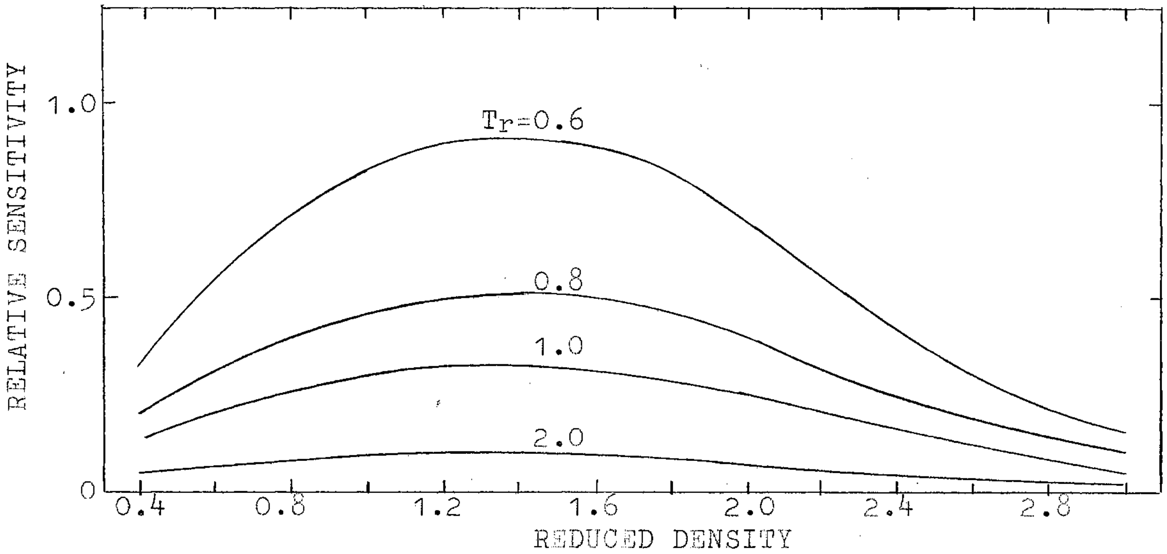


Figure 7. Relative Sensitivity Of Pressure To c

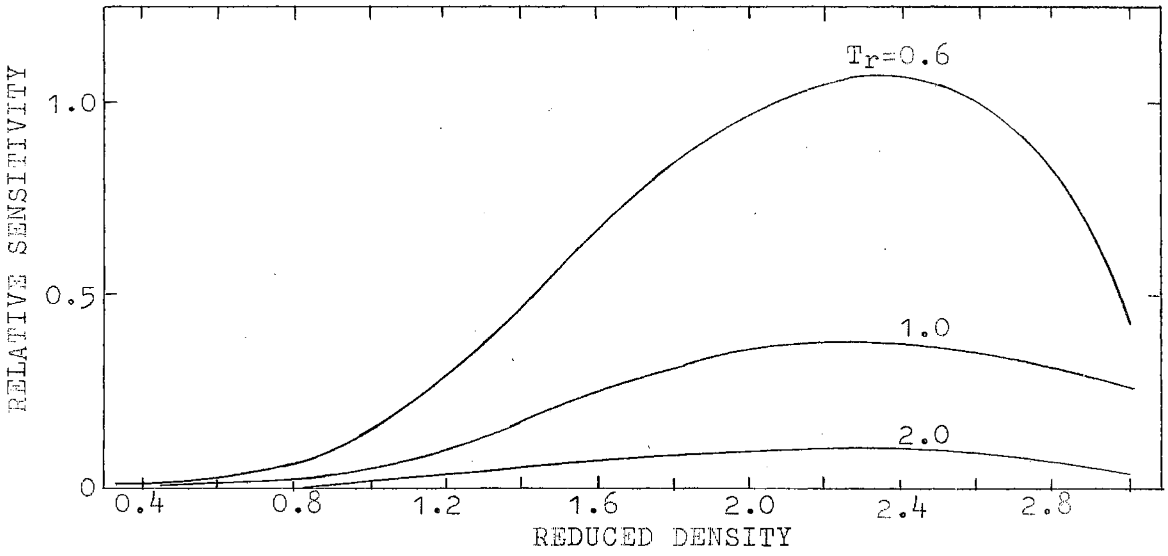


Figure 8. Relative Sensitivity Of Pressure To γ

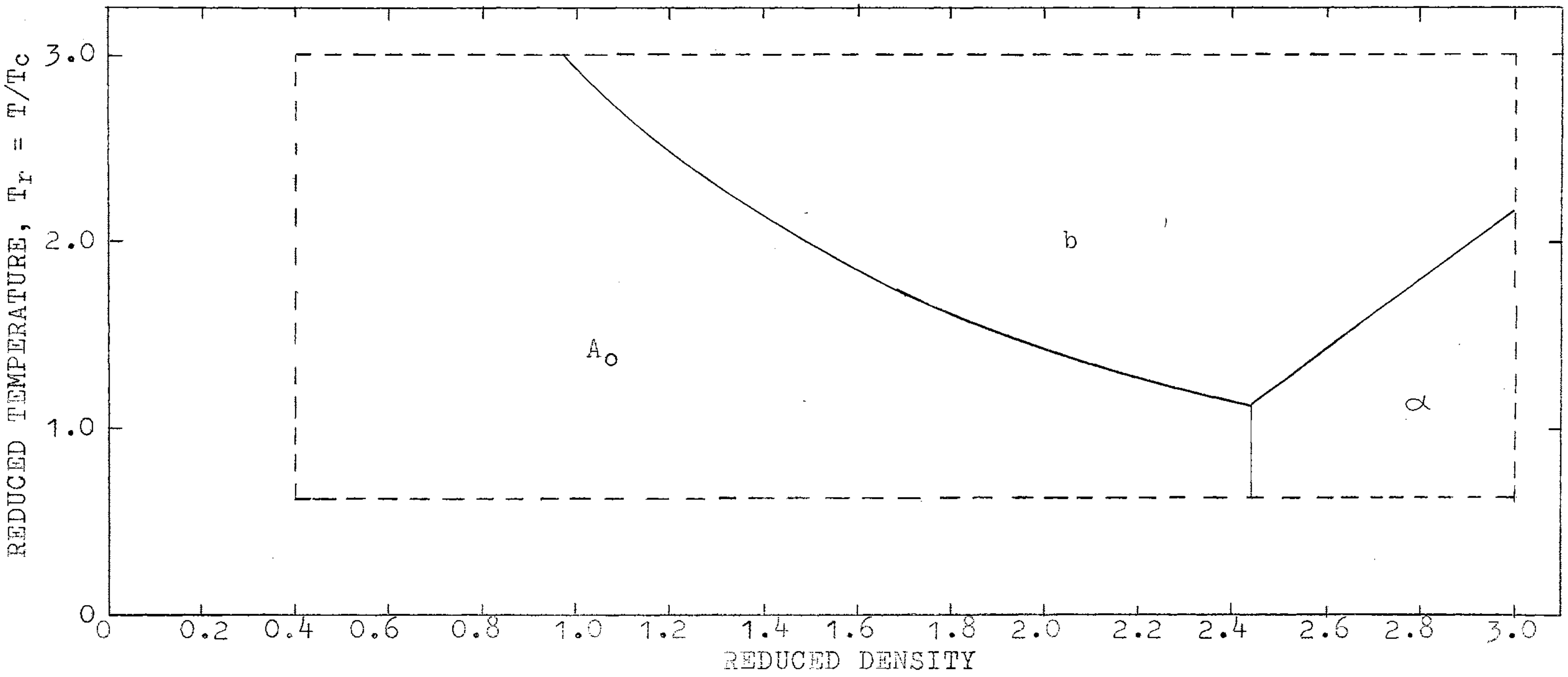


Figure 9. Graphical Representation Of BWR Parameters Having Greatest Effect On Calculated Pressure

Sensitivity of Fugacity to Each BWR Parameter at Saturation Conditions

The effect of each parameter on predicted fugacities for pure methane at saturated conditions was calculated in a manner similar to the procedure used to find the sensitivity of pressure. That is, the basis for sensitivity of fugacity was the relation

$$\text{fugacity sensitivity} = k_i\left(\frac{\partial f}{\partial k_i}\right)_{T,\rho}$$

where f is the pure component fugacity. The derivative $(\partial f/\partial k_i)_{T,\rho}$ is the rate of change in fugacity with k_i at the saturated temperature and density. The derivatives of fugacity were determined from the equation for pure component fugacities presented by Benedict (4).

$$RT\ln f = RT\ln RT\rho + 2(B_oRT - A_o - \frac{C_o}{T^2})\rho + \frac{3}{2}(bRT - a)\rho^2 + \frac{6}{5}a\alpha\rho^5 + \frac{c\rho^2}{T^2}\left[\frac{1}{\gamma\rho^2} - (\frac{1}{\gamma\rho^2} - \frac{1}{2} - \gamma\rho^2)\exp(-\gamma\rho^2)\right] \qquad (3\text{-}18)$$

Equation (3-18) applies to both liquid and vapor phases. The effects of each parameter on liquid and vapor fugacities were calculated from the following equations.

$$B_o\left(\frac{\partial f}{\partial B_o}\right) = 2RT\rho^2 B_o e^u \qquad (3\text{-}19)$$

$$A_o\left(\frac{\partial f}{\partial A_o}\right) = -2\rho^2 A_o e^u \qquad (3\text{-}20)$$

$$C_o\left(\frac{\partial f}{\partial C_o}\right) = -\frac{2\rho^2}{T^2} C_o e^u \qquad (3\text{-}21)$$

$$b\left(\frac{\partial f}{\partial b}\right) = \frac{3}{2}RT\rho^3 b e^u \qquad (3\text{-}22)$$

$$a\left(\frac{\partial f}{\partial a}\right) = \rho^3 \left(-\frac{3}{2} + \frac{6}{5}\alpha\rho^3\right) a e^u \tag{3-23}$$

$$\alpha\left(\frac{\partial f}{\partial \alpha}\right) = \frac{6}{5}\rho^6 a \alpha e^u \tag{3-24}$$

$$c\left(\frac{\partial f}{\partial c}\right) = \frac{R\rho^3}{T^2} c e^u \left[\frac{1}{\gamma\rho^2} - \left(\frac{1}{\gamma\rho^2} - \frac{1}{2} - \gamma\rho^2\right)\exp(-\gamma\rho^2)\right] \tag{3-25}$$

$$\gamma\left(\frac{\partial f}{\partial \gamma}\right) = \frac{c\gamma\rho^3}{T^2} e^u \left[-\frac{1}{\gamma^2\rho^2} + \left(\frac{1}{\gamma} + \frac{1}{\gamma^2\rho^2} + \frac{\rho^2}{2} - \gamma\rho^4\right)\exp(-\gamma\rho^2)\right] \tag{3-26}$$

In Equations (3-19) thru (3-26) u is given by

$$u = 2\left(B_oRT - A_o - \frac{C_o}{T^2}\right)\frac{\rho}{RT} + \frac{3}{2}(bRT - a)\frac{\rho^2}{RT} + \frac{6}{5}\,\frac{a\alpha\rho^5}{RT}$$
$$+ \frac{c\rho^2}{RT^3}\left[\frac{1}{\gamma\rho^2} - \left(\frac{1}{\gamma\rho^2} - \frac{1}{2} - \gamma\rho^2\right)\exp(-\gamma\rho^2)\right]$$

Calculations were made over a range of reduced temperatures from 0.5 to 0.95 for liquid and vapor phases. Saturated liquid and vapor densities used in Equations (3-19) thru (3-26) were calculated with the BWR equation.

Again A_o was used as a basis for determining relative sensitivities of fugacities. Figure 10 shows the absolute sensitivity of fugacity to A_o. The equations for relative sensitivities are as follows.

$$\frac{B_o\left(\frac{\partial f}{\partial B_o}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = -RT \tag{3-27}$$

$$\frac{A_o\left(\frac{\partial f}{\partial A_o}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = 1 \qquad (3\text{-}28)$$

$$\frac{C_o\left(\frac{\partial f}{\partial c_o}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = \frac{1}{T^2} \qquad (3\text{-}29)$$

$$\frac{b\left(\frac{\partial f}{\partial b}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = -\frac{3}{4} RT\rho \qquad (3\text{-}30)$$

$$\frac{a\left(\frac{\partial f}{\partial a}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = \frac{3}{4}\rho - \frac{3}{5}\alpha\rho^4 \qquad (3\text{-}31)$$

$$\frac{\alpha\left(\frac{\partial f}{\partial \alpha}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = \frac{3}{5} a\rho \qquad (3\text{-}32)$$

$$\frac{c\left(\frac{\partial f}{\partial c}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = -\frac{R}{2T\gamma\rho} + \left(\frac{R}{2\gamma T\rho} - \frac{R\rho}{4T} - \frac{R\gamma\rho^3}{2T}\right) \exp\left(-\gamma\rho^2\right) \qquad (3\text{-}33)$$

$$\frac{\gamma\left(\frac{\partial f}{\partial \gamma}\right)}{A_o\left(\frac{\partial f}{\partial A_o}\right)} = -\frac{c\rho^2}{2T^2}\left[\frac{1}{\gamma\rho^2} - \left(\frac{1}{\gamma\rho^2} - \frac{1}{2} - \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right)\right] \qquad (3\text{-}34)$$

Results of the relative fugacity sensitivities are shown in Figures 11-14. A comparison of these results indicate that liquid fugacity is most sensitive to the parameter c over the entire range of reduced temperatures investigated. The parameter A_0 has the greatest effect on vapor fugacities at all but very low reduced temperatures and at temperatures near the critical point. Below a reduced temperature of about 0.55 α becomes the most significant parameter for the vapor fugacity. Above a reduced temperature of about 0.88 vapor fugacity is most affected by c. Therefore, results of this preliminary investigation indicated that c and A_0 may be most suited for modification when fugacity calculations are involved.

Improvement of Parameters to Predict Vapor Pressures

In general, a set of BWR parameters determined from p-v-T properties of a pure component can be used to predict saturated phase properties of that component at reduced temperatures down to about 0.6. However, at reduced temperatures below 0.6, the equation must be modified in order to satisfactorily predict saturated phase properties. Benedict (6) suggested that the prediction of pure component vapor pressures at low temperatures could be improved by adjusting C_0 at every temperature so that agreement with observed vapor pressures is obtained.

In this investigation each BWR parameter, in turn, was studied to determine its variation with temperature to fit vapor pressures at low temperatures. Ahn's (1) parameters for methane were used along with vapor pressure data on methane presented by Din (11). Ahn's parameters were evaluated using the data of Vennix (29) using non-linear regression techniques with compressibility factor as the dependent variable. The procedure used was to hold seven parameters constant and calculate the eighth parameter at each temperature so that the

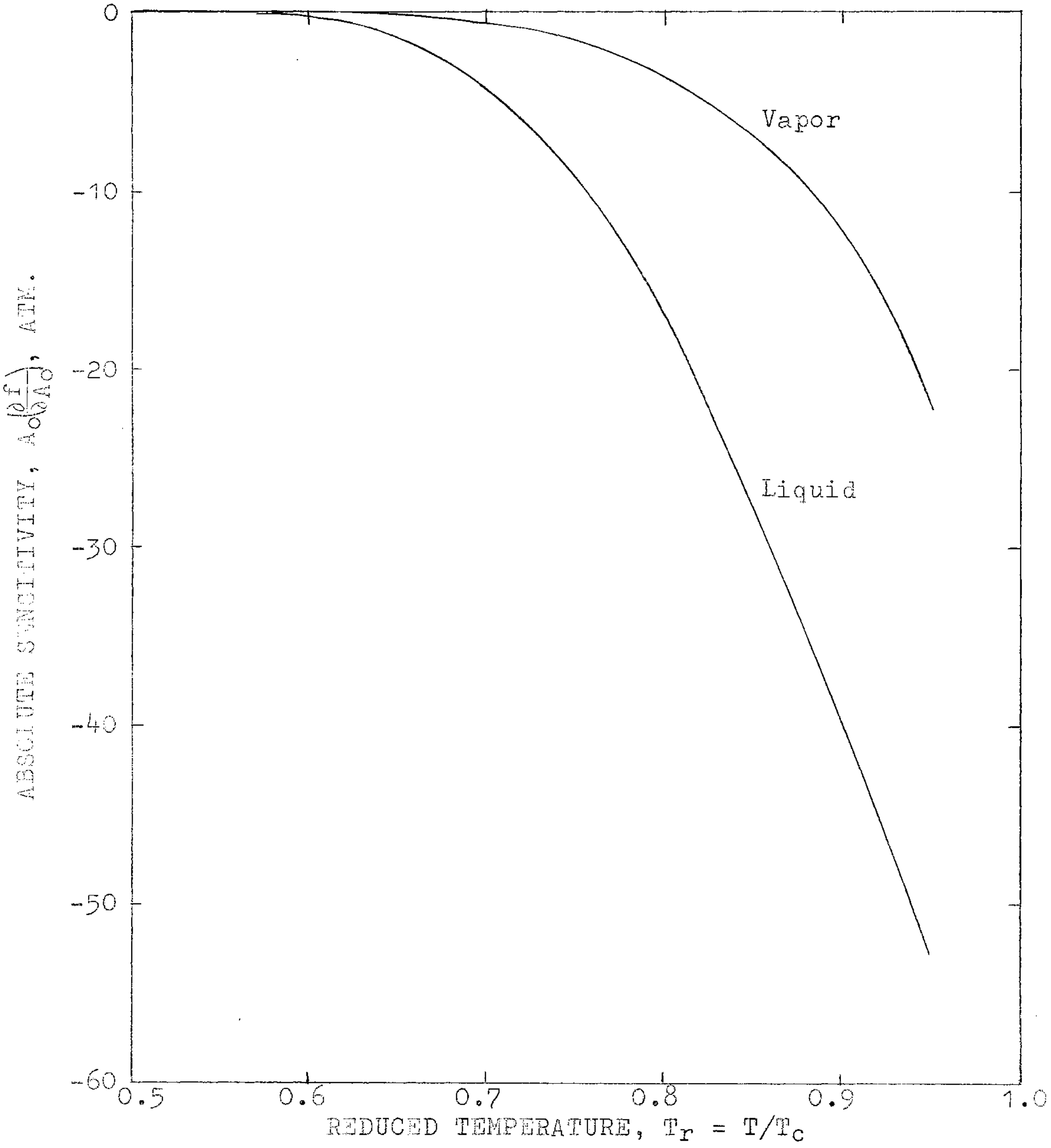


Figure 10. Absolute Sensitivity Of Fugacity To A_o

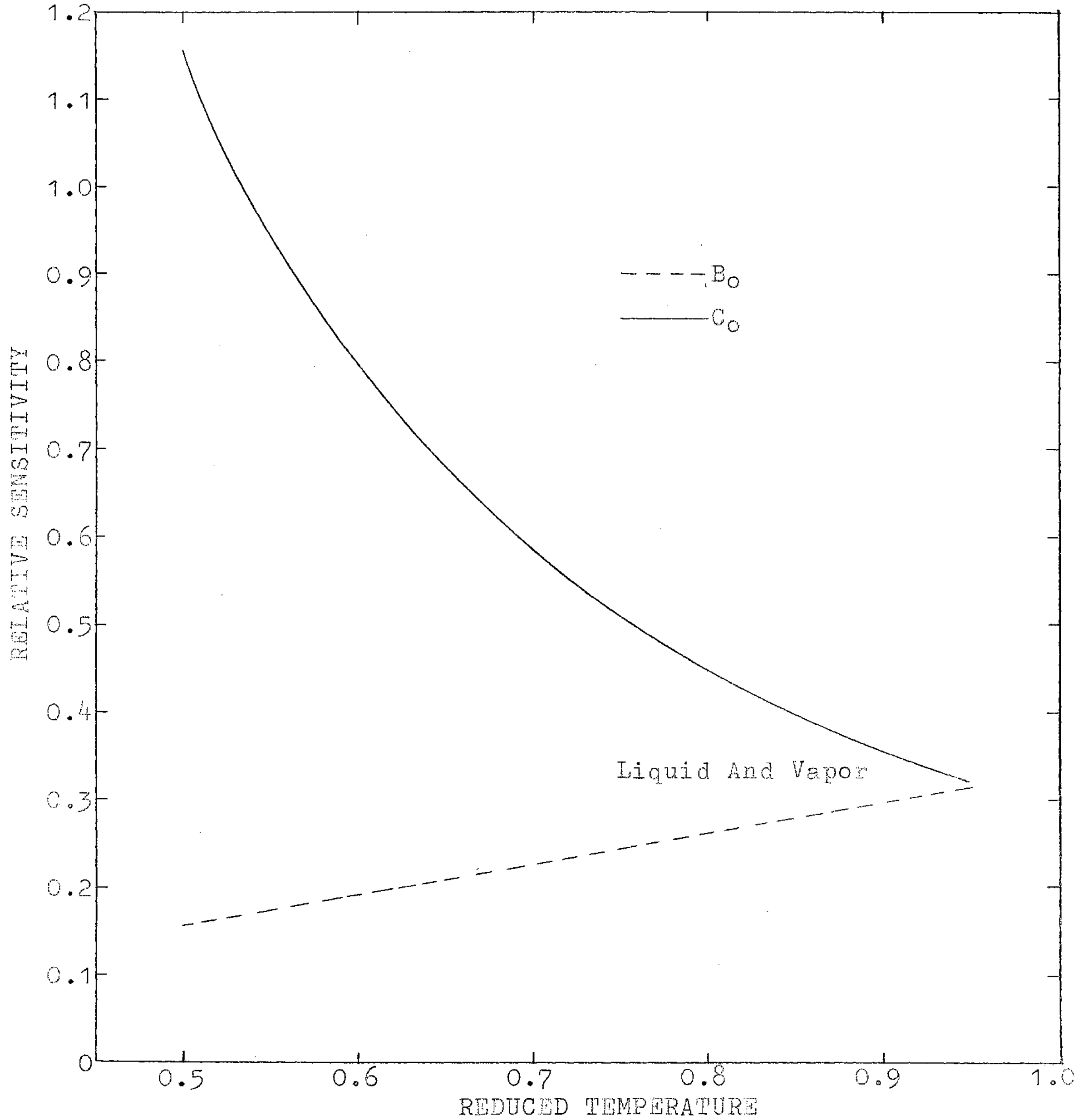


Figure 11. Relative Sensitivity Of Fugacity To B_o And C_o

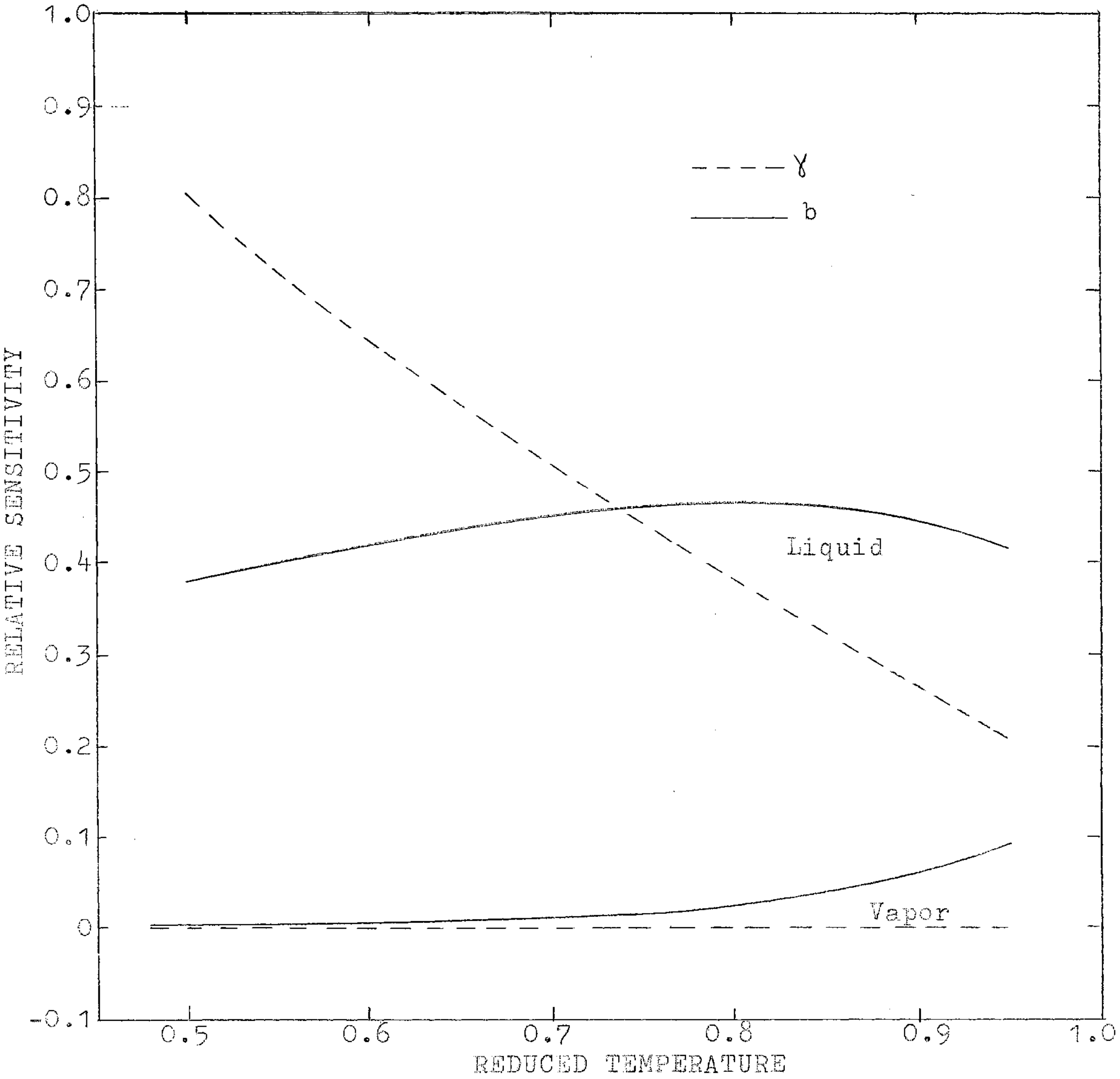


Figure 12. Relative Sensitivity Of Fugacity To b and γ

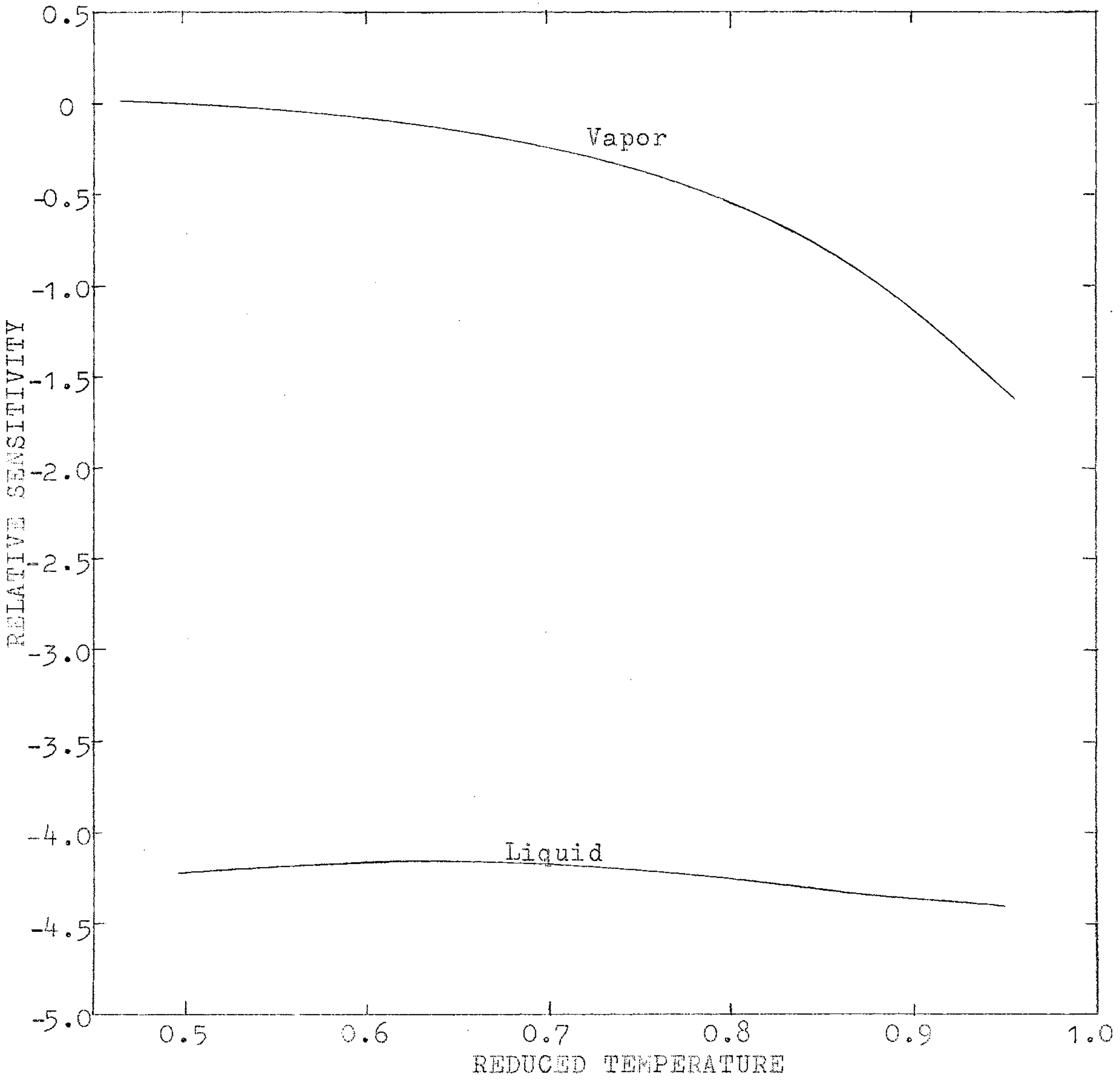


Figure 13. Relative Sensitivity Of Fugacity To c

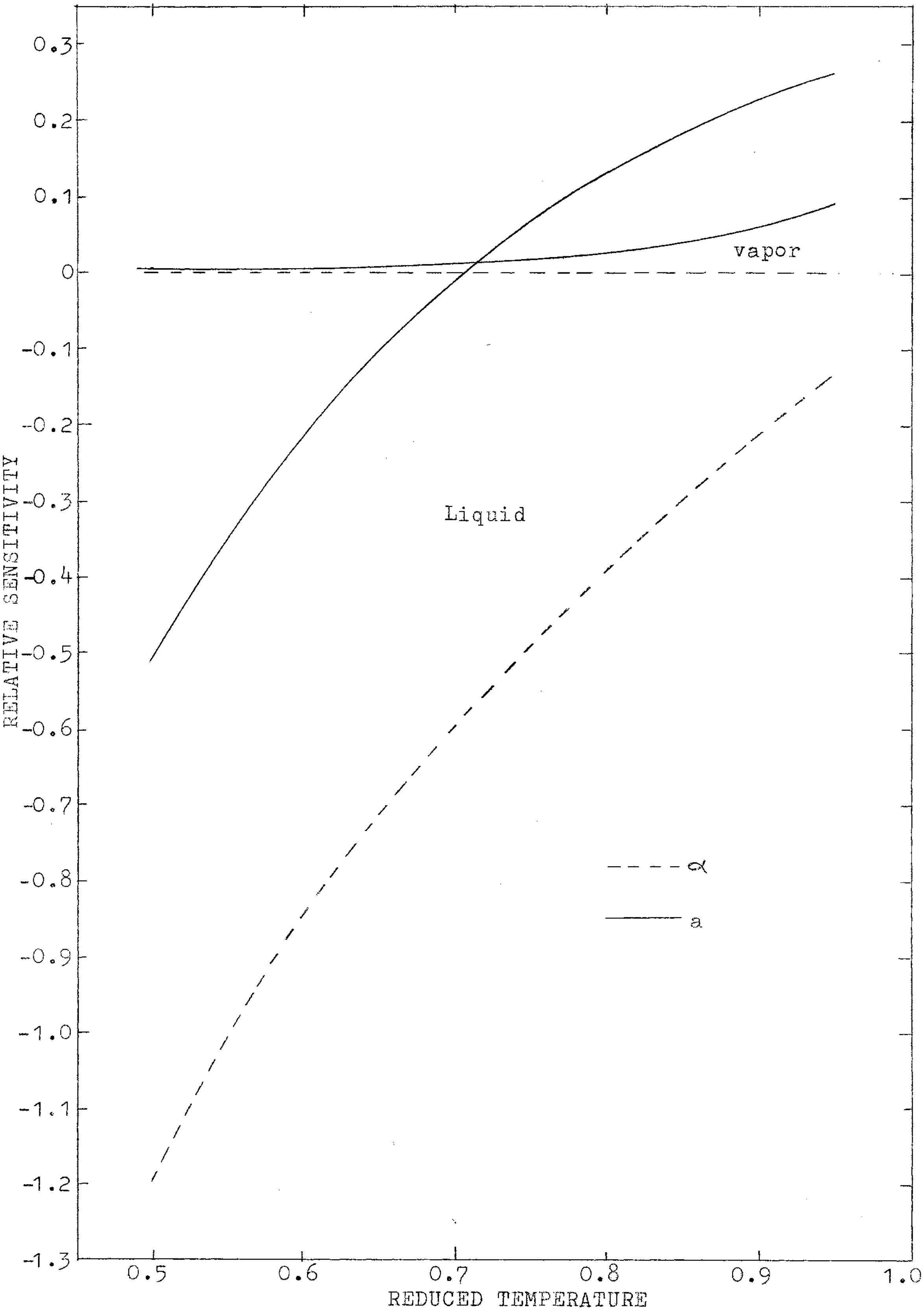


Figure 14. Relative Sensitivity Of Fugacity To 'a' and α

calculated vapor pressure was equal to the experimental value. Eighteen data points covering a range of temperatures from 100° to 185° Kelvin ($T_r = 0.52$ to 0.97) were used.

Calculation of pure component vapor pressures involves a trial and error procedure and included satisfaction of the following criteria:

$$P(\rho^L) = P(\rho^V)$$

$$f(\rho^L) = f(\rho^V)$$

where ρ^L is the saturated liquid density and ρ^V is the saturated vapor density. A detailed explanation of the trial and error methods used to calculate pure component saturated phase properties is given in Appendix A.

The method used to calculate a parameter at each temperature was as follows:

1. Calculate vapor pressure with original parameters.
2. Calculate error in vapor pressure.

$$\text{error} = \frac{P_{obs} - P_{calc}}{P_{obs}}$$

3. Calculate per cent change in pressure per per cent change in k_i.

$$\text{per cent change} = \frac{\dfrac{\Delta P}{P}}{\dfrac{\Delta k_i}{k_i}} = \frac{k_i}{P}\,\frac{\Delta P}{\Delta k_i}$$

4. Calculate the correction factor, $\Delta k_i/k_i$.

$$\frac{\frac{P_{obs} - P_{calc}}{P_{obs}}}{\frac{k_i}{P}\frac{\Delta P}{\Delta k_i}} \approx \frac{\Delta k_i}{k_i}$$

5. Calculate the new value for k_i.

$$k_i = k_i + k_i \frac{\Delta k_i}{k_i} = k_i + \Delta k_i$$

Steps 2 thru 5 were repeated until

$$P_{calc} = P_{obs}$$

A new value for the constant k_i was calculated at each temperature; this procedure was repeated for each parameter. The results of these calculations are shown in Figures 15 thru 18.

The results indicate that any of the eight parameters may be fit to a polynomial curve as a function of temperature and accurately predict vapor pressures at low temperatures. An interesting discovery made during vapor pressure calculations using 'a' was the failure of this parameter to converge on a value that resulted in calculated vapor pressures equal to observed vapor pressures at temperatures less than 125° K ($T_r = 0.654$). A plot of pressure versus 'a' at 100° K showed that the vapor pressure passed through a maximum value less than the observed vapor pressure.

Sensitivity of Vapor Pressure to Each BWR Parameter

The final preliminary investigation for pure methane was to determine how the predicted vapor pressure was affected by each BWR parameter. Vapor pressure sensitivities were determined by calculating

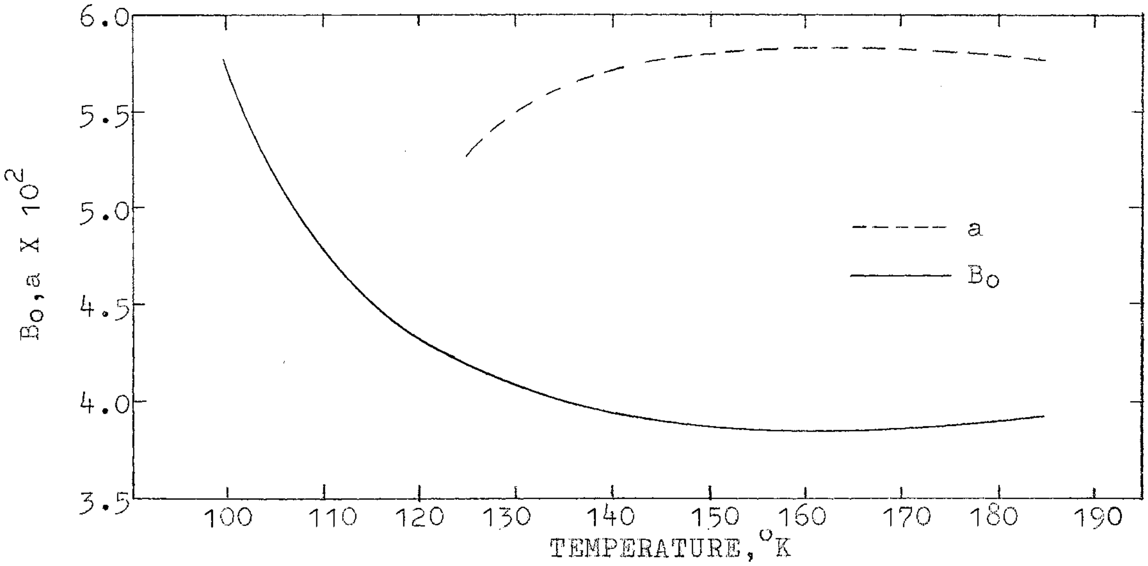


Figure 15. Temperature Variation Of B_o And 'a' In Subcritical Region Of Methane

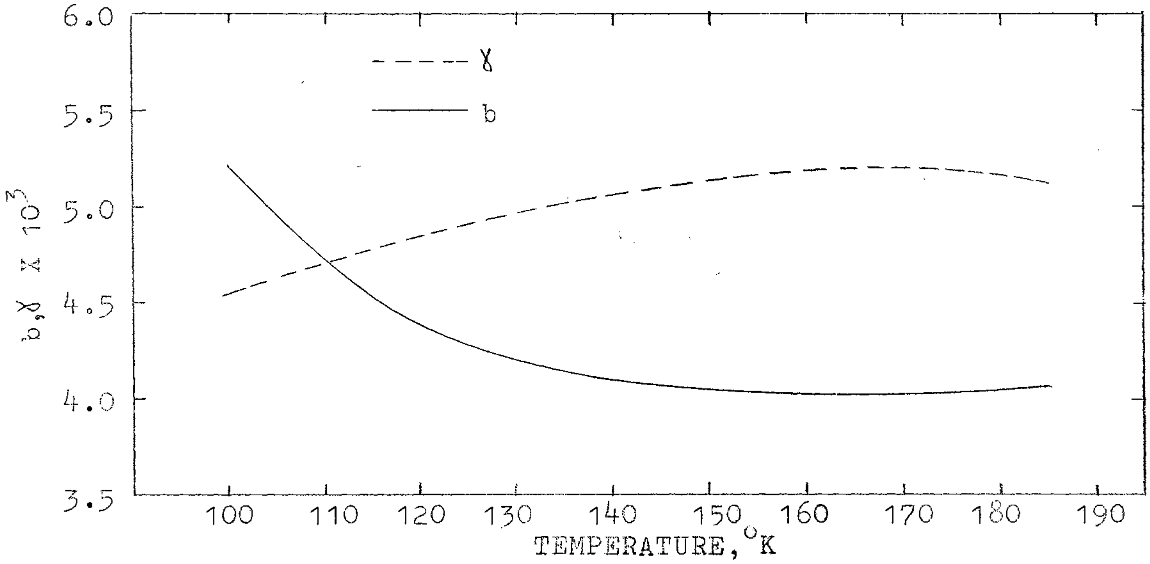


Figure 16. Temperature Variation Of b And γ In Subcritical Region Of Methane

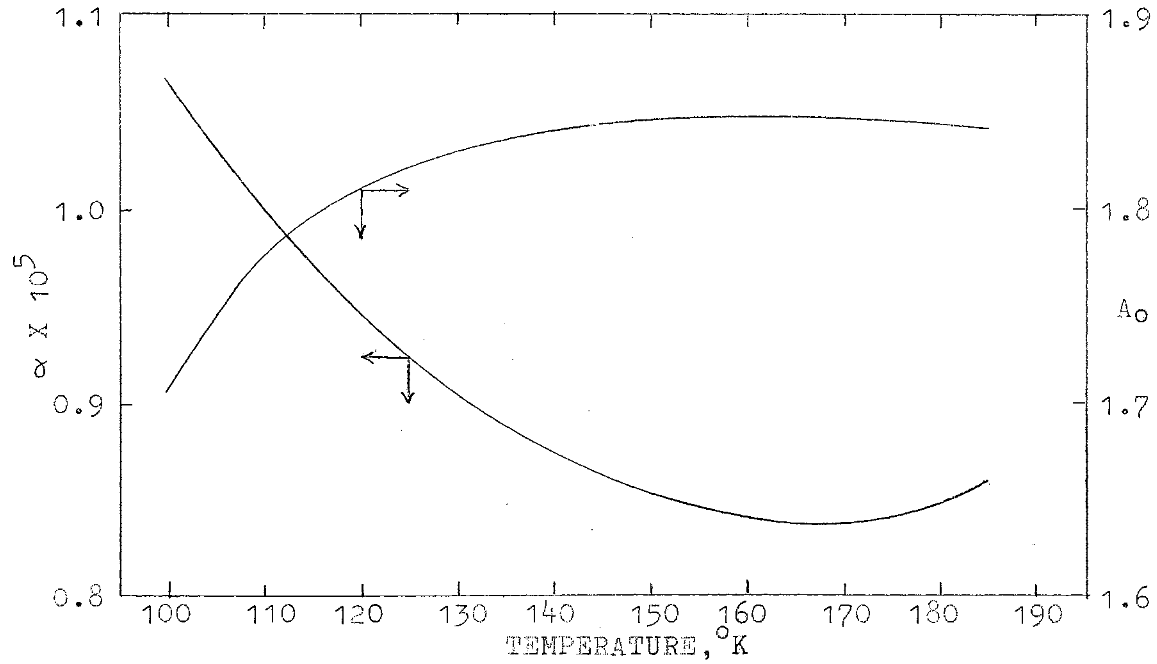


Figure 17. Temperature Variation Of A_o And α In Subcritical Region Of Methane

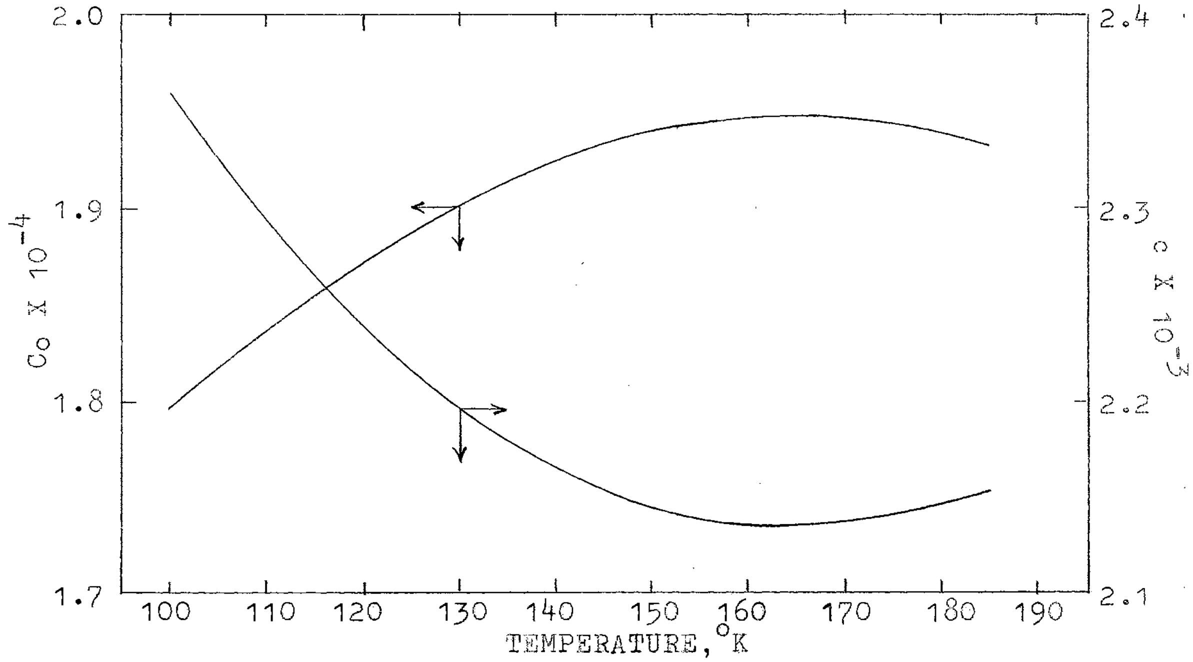


Figure 18. Temperature Variation Of C_o And c In Subcritical Region Of Methane

the per cent change in vapor pressure per per cent change in each parameter.

$$\text{vapor pressure sensitivity} = \left(\frac{P_1 - P_2}{k_{i\,1} - k_{i\,2}} \right) \frac{k_{i\,1}}{P_1}$$

where P_1 is the vapor pressure calculated with unchanged k_i; $k_{i\,1}$, the unchanged k_i; P_2, vapor pressure calculated with k_i change one per cent; and $k_{i\,2}$ is k_i changed one per cent.

Calculations were made for each parameter at reduced temperatures from 0.5 to 0.95. Ahn's parameters for methane were also used in these calculations. The results are shown in Figure 19. These results indicate that A_o has the largest effect on predicted vapor pressures over the entire range of temperatures studied except below a reduced temperature of about 0.54 where the sensitivity to C_o becomes more significant.

Since A_o has the greatest effect on predicted vapor pressures, it may be best suited for modification to a function of temperature at subcritical temperatures. However, if extrapolation to extremely low temperatures is required, C_o may be more suitable for modification since it has the greatest effect on vapor pressure at reduced temperatures less than 0.54.

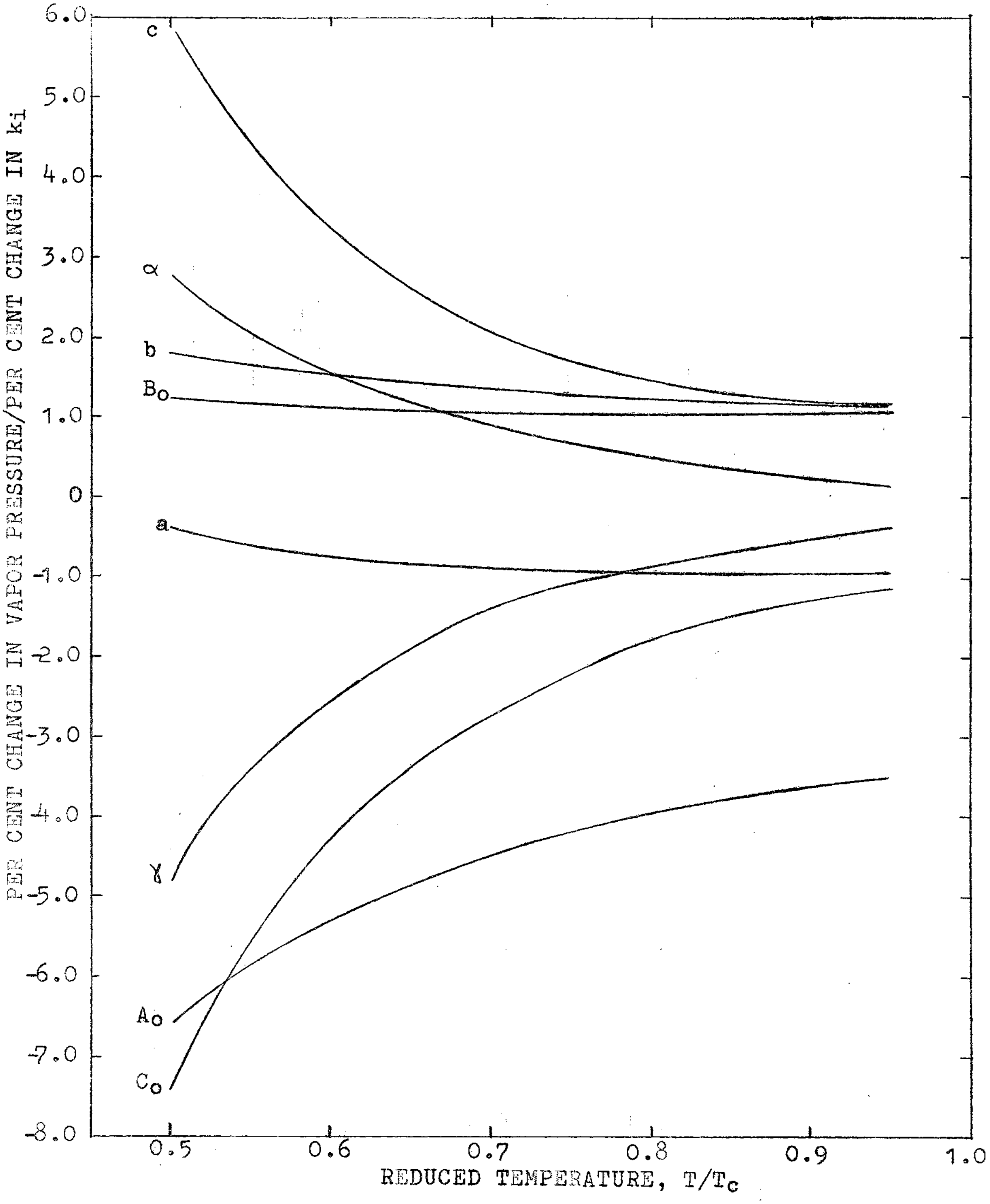


Figure 19. Sensitivity Of Vapor Pressure To The BWR Parameters

CHAPTER IV

SIMULTANEOUS MODIFICATION OF TWO BWR PARAMETERS TO PREDICT SATURATED PHASE PROPERTIES

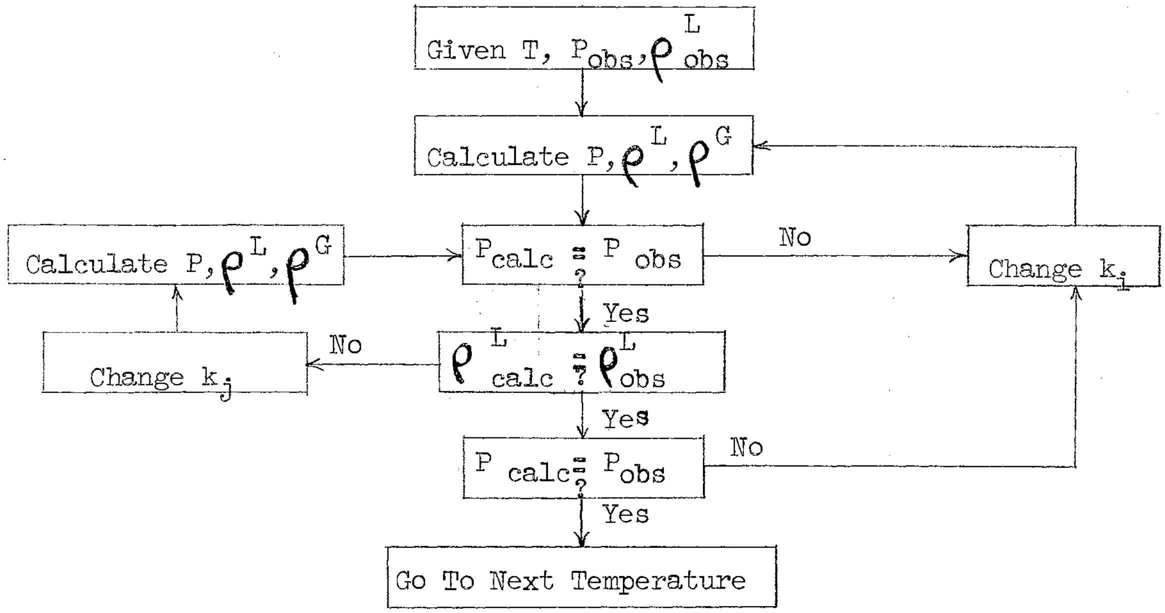
Benedict (6) indicated that the BWR equation was not satisfactory when extrapolations were made to temperatures below which the equation has been fitted. Since a substantial error in vapor pressures predicted by the equation occurs at low temperatures, fugacities in mixtures evaluated at such temperatures would also be expected to be in error. Therefore, Benedict suggested that the parameter C_o be adjusted at low temperatures so that agreement with observed vapor pressures is obtained.

The preliminary investigations previously discussed indicated that C_o would have to be fitted to a polynomial function of temperature if accurate vapor pressures are to be calculated at low temperatures. The same would also hold true if any of the other seven parameters were to be made temperature dependent. For example, Chao (7) found that an equation of the fifth degree in absolute temperature was required to adequately represent C_o for methane over the temperature range from -288° F to the critical point (-116° F). Cox (10) recently modified C_o and 'a' to be linear functions of reciprocal temperature, but he gave no explanation for his choice of such a functional form. The desired goal of this study was to examine the actual temperature dependence of pairs of parameters, and to determine which pairs, if any, could be represented by simple functional dependence on temperature.

Two techniques were used for adjusting the two BWR parameters simultaneously. The first method involved the use of experimental vapor pressures and saturated liquid densities. The second procedure involved only experimental vapor pressures. In both cases the two parameters were calculated in order to determine their temperature variation.

Modification to Predict Vapor Pressure And Saturated Liquid Density

The data for methane presented by Din (11) were used to calculate two parameters as functions of temperature over the temperature range of 100° K to 185° K which corresponds to a reduced temperature range from 0.52 to 0.97. The following diagram briefly describes the calculations made at each temperature.



Simultaneous Fit of Vapor Pressure and Liquid Density

The saturated phase properties were calculated by the trial and error procedure explained in Appendix A. These properties were first calculated with unmodified constants. Then the observed and calculated vapor pressures were compared. If the pressures did not agree, one parameter was changed by the following technique.

$$k_i = k_i + \Delta k_i \tag{4-1}$$

$$\Delta k_i = \frac{\dfrac{P_{obs} - P_{calc}}{P_{obs}}}{\dfrac{k_i}{P}\left(\dfrac{\Delta P}{\Delta k_i}\right)} \tag{4-2}$$

In Equation (4-2), $\Delta P/\Delta k_i$ is the rate of change of vapor pressure with k_i. The parameter k_i was adjusted until the calculated vapor pressure equaled the experimental vapor pressure.

After agreement of vapor pressures was obtained, calculated and observed saturated liquid densities were compared. If the two densities were not equal, a second parameter was changed until good agreement was obtained. The method used to adjust the parameter for convergence on a saturated liquid density was as follows.

$$k_j = k_j + \Delta k_j \tag{4-3}$$

$$\Delta k_j = \frac{dk}{d\rho} \Delta \rho \tag{4-4}$$

$$\Delta \rho = \rho_{obs} - \rho_{calc} \tag{4-5}$$

The derivative $(dk_j/d\rho)$ was estimated by dividing $(dP/dk_j)_{T,\rho}$ by $(dP/d\rho)_{T,k}$.

$$\frac{dk_j}{d\rho} = \frac{\left(\frac{dP}{dk_j}\right)_{T,\rho}}{\left(\frac{dP}{d\rho}\right)_{T,k}} \tag{4-6}$$

The two derivatives on the right side of Equation (4-6) were evaluated from the BWR equation.

$$\left(\frac{dP}{d\rho}\right)_{T,k} = RT + 2(B_oRT-A_o-\frac{C_o}{T^2})\rho + 3(bRT-a)\rho^2$$

$$+ 6a\alpha\rho^5 + \frac{c\rho^2}{T^2}(3+3\gamma\rho^2-2\gamma^2\rho^4)\exp(-\gamma\rho^2) \tag{4-7}$$

The derivative $(dP/dk_j)_{T,\rho}$ was evaluated for each parameter from the following equations.

$$\frac{dP}{dB_o} = RT\rho^2 \tag{4-8}$$

$$\frac{dP}{dA_o} = -\rho^2 \tag{4-9}$$

$$\frac{dP}{dC_o} = \frac{-\rho^2}{T^2} \tag{4-10}$$

$$\frac{dP}{db} = RT\rho^3 \tag{4-11}$$

$$\frac{dP}{da} = -\rho^3 + \alpha\rho^6 \tag{4-12}$$

$$\frac{dP}{d\alpha} = a\rho^6 \tag{4-13}$$

$$\frac{dP}{dc} = \frac{\rho^3}{T^2}(1+\gamma\rho^2)\exp(-\gamma\rho^2) \tag{4-14}$$

$$\frac{dP}{d\gamma} = \frac{-c\gamma\rho^7}{T^2} \exp\left(-\gamma\rho^2\right) \qquad (4\text{-}15)$$

After a value of liquid density equal to the observed saturated liquid density was calculated, the calculated vapor pressure was again compared with the observed value. If the pressure did not agree, the entire procedure was repeated. If the pressures were equal, the routine was continued to the next temperature, and the two parameters were recalculated to predict the observed values of vapor pressure and liquid density at that temperature. Values for both parameters were calculated at each temperature.

Calculations were made with several pairs of parameters using Ahn's (1) and Chao's (7) constants for methane. Results of comparable accuracy were obtained with four different pairs of parameters using Ahn's constants. The four pairs of parameters were A_o and γ, γ and α, C_o and γ, and c and γ.

The temperature dependence of both parameters was found as a function of the form

$$k_i = A + B/T$$

which seemed as adequate as any other functional form. Exact fit would require expressions of considerable complexity. The constants A and B were determined by simple linear regression of the calculated parameters. In his study, Cox (10) assumed that linear functions of reciprocal temperature were adequate. He then utilized p-v-T and enthalpy data to fit C_o and 'a' to such a function. Figures 20, 21, 22, and 23 give comparisons of the parameters - A_o and γ, γ and α, C_o and γ, c and γ - calculated to give exact vapor pressures and saturated liquid densities with the results of curve fitting the parameters to a function of reciprocal temperature. Tables I, II, III, and IV show the results of calculations with the four pairs of constants calculated from the equations

$$\text{(a)}\quad A_0 = 1.7040920 + \frac{22.4312}{T}$$

$$\gamma = 6.6231900\text{x}10^{-3} - \frac{.2451300}{T}$$

$$\text{(b)}\quad \gamma = 6.1093400\text{x}10^{-3} - \frac{.1398400}{T}$$

$$\alpha = 8.101000\text{x}10^{-5} + \frac{.001080}{T}$$

$$\text{(c)}\quad C_0 = 17871.440 + \frac{246550.0}{T}$$

$$\gamma = 6.6234200\text{x}10^{-3} - \frac{.2453100}{T}$$

$$\text{(d)}\quad c = 2281.7705 - \frac{23894.062}{T}$$

$$\gamma = 6.4228885\text{x}10^{-3} - \frac{0.218149}{T}$$

Each pair of constants was calculated with Ahn's parameters and should not be used with another set of parameters. Ahn's constants for methane are listed in Table V.

Although the modified parameters were adjusted for vapor pressures and liquid densities, saturated vapor densities were also accurately predicted. Thus, a single set of parameters can be used for both phases.

The preliminary investigations previously discussed indicated that the parameters c and A_0 may be most suitable for modification. Results of varying A_0 and c simultaneously did not result in accurate predicted properties, but the two parameters were successfully modified in separate cases.

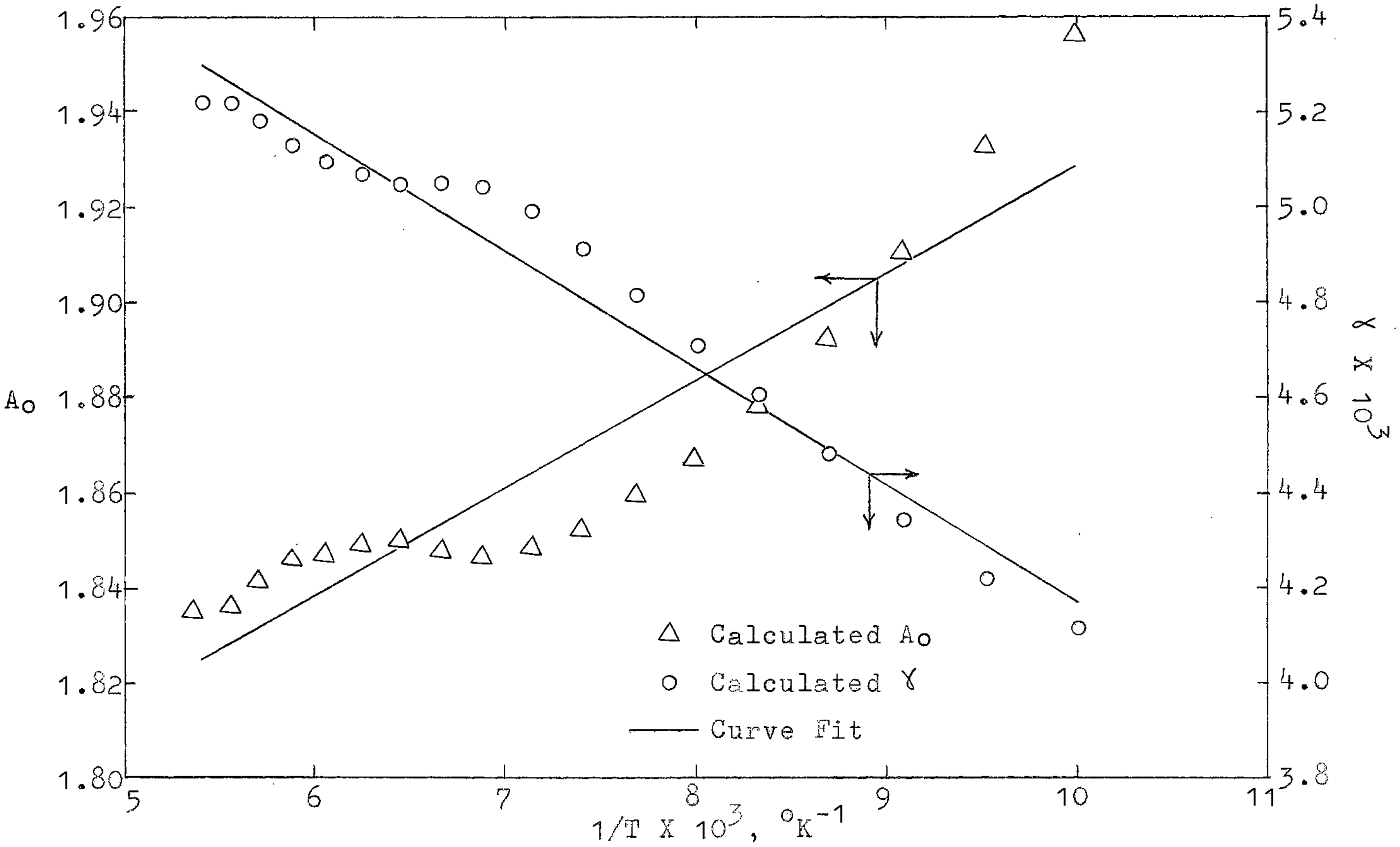


Figure 20. Temperature Dependence Of A_o And γ Simultaneously Determined From Vapor Pressures And Liquid Densities

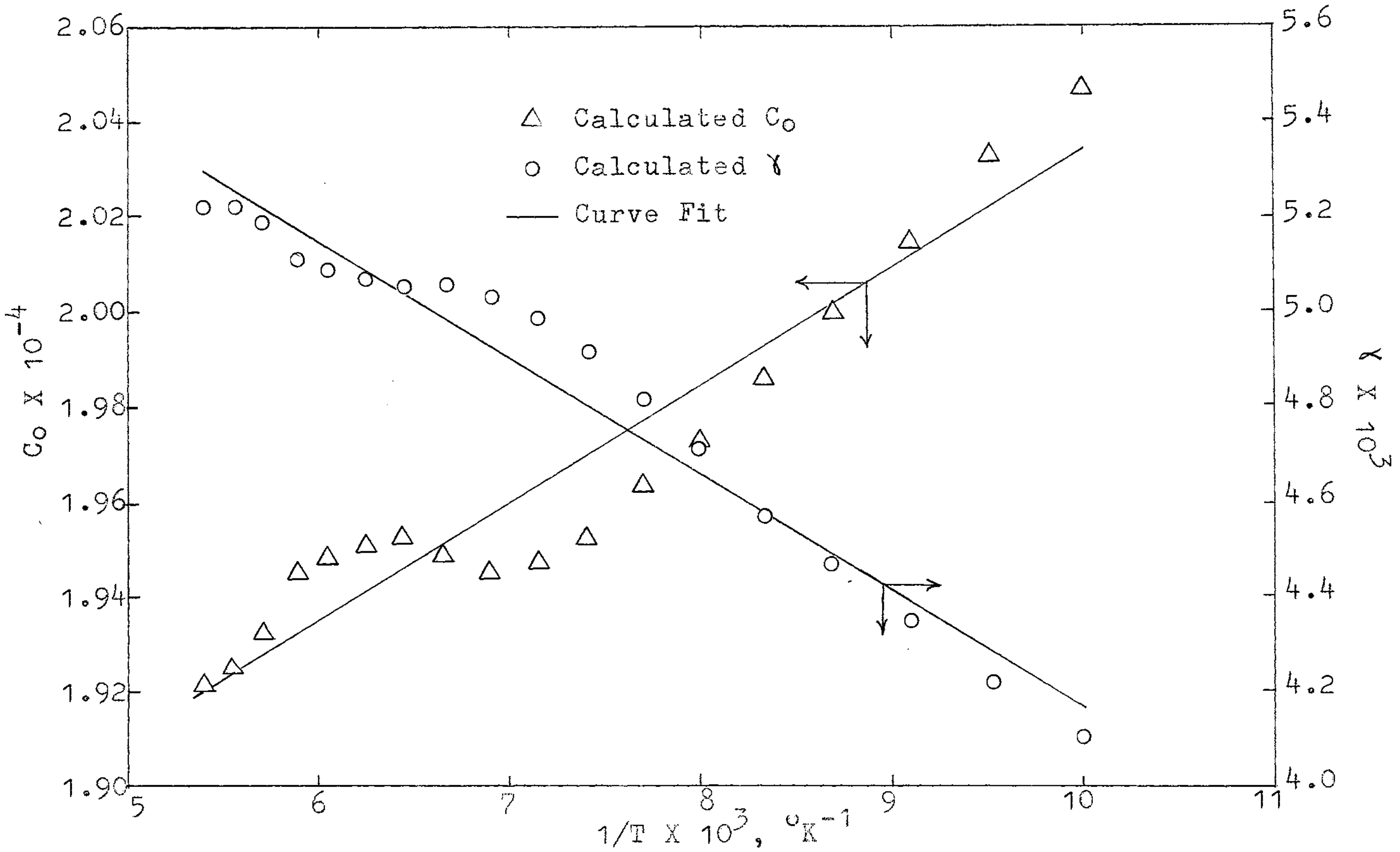


Figure 21. Temperature Dependence Of C_o And γ Simultaneously Determined From Vapor Pressures And Liquid Densities

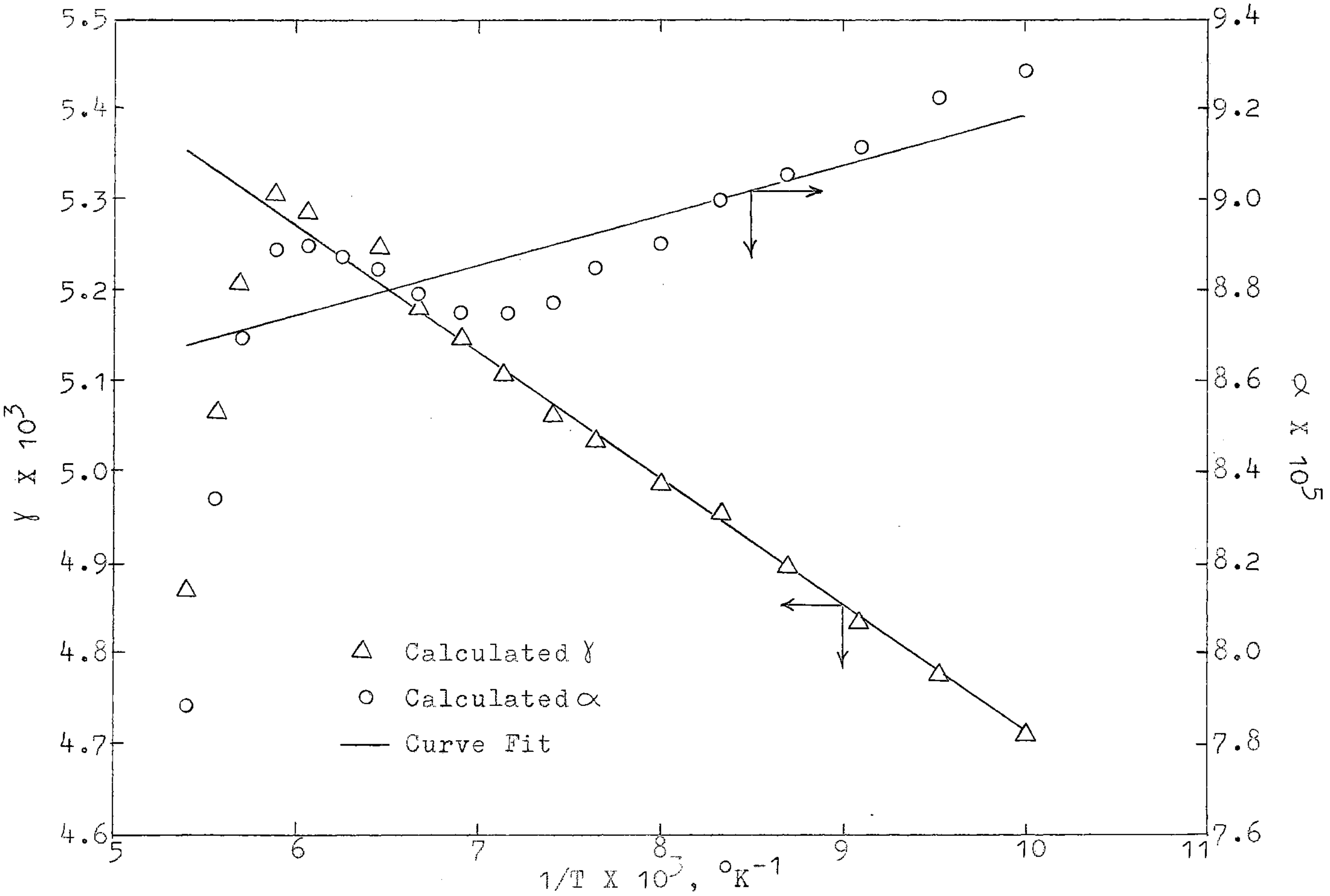


Figure 22. Temperature Dependence Of γ And α Simultaneously Determined From Vapor Pressures And Liquid Densities

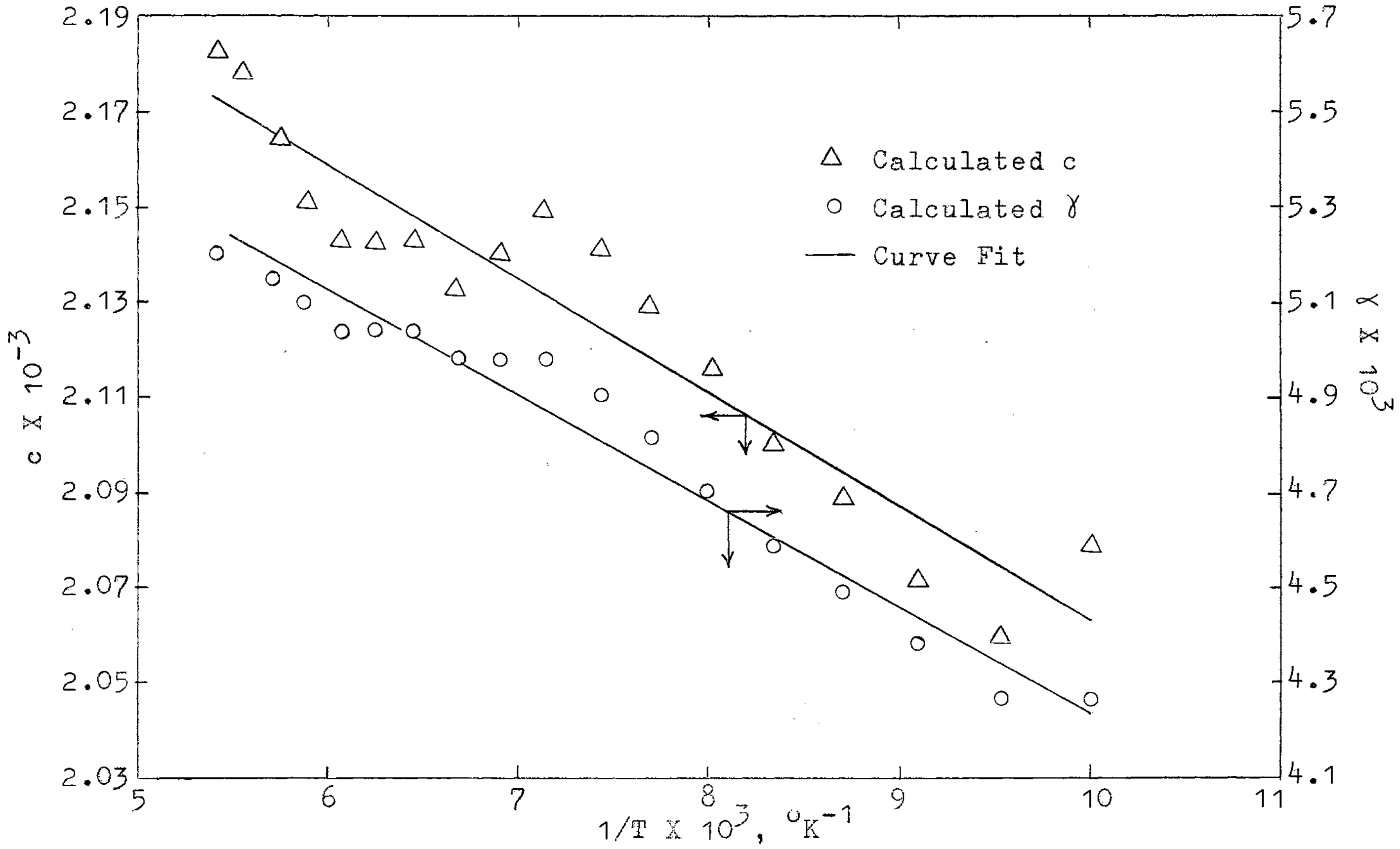


Figure 23. Temperature Dependence Of c And γ Simultaneously Determined From Vapor Pressures And Liquid Densities

TABLE I

CALCULATED SATURATED PHASE PROPERTIES OF METHANE WITH TEMPERATURE DEPENDENT A_o AND γ

Temperature, Degrees Kelvin	Vapor Pressure, Atmospheres	% Deviation*	Liquid Volume, liters/gm-mole	% Deviation*	Vapor Volume liters/gm-mole	% Deviation*
100	0.355	-3.24	0.03630	0.29	22.6700	3.26
105	0.562	0.56	0.03689	0.31	14.9400	0.01
110	0.862	2.13	0.03753	0.27	10.1100	-1.51
115	1.283	2.76	0.03821	0.19	7.0270	-2.25
120	1.853	2.75	0.03893	0.14	5.0110	-2.28
125	2.604	2.44	0.03970	-0.05	3.6570	-1.81
130	3.569	1.98	0.04052	-0.20	2.7260	-1.55
135	4.782	1.50	0.04140	-0.35	2.0690	-1.12
140	6.279	0.94	0.04236	-0.44	1.596	-1.27
145	8.096	0.44	0.04340	-0.44	1.248	-0.32
150	10.269	0.01	0.04456	-0.33	0.9872	-0.58
155	12.836	-0.36	0.04585	-0.18	0.7881	-0.45
160	15.837	-0.62	0.04734	-0.06	0.6336	-0.45
165	19.312	-0.90	0.04907	0.02	0.5116	-0.23
170	23.306	-1.33	0.05116	0.04	0.4136	-0.42
175	27.865	-1.36	0.05380	-0.21	0.3335	0.52
180	33.044	-1.64	0.05734	-0.50	0.2662	-0.24
185	38.906	-1.98	0.06272	-0.58	0.2076	1.09
Maximum % Deviation		3.24		0.58		3.26
Absolute Average Deviation		1.50		0.26		1.08

$$* \ \% \text{ Deviation} = \frac{\text{exp-calc}}{\text{exp}} \times 100$$

TABLE II

CALCULATED SATURATED PHASE PROPERTIES OF METHANE WITH TEMPERATURE DEPENDENT γ AND α

Temperature, Degrees Kelvin	Vapor Pressure, Atmospheres	% Deviation*	Liquid Volume, liters/gm-mole	% Deviation*	Vapor Volume, liters/gm-mole	% Deviation*
100	0.335	2.49	0.03623	0.47	24.035	-2.58
105	0.555	1.78	0.03690	0.28	15.139	-1.34
110	0.873	0.89	0.03759	0.10	9.985	-0.27
115	1.316	0.23	0.03830	-0.05	6.848	0.37
120	1.911	-0.29	0.03904	-0.14	4.855	0.90
125	2.686	-0.63	0.03981	-0.33	3.541	1.42
130	3.671	-0.84	0.04062	-0.46	2.645	1.44
135	4.898	-0.88	0.04149	-0.56	2.017	1.41
140	6.396	-0.90	0.04242	-0.59	1.565	0.72
145	8.197	-0.80	0.04343	-0.50	1.231	1.01
150	10.334	-0.62	0.04454	-0.30	0.9809	0.06
155	12.838	-0.38	0.04578	-0.01	0.7890	-0.55
160	15.746	-0.04	0.04718	0.28	0.6392	-1.34
165	19.088	-0.27	0.04880	0.57	0.5205	-1.98
170	22.905	0.41	0.05073	0.80	0.4248	-3.14
175	27.237	0.92	0.05312	1.05	0.3463	-3.30
180	32.128	1.18	0.05622	1.46	0.2804	-5.57
185	37.631	1.36	0.06064	2.76	0.2234	-6.42
Maximum % Deviation		2.49		2.76		6.42
Absolute Average Deviation		0.83		0.59		1.88

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* % Deviation $= \frac{\text{exp-calc}}{\text{exp}} \times 100$

TABLE III

CALCULATED SATURATED PHASE PROPERTIES OF METHANE WITH TEMPERATURE DEPENDENT C_o AND γ

Temperature, Degrees Kelvin	Vapor Pressure Atmosphere	% Deviation*	Liquid Volume, liters/gm-mole	% Deviation*	Vapor Volume, liters/gm-mole	% Deviation*
100	0.338	1.66	0.03622	0.50	23.815	-1.64
105	0.553	2.08	0.03687	0.38	15.177	-1.60
110	0.866	1.68	0.03754	0.24	10.060	-1.03
115	1.304	1.17	0.03825	0.09	6.910	-0.53
120	1.894	0.59	0.03899	-0.02	4.896	0.06
125	2.666	0.11	0.03978	-0.24	3.565	0.74
130	3.652	-0.30	0.04060	-0.41	2.658	0.97
135	4.882	-0.55	0.04149	-0.56	2.022	1.17
140	6.388	-0.77	0.04244	-0.64	1.565	0.69
145	8.202	-0.87	0.04348	-0.62	1.229	1.19
150	10.357	-0.85	0.04462	-0.47	0.9771	0.45
155	12.886	-0.75	0.04589	-0.25	0.7843	0.04
160	15.823	-0.53	0.04733	-0.05	0.6343	-0.57
165	19.203	-0.33	0.04900	0.16	0.5155	-1.01
170	23.066	-0.29	0.05099	0.29	0.4199	-1.94
175	27.448	0.15	0.05346	0.41	0.3415	-1.89
180	32.403	0.33	0.05669	0.63	0.2757	-3.82
185	37.969	0.48	0.06137	1.58	0.2188	-4.26
Maximum % Deviation		2.08		1.58		4.26
Absolute Average Deviation		0.75		0.42		1.31

$$* \ \% \text{ Deviation} = \frac{\text{exp-calc}}{\text{exp}} \times 100$$

TABLE IV

CALCULATED SATURATED PHASE PROPERTIES OF METHANE WITH TEMPERATURE DEPENDENT c AND γ

Temperature, Degrees Kelvin	Vapor Pressure Atmospheres	% Deviation*	Liquid Volume, liters/gm-mole	% Deviation*	Vapor Volume, liters/gm-mole	% Deviation*
100	0.336	2.44	0.03627	0.36	24.026	-2.54
105	0.553	2.18	0.03692	0.23	15.205	-1.79
110	0.868	1.45	0.03760	0.08	10.046	-0.88
115	1.308	0.81	0.03831	-0.07	6.890	-0.25
120	1.901	0.20	0.03906	-0.18	4.881	0.36
125	2.676	-0.27	0.03984	-0.40	3.555	1.02
130	3.664	-0.62	0.04067	-0.56	2.652	1.18
135	4.894	-0.81	0.04155	-0.71	2.019	1.32
140	6.400	-0.96	0.04251	-0.79	1.564	0.77
145	8.212	-0.98	0.04355	-0.77	1.229	1.20
150	10.362	-0.89	0.04469	-0.63	0.9777	0.38
155	12.887	-0.76	0.04597	-0.43	0.7851	-0.07
160	15.814	-0.47	0.04742	-0.23	0.6354	-0.74
165	19.183	-0.23	0.04911	-0.05	0.5167	-1.23
170	23.031	-0.13	0.05112	0.04	0.4210	-2.22
175	27.399	0.33	0.05362	0.11	0.3425	-2.18
180	32.325	0.57	0.05691	0.24	0.2767	-4.19
185	37.876	0.72	0.06167	1.11	0.2195	-4.57
Maximum % Deviation		2.44		1.11		4.57
Absolute Average Deviation		0.82		0.39		1.49

* % Deviation = $\frac{\text{exp-calc}}{\text{exp}}$ X 100

TABLE V

BWR PARAMETERS* FOR METHANE IN TWO PHASE REGION

B_o	0.038997200	0.038997200
A_o	$1.7040920 + \frac{22.431200}{T}$	1.841062
C_o	19317.440	19317.440
b	0.00406537	0.00406537
a	0.05767643	0.05767643
α	0.00008638	$8.10100\text{x}10^{-5} + \frac{0.001080}{T}$
c	2154.0	
γ	$6.623190\text{x}10^{-3} - \frac{0.245130}{T}$	$6.109340\text{x}10^{-3} - \frac{0.139840}{T}$
B_o	0.038997200	0.038997200
A_o	1.841062	1.841062
C_o	$17871.440 + \frac{246550.0}{T}$	19317.440
b	0.00406537	0.00406537
a	0.05767643	0.05767643
α	0.00008638	0.00008638
c	2154.0	$2281.7705 - \frac{23894.062}{T}$
γ	$6.623420\text{x}10^{-3} - \frac{0.245310}{T}$	$6.4228885\text{x}10^{-3} - \frac{0.218149}{T}$

* Consistent with metric units:

temperature in degrees Kelvin
pressure in atmospheres
density in gm-moles/liter
R = 0.08207

Modification to Fit Vapor Pressures

Often, particularly at low temperatures, saturated liquid density data are unavailable while vapor pressure data can be found. Therefore, the technique devised to calculate the temperature dependence of two parameters simultaneously using vapor pressures and saturated liquid densities cannot always be used.

A method for finding the temperature dependence of two parameters from vapor pressures only was developed and consisted of the following steps.

1. Curve fit two parameters to vapor pressures at two consecutive temperatures, and repeat over the complete temperature range desired.
2. Fit the calculated parameters to equations of the form

$$k_i = A + \frac{B}{T}$$

A non-linear curve fit program (15) was used to do the calculations in step 1. Din's (11) vapor pressure data for methane at temperatures from 100° to 185° K were again used. Two parameters were fitted to vapor pressure at 100° and 105°, 105° and 110°, 110° and 115°, etc. Thus, one value of each parameter was calculated for every two adjacent vapor pressures. These calculated parameters were then fitted to the linear equation in step 2.

Calculations of the temperature dependent parameters derived from vapor pressures were made for several pairs of constants. The best results were obtained with the parameters C_o and γ using Ahn's parameters. Calculated vapor pressures deviated less than two per cent from observed vapor pressures. The temperature dependence of C_o and γ

were calculated by the equation

$$C_o = 11755.086 + \frac{1313422.1}{T}$$

$$\gamma = 9.0851799 \times 10^{-3} - \frac{0.67982177}{T}$$

Results of calculations with the above temperature dependent parameters are shown in Table VI, and their temperature dependence is shown in Figure 24. Although vapor pressures were calculated within reasonable accuracy, the calculated saturated liquid densities showed increasingly large errors at low temperatures.

A comparison of the functions of C_o and γ determined from vapor pressures only with C_o and γ found from vapor pressures and saturated liquid densities reveals that the values of the constants A and B are significantly different in each case. This difference in the values of C_o and γ may explain why saturated liquid densities were not accurately predicted for the case in which only vapor pressures were used.

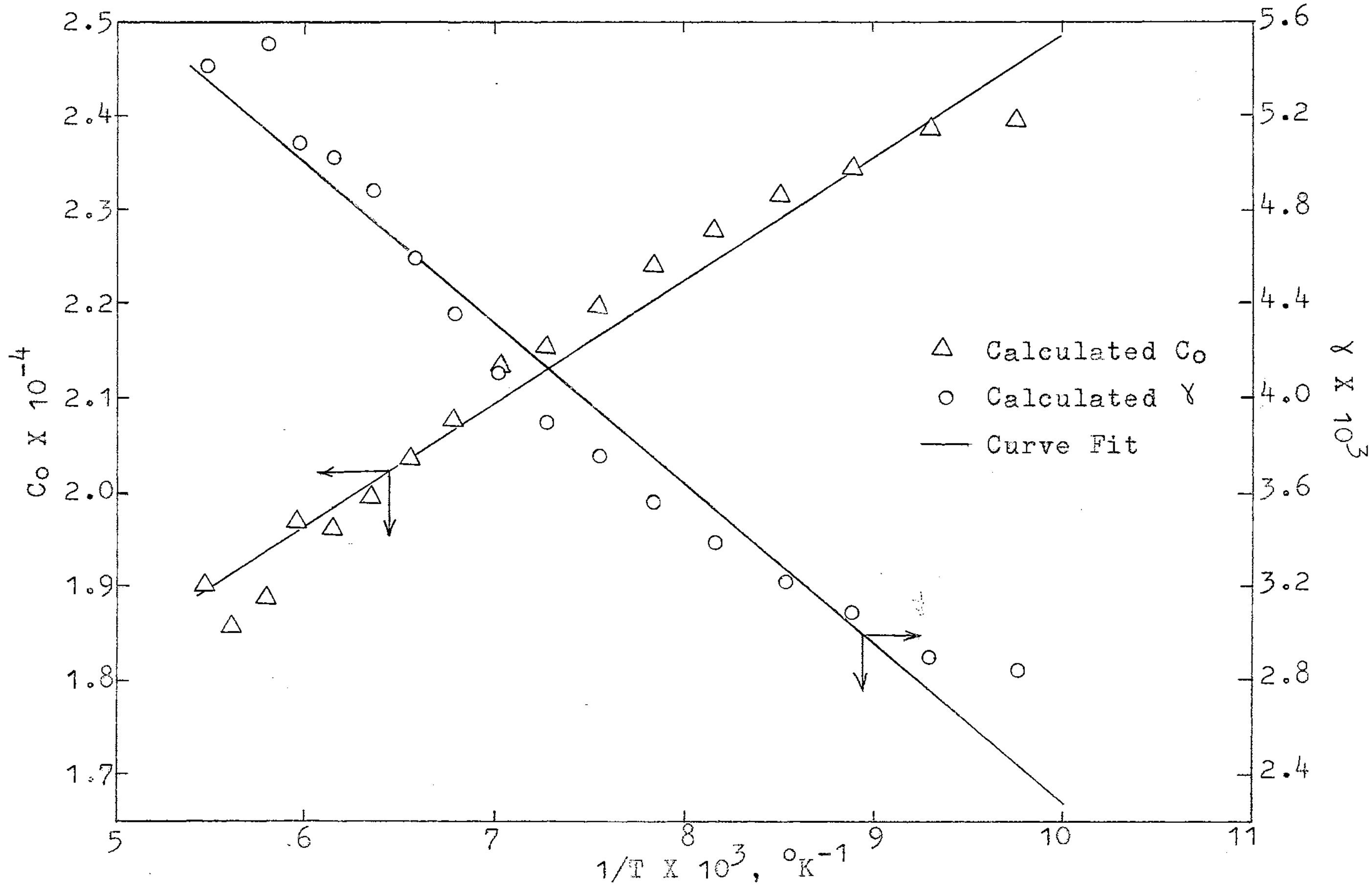


Figure 24. Temperature Dependence Of C_o and γ Simultaneously Determined With Vapor Pressures

TABLE VI

CALCULATED SATURATED PHASE PROPERTIES OF METHANE WITH TEMPERATURE DEPENDENCE OF C_o AND γ DETERMINED WITH VAPOR PRESSURE DATA

Temperature, Degrees Kelvin	Vapor Pressure, Atmospheres	% Deviation*	Liquid Volume liters/gm-mole	% Deviation*	Vapor Volume, liters/gm-mole	% Deviation*
100	0.340	1.11	0.05027	-38.11	23.624	-0.83
105	0.576	-1.96	0.04737	-27.99	14.515	2.83
110	0.899	-1.99	0.04500	-19.58	9.650	3.10
115	1.238	-0.69	0.04355	-13.77	6.748	1.82
120	1.895	0.54	0.04289	-10.01	4.871	0.57
125	2.633	1.34	0.04274	- 7.70	3.596	-0.11
130	3.580	1.68	0.04292	- 6.14	2.703	-0.72
135	4.770	1.75	0.04334	- 5.05	2.065	-0.91
140	6.241	1.55	0.04395	- 4.22	1.599	-1.47
145	8.029	1.27	0.04471	- 3.48	1.254	-0.82
150	10.170	0.97	0.04564	- 2.76	0.9942	-1.30
155	12.702	0.69	0.04672	- 2.07	0.7952	-1.35
160	15.664	0.49	0.04800	- 1.45	0.6403	-1.53
165	19.093	0.25	0.04951	- 0.87	0.5181	-1.51
170	23.034	-0.15	0.05134	- 0.39	0.4199	-1.95
175	27.539	-0.18	0.05363	0.09	0.3396	-1.30
180	32.662	-0.47	0.05665	0.71	0.2723	-2.53
185	38.463	-0.82	0.06105	2.10	0.2142	-2.04
Maximum % Deviation		1.99		38.11		3.10
Absolute Average Deviations		0.99		8.19		1.48

$$* \ \% \text{ Deviation} = \frac{\text{exp-calc}}{\text{exp}} \times 100$$

CHAPTER V

BWR PARAMETERS DETERMINED FROM VOLUMETRIC DATA USING NON-LINEAR REGRESSION

Regression of thermodynamic or p-v-T data to determine BWR equation parameters is a problem in non-linear regression because the parameter γ is involved in the exponential term of the equation. However, the problem can be linearized by assuming values of γ. Values of γ must be assumed and the other seven parameters determined by linear regression until some error function is a minimum. If non-linear regression techniques are used, all eight parameters can be calculated in one regression.

A non-linear curve fit computer program (15) was used for regression of Vennix's (29) low temperature volumetric data on methane to determine all eight parameters in the BWR equation. Two methods were used. One method imposed no restrictions on the regression while the second method employed critical point constraints so that the critical region of methane would be accurately represented.

Regression With No Constraints

One hundred and twenty-six points were selected from the p-v-T data of Vennix. These included data at densities up to twice the critical density. No densities greater than twice the critical density were included because the BWR equation is generally considered to be accurate only to a reduced density of about two. Temperatures ranged from 170° to 290° Kelvin, corresponding to reduced temperatures of 0.89 to 1.52.

The eight parameters - B_o, A_o, C_o, b, a, α , c, γ - that resulted in the minimum sum of the squares of the errors in predicted compressibility factor were determined. The sum of squares of errors was calculated as follows.

$$\text{error sum of squares} = \sum_i (Z_{exp,i} - Z_{calc,i})^2$$

Compressibility factors were calculated by the equation

$$Z_{calc,i} = 1 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3})\rho + (b - \frac{a}{RT})\rho^2 + \frac{a\alpha}{RT}\rho^5 + \frac{c\rho^2}{RT^3}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (5\text{-}1)$$

Compressibility was chosen as the variable because of the relatively small range in Z as compared to pressure or density. The input data included compressibility factors, temperatures, and densities.

Since the non-linear program used required reasonable initial guesses for the BWR parameters, two sets of parameters were determined. In one case, constants determined by Chao (7) were used as initial values while Ahn's (1) constants were used as initial values in the second case. The final results were the same in each case. The eight parameters determined with no constraints are given in Table VII. Of the 126 calculated compressibility factors, the largest per cent error was 2.66 and occurred in the liquid region (T = 190° K, P = 44.8 atm., and Z = 0.2225). The absolute average per cent error was 0.31, and the sum of squares was 4.72303×10^{-4}, giving a root mean square error of 0.0019.

Regression with Critical Point Constraints

Conditions of interest are often near the critical region of a particular component. As conditions approach the critical point the properties undergo a rapid change. For the BWR equation to be of maximum use for engineering calculations, it should accurately represent the critical region. Therefore, critical point relations with which to obtain an exact fit at the critical point were derived.

The critical point relations were derived from Equation (3-1) and conditions which exist at the critical point. At the critical temperature, pressure and density, Equation (3-1) becomes

$$P_c = \rho_c RT_c + \left(B_o RT_c - A_o - \frac{C_o}{T_c^2}\right)\rho_c^2 + (bRT_c - a)\rho_c^3$$

$$+ a\alpha\rho_c^6 + \frac{c\rho_c^3}{T_c^2}(1 + \gamma\rho_c^2)\exp(-\gamma\rho_c^2) \qquad (5\text{-}2)$$

Other conditions which must be satisfied at the critical point are

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c,\rho_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c,\rho_c} = 0$$

The first and second derivatives of pressure with respect to density obtained from the BWR equation are

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c,\rho_c} = 0 = RT_c + 2\left(B_o RT_c - A_o - \frac{C_o}{T_c^2}\right)\rho_c + 3(bRT_c - a)\rho_c^2$$

$$+ 6a\alpha\rho_c^5 + \frac{c\rho_c^2}{T_c^2}(3 + 3\gamma\rho_c^2 - 2\gamma^2\rho_c^4)\exp(-\gamma\rho_c^2) \qquad (5\text{-}3)$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c, \rho_c} = 0 = 2(B_0RT_c - A_0 - \frac{C_0}{T_c^2}) + 6(bRT_c - a)\rho_c$$

$$+ 30a\alpha\rho_c^4 + \frac{c\rho_c}{T_c^2}(6 + 6\gamma\rho_c^2 - 18\gamma^3\rho_c^4 + 4\gamma^3\rho_c^6)\exp(-\gamma\rho_c^2) \tag{5-4}$$

Equations (5-2), (5-3), and (5-4) were used to obtain expressions for α, b, and A_0 in terms of the remaining parameters. The resulting expressions were substituted into Equation (5-1), resulting in an equation containing only five unknown parameters. The five unknown parameters were found by regression of p-v-T data. The equations derived for α, b, and A_0 were

$$\alpha = \frac{P_c - \frac{RT_c\rho_c}{3} + \frac{c\gamma^2\rho_c^7}{3T_c^2}(5 - 2\gamma\rho_c^2)\exp(-\gamma\rho_c^2)}{2a\rho_c^6} \tag{5-5}$$

$$b = \frac{a}{RT_c}(1 - 4\alpha\rho_c^3) + \frac{1}{\rho_c^2} - \frac{2P_c}{RT_c\rho_c^3} - \frac{c}{RT_c^3}(1 + \gamma\rho_c^2 - 2\gamma^2\rho_c^4)\exp(-\gamma\rho_c^2) \tag{5-6}$$

$$A_0 = B_0RT_c - \frac{C_0}{T_c^2} - \frac{P_c}{\rho_c^2} + \frac{RT_c}{\rho_c} + (bRT_c - a)\rho_c$$

$$+ a\alpha\rho_c^4 + \frac{c\rho_c}{T_c^2}(1 + \gamma\rho_c^2)\exp(-\gamma\rho_c^2) \tag{5-7}$$

A detailed derivation of Equations (5-5), (5-6), and (5-7) is given in Appendix B.

Equations (5-5), (5-6), and (5-7) were used to express α, b, and

A_o in Equation (5-1), and Vennix's p-v-T data were regressed to obtain values for the remaining five parameters. The non-linear regression program was used to fit the data. The same 126 data points previously used to determine parameters with no constraints were applied to determine B_o, C_o, a, c, and γ. Chao's and Ahn's parameters were used as initial values in two separate regressions. The final results were the same for each case. The resulting parameters, and α, b, and A_o calculated from Equations (5-5), (5-6), and (5-7), are presented in Table VII. The largest per cent error in compressibility factors was 5.06 and occurred in the liquid region ($T = 180°$ K, $P = 36.4$ atm., and $Z = 0.1394$). The absolute average per cent error was 0.63, and the sum of squares of error was 2.0901×10^{-3}, giving a root mean square error of 0.0041.

In order to check how well the critical point was represented, the critical temperature, pressure, and density were calculated. The predicted critical pressure deviated from the experimental value by 0.31 per cent. The predicted critical density deviated by 0.01 per cent, and the predicted critical temperature was in error by 0.37 per cent. The first and second derivatives of pressure with respect to density were also calculated with the predicted critical properties. The results were

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c, \rho_c} = -0.000226 \text{ liter atm/gm-mole}$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c, \rho_c} = -0.00000858 \text{ (liters/gm-mole)}^2\text{atm}$$

These results indicate that the parameters determined with critical point relations give a satisfactory representation of the critical point.

TABLE VII

BWR PARAMETERS* FOR METHANE

	No Constraints	Critical Point Constraints
B_o	0.038072727	0.053535034
A_o	1.7726941	2.2053264
C_o	22103.202	18419.350
b	0.0040435676	0.0031464092
a	0.061906551	0.036962871
α	8.5228311×10^{-5}	1.4324446×10^{-4}
c	2411.7510	2458.8853
γ	0.0050606757	0.0061359898

* Consistent with metric units

Use of BWR Parameters to Predict Vapor Pressures

The two sets of parameters for methane determined, as described above, were used to predict vapor pressures in the temperature range of 133.73 to 188.801 (T_r = 0.7 to 0.988) degrees Kelvin. The calculated vapor pressures were compared with the experimental data of

Vennix (29); the comparisons are shown in Table VIII. Best results were obtained with the parameters determined by the use of critical point constraints. However, below 144.417 degrees the errors begin to increase substantially, indicating the need for modified parameters at low temperatures. The parameters determined with no constraints give good results at temperatures down to 154.309 degrees. Below that temperature the errors increase as temperature decreases.

BWR Parameters For Hydrogen Sulfide

The p-v-T data of Reamer, Sage, and Lacey (23) were used to determine BWR parameters for hydrogen sulfide. Ninety-seven data points were selected. The data included densities up to twice the critical density. Temperatures ranged from 40° to 340° F ($T_r = 0.74$ to 1.19) and pressures from 100 to 10,000 psia were included. Parameters were determined using critical point constraints as previously described and with no constraints. The non-linear curve fit program was used in both cases to fit the data. The parameters thus determined are presented in Table X. Maximum deviation, average deviation, error sum of squares, and root mean square errors for each set of parameters are listed in Table IX. In each case the largest deviations appeared in the liquid region with the error becoming less as compressibility factor increased. The parameters determined with critical point constraints were used to calculate the critical temperature, pressure, and density. The predicted critical temperature and density were the same as the experimental values, and the critical pressure was in error by 0.02 per cent. The first and second derivatives of pressure with density were

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c, \rho_c} = -0.00223$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c, \rho_c} = -0.0000124$$

Previously, Kate (17) fitted the same hydrogen sulfide data as those used in this study to determine the eight BWR parameters with no constraints. Kate's parameters resulted in a maximum error in compressibility of 1.91 per cent. The absolute average per cent error was 0.44 and the sum of squares of error was $1.2526\mathrm{x}10^{-3}$. Vapor pressures were calculated using Kate's parameters and the parameters determined in this investigation using critical point constraints. In Table XI the calculated vapor pressures are compared with the experimental vapor pressures of Reamer, Sage, and Lacey (23). The two sets of parameters yielded only slightly different results. The values calculated with the parameters having critical point constraints are slightly more accurate near the critical temperature and the lower temperatures. Thus, the critical point constraints improve the BWR equation for calculations in the critical region, and extend its usefulness to lower temperatures without further improvements.

TABLE VIII

COMPARISON OF CALCULATED VAPOR PRESSURES WITH EXPERIMENTAL DATA FOR METHANE

Temperature, Degrees Kelvin	Experimental Vapor Pressure, (29) Atmospheres	Per Cent Deviation	
		No Constraints	Critical Point Constraints
133.730	4.493	7.64	2.05
136.409	5.218	6.37	1.61
138.726	5.904	5.30	1.19
144.417	7.886	3.45	0.71
148.821	9.714	2.33	0.44
154.309	12.395	1.29	0.23
158.213	14.601	0.77	0.16
161.861	16.903	0.41	0.12
165.876	19.728	0.14	0.11
166.017	19.764	-0.22	-0.24
170.407	23.221	-0.41	-0.27
174.332	26.722	-0.26	-0.10
176.443	28.775	-0.09	0.06
177.953	30.278	-0.07	0.04
180.688	33.061	-0.27	-0.30
182.179	34.719	-0.16	-0.29
184.703	37.712	0.15	-0.20
186.524	39.950	0.28	-0.28
188.113	42.016	0.49	-0.33
188.593	42.651	0.54	-0.37
188.801	42.988	0.69	-0.26

TABLE IX

DEVIATION OF PREDICTED COMPRESSIBILITY FACTOR OF HYDROGEN SULFIDE

	No Constraints	Critical Point Constraints
Maximum % error	2.13	7.79
Absolute average % error	0.30	0.92
Sum of squares of error	$3.8936\text{x}10^{-4}$	$2.3454\text{x}10^{-3}$
Root mean square	0.0020	0.0050

TABLE X

BWR PARAMETERS* FOR HYDROGEN SULFIDE

	No Constraints	Critical Point Constraints
B_o	0.033090020	0.065229021
A_o	2.7278084	4.4758284
C_o	256409.65	170631.89
b	0.004605990	0.0028082480
a	0.17896812	0.078536646
α	$6.4931218\text{x}10^{-5}$	$1.4294689\text{x}10^{-4}$
c	23902.765	21123.360
γ	0.0043076199	0.0058352116

* Consistent with metric units

TABLE XI

COMPARISON OF CALCULATED VAPOR PRESSURES WITH EXPERIMENTAL DATA FOR HYDROGEN SULFIDE

Temperature, Degrees Kelvin	Experimental Vapor Pressure (23), Atmospheres	Per Cent Deviation	
		Kate's Parameters	This Study
283.61	13.609	2.85	0.85
299.33	20.414	1.04	0.72
311.61	27.218	0.28	0.75
321.88	34.023	-0.16	0.66
330.77	40.827	-0.27	0.63
338.66	47.632	-0.30	0.51
345.72	54.437	-0.13	0.45
352.05	61.241	0.26	0.49
358.11	68.046	0.21	0.16
363.61	74.850	0.65	-0.11

CHAPTER VI

SECOND AND THIRD VIRIAL COEFFICIENTS IN THE BWR EQUATION

McMath (20) suggested that an improved BWR equation could be developed by proper use of experimental data on second and third virial coefficients. McMath stated that the second and third virial coefficients should be fitted to experimental data to determine the parameters B_o, A_o, C_o and b, a, and c, respectively. The remaining two parameters, α and γ, could then be found using experimental p-v-T data.

The BWR equation has the following form explicit in compressibility factor.

$$Z = 1 + \left(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right)\rho + \left(b - \frac{a}{RT}\right)\rho^2 + \frac{a\alpha\rho^5}{RT} + \frac{c\rho^2}{RT^3}(1+\gamma\rho^2)\exp(-\gamma\rho^2) \qquad (6\text{-}1)$$

The exponential term in Equation (6-1) may be expanded into an infinite power series.

$$\exp(-\gamma\rho^2) = 1 - \gamma\rho^2 + \frac{\gamma^2\rho^4}{2} - \frac{\gamma^3\rho^6}{6} + \cdots \qquad (6\text{-}2)$$

Equation (6-1) may be written in an open-ended virial form by substituting Equation (6-2) into Equation (6-1) and rearranging according to increasing powers of density.

$$Z = 1 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3})\rho + (b - \frac{a}{RT} + \frac{c}{RT^3})\rho^2$$

$$+ \frac{a\alpha\rho^5}{RT} - \frac{c\gamma^2\rho^6}{2RT^3} + \cdots \qquad (6\text{-}3)$$

The virial equation of state may be written as

$$Z = 1 + B(T)\rho + C(T)\rho^2 + \cdots \qquad (6\text{-}4)$$

where B(T) and C(T) are the second and third virial coefficients, respectively. Comparing corresponding terms of Equations (6-3) and (6-4), the second and third virial coefficients are given by the BWR equation as

$$B(T) = B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} \qquad (6\text{-}5)$$

$$C(T) = b - \frac{a}{RT} + \frac{c}{RT^3} \qquad (6\text{-}6)$$

The second virial coefficient, Equation (6-5), was fitted to experimental pure component methane virial coefficients presented by Hoover (16) in order to evaluate the parameters B_o, A_o, and C_o. The experimental second virial coefficients represented the temperature range from 131.93 to 273.15 degrees Kelvin. The curve fitted equation gave values of the second virial coefficients that were within 0.29 per cent of the experimental values. The three parameters thus obtained were

$B_o = 0.078919$

$A_o = 2.86532$

$C_o = 7203.32$

The second virial coefficients are shown in Table XII.

The third virial coefficient, Equation (6-6), was fitted to experimental data of Hoover (16). Experimental third virials also covered the temperature range of 131.93 to 273.15 degrees K. However, Equation (6-6) could not be made to give a good fit of the data. The third virials were then fitted to the following equation, which was suggested by Chueh and Prausnitz (8):

$$C(T) = V_c^2(a_1 T_r^{-0.25} + a_2 T_r^{-5}) \left[1 - \exp(1 - a_3 T_r^2)\right] \qquad (6\text{-}7)$$

where V_c is the critical volume; T_r, the reduced temperature; and a_1, a_2, and a_3 are constants determined by non-linear regression of the experimental third virial coefficients. The third virials thus calculated had maximum error of 3.67 per cent and an absolute average per cent error of 1.87. These errors in calculated third virials were within the range of expected experimental uncertainty claimed by Hoover. The results are shown in Table XIII.

Equations (6-5) and (6-7) were then substituted into the following form of the BWR equation.

$$Z = 1 + B(T)\rho + \left(C(T) - \frac{c}{RT^3}\right)\rho^2 + \frac{a\alpha\rho^5}{RT} + \frac{c\rho^2}{T^3}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (6\text{-}8)$$

The volumetric data for methane of Vennix (29) were then fitted to Equation (6-8) in order to determine values of a, c, and γ that gave the lowest possible sum of squares of error in compressibility factor. The 126 data points used included densities up to twice the critical density and covered the temperature range of 170° to 270° K. The non-linear curve fit program was used to fit the data. The absolute average per cent error in predicted compressibility factors was 7.24 with a maximum error of 67 per cent. The sum of squares of error was 0.383558.

Although the use of virial coefficients to improve the BWR equation was not satisfactory, some trends were noted. The largest errors in compressibility factor occurred at temperatures of 190° and lower. These temperatures correspond to the range of temperatures not represented in the experimental virial coefficients. No data on the virials at temperatures between 131.93 and 191.06 degrees K were available. Table XIII shows that Equation (6-7) fits the experimental data. However, the region between 131.93 and 191.06 degrees may not be satisfactorily represented since the third virial undergoes a drastic change.

Figure 61 compares experimental third virial coefficients with those calculated with Equation (6-7) and values predicted from the usual expression for C(T) [Equation (6-6)] from the BWR equation. The differences calculated from both expressions at low temperatures could explain why the calculated compressibility factors showed considerable error at the lower temperatures. At reduced temperatures below about 0.95, the third virial calculated from the usual equation does not give the correct qualitative behavior.

TABLE XII

COMPARISON OF CALCULATED SECOND VIRIAL COEFFICIENTS OF METHANE WITH EXPERIMENTAL DATA

Temperature, Degrees, Kelvin	Experimental Data (16)		% Deviation
	B(T) cc/gm-mole	% Maximum Probable Error	
131.93	-224.	9.0	0.00
191.06	-116.31	1.0	0.11
200.00	-106.68	1.0	0.03
215.00	- 92.51	0.4	0.28
240.00	- 72.72	0.3	0.29
273.15	- 53.28	0.2	0.09

TABLE XIII

COMPARISON OF CALCULATED THIRD VIRIAL COEFFICIENTS OF METHANE WITH EXPERIMENTAL DATA

Temperature, Degrees, Kelvin	Experimental Data (16)		% Deviation
	C(T) $(cc/gm\text{-}mole)^2$	% Maximum Probable Error	
131.93	-13600.	90.0	0.00
191.06	4741.	10.0	1.69
200.00	4351.	10.0	3.67
215.00	4169.	4.0	1.28
240.00	3508.	3.0	2.39
273.15	2669.6	2.0	2.19

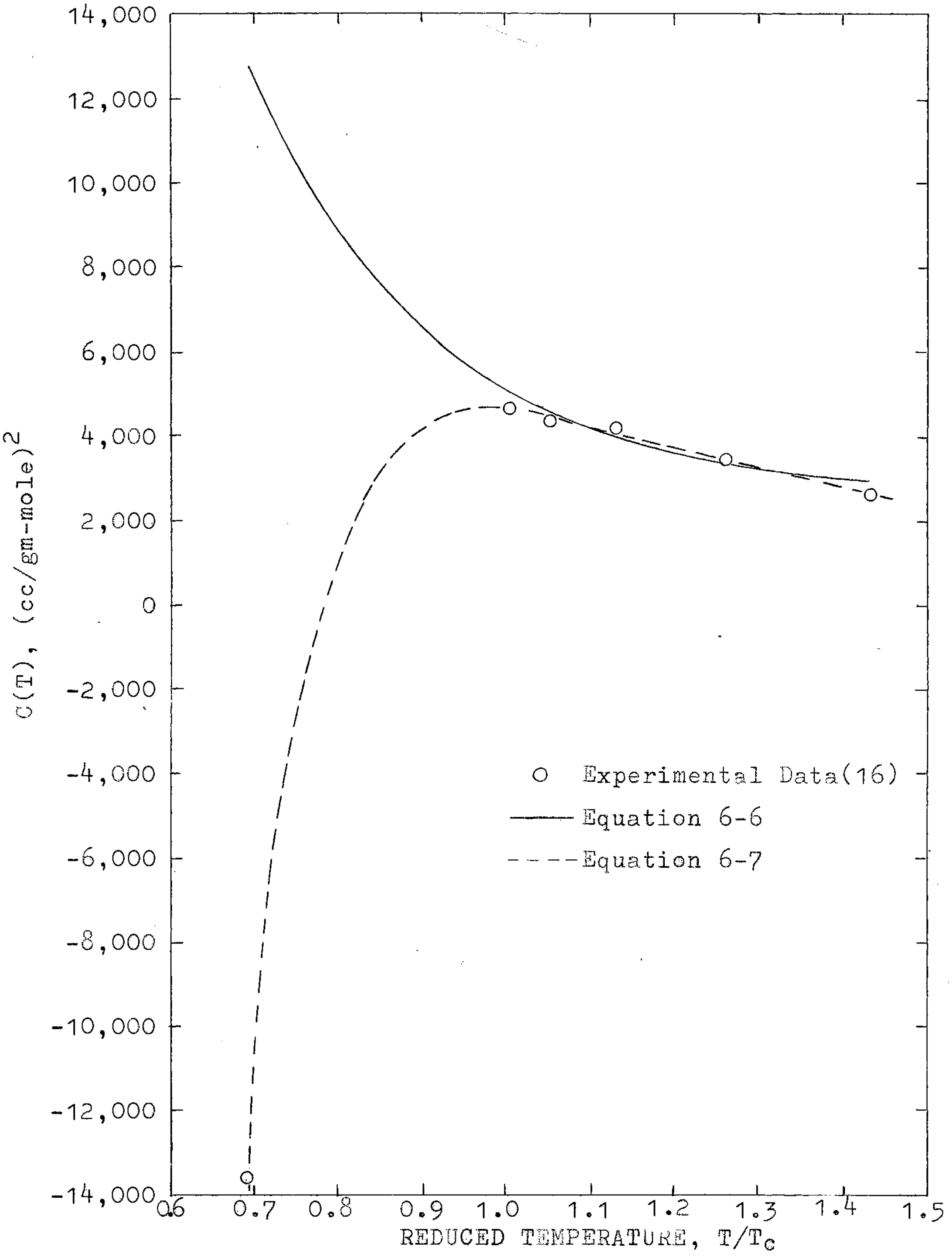


Figure 25. Third Virial Coefficients For Methane

CHAPTER VII

VAPOR-LIQUID EQUILIBRIA FOR METHANE-HYDROGEN SULFIDE MIXTURES USING THE BWR EQUATION

Although the BWR equation can be modified to accurately predict pure component behavior, previous investigations have indicated that the results for mixtures are not always satisfactory. In particular, mixtures containing hydrocarbons with a wide boiling range or mixtures of non-hydrocarbons with hydrocarbons could not be fully represented by the BWR equation without further modification. Stotler and Benedict (28) suggested that one of the interaction constants [corresponding to the parameter A_o in Equation (7-1)] be fitted to experimental data for mixtures. The suggestion that A_o be modified indicated that the simple mixing rules which were set up to compute the interaction constants may not be applicable to all cases. In this investigation, vapor-liquid equilibria calculations were made for methane-hydrogen sulfide mixtures in order to test the mixing rules for this particular system.

Basic BWR Equation

Equation (3-1) may be applied to mixtures as well as pure components.

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

$$+ \ a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1+\gamma\rho^2) \exp(-\gamma\rho^2) \qquad (3\text{-}1)$$

Mixing rules suggested by the original authors of the BWR equation (5) give the parameters as functions of composition and pure component parameters. These rules, listed below, were used in the present work.

$$\begin{aligned}
B_o &= \sum x_i B_{oi} \\
A_o &= (\sum x_i A_{oi}^{\frac{1}{2}})^2 \\
C_o &= (\sum x_i C_{oi}^{\frac{1}{2}})^2 \\
b &= (\sum x_i b_i^{1/3})^3 \\
a &= (\sum x_i a_i^{1/3})^3 \qquad (7\text{-}1) \\
\alpha &= (\sum x_i \alpha_i^{1/3})^3 \\
c &= (\sum x_i c_i^{1/3})^3 \\
\gamma &= (\sum x_i \gamma_i^{\frac{1}{2}})^2
\end{aligned}$$

The mixing rules are applied to both liquid and vapor phases. The Lorentz mixing rule for B_o was suggested by Benedict (5) as a possible alternative for the linear mixing rule. The Lorentz mixing rule is

$$B_o = \sum x_i x_j (B_{oi}^{1/3} + B_{oj}^{1/3})^3/8 \qquad (7\text{-}2)$$

Benedict stated that results obtained using the two mixing rules were only slightly different. Therefore, the linear mixing rule was used for this investigation because of its simplicity and ease of application.

The criteria applied for vapor-liquid equilibria calculations of binary mixtures were the following.

$$P(\rho^{V}, y_i, T) = P(\rho^{L}, x_i, T)$$

$$RT\ln f_i(\rho^{L}, x_i, T) = RT\ln f_i(\rho^{V}, y_i, T)$$

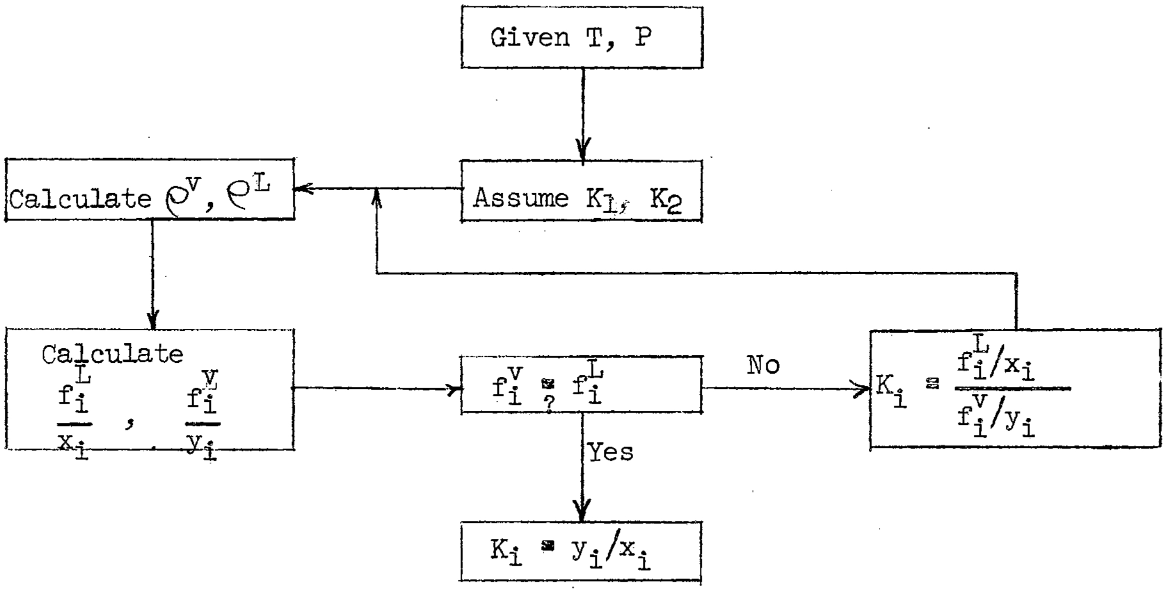
Temperature and pressure were specified and ρ^L, ρ^V, x_1, y_1, x_2, and y_2 were found by trial and error.

Liquid and vapor densities were calculated from Equation (3-1) using the Newton-Raphson convergence technique. Fugacities were calculated from the following equation.

$$\begin{aligned} RT\ln\frac{f_i}{x_i} &= RT\ln\rho RT + \left[(B_o + B_{oi})RT - 2(A_oA_{oi})^{\frac{1}{2}} - \frac{2(C_oC_{oi})^{\frac{1}{2}}}{T^2}\right]\rho \\ &+ \frac{3}{2}\left[RT(b^2b_i)^{1/3} - (a^2a_i)^{1/3}\right]\rho^2 + \frac{3}{5}\left[a(\alpha^2\alpha_i)^{1/3} + \alpha(a^2a_i)^{1/3}\right]\rho^5 \\ &+ 3\rho^2\frac{(c^2c_i)^{1/3}}{T^2}\left[\frac{1-\exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2}\right] \\ &- \frac{2\rho^2 c}{T^2}\left(\frac{\gamma_i}{\gamma}\right)^{\frac{1}{2}}\left[\frac{1-\exp(-\gamma\rho^2)}{\gamma\rho^2} - \exp(-\gamma\rho^2) - \frac{\gamma\rho^2\exp(-\gamma\rho^2)}{2}\right] \end{aligned} \tag{7-3}$$

In Equation (7-3), the non-subscripted parameters were calculated with the mixing rules, and the subscript i refers to pure component parameters.

The procedure used for calculating equilibrium compositions is shown in the following simplified outline.



Vapor-Liquid Equilibria Calculation Scheme

The first step was to assume values of the equilibrium ratios, K_1 and K_2. The liquid and vapor compositions were then calculated from the equations

$$x_1 = \frac{K_2-1}{K_2-K_1}$$

$$x_2 = 1 - x_1$$

$$y_i = x_i K_i$$

Using the mole fractions thus calculated the mixture parameters for both phases were determined from Equations (7-1). Next, liquid and vapor densities were calculated using Equation (3-1). Finally, liquid and vapor fugacities for both components were calculated. If the liquid and vapor fugacities were not equal, new K-values were calculated by the equation

$$K_i = \frac{f_i^L/x_i}{f_i^V/y_i} \tag{7-4}$$

The procedure was then repeated. When the vapor and liquid fugacities of both components were the same (a tolerance of 0.1 per cent was used). Equation (7-4) reduced to

$$K_i = \frac{y_i}{x_i}$$

Thus, the final K-values were determined.

Vapor-liquid equilibria calculations were made for methane-hydrogen sulfide mixtures at 277.78, 310.96, and 344.26 degrees K at pressures up to 119.08 atmospheres. Initially, no modifications were applied to the BWR equation and two sets of parameters were used. In one case, the parameters used for both components were those determined with no constraints. In the second case, the pure component parameters were those determined with critical point constraints. Best results were obtained using the parameters with critical point constraints. However, the liquid phase compositions were not satisfactory in either case. These results indicated that some modification was needed in order to improve the BWR equation for the methane-hydrogen sulfide mixtures.

Since the temperatures considered were above the critical temperature of methane, the use of temperature dependent parameters for pure methane was not considered. Although the temperatures were below the critical temperature of hydrogen sulfide, temperature dependent parameters for hydrogen sulfide were not needed. The results in Table XI showed that the unmodified parameters accurately represent the subcritical region of hydrogen sulfide at temperatures as low as 283.6 degrees K.

Modified Mixing Rule for A_o

Since there was no need to modify the pure component parameters, indications were that the mixing rules needed to be adjusted. An empirical interaction coefficient, Θ, was introduced into the usual mixing rule for A_o. The modified rule for a binary mixture was

$$A_o = x_i^2 A_{oi} + 2x_i x_j \Theta (A_{oi} A_{oj})^{\frac{1}{2}} + x_j^2 A_{oj} \qquad (7\text{-}5)$$

When $\Theta = 1$, Equation (7-5) reverts to the usual rule, Equation (7-1).

When the interaction constant was applied to A_o, the equation for fugacity, Equation (7-3), had to be modified also. The term

$$2(A_o A_{oi})^{\frac{1}{2}}$$

in Equation (7-3), which was derived from the usual mixing rule, was replaced by

$$2 \left[x_i A_{oi} + x_j \Theta (A_{oi} A_{oj})^{\frac{1}{2}} \right]$$

for component i. Derivation of the modified fugacity equation is given in Appendix C.

The value of Θ that resulted in the most accurate vapor-liquid equilibria calculations was found, by trial and error calculations, to be 0.898 for the parameters with critical point constraints and 0.892 for the parameters having no constraints. Phase compositions calculated using parameters with constraints are compared with experimental data (24) in Figures 29, 30, and 31. Figures 26, 27, and 28 show the results obtained using parameters with no constraints. The use of an empirical interaction coefficient improved the equilibrium calculations considerably. Compositions of both phases were accurately predicted with each set of parameters using their respective value of Θ. However, best results were again obtained using the parameters with critical point constraints. Predicted liquid and vapor compositions are compared with the experimental data of Reamer, Sage, and Lacey (24) in Table XIV.

Recently, Masuda and Yorizane (19) determined BWR parameters specifically for prediction of vapor-liquid equilibrium of hydrogen sulfide. They then used their parameters for hydrogen sulfide in conjunction with Benedict's constants (6) for methane to calculate equilibrium compositions of the methane-hydrogen sulfide system. The same constants used by Masuda and Yorizane were applied in this study to predict equilibrium compositions at 277.78, 310.96, and 344.26 degrees K. The results are compared with the data of Reamer, Sage, and Lacey in Table XIV. Although the vapor phase was well represented, the liquid phase compositions deviated considerably.

Kate (17) applied the BWR equation with the modified mixing rule for A_o to experimental data on gas phase partial volumes of hydrogen sulfide in methane at infinite dilution at 100° F and pressures of

100 to 2,000 psia. Using his parameters for hydrogen sulfide and Douslin's (12) methane parameters, Kate found the value of Θ to be 0.8673. Kate's hydrogen sulfide parameters and Θ and Douslin's methane parameters were used to predict phase compositions. The results are shown in Table XIV. Vapor phase calculations showed small deviations, but predicted liquid phase compositions varied considerably from experimental compositions.

TABLE XIV

PHASE COMPOSITIONS OF METHANE-HYDROGEN SULFIDE MIXTURES

Comparison of Parameters With Critical Point Constraints And Parameters With No Constraints for Phase Equilibria Calculations

Temp. °K	Pressure Atm	Experimental (24) Hydrogen Sulfide Mole Fractions		Calculated Hydrogen Sulfide Mole Fractions With $A_{o12}=0.898(A_{o1}A_{o2})^{\frac{1}{2}}$ and Critical Point Constraints				Calculated Hydrogen Sulfide Mole Fractions With $A_{o12}=0.898(A_{o1}A_{o2})^{\frac{1}{2}}$ and No Constraints			
		Liquid	Vapor	Liquid	Error exp-calc	Vapor	Error exp-calc	Liquid	Error exp-calc	Vapor	Error exp-calc
277.78	13.61	0.9943	0.8629	0.9947	-0.0004	0.8600	0.0029	0.9909	0.0034	0.7529	0.1100
	27.22	0.9646	0.4874	0.9608	0.0038	0.4825	0.0049	0.9570	0.0076	0.4183	0.0691
	68.05	0.8750	0.2768	0.8534	0.0216	0.2744	0.0024	0.8514	0.0236	0.2336	0.0432
	88.46	0.8132	0.2694	0.7944	0.0188	0.2612	0.0082	0.7948	0.0184	0.2209	0.0485
	108.87	0.7202	0.2925	0.7300	-0.0098	0.2714	0.0211	0.7353	-0.0151	0.2297	0.0628
	119.08	0.6508	0.3172	0.6954	-0.0446	0.2834	0.0338	0.7020	-0.0512	0.2415	0.0757
310.96	27.22	0.9993	0.9883	0.9988	0.0005	0.9832	0.0051	0.9950	0.0043	0.9344	0.0539
	40.83	0.9745	0.7312	0.9688	0.0057	0.7232	0.0080	0.9636	0.0109	0.6835	0.0477
	68.05	0.9172	0.5393	0.9073	0.0099	0.5277	0.0116	0.8975	0.0197	0.4911	0.0482
	88.46	0.8610	0.4818	0.8574	0.0036	0.4751	0.0067	0.8440	0.0170	0.4390	0.0428
	108.87	0.7808	0.4805	0.8026	-0.0218	0.4607	0.0198	0.7842	-0.0034	0.4245	0.0560
	119.08	0.7275	0.5053	0.7736	-0.0461	0.4642	0.0411	0.7486	-0.0211	0.4291	0.0762
344.26	54.44	0.9969	0.9804	0.9962	0.0007	0.9779	0.0025	0.9927	0.0042	0.9599	0.0205
	61.24	0.9833	0.9054	0.9828	0.0005	0.9130	-0.0076	0.9771	0.0062	0.8899	0.0155
	68.05	0.9691	0.8447	0.9691	0.0000	0.8615	-0.0168	0.9610	0.0081	0.8353	0.0094
	81.66	0.9378	0.7633	0.9393	-0.0015	0.7865	-0.0232	0.9277	0.0101	0.7593	0.0140
	95.26	0.8979	0.7189	0.9077	-0.0098	0.7443	-0.0254	0.8891	0.0098	0.7115	0.0074
	108.87	0.8453	0.7420	0.8706	-0.0253	0.7242	0.0178	0.8413	0.0040	0.6886	0.0534

Absolute Avg. Deviation=0.0131 Absolute Avg. Deviation=0.0303

TABLE XIV (Continued)

Comparison of Kate's (17) and Masuda's (19) BWR Parameters for Phase Equilibria Calculations

Temp, °K	Pressure Atm	Experimental (24) Hydrogen Sulfide Mole Fractions		Calculated Hydrogen Sulfide Mole Fractions With $A_{o12}=0.8673(A_{o1}A_{o2})^{\frac{1}{2}}$ And Kate's Parameters				Calculated Hydrogen Sulfide Mole Fractions With $A_{o12}=(A_{o1}A_{o2})^{\frac{1}{2}}$ And Masuda's Parameters			
		Liquid	Vapor	Liquid	Error exp-calc	Vapor	Error exp-calc	Liquid	Error exp-calc	Vapor	Error exp-calc
277.78	13.61	0.9943	0.8629	0.9988	-0.0045	0.8404	0.0225	0.9957	-0.0014	0.9287	-0.0658
	27.22	0.9646	0.4874	0.9924	-0.0278	0.4802	0.0072	0.9399	0.0247	0.5152	-0.0278
	68.05	0.8750	0.2768	0.9743	-0.0993	0.2825	-0.0057	0.7455	0.1295	0.2875	-0.0107
	88.46	0.8132	0.2694	0.9661	-0.1259	0.2631	0.0063	0.6243	0.1889	0.2776	-0.0082
	108.87	0.7202	0.2925	0.9568	-0.2384	0.2561	0.0364	--		--	
	119.08	0.6508	0.3172	0.9550	-0.3042	0.2549	0.0623	--		--	
310.96	27.22	0.9993	0.9883	0.9997	-0.0004	0.9873	0.0010	0.9997	-0.0004	0.9966	-0.0083
	40.83	0.9745	0.7312	0.9916	-0.0171	0.7377	-0.0065	0.9576	0.0169	0.7273	0.0039
	68.05	0.9172	0.5393	0.9754	-0.0582	0.5493	-0.0100	0.8625	0.0547	0.5262	0.0131
	88.46	0.8610	0.4818	0.9633	-0.1023	0.4954	-0.0136	0.7758	0.0852	0.4766	0.0052
	108.87	0.7808	0.4805	0.9515	-0.1707	0.4703	0.0102	0.6620	0.1188	0.4854	-0.0049
	119.08	0.7275	0.5053	0.9455	-0.2180	0.4632	0.0421	--		--	
344.26	54.44	0.9969	0.9804	0.9989	-0.0020	0.9849	-0.0045	0.9921	0.0048	0.9625	0.0179
	61.24	0.9833	0.9054	0.9933	-0.0100	0.9205	-0.0151	0.9737	0.0096	0.8929	0.0125
	68.05	0.9691	0.8477	0.9877	-0.0186	0.8708	-0.0261	0.9538	0.0153	0.8375	0.0072
	81.66	0.9378	0.7633	0.9760	-0.0382	0.8007	-0.0374	0.9079	0.0299	0.7852	0.0051
	95.26	0.8979	0.7189	0.9640	-0.0661	0.7577	-0.0388	0.8587	0.0412	0.7201	-0.0012
	108.87	0.8453	0.7420	0.9514	-0.1061	0.7310	-0.0110	--		--	

Absolute Average Deviation = 0.0553

Absolute Average Deviation = 0.0326

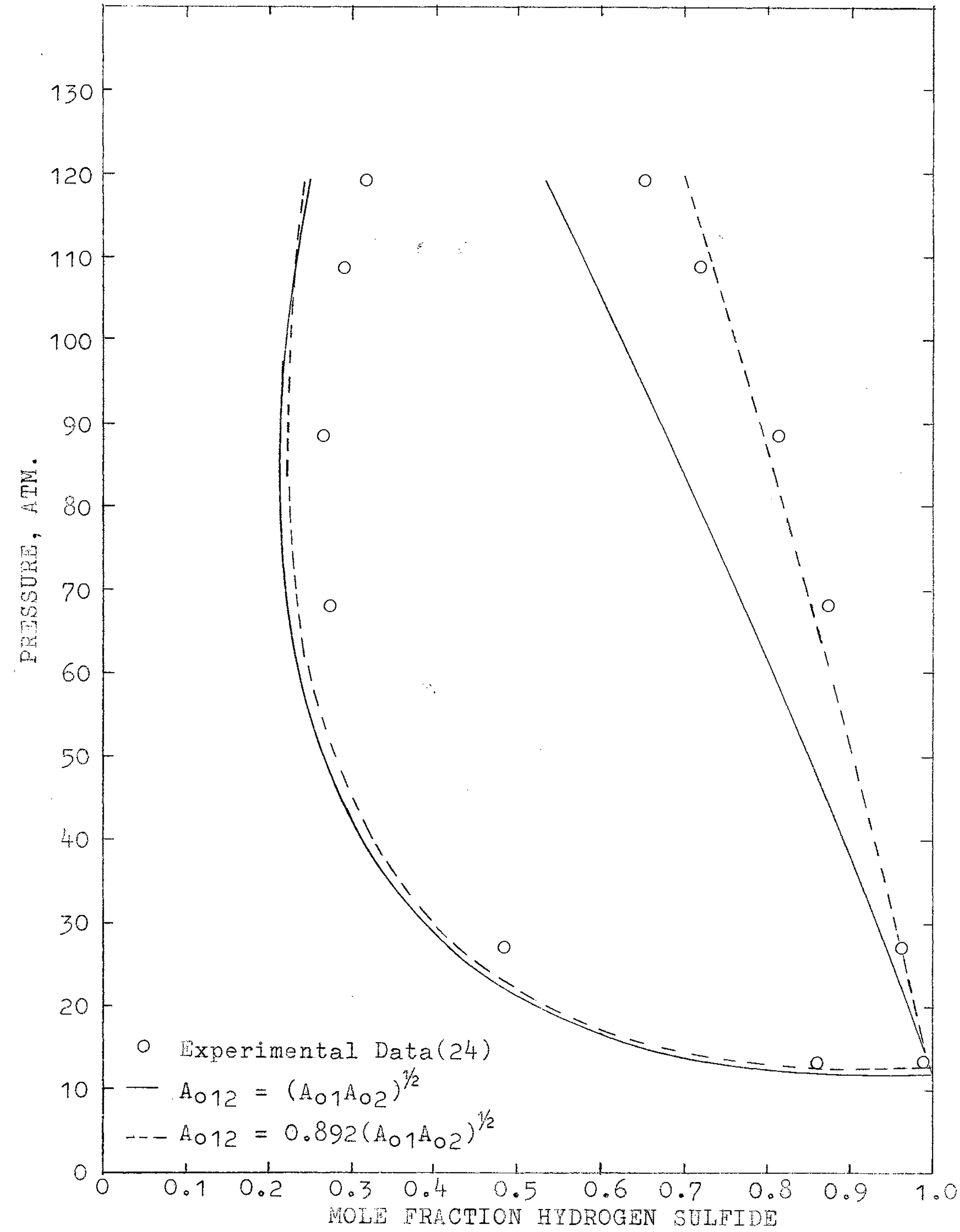


Figure 26. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 277.78°K Calculated With BWR Parameters Having No Constraints

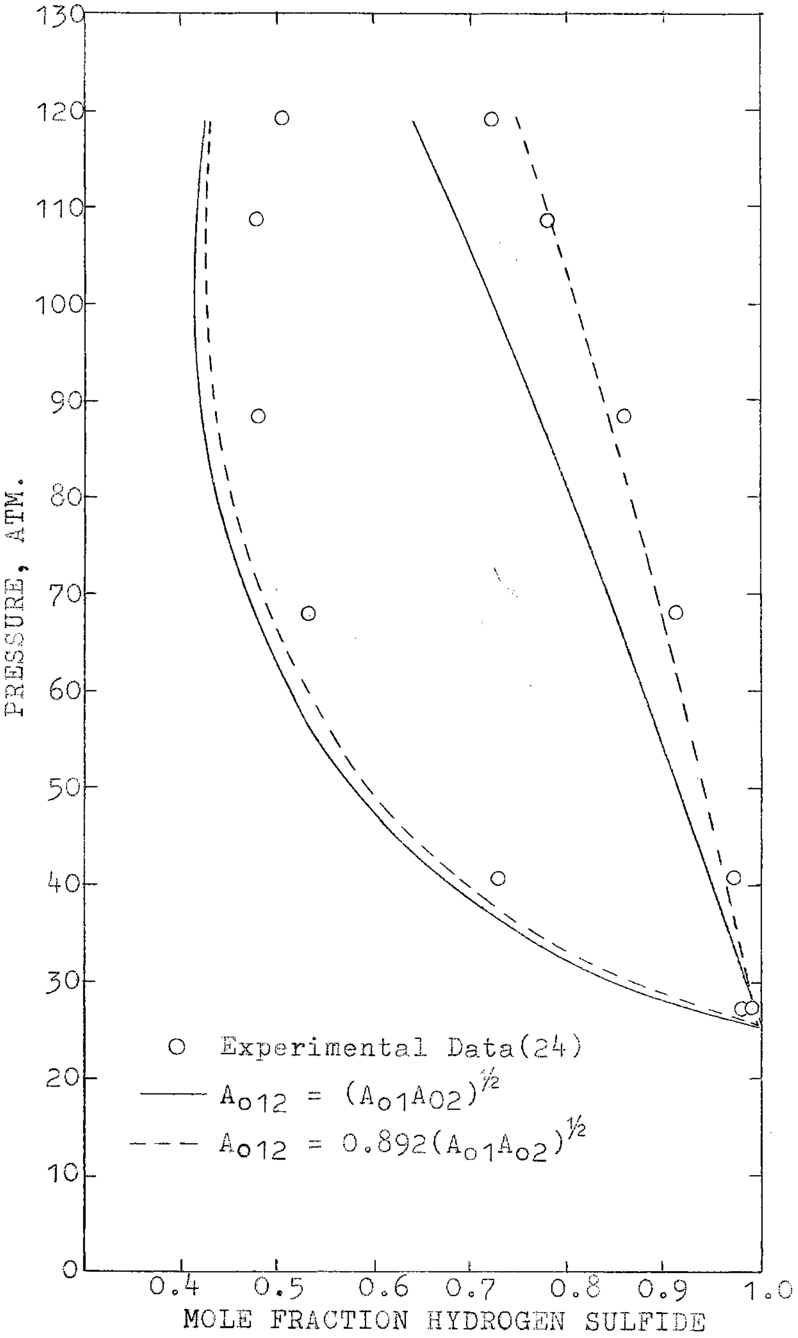


Figure 27. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 310.96° K Calculated With BWR Parameters Having No Constraints

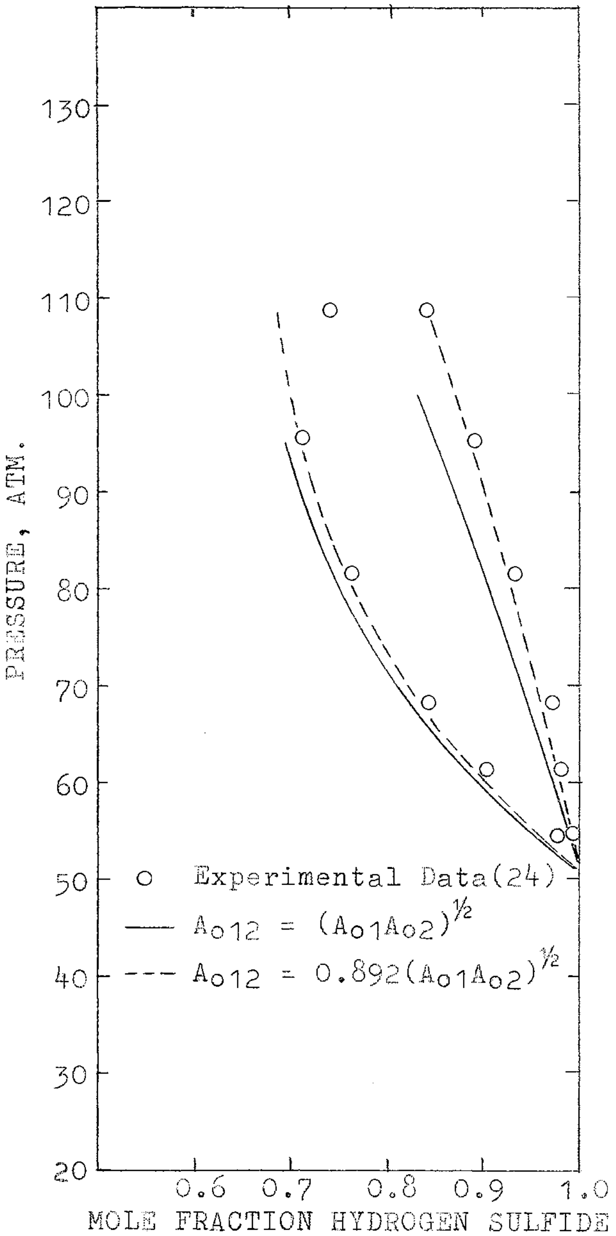


Figure 28. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 344.26° K Calculated With BWR Parameters Having No Constraints

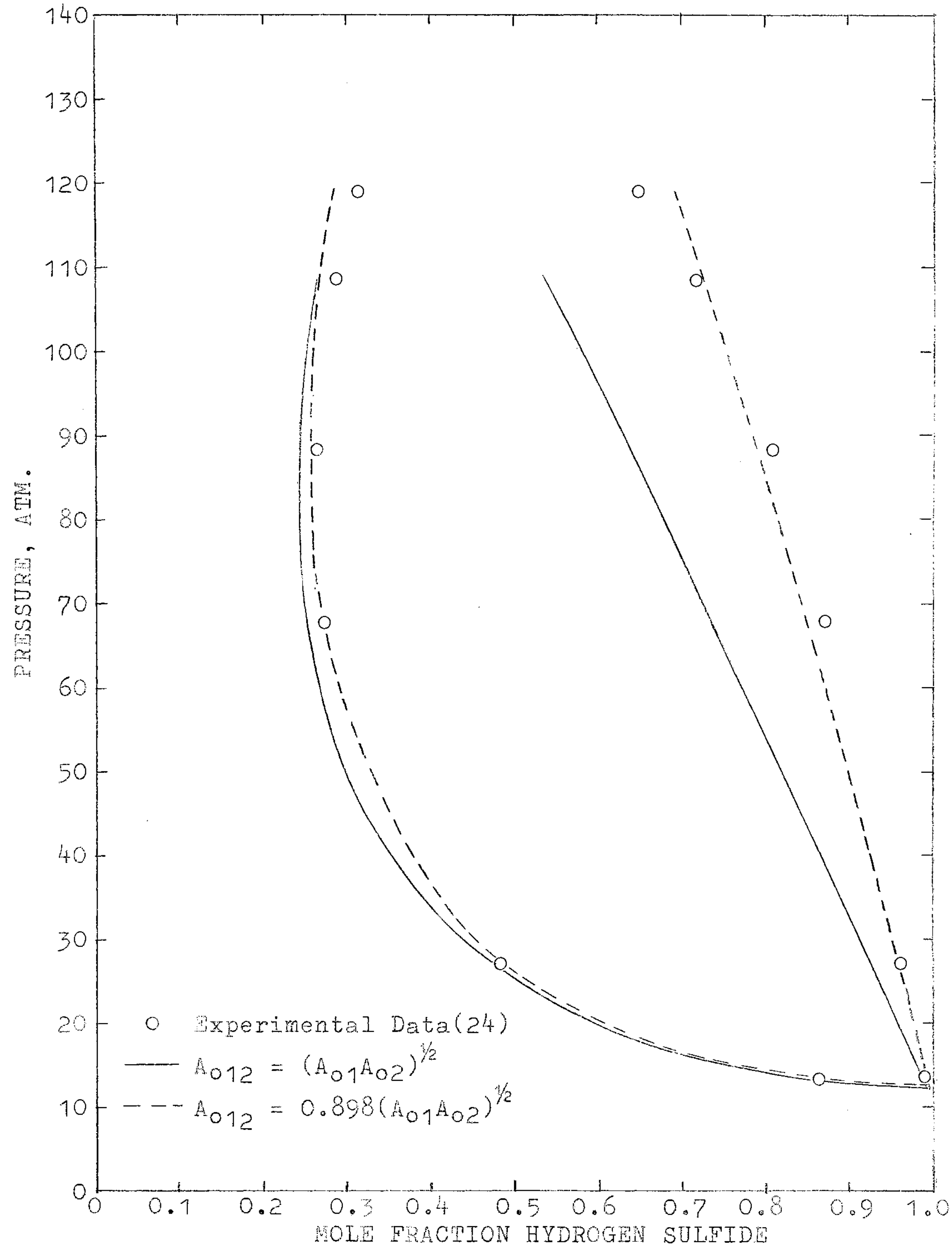


Figure 29. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 277.78°K Calculated With BWR Parameters Having Critical Point Constraints

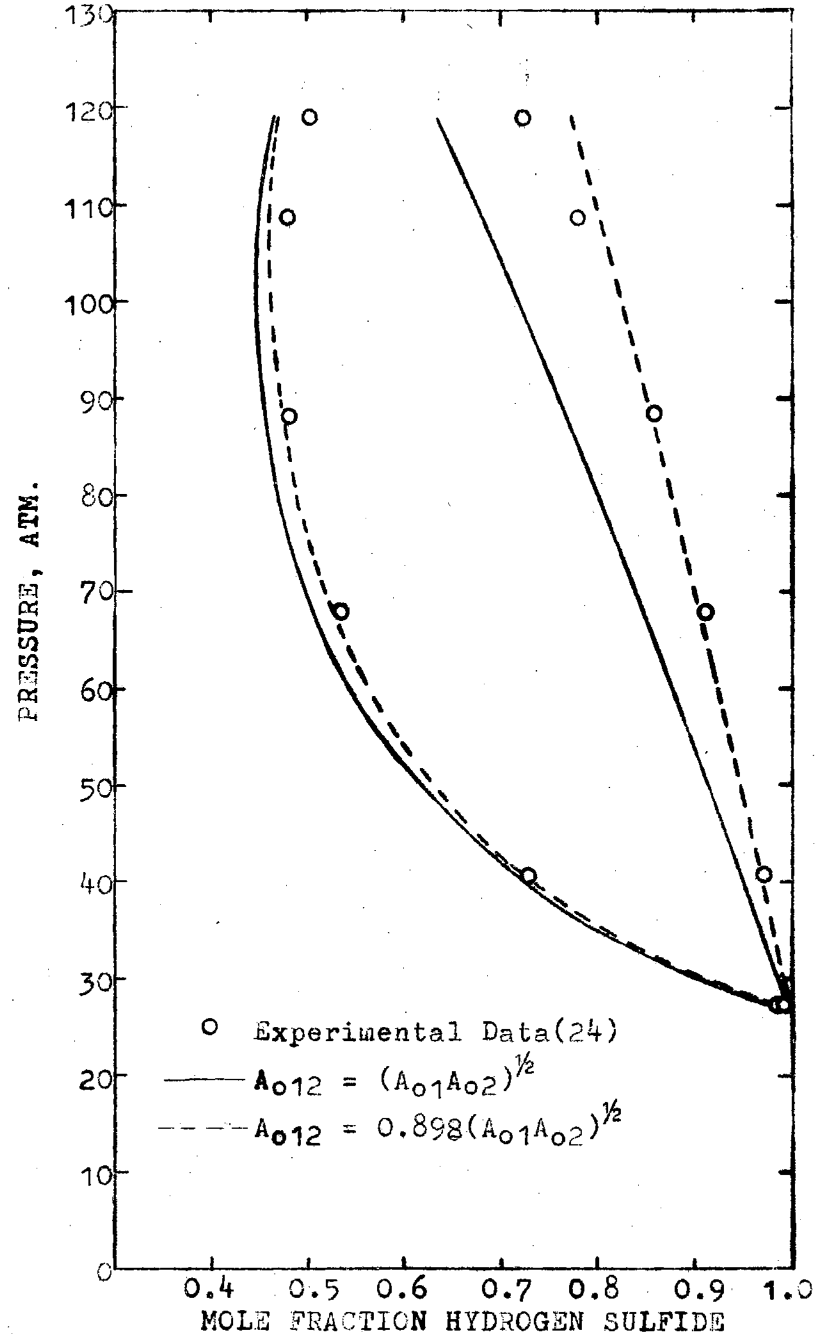


Figure 30. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 310.96° K Calculated With BWR Parameters Having Critical Point Constraints

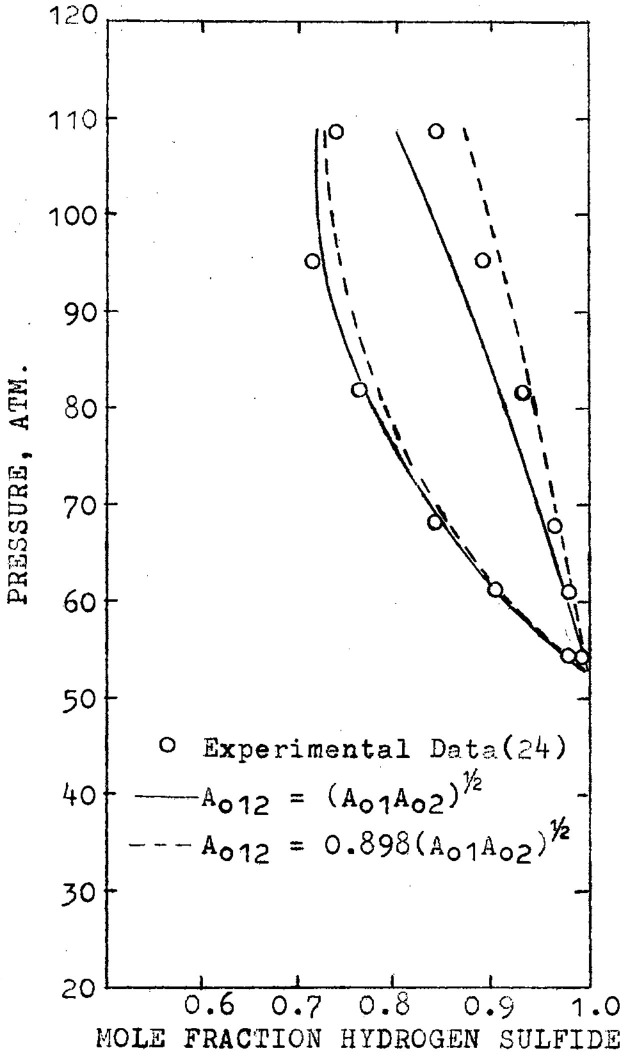


Figure 31. Equilibrium Compositions Of Methane-Hydrogen Sulfide Mixtures At 344.26° K Calculated With BWR Parameters Having Critical Point Constraints

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

This study was concerned with several possible modifications of the Benedict-Webb-Rubin equation. Specific investigations included (a) preliminary investigations to determine the effects of each of the eight BWR parameters on calculated pressure, saturated phase fugacity, and vapor pressure for methane, (b) simultaneous fit of two BWR parameters to predict saturated phase properties, (c) non-linear regression of p-v-T data to determine pure component BWR parameters for methane and hydrogen sulfide, and (d) vapor-liquid equilibria calculations with the BWR equation for methane-hydrogen sulfide mixtures.

The major conclusions of this investigation are

1. Pressure and vapor pressure are most sensitive to changes in the parameter A_o, while c had the greatest effect on saturated phase fugacities, thus indicating that these parameters may be best suited for modification.
2. The simultaneous fit of two constants to vapor pressures or vapor pressures and saturated liquid densities reveal a temperature dependence of the parameters which is not of an apparent simple functional form.
3. Two BWR parameters can be fitted simultaneously to vapor pressures and saturated liquid densities.

Specifically, four pairs of parameters - A_0 and γ, C_0 and γ, γ and α, c and γ gave results of comparable accuracy when fitted as linear functions of reciprocal temperature to vapor pressures and liquid densities for methane.

4. Although the simultaneous fit of two BWR parameters to vapor pressures only could be made, the results were not satisfactory with respect to prediction of saturated liquid densities.
5. The use of experimental second and third virial coefficients to determine six BWR parameters did not result in satisfactory representation of p-v-T behavior, especially in the region below the critical temperature where the third virial predicted by the BWR equation does not give the correct qualitative behavior.
6. BWR parameters which yield exact fit to the critical point conditions were determined for the pure components methane and hydrogen sulfide.
7. Predictions of vapor-liquid equilibria using the BWR equation with the usual mixing rules and parameters for hydrogen sulfide and methane determined in this study did not yield satisfactory results.
8. The use of BWR parameters constrained to critical point behavior for the heavy component, hydrogen sulfide, in the methane-hydrogen sulfide system gave improved results relative to unconstrained parameters when basic mixing rules were used.

9. An empirical interaction coefficient applied to the mixing rule of A_o improved the vapor-liquid equilibria calculations for the methane-hydrogen sulfide system, with the most accurate results being obtained using pure component parameters satisfying the critical point conditions.

The results of this investigation have led to the following recommendations:

1. A study should be made to see if the empirical interaction coefficient in the mixing rule of A_o based on vapor-liquid equilibria can be applied to p-v-T and enthalpy-entropy calculations.
2. The BWR equation could be modified for three binary mixtures and the results applied to a ternary system to see if calculated ternary data is better predicted.

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APPENDIX A

APPENDIX A

METHOD FOR CALCULATING PURE COMPONENT SATURATED PHASE PROPERTIES WITH THE BWR EQUATION

The calculation of saturated phase properties involves a rather lengthy trial and error procedure. Only one variable needs to be specified. In this case the known variable is temperature. A vapor and liquid phase will be in equilibrium if and only if the following conditions are satisfied:

$$P^L = P^V$$

$$T^L = T^V$$

$$f^L = f^V$$

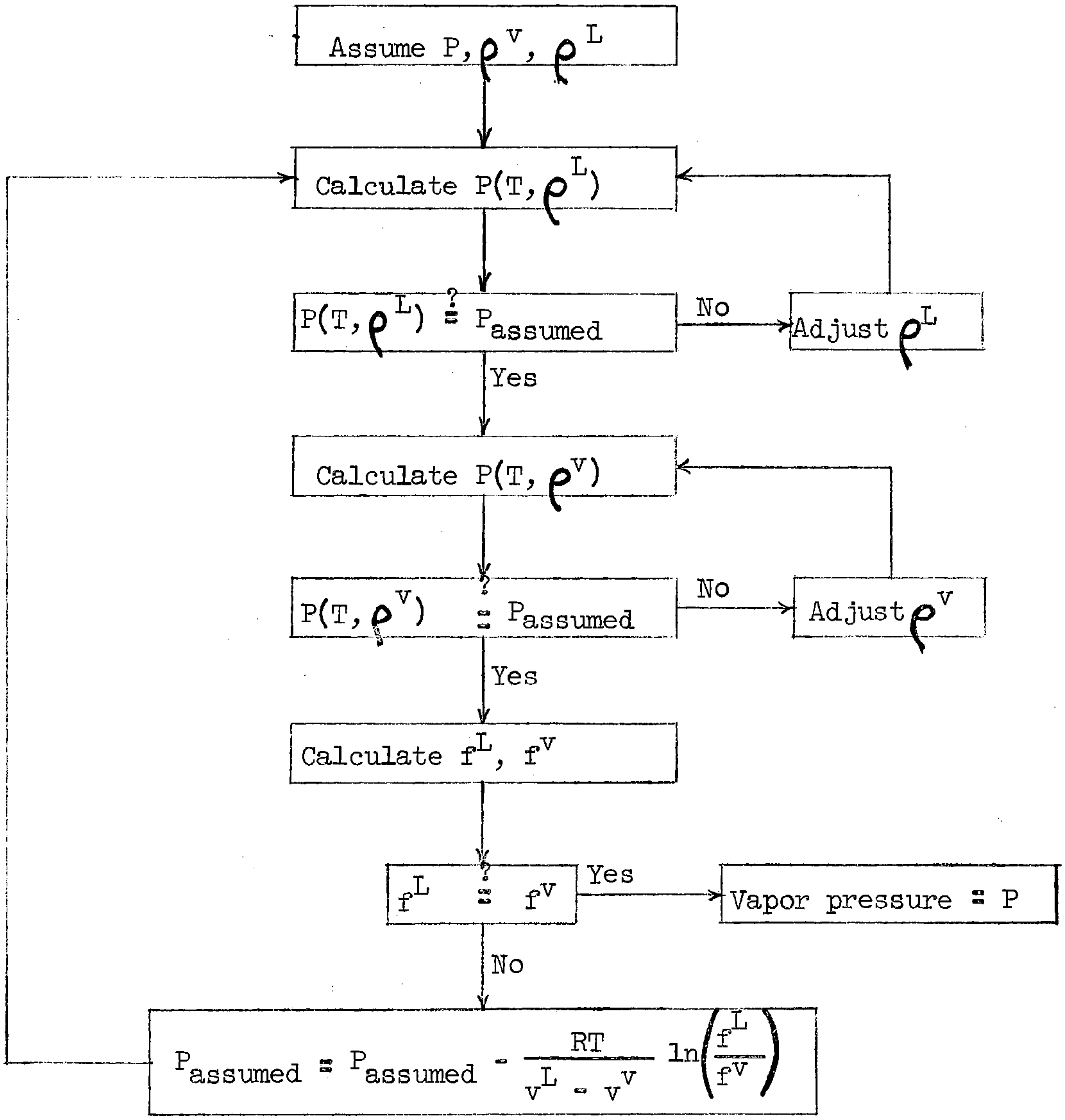
Equation (3-1) was used to calculate vapor pressures.

$$P = RT\rho + \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1+\gamma\rho^2)\exp(-\gamma\rho^2) \tag{3-1}$$

and Equation (3-18) was used to calculate liquid and vapor fugacities.

$$RT\ln f = RT\ln RT\rho + 2\left(B_oRT - A_o - \frac{C_o}{T^2}\right)\rho + \frac{3}{2}(bRT - a)\rho^2 + \frac{6}{5}a\alpha\rho^5 + \frac{c\rho^2}{T^2}\left[\frac{1}{\gamma\rho^2} - \left(\frac{1}{\gamma\rho^2} - \frac{1}{2} - \gamma\rho^2\right)\exp(-\gamma\rho^2)\right] \tag{3-18}$$

The following is a simplified flow diagram of the procedure used to calculate the saturated phase properties at a known temperature.



Flow Diagram for Calculation of Pure Component Saturated Phase Properties

The following equation was used to estimate the vapor pressure.

$$P = P_c \exp\left(5.39 - \frac{5.39}{T_r}\right) \qquad \text{(A-1)}$$

Equation (A-1) was derived from a plot of $1/T_r$ versus P/P_c (13). The saturated liquid volume was estimated by the equation (22)

$$V^L = V_c Z_c^{(1-T_r)^{2/7}} \qquad \text{(A-2)}$$

Equation (3-1) was then used to calculate the pressure. If the calculated pressure did not equal the assumed pressure, the liquid density was changed by way of the Newton-Raphson technique as follows:

$$\rho_2^L = \rho_1^L - \frac{G(\rho^L)}{G'(\rho^L)} \qquad \text{(A-3)}$$

where

$$G(\rho^L) = P_{calc} - P_{assumed} \qquad \text{(A-4)}$$

$$G'(\rho^L) = \frac{\partial\,[G(\rho^L)]}{\partial \rho} \qquad \text{(A-5)}$$

Equation A-5 is the derivative of the BWR equation with respect to density.

$$G'(\rho^L) = RT + 2\left(B_oRT - A_o - \frac{C_o}{T^2}\right)\rho + 3(bRT-a)\rho^2$$

$$+ 6a\alpha\rho^5 + \frac{c\rho^2}{T^2}\left(3 + 3\gamma\rho^2 - 2\gamma^2\rho^4\right)\exp(-\gamma\rho^2) \qquad \text{(A-6)}$$

Saturated vapor density was estimated from an assumed compressibility factor.

$$\rho^v = \frac{P_{assumed}}{RT\ Z_{assumed}}$$

Pressure was then calculated with the estimated vapor density. If the calculated pressure was not equal to the assumed pressure, the Newton-Raphson technique was again used to change ρ^V.

When values of ρ^V and ρ^L that resulted in the assumed pressure were found, Equation (3-18) was used to calculate liquid and vapor fugacities. If the fugacities were not equal, a new assumed pressure was calculated from Equation (A-7).

$$P_2 = P_1 - \left(\frac{RT}{V^L - V^V}\right) \ln\left(\frac{f^L}{f^V}\right) \tag{A-7}$$

Equation (A-7) was derived as follows.

Fugacity is given by the equation

$$RTd\ln f = VdP$$

or

$$d\ln f = \frac{V}{RT} dP \tag{A-8}$$

Equation (A-8) can be written for liquid and vapor phases

$$d\ln f^L = \frac{V^L}{RT} dP \tag{A-9}$$

$$d\ln f^V = \frac{V^V}{RT} dP \tag{A-10}$$

Division of Equation (A-9) by Equation (A-10) results in

$$d\ln \frac{f^L}{f^V} = \frac{V^L - V^V}{RT} dP \tag{A-11}$$

Equation (A-11) can now be integrated assuming that the change V^L-V^V is negligible.

$$RT \int_{\ln(f^L/f^V)}^{0} d\ln(f^L/f^V) = \int_{P_1}^{P_2} (V^L - V^V)dP$$

or

$$-\ln\left(\frac{f^L}{f^V}\right) = \frac{V^L - V^V}{RT}(P_2 - P_1) \tag{A-12}$$

Rearranging Equation (A-12) gives

$$P_2 = P_1 - \left(\frac{RT}{V^L - V^V}\right)\ln\left(\frac{f^L}{f^V}\right) \tag{A-13}$$

The pressure thus calculated becomes the new assumed vapor pressure, and the trial and error procedure is repeated. Iterations were repeated until the liquid and vapor fugacities were equal.

APPENDIX B

APPENDIX B

DERIVATION OF CRITICAL POINT RELATIONS

The critical point relations used in the non-linear curve fit of the BWR equation with exact critical point behavior were derived from Equation (3-1) as follows.

At the critical point, Equation (3-1) becomes

$$P_c = RT_c\rho_c + \left(B_oRT_c - A_o - \frac{C_o}{T_c^2}\right)\rho_c^2 + (bRT_c - a)\rho_c^3$$
$$+ a\alpha\rho_c^6 + \frac{c\rho_c^3}{T_c^2}(1 + \gamma\rho_c^2)\exp(-\gamma\rho_c^2) \qquad \text{(B-1)}$$

Also, at the critical point

$$\left(\frac{\partial P}{\partial \rho}\right)_{\rho_c, T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{\rho_c, T_c} = 0$$

The first and second derivatives were given by Equations (5-5) and (5-6), respectively. By multiplying Equation (5-2) by $2/\rho_c$ and subtracting Equation (5-5), the following equation is obtained.

$$2\frac{P_c}{\rho_c} = RT_c - (bRT_c - a)\rho_c^2 - 4a\alpha\rho_c^5$$
$$- \frac{c\rho_c^2}{T_c^2}(1 + \gamma\rho_c^2 - 2\gamma^2\rho_c^4)\exp(-\gamma\rho_c^2) \qquad \text{(B-2)}$$

In Equation (B-2), A_o, B_o, and C_o have been eliminated. The same parameters can be eliminated from Equation (5-6) by multiplying Equation (5-2) by $2/\rho_c^2$ and subtracting Equation (5-6). The resulting equation is

$$P_c = RT_c\rho_c - 2(bRT_c - a)\rho_c^3 - 14a\alpha\rho_c^6 - \frac{c\rho_c^3}{T_c^2}(2 + 2\gamma\rho_c^2 - 9\gamma^2\rho_c^4 + 2\gamma^3\rho_c^6)\exp(-\gamma\rho_c^2) \qquad \text{(B-3)}$$

Then Equation (B-3) was multiplied by $1/2\rho_c$ and subtracting from Equation (B-2) to obtain

$$P_c = \frac{1}{3}RT_c\rho_c + 2a\alpha\rho_c^6 - \frac{1}{3}\frac{c\rho_c^3}{T_c^2}(5\gamma^2\rho_c^4 - 2\gamma^3\rho_c^6)\exp(-\gamma\rho_c^2) \qquad \text{(B-4)}$$

Equation (B-4) was solved for α to obtain Equation (5-7).

$$\alpha = \frac{P_c - \dfrac{RT_c\rho_c}{3} + \dfrac{c\gamma^2\rho_c^2}{3T_c^2}(5 - 2\gamma\rho_c^2)\exp(-\gamma\rho_c^2)}{2a\rho_c^6} \qquad \text{(5-7)}$$

Equation (B-2) was then solved for b to obtain Equation (5-8)

$$b = \frac{a}{RT_c}(1 - 4\alpha\rho_c^3) + \frac{1}{\rho_c^2} - \frac{2P_c}{RT_c\rho_c^3} - \frac{c}{RT_c^3}(1 + \gamma\rho_c^2 - 2\gamma^2\rho_c^4)\exp(-\gamma\rho_c^2) \qquad \text{(5-8)}$$

Equation (B-1) was then rearranged to obtain Equation (5-9)

$$A_o = B_oRT_c - \frac{C_o}{T_c^2} - \frac{P_c}{\rho_c^2} + \frac{RT_c}{\rho_c} + (bRT_c - a)\rho_c + a\alpha\rho_c^4 + \frac{c\rho_c}{T_c^2}(1 + \gamma\rho_c^2)\exp(-\gamma\rho_c^2) \qquad \text{(5-9)}$$

APPENDIX C

APPENDIX C

DERIVATION OF FUGACITY EQUATION FOR MIXTURES WITH MODIFIED A_o

The fugacity of component i in a mixture is obtained from the residual work content as follows:

$$RT\ln f_i = \left(\frac{\partial N\tilde{A}}{\partial n_i}\right)_{T,V,n_j} + RT\ln \rho RTx_i \qquad (C-1)$$

where n_i is the number of moles of component i and $N = \sum n_i$. The residual work content is obtained from the equation

$$\tilde{A} = \int_o^{\rho} \frac{P-RT\rho}{\rho^2}\, d\rho \qquad (C-2)$$

Equation (3-1) is substituted into Equation (C-2) to obtain

$$\tilde{A} = (B_oRT-A_o - \frac{C_o}{T^2})\rho + (bRT-a)\frac{\rho^2}{2} + \frac{a\alpha\rho^5}{5}$$

$$+ \frac{c\rho^2}{T^2}\left[\frac{1-\exp(-\gamma\rho^2)}{\gamma\rho^2} - \frac{\exp(-\gamma\rho^2)}{2}\right] \qquad (C-3)$$

Equation (C-3) is substituted into Equation (C-1) to arrive at Equation (7-7).

In order to derive the fugacity equation with modified A_o, only the first group of parameters in Equation (C-3) will be discussed.

With $\rho = N/V$, $N\tilde{A}$ becomes

$$N\tilde{A} = N\left(B_oRT - A_o - \frac{C_o}{T^2}\right)\frac{N}{V} + \dots \qquad \text{(C-4)}$$

where

$$B_o = \frac{1}{N}\sum n_i B_{oi} \qquad \text{(C-5)}$$

$$A_o = \frac{1}{N^2}\left[n_i^2 A_{oi} + 2n_in_j\,\Theta\,(A_{oi}A_{oj})^{\frac{1}{2}} + n_j^2 A_{oj}\right] \qquad \text{(C-6)}$$

$$C_o = \frac{1}{N^2}\left[\sum n_i C_{oi}^{\frac{1}{2}}\right]^2 \qquad \text{(C-7)}$$

Equation (C-4) becomes

$$N\tilde{A} = \left[(N\sum n_iB_{oi})RT - \left(n_i^2A_{oi} + 2n_in_j\,\Theta\,(A_{oi}A_{oj})^{\frac{1}{2}} + n_j^2\,A_{oj}\right) - \frac{(\sum n_iC_{oi}^{\frac{1}{2}})^2}{T^2}\right]\frac{1}{V} + \dots \qquad \text{(C-8)}$$

The derivative of $N\tilde{A}$ with respect to n_i at constant n_j, V, and T is

$$\left(\frac{\partial N\tilde{A}}{\partial n_i}\right)_{T,V,n_j} = \frac{1}{V}\left[(NB_{oi} + \sum n_iB_{oi})RT - 2\left(n_iA_{oi} + n_j\,\Theta\,(A_{oi}A_{oj})^{\frac{1}{2}}\right) - \frac{2(\sum n_iC_{oi}^{\frac{1}{2}})C_{oi}^{\frac{1}{2}}}{T^2}\right] + \dots \qquad \text{(C-9)}$$

After rearranging

$$\left(\frac{\partial N\tilde{A}}{\partial n_i}\right)_{T,V,n_j} = \left[(B_{oi} + B_o)RT - 2\left(x_iA_{oi} + x_j\,\Theta\,(A_{oi}A_{oj})^{\frac{1}{2}}\right) - \frac{2(C_oC_{oi})^{\frac{1}{2}}}{T^2}\right]\rho + \dots \qquad \text{(C-10)}$$

Substitution of (C-10) into Equation (C-1) results in the equation for fugacity with modified A_o.

$$RT\ln f_i = RT\ln \rho RT x_i + \Big[(B_{oi} + B_o)RT - 2\Big(x_i A_{oi} + x_j\, \Theta (A_{oi}A_{oj})^{\frac{1}{2}}\Big) - \frac{2(C_o C_{oi})^{\frac{1}{2}}}{T^2}\Big]\rho + \cdots \qquad \text{(C-11)}$$

APPENDIX D

COMPUTER PROGRAM FOR CALCULATING PURE COMPONENT SATURATED PHASE PROPERTIES AND SIMULTANEOUSLY DETERMINING TEMPERATURE DEPENDENCE OF TWO BWR PARAMETERS FROM VAPOR PRESSURES AND LIQUID DENSITIES

```
      COMMON/COM/NC,NON
      DIMENSION T(50),PEX(50),VLE(50),C(8),VVEX(50),VL(50),DL(50),P1(50)
     1,P(50),CORR(8,50),TR(50),DV(50),CO1(50),CO2(50),VLEX(50),S(50),TT(
     250)
      DOUBLE PRECISION C,DL,S,TT,DV
C
C     SUBROUTINES
C          VPRESS   CALCULATES VAPOR PRESSURES, LIQUID DENSITY, AND VAPOR DENSIT
C          DEVIAT     CALCULATES DEVIATIONS OF CALCULATED VARIABLES FROM EXPERIM
C                     ENTAL
C          CONSON     CALCULATES TWO BWR CONSTANTS(SPECIFIED) AT EACH TEMP.
C         CURV     PREPARES VARIABLES FOR CURVE FIT
C          CURVFT     FITS THE TWO BWR CONSTANTS AS A LINEAR FUNCTION OF 1/T
C
C
C     VARIABLES
C          N  NUMBER OF EXPERIMENTAL DATA POINTS
C     NC    NUMBER OF PAIRS OF CONSTANTS TO BE USED
C          TC    CRITICAL TEMPERATURE
C         PC    CRITICAL PRESSURE
C         DC    CRITICAL DENSITY
C        ZMAX   COMPRESSIBILITY USED TO BEGIN VAPOR DENSITY CALCULATIONS
C          T(I)    TEMPERATURE
C         PEX(I)    OBSERVED VAPOR PRESSURE
C          VLE(I)    OBSERVED SATURATED LIQUID VOLUME
C         VVEX(I)    OBSERVED SATURATED VAPOR VOLUME
C          C(J)    BWR CONSTANTS
C          KA,KB    CONSTANTS TO MODIFIED
C          R    GAS CONSTANT
C          VL(I)    SATURATED LIQUID VOLUME
C         DL(I)    SATURATED LIQUID DENSITY
C          P1(I)    CALCULATED VAPOR PRESSURE (UNMODIFIED CONSTANTS)
C         NN    CONTROL INDEX
C          K    CONTROL INDEX
C          LET    CONTROL INDEX
C
C
C     DIMENSIONS
C         PRESSURE     ATMOSPHERES
C          DENSITY    GRAM-MOLES/LITER
C          TEMPERATURE    DEGREES  KELVIN
C         GAS CONSTANT    LITER-ATM/GM-MOLE K
C          VVEX(I)    CC/GM-MOLE
C          VLE(I)    CC/GM-MOLE
    1 FORMAT(2I5,2F10.3,F6.3,F8.4)
    2 FORMAT(7F10.3)
    3 FORMAT(4E15.8)
    4 FORMAT(1H1,8X,2HB0,12X,2HA0,13X,2HC0,14X,1HB,14X,1HA,14X,2HAL,13X,
     11HC,13X,1HG/)
    5 FORMAT(1X,8E15.8///)
    6 FORMAT(2I5)
      READ(5,1)N,NC,TC,PC,ZMAX,DC
      READ(5,1)NO,NON
C     NO CONTROLS WHICH DATA IS TO BE READ
C         NO=1 TEMPERATURE ONLY IS READ
C         NO=2 TEMPERATURE AND EXPERIMINTAL VAPOR PRESSURE
C         NO=3 TEMP, PRESSURE,AND LIQUID VOLUME
C         NO=4 TEMP, PRESS, LIQUID VOLUME, AND VAPOR VOLUME
C     IF NON =1, TEMPERATURE DEPENDENCE CALCULATIONS ARE BY PASSED AND ONLY
C         P-V-T CALCULATIONS ARE MADE
      READ(5,2)(T(I),I=1,N)
      IF(NO.EQ.1)GO TO 1000
      READ(5,2)(PEX(I),I=1,N)
      IF(NO.EQ.2)GO TO 1000
      READ(5,2)(VLE(I),I=1,N)
      IF(NO.EQ.3)GO TO 1000
      READ(5,2)(VVEX(I),I=1,N)
 1000 CONTINUE
 1019 CONTINUE
 1020 READ(5,3)(C(I),I=1,8)
      WRITE(6,4)
      WRITE(6,5)(C(I),I=1,8)
      IF(NON.EO.1)GO TO 1026
 1025 READ(5,6)KA,KB
 1026 R=.08207
      NN=0
      K=0
      LET=0
      CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      DO 1015 I=1,N
      P(I)=S(I)
      TR(I)=TT(I)
      VL(I)=1./DL(I)
 1015 P1(I)=P(I)
      CALL DEVIAT(KA,KB,N,PEX,P,TR,T,VLE,DL,VVEX,DV,VLEX)
      IF(NON.EQ.1) GO TO 1030
      DO 800 J=1,8
      DO 800 I=1,N
  800 CORR(J,I)=0
      CALL CONSON(KA,KB,C,N,P1,CORR,PEX,T,VLEX,DC,PC,TC,R,NN,K,LET,ZMAX,
     1TR,VLE,VVEX,CO1,CO2)
      CALL CURVE(N,T,CO1,CO2,AA,BA,AB,BB)
      LET=1
      NN=0
      CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      DO 2000 I=1,N
      P(I)=S(I)
 2000 TR(I)=TT(I)
      CALL DEVIAT(KA,KB,N,PEX,P,TR,T,VLE,DL,VVEX,DV,VLEX)
```

```
 1030 NC=NC-1
      IF(NC.EQ.0)GO TO 1040
      GO TO 1020
 1040 CONTINUE
      CALL EXIT
      END
      SUBROUTINE VPRESS(DC,PC,TC,R,N,NN,K,LET,C,H,DL,P,ZMAX,DV,TR,KA,KB,
     1M,AA,BA,AB,BB)
      DIMENSION C(8),T(50),TR(50),DL(50),P(50),DV(50),FL(50),FV(50),PR(5
     10),H(50)
      DOUBLE PRECISION C,DL
      DOUBLE PRECISION AA,BA,AB,BB,VOL,CON1,CON2,P,PA,FPD
      DOUBLE PRECISION VC,DC,ZC,PC,R,TC,T,TR,FD
      DOUBLE PRECISION ZMAX,ZV,DV,DOC
      DO 100 I=1,N
  100 T(I)=H(I)
C
C     VARIABLES
C            VC     CRITICAL VOLUME
C            ZC     CRITICAL COMPRESSIBILITY FACTOR
C            M     CONTROL INDEX
C            K     CONTROL INDEX
C            NOC     CONTROL INDEX
C            CON1     FIRST BWR CONSTANT TO BE MODIFIED
C            CON2     SECOND BWR CONSTANT TO BE MODIFIED
C            AA,BB     CONSTANTS IN TEMPERATURE DEPENDENT FORM OF FIRST
C                      CONSTANT,C(KA)
C            AB,BB     CONSTANTS IN TEMPERATURE DEPENDENT FORM OF SECOND
C                      BWR CONSTANT, C(KB)
C            TR(I)     REDUCED TEMPERATURE
C            PA    FIRST ASSUMED PRESSURE
C            VOL    FIRST ESTIMATE OF LIQUID VOLUME
C            FL(I)    LIQUID FUGACITY
C            FV(I)    VAPOR FUGACITY
C
C
      VC=.10D 01/DC
      ZC=PC*VC/(R*TC)
      NO=N
      IF(NN.EQ.0)K=1
      IF(NN.GT.0)K=M
      IF(NN.GT.0)NO=NN
      NOC = 0
      DO 505 I=K,NO
      IF(LET.EQ.0)GO TO 200
      CON1=C(KA)
      CON2=C(KB)
      C(KA)=AA+BA/T(I)
      C(KB)=AB+BB/T(I)
  200 TR(I)=T(I)/TC
      PA=PC*DEXP(.539D 01-.539D 01/TR(I))
C     EQUATION FOR PA IS DERIVED FROM FIGURE 18.3, PAGE 195 OF
C     APPLIED HYDROCARBON THERMODYNAMICS BY W. C. EDMISTER
      VOL=VC*ZC**((.10D 01-TR(I))**(2./7.))
  280 DL(I)=1./VOL
  290 PUI)=R*T(I)*DL(I)+(C(1)*R*T(I)-C(2)-C(3)/T(I)**2.)*DL(I)**2.+(C(4)
     1*R*T(I)-C(5))*DL(I)**3.+C(5)*C(6)*DL(I)**6.+(C(7)*DL(I)**3./T(I)**
     22.)*(.1D 01+C(8)*DL(I)**2.)*DEXP(-C(8)*DL(I)**2.)
C     CHECK TO SEE IF CALCULATED PRESSURE=ASSUMED PRESSURE
      IF(DABS((PA-P(I))/PA)-.1D-02)300,300,310
C     ASSUME NEW DENSITY IF PRESSURES DO NOT AGREE
C     NEWTON RAPHSON ITERATION IS USED TO CONVERGE ON DENSITY
  310 FD=P(I)-PA
      FPD=R*T(I)+.2D 01*(C(1)*R*T(I)-C(2)-C(3)/T(I)**2.)*DL(I)+.3D 01*(C
     1(4)*R*T(I)-C(5))*DL(I)**2.+.6D 01*C(5)*C(6)*DL(I)**5.+(C(7)*DL(I)*
     2*2./T(I)**2.)*(.3D 01+.3D 01*C(8)*DL(I)**2.-.20D 01*C(8)**2.*DL(I)
     3**4.)*DEXP(-C(8)*DL(I)**2.)
C     FPD IS DERIVATIVE OF PRESSURE WITH RESPECT TO DENSITY
      IF(FPD)305,305,315
C     IF FPD IS NEGATIVE, EQUATION WILL NOT CONVERGE
  305 DL(I)=.11D 01*DL(I)
      GO TO 290
  315 DL(I)=DL(I)-FD/FPD
      GO TO 290
  300 CONTINUE
C     CALCULATE VAPOR DENSITY
      ZV=ZMAX
      DV(I)=PA/(ZV*R*T(I))
      IF (NOC.EQ.1) DV(I) = DOC
C     DOC IS DENSITY CALCULATED IN PREVIOUS TRIAL
      IF (NOC.EQ.2) DV(I) = DV(I-1)
  390 PUI)=R*T(I)*DV(I)+(C(1)*R*T(I)-C(2)-C(3)/T(I)**2.)*DV(I)**2.+(C(4)
     1*R*T(I)-C(5))*DV(I)**3.+C(5)*C(6)*DV(I)**6.+(C(7)*DV(I)**3./T(I)**
     22C)*(.10D 01+C(8)*DV(I)**2.)*DEXP(-C(8)*DV(I)**2.)
      DOC = DV(I)
      IF(DABS((PA-P(I))/PA)-.10D-03)400,400,410
  410 FD=P(I)-PA
      FPD=R*T(I)+.2D 01*(C(1)*R*T(I)-C(2)-C(3)/T(I)**2.)*DV(I)+.30D 01*(
     1CU4)*R*T(I)-C(5))*DV(I)**2.+.60D 01*C(5)*C(6)*DV(I)**5.+(C(7)*DV(I
     2)M*2./T(I)**2.)*(.30D 01+.30D 01*C(8)*DV(I)**2.-.20D 01*C(8)**2.*D
     3V(I)**4.)*DEXP(-C(8)*DV(I)**2.)
      IF(FPD)405,405,415
C     IF FPD IS NEGATIVE, EQUATION WILL NOT CONVERGE
  405 DV(I)=.99D 00*DV(I)
      GO TO 390
  415 DV(I)=DV(I)-FD/(FPD)
      GO TO 390
  400 CONTINUE
C     CALCULATE LIQUID AND VAPOR FUGACITIES
      RFL=R*T(I)*DLOG(R*T(I)*DL(I))+2.*(C(1)*R*T(I)-C(2)-C(3)/(T(I)**2))
     1*DL(I)+1.5*(C(4)*R*T(I)-C(5))*DL(I)**2+1.2*C(5)*C(6)*DL(I)**5+((C(
     27D*DL(I)**2)/(T(I)**2))*((1./(C(8)*DL(I)**2))-(1./(C(8)*DL(I)**2)-
     3.5-C(8)*DL(I)**2)*DEXP(-C(8)*DL(I)**2))
      RFV=R*T(I)*DLOG(R*T(I)*DV(I))+2.*(C(1)*R*T(I)-C(2)-C(3)/(T(I)**2))
     1*DV(I)+1.5*(C(4)*R*T(I)-C(5))*DV(I)**2+1.2*C(5)*C(6)*DV(I)**5+((C(
     27D*DV(I)**2)/(T(I)**2))*((1./(C(8)*DV(I)**2))-(1./(C(8)*DV(I)**2)-
     3.5-C(8)*DV(I)**2)*DEXP(-C(8)*DV(I)**2))
C     RFL=R*T*LN(FL)     FL IS LIQUID FUGACITY
C     RFV=R*T*LN(FV)     FV IS VAPOR FUGACITY
      CHECK=RFL/(R*T(I))
      IF(CHECK-85.)401,401,402                                          CHECK
C     IF CHECK IS GREATER THAN 85, COMPUTER WILL NOT CALCULATE THE
C     EXPONENT IN STATEMENT 401, AND CALCULATION IS BYPASSED TO ASSUME
C     A NEW PRESSURE
  402 FLOFV=(DEXP(RFL/(9.*R*T(I)))/DEXP(RFV/(9.*R*T(I))))**9             CHECK
      WRITE(6,10)CHECK
   10 FORMAT(1X,E15.8)
      PA=PA-((R*T(I)/(1./DL(I)-1./DV(I)))*ALOG(FLOFV))                  CHECK
      GO TO 280                                                         CHECK
  401 FL(I)=DEXP(RFL/(R*T(I)))
      FV(I)=DEXP(RFV/(R*T(I)))
C     CHECK TO SEE IF LIQUID AND VAPOR FUGACITIES ARE EQUAL
      IF(ABS(FV(I)-FL(I))-.0100)430,430,440
  430 IF(ABS((FV(I)-FL(I))/FV(I))-.0001)450,450,440
C     IF LIQUID AND VAPOR FUGACITIES ARE EQUAL, ASSUMED PRESSURE IS OK
C      OTHERWISE A NEW PRESSURE IS ASSUMED
```

```
C      ASSUME NEW PRESSURE
  440 PA=PA-((R*T(I)/(1./DL(I)-1./DV(I)))*ALOG(FL(I)/FV(I)))
      NOC = 1
      GO TO 280
  450 TR(I)=T(I)/TC
      NOC = 2
      IF(LET.EQ.0)GO TO 505
      C(KA)=CON1
      C(KB)=CON2
  505 PR(I)=P(I)/PC
      RETURN
      END
      SUBROUTINE DEVIAT(KA,KB,N,PEX,P,TR,T,VLE,DL,VVEX,DV,VLEX)
      COMMON/COM/NO,NON
      DIMENSION PEX(50),P(50),ERROR(50),TR(50),T(50),VLEX(50),VLE(50),VL
     1(50),DL(50),ERRORV(50),VVEX(50),VV(50),DV(50)
      DOUBLE PRECISION C,DL,DV
C
C      VARIABLES
C          SUMP     SUM OF VAPOR PRESSURE DEVIATIONS
C           SUMVL     SUM OF LIQUID DENSITY DEVIATION
C           SUMVV     SUM OF VAPOR DENSITY DEVIATIONS
C           ERROR(I)     VAPOR PRESSURE DEVIATION
C           ERRORV(I)     LIQUID DENSITY DEVIATION
C           ERR     VAPOR DENSITY DEVIATION
C           AVGP     AVERAGE DENSITY DEVIATION
C           AVGL     AVERAGE LIQUID DENSITY DEVIATION
C           AVGVV     AVERAGE VAPOR DENSITY DEVIATION
C
C
    2 FORMAT(5X,29HAVERAGE VAPOR PRESSURE ERROR=,F8.4/5X,28HAVERAGE LIQU
     1ID VOLUME ERROR=,F8.4/5X,27HAVERAGE VAPOR VOLUME ERROR=,F8.4)
    6 FORMAT(10X,2HTR,10X,3HT,K,10X,7HPEX,ATM,10X,7HPCA,ATM,10X,9HPCT ER
     1ROR/)
    1 FORMAT(5X,1HC,I1,6H AND C,I1,29H ARE FUNCTIONS OF TEMPERATURE)
    7 FORMAT(7X,F6.3,6X,F8.3,8X,F7.3,10X,F7.3,16X,F11.3)
    8 FORMAT(7X,F6.3,6X,F8.3,12X,F9.5,12X,F9.5,11X,F10.4)
    9 FORMAT(///10X,2HTR,10X,3HT,K,15X,4HVLEX,13X,4HVLCA,13X,9HPCT ERROR
     1/)
   10 FORMAT(///10X,2HTR,10X,3HT,K,15X,4HVVEX,13X,4HVVCA,13X,9HPCT ERROR
     1/)
      SUMP=0.
      SUMVL=0.
      SUMVV=0.
      IF(NON.EQ.1)GO TO 50
      WRITE(6,1)KA,KB
   50 WRITE(6,6)
      DO 1000 I=1,N
      ERROR(I)=(PEX(I)-P(I))*100./PEX(I)
      SUMP=SUMP+ABS(ERROR(I))
 1000 WRITE(6,7)TR(I),T(I),PEX(I),P(I),ERROR(I)
      IF(NO.LT.3)GO TO 75
      WRITE(6,9)
      DO 1005 I=1,N
      VLEX(I)=VLE(I)/1000.
      VL(I)=1./DL(I)
      ERRORV(I)=(VLEX(I)-VL(I))*100./VLEX(I)
      SUMVL=SUMVL+ABS(ERRORV(I))
 1005 WRITE(6,8)TR(I),T(I),VLEX(I),VL(I),ERRORV(I)
   75 IF(NO.LT.4)GO TO 85
      WRITE(6,10)
      DO 1010 I=1,N
      VVEX(I)=VVEX(I)/1000.
      VV(I)=1./DV(I)
      ERR=(VVEX(I)-VV(I))*100./VVEX(I)
      SUMVV=SUMVV+ABS(ERR)
      WRITE(6,8)TR(I),T(I),VVEX(I),VV(I),ERR
 1010 VVEX(I)=VVEX(I)*1000.
   85 IF(NO.LT.4)GO TO 95
      TOT=N
      AVGP=SUMP/TOT
      AVGVL=SUMVL/TOT
      AVGVV=SUMVV/TOT
      WRITE(6,2)AVGP,AVGVL,AVGVV
   95 CONTINUE
      RETURN
      END
      SUBROUTINE CONSON(KA,KB,C,N,P1,CORR,PEX,T,VLEX,DC,PC,TC,R,NN,K,LET
     1,ZMAX,TR,VLE,VVEX,CO1,CO2)
      DIMENSION C(8),P1(50),P(50),PCTC(8,50),CORR(8,50),VL(50),DL(50),VV
     1(50),DV(50),ERROR(50),PEX(50),COMP(5,50),VLEX(50),DPDK(8,50),DPDV(
     28T50),DELTAV(8,50),DK(8,50),DKC(8,50),T(50),TR(50),VVEX(50),CO1(50
     3),CO2(50),VLE(50),S(50),TT(50)
      DOUBLE PRECISION C,DL,S,TT,CONS,DV
C
C      VARIABLES
C          DELP     VAPOR PRESSURE CALCULATED WITH UNMODIFIED CONSTANTS-
C                     PRESSURE CALCULATED WITH C(KA) CHANGED ONE PER CENT
C          PCTC(J,I)     PER CENT OF PRESSURE/PER CENT CHANGE OF CEKA)
C          CORR(J,I)     TOTAL CORRECTION FACTOR FOR C(KA)
C          COMP(J,I)     CORRECTION FACTOR FOR ONE TRIAL OF C(KA)
C          DPDK(KB,I)     DERIVATIVE OF PRESSURE WITH RESPECT TO C(KB)
C          DPDV(J,I)     DERIVATIVE OF PRESSURE WITH RESPECT TO DENSITY
C          DELTAV(KB,I)     OBSERVED- CALCULATED LIQUID DENSITY
C          DKC(KB,I)     CORRECTION FACTOR FOR C(KB)
C
C
    1 FORMAT(1H1,21H RESULTS OF VARYING C,I1,6H AND C,I1,42H BY CORRECTI
     1NG THROUGH PRESSURE AND VOLUME//10X,3HT,K,10X,5HP,ATM,10X,2HVL,10X
     2,1HC,I1,12X,1HC,I1/)
    2 FORMAT(7X,F8.3,6X,F7.3,6X,F8.5,1X,E15.8,1X,E15.8,5X,F12.4)
      WRITE(6,1)KA,KB,KA,KB
      J=KA
C      C(KA) IS CHANGED TO CALCULATE OBSERVED VAPOR PRESSURE
      C(J)=.99*C(J)
      CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      DO 50 I=1,N
      P(I)=S(I)
      TR(I)=TT(I)
      DELP=P1(I)-P(I)
   50 PCTC(J,I)=100.*DELP/P(I)
      C(J)=C(J)/.99
      I=1
      M=1
      NN=NN+1
   80 C(J)=(1.+CORR(J,I)/100.)*C(J)
      CONS=C(J)
      CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      P(I)=S(I)
      TR(I)=TT(I)
      VL(I)=1./DL(I)
      VV(I)=1./DV(I)
 1315 ERROR(I)=(PEX(I)-P(I))*100./PEX(I)
 1325 IF(ABS(ERROR(I))-.10)1400,1400,1350
```

```
 1350 COMP(J,I)=ERROR(I)/PCTC(J,I)
   10 FORMAT(10X,E15.6,E15.8)
      WRITE(6,10)P(I),C(KA)
 1300 C(J)=C(J)/(1.+CORR(J,I)/100.)
      CORR(J,I)=CORR(J,I)+COMP(J,I)
      GO.TO 80
   90 CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      P(I)=S(I)
      TR(I)=TT(I)
      VL(I)=1./DL(I)
      VV(I)=1./DV(I)
      CORR(J,I)=0
      COMP(J,I)=0
      ERROR(I)=(PEX(I)-P(I))*100./PEX(I)
      GO TO 1325
 1400 CONTINUE
  200 IF(ABS((VLEX(I)-VL(I))/VLEX(I))-.005)350,350,250
      C(KB) IS CHANGED TO CALCULATE OBSERVED LIQUID DENSITY
  250 IF(KB.EQ.1)DPDK(KB,I)=R*T(I)*DL(I)**2
      IF(KB.EQ.2)DPDK(KB,I)=-DL(I)**2
      IF(KB.EQ.3)DPDK(KB,I)=-DL(I)**2/T(I)**2
      IF(KB.EQ.4)DPDK(KB,I)=R*T(I)*DL(I)**3
      IF(KB.EQ.5)DPDK(KB,I)=-DL(I)**3+C(6)*DL(I)**6
      IF(KB.EQ.6)DPDK(KB,I)=C(5)*DL(I)**6
      IF(KB.EQ.7)DPDK(KB,I)=(DL(I)**3/T(I)**2)*(1.+C(8)*DL(I)**2)*DEXP(-
     1C(8)*DL(I)**2)
      IF(KB.EQ.8)DPDK(KB,I)=-(C(7)*C(8)*DL(I)**7/T(I)**2)*DEXP(-C(8)*DL(
     1I)**2)
      J=KB
      DPDV(J,I)=R*T(I)+2.*(C(1)*R*T(I)-C(2)-C(3)/(T(I)**2))*DL(I)+3.*(C(
     14D*R*T(I)-C(5))*DL(I)**2+6.*C(5)*C(6)*DL(I)**5+(C(7)*(DL(I)**2)/(T
     2(I)**2))*(3.+3.*C(8)*DL(I)**2-2.*(C(8)**2)*DL(I)**4)*DEXP(-C(8)*DL
     1(I)**2)
      J=KA
  100 DELTAV(KB,I)=VLEX(I)-VL(I)
  110 DK(KB,I)=DPDK(KB,I)/DPDV(KB,I)
      DKC(KB,I)=(1./VLEX(I)-DL(I))/DK(KB,I)
  255 C(KB)=C(KB)-DKC(KB,I)
  270 CALL VPRESS(DC,PC,TC,R,N,NN,K,LET,C,T,DL,S,ZMAX,DV,TT,KA,KB,M,AA,B
     1A,AB,BB)
      P(I)=S(I)
      TR(I)=TT(I)
      VL(I)=1./DL(I)
      VV(I)=1./DV(I)
      ERVL=1./VLEX(I)-DL(I)
      WRITE(6,10)ERVL,C(KB)
      IF(ABS((VLEX(I)-VL(I))/VLEX(I))-.001)300,300,250
  300 IF(ABS((PEX(I)-P(I))/PEX(I))-.0010)350,350,1315
  350 WRITE(6,2)T(I),P(I),VL(I),CONS,C(KB),VV(I)
      CO1(I)=C(KA)
      CO2(I)=C(KB)
      NN=NN+1
      I=I+1
      M=M+1
      IF(I-N)80,80,400
  400 NN=0
      CALL DEVIAT(KA,KB,N,PEX,P,TR,T,VLE,DL,VVEX,DV,VLEX)
      RETURN
      END
      SUBROUTINE CURVE(N,T,CO1,CO2,AA,BA,AB,BB)
      DIMENSION T(50),CO1(50),CO2(50),X(50),Y(50)
      DOUBLE PRECISION C,DL
C
C     VARIABLES
C          X(I)     1/TEMP
C          CO1(I)     C(KA) AT T(I)
C          CO2(I)     C(KB) AT T(I)
C
C
C     CONSTANTS ARE REPRESENTED BY C(J)=A+B/T
      DO 100 I=1,N
      X(I)=1./T(I)
  100 Y(I)=CO1(I)
      CALL CURVFT(X,Y,BETA0,BETA1,N)
      AA=BETA0
      BA=BETA1
      DO 200 I=1,N
  200 Y(I)=CO2(I)
      CALL CURVFT(X,Y,BETA0,BETA1,N)
      AB=BETA0
      BB=BETA1
      RETURN
      END
      SUBROUTINE CURVFT(X,Y,BETA0,BETA1,N)
      DIMENSION X(50),Y(50)
      DOUBLE PRECISION C,DL
C     THIS IS A SIMPLE LINEAR REGRESSION ONLY
C     THIS PROGRAM DOES SIMPLE LINEAR REGRESSION USING THE DOOLITTLE METHOD
C     Y IS THE DEPENDENT VARIABLE
    1 FORMAT(I5)
    2 FORMAT(2E15.8)
    3 FORMAT(5X,27HFOR AN EQUATION OF THE FORM/10X,6HY=A+BX/5X,6HFIT TO,
     1I5,39H DATA POINTS, THE CONSTANTS A AND B ARE/10X,3HA= ,E15.8/10X,
     23HB= ,E15.8)
      SUMX=0.
      SUMY=0.
      SUMXSQ=0.
      SUMXY=0.
      DO 100 I=1,N
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
      SUMXSQ=SUMXSQ+X(I)**2
  100 SUMXY=SUMXY+X(I)*Y(I)
      EL=N
      A=SUMX/EL
      B=SUMY/EL
      CC=1./EL
C     EL IS THE LEADING ELEMENT
      D=SUMXSQ-A*SUMX
      E=SUMXY-A*SUMY
C     A IS THE PIVOT
      F=-A
      EL2=D
      G=E/D
      H=F/D
      O=1./D
      BETA1=G
      BETA0=B-BETA1*A
      WRITE(6,3)N,BETA0,BETA1
      RETURN
      END
```

APPENDIX E

COMPUTER PROGRAM FOR BINARY MIXTURE VAPOR-LIQUID EQUILIBRIA CALCULATIONS

```
C       EQUILIBRIUM CALCULATIONS FOR BINARY MIXTURES USING B-W-R EQUATION
C
C       SUBROUTINES
C           COMPOS  CALCULATES LIQUID AND VAPOR COMPOSITIONS FROM K VALUES
C           CONST  CALCULATES BWR CONSTANTS FOR THE MIXTURE IN LIQUID
C           AND VAPOR PHASES
C           EQUIL  CONTROLS EQUILIBRIUM CALCULATIONS
C           DENSI  CALCULATES SATURATED LIQUID AND VAPOR DENSITIES
C            FUGAC  CALCULATES LIQUID AND VAPOR FUGACITIES
C
C
C       VARIABLES
C            NCP-NUMBER OF COMPONENTS
C          N-NUMBER OF ISOTHERMS
C           NCO-CONTROL INDEX
C              0  BASIC BWR EQUATION WITH NO MODIFICATIONS TO CONSTANTS
C             1  TWO CONSTANTS OF COMPONENT 1 ARE TEMPERATURE DEPENDENT
C             2  TWO CONSTANTS OF COMPONENT 2 ARE TEMPERATURE DEPENDENT
C             3  TWO CONSTANTS OF BOTH COMPONENTS ARE TEMPERATURE DEPENDENT
C           NTO-CONTROL INDEX
C             0  BASIC BWR EQUATION WITH NO MODIFICATIONS TO MIXING RULES
C             1  INTERACTION COEFFICIENT IS ADDED TO MIXTURE RULE OF A0
C           ZMAX-INITIAL GUESS FOR COMPRESSIBILITY FACTOR USED TO CALCULATE
C            VAPOR DENSITY
C           R-GAS CONSTANT  L-ATM/G-MOLE K
C           TC CRITICAL TEMPERATURE
C           PC CRITICAL PRESSURE
C           DC CRITICAL DENSITY
C           C PURE COMPONENT CONSTANTS FOR BWR EQUATION
C           JA,JB NUMBERS CORRESPONDING TO THE TWO CONSTANTS OF COMPONENT
C            1 THAT ARE TEMPERATURE DEPENDENT
C           KA,KB NUMBERS CORRESPONDING TO THE TWO CONSTANTS OF COMPONENT
C            2 THAT ARE TEMPERATURE DEPENDENT
C         THE CONSTANTS ARE NUMBERED AS THEY APPEAR THE EQUATION
C        TEMPERATURE DEPENDENCE IS OF THE FORM C=A.B/T
C           CI INTERACTION COEFFICIENT FOR MODIFIED MIXTURE RULE
C           T TEMPERATURE,K
C           MO NUMBER OF MIXTURES AT TEMPERATURE T
C           S EQUILIBRIUM RATIO
C           PO OBSERVED PRESSURE
C           KK CONTROL INDEX
C           X LIQUID MOLE FRACTION
C           Y VAPOR MOLE FRACTION
C            CV CONSTANT FOR MIXTURE IN VAPOR PHASE
C           CL CONSTANT FOR MIXTURE IN LIQUID PHASE
C           DL SATURATED LIQUID DENSITY
C           DV SATURATED VAPOR DENSITY
C
C
C       DIMENSIONS
C           TEMPERATURES  DEGREES KELVIN
```

```
C          PRESSURES  READ IN AS PSIA THEN CONVERTED TO ATM. FOR CALCULATIONS
C          DENSITYS  GRAM-MOLES/LITER
      DIMENSION TC)3*,PC)3*,DC)3*,C)3,8*,X)3,20*,Y)3,20*,CV)8*,CL)8*,S)3
     1,20*,FY)3*,FX)3*
      COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
    1 FORMAT)4I5,5F10.3*
    2 FORMAT)8F10.3*
    3 FORMAT)5E15.8*
    4 FORMAT)F10.3,I5*
    5 FORMAT)5X,F8.2,3X,F6.4,2X,F6.4,3X,F8.3,4X,F6.4,2X,F6.4,3X,F8.3,3X,
     1F8.4,2X,F8.4*
    6 FORMAT)1H1,5X,9HPRESSURE,,7X,12HLIQUID PHASE,18X,11HVAPOR PHASE,15
     1XT11HEQUILIBRIUM/7X,4HATM.,7X,13HMOLE FRACTION,3X,7HDENSITY,6X,13H
     2MOLE FRACTION,3X,7HDENSITY,10X,5HRATIO/24X,2A4,2X,8HGM-MOLE/,11X,2
     3A4,2X,8HGM-MOLE/,12X,2A4,/15X,2A4,1X,2A4,3X,5HLITER,4X,2A4,1X,2A4,
     44X,5HLITER,4X,2A4,1X,2A4/*
    7 FORMAT)5X,8E15.8*
    8 FORMAT)6A4*
    9 FORMAT)38X,2HT=,F7.2,2H K/*
   11 FORMAT)2I5,4E15.8*
      READ)5,13*CI
   13 FORMAT)F10.4*
      READ)5,8*CO1,CO2,CO3,CO4,CO5,CO6
      READ)5,1*NCP,N,NCO,NTO,ZMAX,R
      WRITE)6,1*NCO,NTO
      READ)5,2*)TC)J*,J=1,NCP*
      READ)5,2*)PC)J*,J=1,NCP*
      READ)5,2*)DC)J*,J=1,NCP*
C     NCP=NUMBER OF COMPONENTS
C      R IS THE GAS CONSTANT   L-ATM/G-MOLE K
C     ZMAX IS THE FIRST GUESS FOR VAPOR COMPRESSIBILITY FACTOR
C      TC IS CRITICAL TEMP
C     PC IS CRITICAL PRESSURE
C     DC IS CRITICAL DENSITY
C     DIMENSIONS ARE   TEMP,DEGREESS KELVIN   PRESS,ATM   DENSITY,G-MOLE/LITER
      READ)5,3*))C)J,L*,L=1,8*,J=1,NCP*
      IF)NCO.EQ.0*GO TO 15
      IF)NCO.EQ.3*GO TO 14
      IF)NCO.EQ.1*READ)5,11*JA,JB,AA,AB,BA,BB
      IF)NCO.EQ.2*READ)5,11*KA,KB,CA,CB,DA,DB
      GO TO 15
   14 READ)5,11*JA,JB,AA,AB,BA,BB
      READ)5,11*KA,KB,CA,CB,DA,DB
   15 WRITE)6,7*))C)J,L*,L=1,8*,J=1,NCP*
C     N IS THE NUMBER OF ISOTHERMS
      NO=N
      N=1
      WRITE)6,6*CO3,CO4,CO3,CO4,CO3,CO4,CO1,CO2,CO5,CO6,CO1,CO2,CO5,CO6,
     1CO1,CO2,CO5,CO6
   10 READ)5,4*T,MO
      WRITE)6,9*T
C     MO IS THE NUMBER OF MIXTURES AT THIS ISOTHERM
```

```
      M=1
   20 READ)5,2*)S)J,M*,J=1,NCP*
      READ)5,2*PO
      PO=PO/14.696
      KK=0
   25 CALL COMPOS)S,X,Y,M*
   30 CALL CONST)X,Y,C,NCP,S,CV,CL,M,T,TC*
C     SIS THE FIRST K-VALUE GUESS
C     CV AND CL ARE CONSTANTS FOR THE MIXTURE IN VAPOR AND LIQUID PHASES
C     PO IS THE OBSERVED VAPOR PRESSURE
      CALL EQUIL)PC,TC,DC,X,Y,CV,CL,NCP,T,R,ZMAX,C,PO,FY,FX,KC,S,M,KK,DL
     1,DV*
      IF)KC.EQ.1*GO TO 25
   50 WRITE)6,5*PO,X)1,M*,X)2,M*,DL,Y)1,M*,Y)2,M*,DV,S)1,M*,S)2,M*
      M=M.1
      IF)M.LE.MO*GO TO 20
      N=N.1
      IF)N.LE.NO*GO TO 10
      CALL EXIT
      END
      SUBROUTINE COMPOS)S,X,Y,M*
      DIMENSION S)3,20*,X)3,20*,Y)3,20*
      COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
      XE1,M*=)S)2,M*-1.*/)S)2,M*-S)1,M**
      X)2,M*=1.-X)1,M*
      DO 10 J=1,2
   10 Y)J,M*=X)J,M**S)J,M*
      RETURN
      END
      SUBROUTINE CONST)X,Y,C,NCP,S,CV,CL,M,T,TC*
      DIMENSION X)3,20*,Y)3,20*,C)3,8*,S)3,20*,CL)8*,CV)8*,TC)3*
      COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
      IF)NCO.EQ.0*GO TO 5
      IF)NCO.EQ.1*GO TO 3
      IF)NCO.EQ.2*GO TO 4
      IF)T.GT.TC)1**GO TO 2
      C)1,JA*=AA.AB/T
      C)1,JB*=BA.BB/T
    2 IF)T.GT.TC)2**GO TO 5
      C)2,KA*=CA.CB/T
      C)2,KB*=DA.DB/T
      GO TO 5
    3 IF)T.GT.TC)1**GO TO 5
      C)1,JA*=AA.AB/T
      C)1,JB*=BA.BB/T
      GO TO 5
    4 IF)T.GT.TC)2**GO TO 5
      C)2,KA*=CA.CB/T
      C)2,KB*=DA.DB/T
    5 DO 10 L=1,8
      CL)L*=0.
   10 CV)L*=0.
      DO 50 J=1,NCP
      CL)1*=CL)1*.X)J,M**C)J,1*
      CV)1*=CV)1*.Y)J,M**C)J,1*
      DO 30 L=2,3
      CL)L*=CL)L*.X)J,M**C)J,L***.5
   30 CV)L*=CV)L*.Y)J,M**C)J,L***.5
      DO 40 L=4,7
      CL)L*=CL)L*.X)J,M**C)J,L***)1./3.*
   40 CV)L*=CV)L*.Y)J,M**C)J,L***)1./3.*
      CL)8*=CL)8*.X)J,M**C)J,8***.5
   50 CV)8*=CV)8*.Y)J,M**C)J,8***.5
```

```
      DO 60 L=2,3
      CL)L*=CL)L***2
   60 CV)L*=CV)L***2
      DO 70 L=4,7
      CL)L*=CL)L***3
   70 CV)L*=CV)L***3
      CL)8*=CL)8***2
   80 CV)8*=CV)8***2
      IF)NTO.EQ.0*GO TO 90
      CL)2*=X)1,M***2*C)1,2*.X)2,M***2*C)2,2*.2.*X)1,M**X)2,M**SQRT)C)1,
     12**C)2,2***CI
      CV)2*=Y)1,M***2*C)1,2*.Y)2,M***2*C)2,2*.2.*Y)1,M**Y)2,M**SQRT)C)1,
     12**C)2,2***CI
   90 CONTINUE
      RETURN
      END
      SUBROUTINE EQUIL)PC,TC,DC,X,Y,CV,CL,NCP,T,R,ZMAX,C,PO,FY,FX,KC,S,M
     1,KK,DL,DV*
      DIMENSION PC)3*,TC)3*,DC)3*,X)3,20*,Y)3,20*,CV)8*,CL)8*,C)3,8*,FX)
     13*,FY)3*,S)3,20*
      COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
      KK=KK.1
      KC=0
      IF)KK.GT.1*D=DL
      IF)KK.GT.1*GO TO 20
      PCR=0.
      TCR=0.
      DCR=0.
      DO 10 J=1,NCP
      PCR=PCR.X)J,M**PC)J*
      TCR=TCR.X)J,M**TC)J*
   10 DCR=DCR.X)J,M**DC)J*
C     PSEUDOCRITICAL CONSTANTS USED TO ESTIMATE LIQUID DENSITY
      TR=T/TCR
   15 D6DCR*)1..1.75*)ABS)1.-TR****)1./3.*..75*)1.-TR**
   17 DD=D
   20 CALL DENSI)PO,D,T,R,CL,1.1,PL*
      DL=D
      IF)KK.GT.1*D=DV
      IF)KK.GT.1*GO TO 30
      Z=ZMAX
      D=PO/)Z*R*T*
   30 CALL DENSI)PO,D,T,R,CV,.99,PV*
      DV=D
      IF)ABS)DL-DV*-.1*35,35,40
   35 KK=1
      D=1.2*DD
      GO TO 17
   40 DO 50 J=1,NCP
      CALL FUGAC)DL,R,T,CL,C,J,FOX,M,X*
C     FUGAC CALCULATES F/X
      CALL FUGAC)DV,R,T,CV,C,J,FOY,M,Y*
      FX)J*=X)J,M**FOX
      FY)J*=Y)J,M**FOY
   50 IF)ABS)FX)J*-FY)J**-.0020.GT.0.*KC=1
      IF)KC.EQ.0*GO TO 80
      DO 60 J=1,NCP
   60 S)J,M*=)FX)J*/X)J,M**/)FY)J*/Y)J,M**
   80 RETURN
      END
      SUBROUTINE DENSI)PO,D,T,R,C,A,P*
      DIMENSION C)8*
      COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
```

```
 10 P6R*T*D.)C)1**R*T-C)2*-C)3*/T**2**D**2.)C)4**R*T-C)5***D**3.C)5**C
   1)6**D**6.)C)7**D**3/T**2**)1..C)8**D**2**EXP)-C)8**D**2*
    IF)ABS))PO-P*/PO*-.001*50,50,20
    NEWTON RAPHSON ITERATION IS USED TO CONVERGE ON A LIQUID DENSITY
 20 FD=P-PO
    FPD=R*T.2.*)C)1**R*T-C)2*-C)3*/T**2**D.3.*)C)4**R*T-C)5***D**2.6.*
   1CE5**C)6**D**5.)C)7**D**2/T**2**)3..3.*C)8**D**2-2.*C)8***2*D**4**
   2EXP)-C)8**D**2*
C   FPD IS THE DERIVATIVE OF BWR EON WITH RESPECT TO DENSITY
    IF)FPD*30,30,40
 30 D=A*D
    GO TO 10
 40 D=D-FD/FPD
    GO TO 10
 50 RETURN
    END
    SUBROUTINE FUGAC)D,R,T,CL,C,J,FOX,M,X*
    DIMENSION CL)8*,C)3,8*,X)3,20*
    COMMON NCO,JA,JB,AA,AB,BA,BB,KA,KB,CA,CB,DA,DB,NTO,CI
    IF)NTO.EQ.0*GO TO 10
    IF)J.EQ.1*BB=))CL)1*.C)J,1***R*T-2.*)X)J,M**C)J,2*.X)2,M**SQRT)C)J
   1,2**C)2,2***CI*-2.*)CL)3**C)J,3****.5/T**2**D
    IF)J.EQ.2*BB=))CL)1*.C)J,1***R*T-2.*)X)J,M**C)J,2*.X)1,M**SQRT)C)J
   1,2**C)1,2***CI*-2.*)CL)3**C)J,3****.5/T**2**D
    GO TO 20
 10 BB=))CL)1*.C)J,1***R*T-2.*)CL)2**C)J,2****.5-2.*)CL)3**C)J,3****.5
   1/T**2**D
 20 CC=1.5*))CL)4***2*C)J,4****)1./3.**R*T-)CL)5***2*C)J,5****)1./3.**
   1*D**2
    DD=.6*)CL)5**)CL)6***2*C)J,6****)1./3.*.CL)6**)CL)5***2*C)J,5****)
   11./3.***D**5
    EE=)3.*D**2/T**2**)CL)7***2*C)J,7****)1./3.**)))1.- EXP)-CL)8**D**2
   1**/)CL)8**D**2*- .5*EXP)-CL)8**D**2**
    FF=-)2.*CL)7**D**2/T**2**)C)J,8*/CL)8****.5*)))1.- EXP)-CL)8**D**2*
   1*/)CL)8**D**2*- EXP)-CL)8**D**2*- .5*CL)8**D**2*EXP)-CL)8**D**2**
    FOX=R*D*T*EXP))BB.CC.DD.EE.FF*/)R*T**
    RETURN
    END
```

APPENDIX F

APPENDIX F

NOMENCLATURE

a = BWR equation parameter

A = constant in linear function of BWR parameter

A_o = BWR equation parameter

$\tilde{A}$ = residual work content

b = BWR equation parameter

B = constant in linear function of BWR parameter

B_o = BWR equation parameter

$B(T)$ = second virial coefficient

c = BWR equation parameter

C_o = BWR equation parameter

$C(T)$ = third virial coefficient

f = fugacity

k_i = general BWR parameter

K_i = phase equilibrium ratio of component i

n_i = moles of component i

N = total number of moles

P = pressure, atm.

P_c = critical pressure

R = universal gas constant

T = absolute temperature

T_c = critical temperature

T_r = reduced temperature

V = volume, liters/gm-mole

V_c = critical volume

V^L = saturated liquid volume

V^V = saturated vapor volume

x_i = liquid mole fraction of component i

y_i = vapor mole fraction of component i

Z = compressibility factor

Greek Symbols

α = BWR equation parameter

γ = BWR equation parameter

ρ = molar density, gm-mole/liter

c = critical density

L = saturated liquid density

v = saturated vapor density

θ = empirical interaction coefficient in modified mixing rule of A_o

Abbreviations

atm = atmospheres

BWR = Benedict-Webb-Rubin

calc = calculated value

exp = experimental values

gm-mole = gram molecular weight

obs = observed value

psia = pounds per square inch absolute

VITA

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Candidate for the Degree of

Master of Science

Thesis: A STUDY OF MODIFICATIONS TO THE BENEDICT-WEBB-RUBIN EQUATION OF STATE-EXTENSION TO LOW TEMPERATURES AND APPLICATIONS TO BINARY MIXTURES

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