

A MODIFICATION OF THE HEYEN
EQUATION OF STATE

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NOMENCLATURE

English Letters

- A = Dimensionless parameter, Equation (2-10)
- A_c = Dimensionless parameter at the critical point, Equation (2-55)
- a = Attractive force parameter, Equation (2-1)
- a_c = Attractive force parameter at the critical point, Equation (2-4)
- B = Dimensionless parameter, Equation (2-11)
- B_c = Dimensionless parameter at the critical point, Equation (2-53)
- b = Co-Volume parameter, Equation (2-1)
- E = Dimensionless parameter, equation (2-52)
- E_c = Dimensionless parameter, at the critical point, Equation (2-54)
- e = Heyen equation of state size parameter, Equation (2-51)
- K = Equilibrium ratio ($K=y/x$)
- k = Binary coefficient of conventional mixing rule, Equation (2-28)
- x = Heyen parameter, Equation (2-57)
- m = Heyen parameter, Equation (2-58)
- n = Heyen parameter, Equation (2-57)
- n = Total no. of moles
- n = No. of Components, Equation (2-60)
- P = Pressure, PSIA
- P_r = Reduced pressure
- q = Dimensionless parameter, Equation (2-61)
- R = Gas Constant, $(\text{Psia})(\text{ft}^3)/(\text{lb mol})(^\circ\text{R})$

R = Fitted parameter in proposed model, Equation (3-30)
 T = Temperature, °R
 T_c = Critical temperature, °R
 T_r = Reduced temperature ($T_r = T/T_c$)
 V = Volume, ft³/lb mole
 V_c = Critical volume, ft³/lb mole
 W = Dimensionless parameter equation (2-61)
 X, Y = Mole fraction in liquid and gas, respectively
 Z = Compressibility factor, = PV/RT
 Z_c = Critical Compressibility factor, = $P_c V_c/RT_c$

Greek Letters

α = Soave coefficient, Equation (2-15)
 β = Heyen coefficient, Equation (2-58)
 θ = Heyen coefficient, Equation (2-58)
 ω = Acentric factor, Equation (2-16)
 δ_{jk} = Interaction coefficient between pure component j and k
 ϕ = Fugacity coefficient

Subscripts

c = Critical condition
 i = Component number, Equation (2-12)
 j = Component number, Equation (2-27)
 k = Component number, Equation (2-61)
 L, ℓ = Liquid phase
 m = Mixture, Equation (2-60).
 n_j = Constant mole (2-23)

P = Constant pressure, Equation (2-23)
r = Reduced temperature, Equation (2-57)
T = Constant temperature, Equation (2-23)
T_c = Constant critical temperature, Equation (2-2)
V = Constant volume
V_c = Constant critical volume, Equation (2-2)
V,g = Gas phase

Superscripts

Λ = Property of a component in a solution
L = Liquid phase
S = Saturated phase
V = Vapor phase
' = Prime
* = Saturated

Abbreviations

API-44 = American Petroleum Institute Project Number 44
ID = Identification number
EOS = Equation of State
n = Normal
DMT = Dimethyl
M = Modified
MT = Methyl
ET = Ethyl
CYC = Cyclo

-C₁ = Methane

-C₂ = Ethane

-C₃ = Propane

-C₄ = Butane

-C₅ = Pentane

-C₆ = Hexane

BUBPT = Bubble Point Temperature

PR = Peng-Robinson Equation of State

RK = Redlich-Kwong Equation of State

SRK = Soave's Redlich-Kwong Equation of State

ESDU = Engineering Science Data Unit

VLE = Vapor Liquid Equilibrium

PVT = Pressure-Volume-Temperature

CHAPTER I

INTRODUCTION

Accurate prediction of the thermodynamic properties of pure and multicomponent mixtures, over a wide range of temperature, pressure, and composition is of paramount importance in the design and operation of most processing units in the petroleum, chemical, and nuclear industries. These properties are required for the design of various unit operations-- distillation and extraction columns, absorbers, flash separators, heat exchangers, and etc.

A very general method for calculating the thermodynamic properties of pure components and their mixtures is by means of equations of state. An equation of state is an analytic expression that relates pressure, temperature, and composition. Since thermodynamic properties are functions of state, an equation of state represents an analytic tool from which these properties may be derived.

A review of the literature provides more than a hundred equations of state (54, 55) and reveals that there is still no satisfactory method for the prediction of thermodynamic properties over a wide range of pressure and temperature.

Previous studies (4) indicate that the Heyen equation of state is a step in the right direction and shows better accuracy in the calculation of volumetric properties compared to the most successful and widely accepted equations of state proposed by Soave-Redlich-Kwong (SRK)

and Peng-Robinson (PR) (49). However, the original Heyen equation of state is limited to high temperature, and low temperature applications have been a subject of much concern. Also, at low reduced temperature, predicted vapor pressures deviate considerably from experimental values (13).

The objective of this work was to modify the Heyen equation of state (50) by proposing a better model for the temperature dependent attractive term α , when the reduced temperature is less than or equal to 0.7 ($T_r \leq 0.7$). The temperature dependent attractive term α is defined as:

$$\alpha = \text{Exp}(k/2(1-T_r^n)) \quad (1-1)$$

where k and n are fitted parameters and T_r is the reduced temperature.

The advantage of this modification over the original Heyen equation of state, as well as modified Soave-Redlich-Kwong (162) and PFGC (163) equations of state were tested by comparing predicted and experimental thermodynamic properties.

Parameters for pure components were obtained by fitting the Heyen equation of state with this revised α expression using nonlinear regression to match experimental pure component vapor pressure from the triple point to the critical point. Volumetric data and the vapor pressure to be used were those of paraffins, olefins, cycloparaffins, aromatics, hydrogen sulfide, nitrogen, carbon dioxide and sulfur dioxide.

This study was extended for mixtures, using the same mixing rules as used by Heyen. Equilibrium K values for different systems--paraffin-paraffin, paraffin-olefin, paraffin-aromatic, olefin-olefin, etc.-- were predicted and compared with the experimental values.

In the evaluation and fitting of the data, the main tool for this

study, was the 'MPMCGC' program developed by Erbar (53). This program needed to be modified in order to handle the Heyen equation of state and the new model proposed as:

$$\alpha = A + M(1 - T_r^R) \quad (1-2)$$

where A and M are obtained through the correlations and R is a fitted parameter.

CHAPTER II

LITERATURE REVIEW

Vapor liquid equilibrium calculations are of great importance to the design and operation of most processing units in the chemical and hydrocarbon processing industries. Thermodynamic properties can be measured experimentally; however, experimental measurements are costly and time consuming. Thus, development of the predictive methods for estimation of thermodynamic properties has been of considerable interest to the present technology. Numerous experimental and theoretical studies have been developed on the subject over the past several decades. Consequently, many useful correlation methods have been developed.

A review of the literature indicates that numerous attempts have been made in the past century to develop an accurate equation of state for real fluids. These attempts cover such a variety of methods, approaches, and a wide range of specific applications, that the discussion and interpretation of all of these techniques would be too lengthy and time consuming. However, in reviewing the published work on equations of state one can perceive a rough historical division into two main types of approaches.

The Theoretical Approach

In this approach an attempt is made to develop equations of state based on either kinetic theory or statistical mechanics involving inter-

molecular forces. Typical publications following this approach are those of Van der Waals (56), Lennard-Jones and Devonshire (57), Hirschfelder, Bird, and Spatz (58), and Flory, Orwall, and Vrij (59).

The Empirical or Semi-Theoretical Approach

Here an attempt is made to deduce the structure of the equations of state from an empirical or semi-theoretical relationship among related variables using the large accumulation of experimental data. Typical of the many publications adopting this approach are those of Clausius (60), Berthelot (61), Dieteric (62), Wohl (63), Keyes (64), NBS (65), Beattie and Bridgeman (66), Benedict, Webb, and Rubin (67), Martin and Hou (69), Pings and Sage (70), Hirschfelder, Buehler, McGee and Sutton (71), Strobridge (72), Gastolnich and Thodos (73), McCarty and Stewart (74), and Goodwin (75).

Besides the above types of approaches, Eubank (76) has divided the equations of state into two categories: analytical and non-analytical. Leland (77) has classified equations of state into four groups: (1) The Van der Waals Type Equations, (2) The Benedict, Webb, and Rubin Type Equations, (3) Reference Fluid Equations, and (4) Augmented Rigid Body Equations. Harmens (168) has distinguished two types of equations of state: the complex virial equations, and the much simpler cubic equations. For further information about any of the above classifications, the reader is referred to reviews and articles by the authors (67, 77, 80, 81, 168).

This literature review focuses attention of the empirical or semi-theoretical, Van der Waals type, equations of state since these are the ones which have had the greatest success in representing data with high

precision over a wide range of conditions (159). Besides, this work itself is the further improvement of such a type of cubic equation of state.

History of Equation of State

The earliest equation of state to describe the volumetric properties of gases dates back at least to the time of Boyle, 300 years ago. These developments led to the famous "Ideal Gas Law" which is given below:

$$PV=RT$$

where

P = Pressure

V = Volume

T = Absolute Temperature

R = Universal Constant

This equation does not adequately describe the volumetric behavior of real gases and many attempts have been made in the past century to develop an equation of state for the real fluids. It was not until 1873 that Van der Waals published his famous equation of state capable of describing equilibrium properties of real gases. The Van der Waals equation of state is:

$$\left(P - \frac{a}{V^2}\right)(V-b) = RT$$

or

$$P = \frac{RT}{V-b} + \frac{a}{V^2} \quad (2-1)$$

The constant "b", known as the co-volume, is considered to reflect the volume of molecules, and the constant "a" is assumed to account for the

attractive force between molecules. The constants "a" and "b" can be obtained from the condition at the critical point

$$\left(\frac{\partial P}{\partial V}\right)_{T_c, V_c} = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \quad (2-2)$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c, V_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \quad (2-3)$$

The equation of state constants require only two of the three critical properties for complete definition. The critical pressure (P_c) and critical temperature (T_c) are usually selected, since these properties are more reliable than the critical volume. Simultaneous solutions of equations (2-1), (2-2) and (2-3) result in:

$$a(P_c, T_c) = \frac{27R^2 T_c^2}{64P_c} \quad (2-4)$$

$$b(P_c, T_c) = \frac{RT_c}{8P_c} \quad (2-5)$$

Although empirical equations of state have been used extensively by many authors since Van der Waals proposed his famous equation, such equations have only recently come into prominence from a theoretical point of view (88). The recent interest in equations of state of the Van der Waals type is due to the papers by Kac, Uhlenbeck and Hemmer (85), and by Lebowitz and Penrose (86) which show that, under certain conditions of the intermolecular potential, one might expect a Van der Waals-like equation with the Maxwell construction to be an exact equation of state.

Because of the number of shortcomings in Van der Waals equation, several investigators, including Clausius (60), Berthelot (61), Dieterici (62), Wohl (63), and Redlich and Kwong (89), improved the Van der Waals equation of state, mainly by modifying the pressure correction term $\frac{a}{V^2}$. Among the many early modified versions (82), the Redlich-Kwong (RK) equation (94) is believed to be the most successful modification (79).

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}(V+b)V} \quad (2-6)$$

This equation was formulated using the assumption that the constant "b" is 0.26 times the critical volume. Despite the doubtful soundness of this assumption, the resultant equation has been shown to be the best two constant equations of state. Its great assets are its simplicity and its accuracy relative to other equations with numerous constants. Its shortcomings are its inability to accurately describe the liquid phase, volumetric properties, and its failure to give consistently good results for fugacity coefficients in mixtures. The results obtained by this method show an increasing error as the acentric factor of the compound increases. Besides the critical compressibility factor, Z_c , predicted by this method has a value of one-third for all the compounds, while the value of Z_c for different compounds varies from 0.24 to 0.32.

Consequently, several attempts have been made in order to improve the original equation by extending its application to liquid phase and mainly to vapor-liquid equilibrium description. For early work the reader is referred to the book by Hirschfelder, Curtis, and Bird (87). Only a few are noted here to indicate the approaches employed. In 1964, Wilson (2, 3) modified the Redlich-Kwong equation of state by making the constant "a" a function of reduced temperature. Also, he introduced

a binary interaction coefficient into the mixing rule for "a" to improve mixture properties. However, his modification had limited success, particularly at high pressure where deviations for vapor pressure predictions are very high.

In 1965, Robinson and Jacoby (90) studied the temperature dependencies of constants "a" and "b" and set both constants as linear functions of temperature. They also reported a number of binary interaction coefficients to be used for the mixing rules of "a".

In 1966, Barner, Pigford, and Schreiner (1) tried to improve Wilson's work by modifying the temperature dependency of Redlich-Kwong equation of state. Despite the fact that Barner's work improved the estimation of enthalpy deviations for non-polar vapors and for vapor-phase mixtures of hydrocarbons, it was not suitable for fugacity calculations.

In 1967, Chueh and Prausnitz (91) proposed an interaction term for a large number of binary mixtures, with particular emphasis on the improvement of the fugacity coefficient prediction. Their improvement incorporates both acentric factor and critical volume as well as an interaction constant specific to each mixture. However, some limitations were found in their modification which resulted in a slight inconsistency in the extent of two-phase region. With the constant established by Chueh and Prausnitz, different coefficients were obtained using volumetric data on the different saturated phases, consequently fugacities were not equal for both phases, a basic requirement for phase equilibrium.

In 1968, Ngo (92) a student of Redlich, presented a modification in which the critical compressibility factor Z_c is introduced in the equa-

tion as the third parameter. Ngo's modification is extremely complex. Even without the deviation function that she introduced to fit the supercritical data, it can not be relied upon for values of $T_r < 0.8$. It was used to calculate the compressibility factor of pure substances, but due to its complexity, it is difficult to use for mixtures.

Gray, Rent, and Zudkevitch (93) in a paper presented at the AIChE meeting, in New Orleans, combined the deviation function approach of RK with Barner's modification to fit compressibility factors and enthalpy data for vapor mixtures of light hydrocarbons. Although the fit near the critical point is improved, the modification has a limited range of applicability.

Wilson (94) presented a complicated relation which is the modification of his earlier paper to improve the calculation of mixture properties. He successfully applied this modification to the nitrogen-hydrogen system. In this case the agreement between experimental results and predicted results is very good. However, for some other cases, especially those containing larger hydrocarbons, agreement is unsatisfactory.

Joffe and Zudkevitch (9) combined the ideas of Wilson (2,3) and Chueh and Prausnitz, and proposed a modification to the Redlich-Kwong equation which solved the discrepancies inherent in the Chueh and Prausnitz modification. However, because of its complex nature it was not widely adopted. Meanwhile, Vogh and Hall (95) correlated the two parameters for hydrogen and helium, but limited their correlation to the supercritical region and without generalization.

In 1971, Chung and Lu (30) introduced a third parameter to the Redlich-Kwong equation. They added a deviation function which is a

generalized function of P_r and T_r . Mixing rules that include the interaction parameter allow the use of equation for multicomponent mixtures. Gravelle and Lu (96), Hsi and Lu (97, 98), and Skamenca and Tassios (99) are among those who have worked on the modification of Van der Waals type equation in 1971.

Up to this point of time, the inability of cubic equations of state to represent the entire fluid range, prevented their use for the vapor liquid equilibrium calculations, and thermodynamic treatment of phase equilibria was mainly based on the Gamma-Phi, or split, equations of state. This approach considers the use of an equation of state for evaluating the properties in the vapor phase, while empirical correlations are used to calculate the thermodynamic properties of the liquid phase. This method tends to suffer from two serious, if not fatal weaknesses, in the hydrocarbon phase equilibrium area. The first of these is peaks or spikes in phase boundaries. They are found in the bubble point curve on the pressure temperature (PT) diagram at the higher pressure on the liquid side of envelope (100). The second one is that the two separate equations of state do not come to a common point, and, as a matter of fact, may never interact when an attempt is made to calculate the bubble point-dew point envelope for the mixture (100). A correlation of vapor-liquid equilibria by means of a single equation of state which predicts properties of both vapor and liquid avoids these difficulties, since the equation is continuous in going from vapor to liquid.

Of course, this fundamental approach has been used in the past with B-W-R (101); but because of some disadvantages and its complexity, it was placed in a position of limited use. Among other investigators who

proposed that the RK equation can be adapted to predict both liquid and vapor properties are Wilson (2,3,94) and Chueh and Prausnitz (91). Their methods were not widely accepted because of some deficiencies which were indicated earlier.

In 1972, Soave showed how to overcome difficulties encountered in the split equations of state. His modification has achieved wide application in chemical engineering practice because of the relative simplicity of the equation itself as compared to the more complicated equations and because of its capability for generating reasonably accurate results relative to other methods in VLE calculation. Thus, Soave's modification of the RK equation of state deserves a more detailed consideration.

Soave's Modification

In 1972, Soave (5,6) modified Redlich-Kwong (RK) equation of state along the same line of thought of Barner et al. (1) and Wilson (2,3,94). This modification consisted of developing a generalized temperature dependence term for the attractive term "a" in the RK and replacing the term $a/T^{0.5}$ with a more general temperature dependent term $a(T)$. The basic form of RK equation of state was modified only slightly. Soave's modification is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (2-7)$$

or

$$P = \frac{RT}{V-b} - \frac{a_c \alpha}{V(V+b)} \quad (2-8)$$

Equation (2-7) can be written in terms of compressibility factor

$$Z^3 - Z^2 + 2(A-B-B^2) - AB = 0 \quad (2-8)$$

where

$$Z = \frac{PV}{RT} \quad (2-9)$$

$$A = \frac{aP}{R^2T^2} \quad (2-10)$$

$$B = \frac{bP}{RT} \quad (2-11)$$

and the values of $a(T)$ were obtained for each substance by fitting of experimental vapor pressure data. The values of $a(T_c)$ and b can be calculated from component critical constants by imposing the requirement that the first and second derivatives of pressure with respect to volume be zero at the critical point:

$$a_i(T_c) = a_{ci} = 0.42747 \frac{R^2T_{ci}^2}{P_{ci}} \quad (2-12)$$

$$b_i = 0.08664035 \frac{RT_{ci}}{P_{ci}} \quad (2-13)$$

At temperatures other than the critical;

$$a_i(T) = a_{ci}\alpha_i(T) \quad (2-14)$$

where α_i could be expressed as a function only of reduced temperature and acentric factor:

$$\alpha_i = [1 + m_i (1 - T_{ri}^{0.5})]^2 \quad (2-15)$$

where

$$m_i(\omega) = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \quad (2-16)$$

consequently

$$A = 0.42747 a_i \frac{P_{ri}}{T_{ri}}$$

and

$$B = 0.08664 \frac{P_{ri}}{T_{ri}} \quad (2-17)$$

The fugacity coefficient of a pure component can be calculated from the equation.

$$\ln \frac{f}{P} = Z-1 - \ln(Z-B) - \frac{A}{B} \ln\left(\frac{Z+B}{Z}\right) \quad (2-18)$$

Soave extended the application of the equation of state to mixtures by using the following mixing rules:

$$a^{0.5} = \sum x_i a_i^{0.5} \quad (2-19)$$

$$b = \sum x_i b_i \quad (2-20)$$

Where a and b referred to the mixtures and a_i , b_i to the pure components.

Then A and B for the mixtures are given by:

$$A = 0.42747 \frac{P}{T^2} \left(\sum x_i \frac{T_{ci}^{0.5} a_i^{0.5}}{P_{ci}^{0.5}} \right)^2 \quad (2-21)$$

$$B = 0.08664 \frac{P}{T} \left(\sum x_i T_{ci} / P_{ci} \right) \quad (2-22)$$

Here x_i is the mole fraction in either the liquid or vapor phases.

The fugacity coefficient for a component in a mixture is given by

$$\ln \phi_i = \int_{\infty}^V \left[\frac{1}{V} - \frac{1}{RT} \left(\frac{dP}{dn_i} \right)_{T,P,n_i} \right] dV - \ln Z \quad (2-23)$$

$$= \frac{b_i}{b} (Z-1) - \ln(Z-B) - \frac{A}{B} \left(2 \frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b} \right) \ln \left(1 + \frac{B}{Z} \right) \quad (2-24)$$

Where the ratios b_i/b and a_i/a are given by:

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{\alpha_i^{0.5} T_{ci}/P_{ci}^{0.5}}{\sum \alpha_i^{0.5} T_{ci}/P_{ci}^{0.5}} \quad (2-25)$$

$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum (x_i T_{ci}/P_{ci})} \quad (2-26)$$

Although the above mixing rules based on Soave's results were adequate for non-polar or slightly polar compounds, they could be improved by introducing empirical correction terms. Later on, Soave (6,7) improved the performance of his equation for polar compounds by modifying the above mixing rules as follows:

$$a = \sum x_i x_j a_{ij} \quad (2-27)$$

where

$$a_{ii} = a_i$$

$$a_{jj} = a_j$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \quad (2-28)$$

and

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (2-29)$$

and

$$b_{ii} = b_i$$

$$b_{jj} = b_j$$

$$b_{ij} = b_{ji} (1 - k_{ij})(b_i + b_j)/2 \quad (2-30)$$

Also, for polar compounds, the trend of α deviates from that expressed by Equation (2-15). A more general expression is required, containing at least two adjustable coefficients, as follows:

$$\alpha = 1 + m(1 - T_r) + n\left(\frac{1}{T_r} - 1\right) \quad (2-31)$$

Experience has shown that the $(1 - k_{ij})$ term is not required for hydrocarbon-hydrocarbon binaries, but is required for nitrogen-hydrocarbon, carbon dioxide, hydrocarbon, and hydrogen sulfide-hydrocarbon binaries (8).

As mentioned earlier, among the research reports attempting to modify the Redlich-Kwong equation of state, Soave's modification is one of the best. It made possible a high precision of prediction of vapor pressures (9). However, despite the important advantages achieved by Soave, the computation of saturated liquid density remains the weak point of cubic equations of state (10,12).

From 1972 to 1976 many attempts were made to improve this deficiency in Soave's method (12, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24). Among the research reports, the best known is the one by Peng-Robinson (12) which will be considered in more detail.

The Peng-Robinson Equation of State

Peng and Robinson (97), noted that the Soave-Redlich-Kwong equation predicts poor saturated liquid volumes and the predicted value of the critical compressibility factor influences the predicted liquid volumes. They developed an equation of state which would predict reasonable values of hydrocarbon liquid densities. They proposed their equation in the form of:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (2-32)$$

The parameters a and b , which are characteristic of each substance, can be correlated to critical temperature and pressure using the necessary condition of existence of the critical point. The final expressions obtained at the critical point are:

$$a_i(T_c) = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}}$$

$$b_i(T_c) = 0.07780 \frac{RT_{ci}}{P_{ci}} \quad (2-33)$$

$$Z_c = 0.307$$

At the temperatures other than the critical,

$$a_i(T) = a_i(T_c) \alpha_i(T_r, \omega) \quad (2-34)$$

$$b_i(T) = b_i(T_c) \quad (2-35)$$

where $\alpha_i(T_r, \omega)$ is a function of reduced temperature and acentric factor and must assume unitary value at the critical point.

$$\alpha_i^{1/2} = 1 + m_i (1 - T_{ri})^{0.5} \quad (2-36)$$

where m_i is a constant characteristic of each substance

$$m_i = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (2-37)$$

Introducing compressibility factor Z , Equation (2-32) can be written as:

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \quad (2-38)$$

where

$$A = \frac{aP}{R^2T^2} \quad (2-39)$$

$$B = \frac{bP}{RT} \quad (2-40)$$

$$Z = \frac{PV}{RT} \quad (2-41)$$

Applying the thermodynamic relationship

$$\ln \frac{f}{p} = \int_0^P \left(\frac{V}{RT} - \frac{1}{p} \right) dp \quad (2-42)$$

to Equation (2-32), Peng and Robinson derived the following equation for the fugacity of a pure component:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (2-43)$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (2-44)$$

$$b = \sum_i x_i b_i \quad (2-45)$$

where

$$a_{ij} = (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \quad (2-46)$$

The fugacity coefficient of component k in the mixture is

$$\ln \frac{f_k}{x_k P} = \frac{b_k}{b} (Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum x_i a_{ik}}{a} - \frac{b_k}{b} \right) \cdot$$

$$\ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right)$$

The PR equation of state has some significant advantages over earlier two-parameter equations of state, and in a short span of time has found wide application in natural gas and petroleum. However, the constant critical compressibility factor limits the range of fluids for which it is accurate. Thus, it is still apparent that further studies are required in the calculation of vapor pressure.

Consequently, from 1976 on, research has continued in an effort to overcome the shortcomings, deficiencies, and handicaps of specific equations of state of RK type (25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38-46), as well as equations of state in general. However, the two-parameter cubic equation of state, which up to this point has been the focus of our study, has suffered from the so called "critical abnormality." Inherent with each equation of this type is an invariant value of the critical compressibility factor Z_c . For the SRK equation $Z_c = 0.333$, and for Peng-Robinson equation $Z_c = 0.30740$. The abnormality lies in the fact that all substances of interest have Z_c between 0.24 and 0.32, so that these two values can never be wholly representative of them. The abnormality interfered with the temperature fitting of the parameters near the critical temperature, and thus affected the accuracy of calculated equilibrium even at pressures well below the critical.

Another possible explanation for the failure to reproduce the liquid state is that the repulsive parameter b in SRK and PR do not change with temperature. This phenomenon disagrees with the kinetic theory (47), which states that parameter b does depend on temperature.

Three Parameter Equations of State

Based on the earlier discussion it appeared that further studies are necessary in the calculation of VLE. This led to re-examination of the variation of the parameters with temperature. Although, these equations of state seemed to be designed for computing densities, success in doing so was only mediocre. Thus, it led to modification of cubic equations of state by using a "third parameter." Even though three parameter equations of state are identical in their formulations, they differ by the method followed by their authors for evaluating the parameters.

Freze and Chevalier (48) in 1978 used equations with three temperature-dependent parameters which allowed them to make Z_c substance dependent, causing both the liquid volume at a particular reduced temperature and critical volume to be reproduced accurately.

In 1980, Harmens and Knapp (41) studied three parameter equations of state. Keeping " b " and " c " constant at their critical values and " a " temperature dependent, they obtained the parameters of an equation of state from density data along the critical isotherm. The variation of the attraction parameter with temperature was evaluated using vapor pressures. At temperatures higher than the critical temperature, density data along the critical isobar was used to evaluate the attraction parameter.

Schmidt and Wenzel (1980) proposed an equation of state of the Van der Waals type which used the critical data, T_c and P_c , and the acentric factor, ω , as input data to yield a substance-dependent critical compressibility factor. By applying the critical conditions and using vapor-pressure data they determined the variation of "a" term with temperature, while keeping other parameters constant at their critical point values.

The three parameter equation of state proposed by Patel and Teja (49) has the following form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + c(V-c)} \quad (2-50)$$

They evaluated their parameters by minimizing deviations in saturated liquid densities and vapor-pressure, while preserving the form of the $a(T)$ law proposed by Soave and keeping "b" and "c" constant.

In 1980, Heyen (50) proposed a cubic equation of state which shows better accuracy in the calculation of volumetric properties, compared to PR equation of state (51). Heyen's method can be singled out by the fact that the co-volume varies with the temperature.

The Heyen Equation of State

In 1980, Heyen (50) proposed a modification of Peng-Robinson equation of state by introducing a third parameter in order to reproduce experimental compressibility factor. Heyen, in his equation, made two parameters temperature dependent. The equation that he proposed can be reduced to PR or SRK models by proper selection of parameter e :

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + (b+e)V-be} \quad (2-51)$$

and in dimensionless form

$$Z^3 + (B-1)Z^2 + (A-B-E-2BE-E^2)Z + (BE^2 + BE-AE) = 0 \quad (2-52)$$

where

$$Z = PV/RT$$

$$A = aP/R^2T^2$$

$$B = bP/RT$$

$$E = eP/RT$$

Temperature dependent a and e were chosen to ensure that the equation of state reproduced experimental saturated liquid densities and vapor pressures. Since equation (2-52) has three equal roots at the critical point, the values of A , B and E for the critical temperature can be obtained from.

$$B_c = 1-3Z_c \quad (2-53)$$

$$E_c^3 + (2-3Z_c) E_c^2 + 3Z_c^2 E_c - Z_c^3 = 0 \quad (2-54)$$

Equation (2-54) can be solved either analytically or by iteration (Newton's Method) with an initial value of

$$E_c = 0.32429Z_c - 0.022005$$

Finally,

$$A_c = B_c + E_c + 2B_cE_c + E_c^2 + 3Z_c^2 \quad (2-55)$$

The details of the derivation of Equation (2-52), A_c , B_c , and C_c are presented in Appendix A.

Temperature dependent parameters are expressed by:

$$a = A_c \frac{R^2 T_c^2}{P_c} \alpha(T_r)$$

$$b = B_c \frac{RT_c}{P_c}$$

$$e = E_c \frac{RT_c}{P_c} \beta(T_r) \quad (2-56)$$

Values of $\alpha(T_r)$ and $\beta(T_r)$ have been calculated by forcing the equation of state to match experimental saturated liquid volume and vapor pressure. It has been pointed out by many authors (14, 21, 52) that the temperature function for α used by Soave and Peng-Robinson does not reproduce the correct temperature behavior of constant "a" at high temperatures. This is mainly because the function becomes zero at finite T_r and then starts to rise with temperature. The approach of real gas behavior to that of an ideal gas at high temperatures requires that $a \rightarrow 0$ as $T_r \rightarrow \infty$. Heyen proposed the following exponential function for α which has the required characteristic (49):

$$\alpha(T_r) = \exp(k(1-T_r^n)) \quad (2-57)$$

$$\beta(T_r) = 1 + m \frac{1 - \exp(\theta(T_r - 1))}{1 + \exp(\theta(T_r - 1))}$$

$$= 1 - m \tanh\left[\frac{\theta}{2}(T_r - 1)\right] \quad (2-58)$$

where β decreases from a maximum asymptotic value at low T_r , to unity for $T_r = 1$. Parameters k , n , m , and θ can be identified for polar and nonpolar components by fitting experimental vapor pressure and saturated volume.

The principle of corresponding states implies that equation of state parameters for normal components should be a unique function of the acentric factor. Simultaneous fit of 562 sets of saturated pressure and volume data for 62 normal components has led to:

$$k = 0.49164 + 0.43882\omega - 0.08821\omega^2$$

$$n = 1.637 + 1.389\omega$$

$$e = 7.2562 + 14.153\omega + 1.33137\omega^2$$

$$m = 0.2333 - 0.06737\omega + 0.49110\omega^2$$

Equation (2-51) can be applied to the mixtures using classical quadratic mixing rules:

$$a_m = \sum_i^n \sum_j^n x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (2-60)$$

$$b_m = \sum_i x_i b_i$$

$$e_m = \sum_i x_i e_i$$

Fugacity coefficients for component k in the mixture are given by:

$$\begin{aligned} \ln \phi_k = & \ln(Z-E) - \frac{A}{W} \left(\frac{r_k}{a} - q_k \right) \ln \delta + \frac{E_k}{Z-E} \\ & + \left(\frac{1}{Z-E} - 1 \right) \left[\frac{1}{2} (E_k + B_k - q_k(E+B) - q_k Z) \right] \end{aligned} \quad (2-61)$$

where

$$W = \sqrt{E^2 + 6BE + B^2}$$

$$\delta = \frac{2Z + E + B + W}{2Z + E + B - W}$$

$$q_k = \frac{(E + 3B) E_k + (B + 3E) B_k}{W^2}$$

$$r_k = 2 \sum_{i=1}^n x_j \sqrt{a_j a_k} (1 - k_{ij})$$

As can be seen, the Heyen equation of state is an empirical equation specially formulated to describe the volumetric and phase behavior of hydrocarbons and their mixtures. Saturated liquid and vapor densities

for 38 components were studied by Patel and Teja (49) for both PR and Heyen. The Heyen type equation gives lower average deviations in both vapor and liquid phases than the PR equation of state.

Later on, Heyen himself used a new mixing rule and obtained better results than Craboski-Daubert (27), Peng-Robinson (21) Schmidt-Wenzel (40) and Hamens-Knapp (41).

However, Vidal (13) in his extensive study of equations of state in general, and three parameter cubic equations of state in particular, compared the obtained results by PR, Kubic, Harmens-Knapp, Schmidt-Wenzel, Patel-Teja, and Heyen equations of state and concluded that:

The calculation of vapor pressure is generally good above the thermal boiling point but it should be noted that the methods appreciably different from the Soave's formulation of the $a(T)$ law may give disappointing results at low temperatures. Because of the great differences between the experimental and the calculated values of the critical compressibility factor, the values of the saturated liquid density cannot be good at high pressure. Heyen's method is an exception to this rule because of the volume temperature variation.

In 1983, Won (51), who worked specifically with the Heyen type equation of state, reached the same conclusion as Vidal for low T_r .

In conclusion, the application of Heyen equation of state at low T_r has been a subject of much concern. At low reduced temperatures, predicted vapor pressure deviates considerably from experimental values. Thus, further work is needed to overcome this shortcoming of the Heyen equation of state. As a result, and also as a part of a continuing study of the evaluation and development of equations of state, this work is an attempt to modify the Heyen equation of state by developing a new α model for low T_r . Hopefully this effort will help overcome the

deficiencies at low T_r and yield a better overall representation of thermodynamic properties of pure components and mixtures.

CHAPTER III

MODEL DEVELOPMENT

Justification

It has been pointed out by many authors (14, 21, 52) that the temperature function for α used by Soave and Peng-Robinson does not reproduce correct temperature behavior of the parameter "a" at high temperature. This is mainly because the function becomes zero at finite T_r and then starts to rise with temperature. The approach of real gas behavior to that of an ideal gas at high temperatures requires that $a \rightarrow 0$ as $T_r \rightarrow \infty$.

Heyen therefore proposed the following empirical functions for α which has the required characteristic (49):

$$\alpha(T_r) = \exp[k(1-T_r^n)] \quad (3-1)$$

where parameters k and n can be identified for polar and nonpolar components by fitting experimental vapor pressure and saturated volume. Based on principles of corresponding states they are unique functions of the acentric factor. Simultaneous fit of 562 sets saturated pressure and volume data for 62 pure components has lead to:

$$n = 1.637 + 1389\omega \quad (3-2)$$

$$k = 0.49146 + 0.43882\omega - 0.08821\omega^2 \quad (3-3)$$

The Heyen equation has been presented in Figure 1, and its related derivation in Appendices A and B.

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + (b+e)V-be} \quad (3-4)$$

$$Z^3 + (B-1)Z^2 + (A-B-E-2BE-E^2)Z + (BE^2 + BE-AE) = 0 \quad (3-5)$$

$$Z = PV/RT \quad (3-6)$$

$$A = aP/R^2T^2 \quad (3-7)$$

$$B = bP/RT \quad (3-8)$$

$$E = eP/RT \quad (3-9)$$

$$B_{ci} = 1-3Z_{ci} \quad (3-10)$$

$$E_{ci}^2 + (2-3Z_{ci})E_{ci} + 3Z_{ci}^2E_{ci} - Z_{ci}^3 = 0 \quad (3-11)$$

$$E_{ci} = 0.32429Z_{ci} - 0.022005 \quad (3-12)$$

$$A_{ci} = B_{ci} + E_{ci} + 2B_{ci}E_{ci} + E_{ci}^2 + 3Z_{ci}^2 \quad (3-13)$$

$$a_i = A_{ci} \frac{R^2T_{ci}^2}{P_{ci}} \alpha_i(T_r) \quad a = \sum_i \sum_j x_i x_j \sqrt{a_i} a_j (1-k_{ij}) \quad (3-14)$$

$$b_i = B_{ci} \frac{RT_{ci}}{P_{ci}} \quad b = \sum x_i b_i \quad (3-15)$$

$$e_i = E_{ci} \frac{RT_{ci}}{P_{ci}} \beta_i(T_r) \quad e = \sum x_i e_i \quad (3-16)$$

$$\alpha_i(T_r) = \text{Exp} [k_i (1-T_{ri}^{n_i})] \quad (3-17)$$

$$\beta_i(T_r) = 1 + m_i \frac{1 - \exp[\theta_i (T_{ri} - 1)]}{1 + \exp[\theta_i (T_{ri} - 1)]} = 1 - m_i \text{Tanh} \left[\frac{\theta_i}{2} (T_{ri} - 1) \right] \quad (3-18)$$

$$k_i = 0.49164 + 0.43882\omega_i - 0.08821\omega_i^2 \quad (3-19)$$

$$n_i = 1.637 + 1.389\omega_i \quad (3-20)$$

$$\theta_i = 7.2562 + 14.153\omega_i + 1.33137\omega_i^2 \quad (3-21)$$

$$m_i = 0.23333 - 0.06737\omega_i + 0.49110\omega_i^2 \quad (3-22)$$

$$\ln \phi_k = \ln(Z-E) - \frac{A}{W} \left(\frac{r}{a} - q_k \right) + \ln \delta + \frac{E_n}{Z-E} + \left(\frac{1}{Z-E} - 1 \right) \left[\frac{1}{2} (E_k + B_k - q_k (E+B) - q_k Z) \right] \quad (3-23)$$

$$W = \sqrt{E^2 + 6BE + B^2} \quad (3-24)$$

$$\delta = \frac{2Z + E + B + W}{2Z + E + B - W} \quad (3-25)$$

$$q_k = \frac{(E + 3B)E_k + (B + 3E)B_k}{W^2} \quad (3-26)$$

$$r_k = 2 \sum_{j=1}^n x_j \sqrt{a_j} a_k (1-k_{jk})$$

Figure 1. The Heyen Equation of State

Despite the important advantages achieved by Heyen (49) over the Peng-Robinson and earlier two parameter cubic equations of state, its application at low T_r has been a subject of much concern. At low reduced temperatures predicted vapor pressures deviate considerably from experimental values. As Vidal (13) in his extensive study of three parameter cubic equations of state concluded:

It should be noted that the methods appreciably different from Soave's formulation of the $a(T)$ may give disappointing results at low temperature.

Since one of the important considerations for any equation of state that is to be used for vapor-liquid equilibrium calculation is whether or not it can accurately predict the vapor pressure of pure substances. Therefore, the principle objective and goal of this work has been to modify the Heyen equation of state by developing a new α model for low T_r which overcomes this deficiency. The assumption is that an improvement in reproducing saturated conditions of pure substances also leads to an improvement for mixtures.

Derivation of The Proposed α Model

As indicated, the Heyen equation of state with the α term is defined as:

$$\alpha_{h_i}^{1/2} = \exp[k_i/2(1-T_{ri}^{n_i})] \quad (3-28)$$

does not predict vapor pressure well at low temperature. However, the SRK equation of state has an α term of the following form:

$$\alpha_{S_i}^{1/2} = 1 + m_i(-T_{ri}^{0.5}) \quad (3-29)$$

which predicts thermodynamic properties better at lower temperature and

pressure (117). A model for α which incorporates the best features of both Soave's and Heyen's models is proposed to overcome this deficiency. The proposed model is as follows:

$$\alpha^{1/2} = A + M(1-T_r^R) \quad (3-30)$$

The term "R" is a fitted parameter. Its value is obtained by fitting the Heyen equation of state with the new α model to pure component vapor pressure data using Chandler's (116) modified version of Marquardt's non-linear fitting algorithm. For obtaining the expressions for A and M the following logic is followed. Since the proposed $\alpha(T_r)$ curve follows the Heyen temperature dependence at values of T_r greater than or equal to 0.7 and the Soave (46) dependence for values of T_r below 0.7, the slopes and the values of α at the match point of $T_r=0.7$ must be identical. Thus, the expressions for α and also partial derivatives of α with respect to T_r should be equal at the point of $T_r=0.7$. Thus, the expressions for the value of A, and the slope M, are obtained by the following correlations:

$$\frac{\partial \alpha_h^{1/2}}{\partial T_r} = \frac{\partial \alpha_{new}^{1/2}}{\partial T_r} \quad \text{at } T_r = 0.7 \quad (3-31)$$

$$\alpha_h^{1/2} = \alpha_{new}^{1/2} \quad \text{at } T_r = 0.7 \quad (3-32)$$

where;

$$\frac{\partial \alpha_h^{1/2}}{\partial T} = -\frac{k}{2} (n)(T_r^{n-1})e^{k/2(1-T_r^n)} \quad \text{at } T_r = 0.7$$

or

$$\frac{\partial \alpha_h^{1/2}}{\partial T_r} = -\frac{k}{2} (n) (T_r^{n-1}) \alpha_h^{1/2} \text{ at } T_r=0.7 \quad (3-33)$$

and

$$\frac{\partial \alpha_{new}^{1/2}}{\partial T_r} = -M(R)(T_r^{R-1}) \text{ at } T_r=0.7 \quad (3-34)$$

substituting Equations (3-33) and (3-34) into Equation (3-31) yields the following expression for M:

$$M = \left(\frac{n}{R}\right) \left(\frac{k}{2}\right) T_r^{n-R} \alpha_h^{1/2} \text{ at } T_r=0.7 \quad (3-35)$$

Substituting the expressions of α_h and α_{new} from Equations (3-28) and (3-30) into the Equation (3-32) and replacing the functional value of M from Equation (3-35) yields

$$A = \left[1 - \left(\frac{n}{2}\right) \left(\frac{k}{2}\right) (T_r^{n-R})(1-T_r^R)\right] (\alpha_h^{1/2}) \Big|_{T_r=0.7} \quad (3-36)$$

Substituting the expressions for A and M from the Equations (3-36) and (3-35) into Equation (3-30) and rearranging results in the following equation:

$$\alpha_{new}^{1/2} = \left\{ 1 - \left(\frac{n}{R} \cdot \frac{k}{2} \cdot T_r^{n-R}\right) \Big|_{T_r=0.7} \left[(1-T_r) \Big|_{T_r=0.7} - (1-T_r) \Big|_{T_r = T_r} \right] \right\} \cdot \alpha_h^{1/2} \Big|_{T_r=0.7} \quad (3-37)$$

which is the final form of the proposed α model. Note from the above equation, at only two points ($T_r = 0.0, 0.7$) does $\alpha_{new}^{1/2} = \alpha_h^{1/2}$.

For a better visual understanding of the new α model compare the earlier ones, the temperature behavior of all three models, namely,

SRK, Heyen and the proposed models have been presented graphically in Figure 2.

Finally, the expression for $\alpha^{1/2}$ can be shown as:

$$\alpha^{1/2} = \begin{cases} \alpha_{\text{new}}^{1/2} & T_r \leq 0.7 \\ \alpha_h^{1/2} & T_r > 0.7 \end{cases}$$

Derivation of the Fugacity Coefficient

The basic relationship for defining phase equilibria is based on the concept of chemical potential. For practical design purposes, however, the use of the fugacity concept, equivalent to chemical potential and of greater physical meaning, is preferred. For vapor-liquid systems in which both phases are at the same temperature and pressure, the criteria of phase equilibria for each component k is expressed in terms of the fugacity of the component k in the liquid and vapor phases. That is:

$$f_k^L = f_k^V \quad (3-39)$$

Equation (3-39) is of limited utility, unless the fugacity can be related to the temperature and pressure of the system, and to the liquid and vapor phase composition, x_n and y_n . The desired relations between the fugacity and experimentally accessible quantities are better expressed if they are replaced with fugacity coefficients which relate

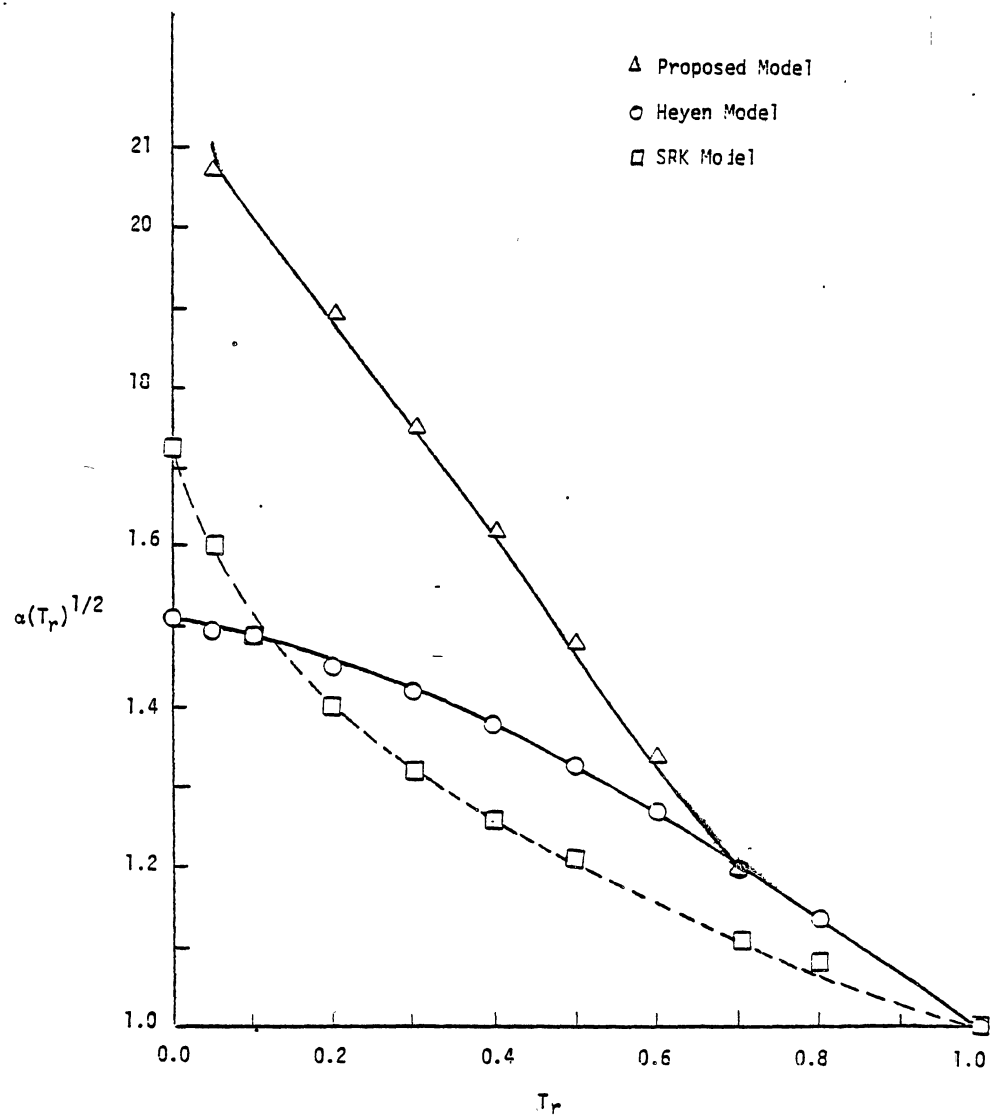


Figure 2. Effect of Temperature on Three Temperature Dependence of Attractive Term Models for Propane

the fugacities to the compositions and the total pressure of the system through the equations.

$$f_k^V = \phi_k^V y_k P \quad \text{or} \quad \phi_k^V = \frac{f_k^V}{y_k P} \quad (3-40)$$

$$f_k^L = \phi_k^L X_k P \quad \text{or} \quad \phi_k^L = \frac{f_k^L}{X_k P} \quad (3-41)$$

The fugacity coefficients in Equations (3-40) and (3-41) are used for calculation of the equilibrium ratio, k_i , and can be derived from Equation (3-4) which applies to both phases. Heyen has presented the final form of the fugacity coefficient equation in his paper (50), but it is not correct. Therefore, it is given correctly here.

Once the equation of state is defined, the fugacity coefficient can be calculated through following general thermodynamic relationships:

$$\ln \phi_k = \int_V^{\infty} \left[\frac{1}{RT} \left(\frac{P}{n_k} \right)_{T,V,n_j} - \frac{1}{V} \right] dV - \ln Z \quad (3-43)$$

Introducing Equation (3-4) into Equation (3-43) and integrating yields the following final and corrected form of the fugacity coefficients equations:

$$\ln \phi_k = \ln(Z-E) - \frac{A}{W} \left(\frac{r_k}{a} - q \right) \ln \delta + \frac{E_k}{Z-E} + \left(\frac{1}{Z-E} - 1 \right) \left[\frac{1}{2} (E_k + B_k - q_k (E+B) - q_k Z) \right] \quad (3-44)$$

The complete derivation of the above equation is given in Appendix B.

Determination of The Parameters And Testing of New α Model

Application of Heyen equation of state with a new α model to a specific fluid requires that numerical values first be accurately determined for the parameters, a , b , e , and any others which enter through arbitrary temperature functions $a(T)$ and $c(T)$ at the given temperature and pressure.

The modified Heyen equation of state in its final form has 6 adjustable parameters, n , m , $k/2$, θ , Z_c , R for each pure component. In order to obtain values of these variables thermodynamic properties, several steps were followed. Initial values were assumed for the six parameters. The modified Heyen equation of state was evaluated over the entire range of vapor pressure and volumetric data. The set of parameters that yielded the lowest absolute average error in vapor pressure predictions were selected. Care was exercised to maintain reasonable quality of prediction for the volumetric properties.

To assist in the fitting of the data for obtaining reliable parameters a very elaborate multiproperty, multicomponent fit program, "MPCGC", for the PFGC (Parameter For Group Contribution) developed by Erbar (115) was used. This program can be divided into five main functional parts: Input, setting property evaluation, fitting, and output. The Input program segment read the data to be used in the program. Data are checked for errors and, if necessary, modified to reduce the chances of program failure in later phases of the calculation. In the setting section of the program, all the required constants and parameters for the evaluation section are calculated. After successful completion of the required calculation in the setting section, the program proceeds

to the evaluation section of the program. This section consists of a number of subprograms dealing with the equilibrium calculation, calculation of several thermodynamic properties, etc. The calculated results are then compared with the experimental data supplied as input data to the program. From here on, depending on the request of the user, there are two options in the program.

1. If the user has requested prediction of the parameters, the program proceeds to the non-linear fitting section of the program. The fitting part consists of several subprograms and is designated to modify the parameters in order to minimize relative errors (objective function) by using Chandler's (116) modified version of Marquardt's non-linear fitting algorithm.

2. If the user has requested only evaluation (this is usually when the best set of parameters have been found), the program skips to the output section after the calculation of volumetric properties and enthalpy departures at the given T and P, and the comparison of the results with the experimental data given as the input data. The output segments of the program input data, the final values of the fitted parameters, a detailed comparison for each individual data point, a summary of the final average, percentage error, and absolute average percentage error for each type of data. The basis used for comparison is the absolute percent error in each point.

Outline of The Procedure

The following steps outline the method used for obtaining the parameters which lead to reliable prediction of thermodynamic properties and, consequently, the evaluation of Heyen equation of state with the new α

model over the entire range of vapor pressure and temperature.

1. Given the experimental critical temperature (T_c), critical pressure (P_c), critical compressibility factor ($Z_{c, \text{exp}}$), and an initial guess for six parameters ($n, m, k/2, \theta, Z_{c, \text{cal}}, R$); the numerical values for $B_c, A_c,$ and E_c are obtained from Equations (3-9), (3-11) and (3-13), respectively.

2. At a given temperature, the values for $\alpha(T_r)$ and $\beta(T_r)$ are calculated from equations (3-38) respectively.

3. At a given temperature, a pressure must be assumed--experimental pressure "P" is a good choice for the first guess.

4. The values of α and β provided by Step 2 will be used to calculate a and e from Equations (3-14) and (3-16). Using Equation (3-15) the numerical value of b is also calculated in this step.

5. Calculated values of $a, b,$ and e along with Equations (3-7), (3-8), and (3-9) are used to calculate the dimensionless values of $A, B,$ and E .

6. Information obtained by Step 5 is used to solve equation (3-5). This equation is cubic in terms of compressibility factor (Z), and has three roots. The smallest one is considered the compressibility factor of saturated liquid. The largest is applied to the vapor phase, and the third is ignored.

7. Calculated compressibility factors for liquid (Z^L) and vapor (Z^V) are used to calculate fugacity coefficients for liquid (ϕ^L) and vapor (ϕ^V).

8. If $\phi^L = \phi^V$ (within a tolerance), calculations proceed to the

next step; otherwise a new pressure "p" must be estimated. $P_{\text{new}} = P_{\text{old}}$.

$\frac{f_k^L}{f_k^V}$, and steps 4 through 8 are repeated using the new pressure.

9. Using equation (3-6) along with the results obtained by steps 6 and 8, saturated volumes of the vapor phase and liquid phase are calculated.

10. Calculated results (vapor pressure, volumetric properties, etc.) are compared with the related experimental values given as data to the program.

If the user has requested an evaluation only, the program prints the initial value of the parameter (without change) and a detailed comparison for each individual data point. Otherwise, the program skips this step and proceeds to Step 12, the non-linear fitting section of the program.

11. In this section, the sums of relative errors in each of the predicted properties are minimized. The parameters are changed, and the designated calculations are carried out on each data point in the total data set, repeatedly. The set of parameters that yields the lowest absolute average error in vapor pressure predictions are selected as the final values. The main tool to optimize the objective function in the non-linear fitting program is Chandler's (116) modified version of Marquardt's non-linear algorithm.

12. If predicted results still are not acceptable, the final values of the fitted parameters are used as initial guesses and the whole procedure is repeated until accurate results are predicted.

Vapor Liquid Equilibrium of Multicomponent
Mixtures and Prediction of K-Values

Using the following mixing rules

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij})$$

$$b = \sum_i x_i b_i$$

$$e = \sum_i x_i e_i$$

The Heyen equation of state with proposed model for α can be extended directly to the mixtures. The k_{ij} are empirical constants to correct the energy of interaction between the two different molecules present so as to optimize the prediction of phase equilibria. These constants are generally small and on the order of 0.0 to 0.25. The interaction coefficients, k_{ij} , increase as molecular size and complexity differences increase. These interaction coefficients are assumed generally to be constant for a given binary pair. Therefore, they are independent of temperature, pressures, density, and composition. Nevertheless, practical experience indicates that this is not always true. Thus, k_{ij} values should be determined at the temperature and pressure where they are being used.

Using the pure component parameters and extensive vapor-liquid equilibrium data for mixtures, binary component interaction parameters are derived which minimize the absolute average error in equilibrium K-ratios over the given pressure and temperature range. However, for mixtures containing hydrocarbon components with hydrocarbons values of

k_{ij} were found to be very close to zero. In this case the assumption of $\delta_{ij} = 0$ is reasonable. K-values were determined by flash calculations except in regions where flash calculations were unstable or calculated liquid fraction errors were high. In these cases the bubble point temperature calculation method was used.

CHAPTER IV

RESULTS

To overcome the shortcoming of Heyen equation of state in predicting the hydrocarbon properties at low temperature a new model of α was developed for $T_r \leq 0.7$.

$$\alpha_{i \text{ new}}^{1/2} = \left\{ 1 - \left(\frac{n_i}{R_i} \frac{k_i}{2} T_{ri}^{(n_i - R_i)} \right)_{T_{ri}=0.7} \left[(1 - T_{ri})_{T_{ri}=0.7} - (1 - T_{ri})_{T_{ri}=T_{ri}} \right] \right\} \alpha_{hi}^{1/2} \quad T_{ri} = 0.7 \quad (3-38)$$

where n_i , k_i , and R_i are fitted parameters. Parameters were obtained for each pure component by fitting the Heyen equation of state with the new α model using Chandler's (116) modified version of Marquardt's non-linear fitting algorithm.

Pure Component Vapor Pressures

Prediction

The program 'MPMCGC' was modified to handle the Heyen equation of state with the newly developed α model. Using available vapor pressure and volumetric data from the literature for a list of pure components most frequently used in the light hydrocarbon industry, parameters for use in modified Heyen equation of state were derived.

The fundamental objective in using non-linear, least-square fitting technique was to minimize the average percent error and absolute average percent error in vapor pressure of each pure component defined as:

$$\text{Average percent deviation} = \frac{\sum[(\text{EXP}-\text{Calc})/\text{Exp}]}{\text{NPTS}} \times 100$$

$$\text{Absolute average percent deviation} = \frac{\sum|[(\text{EXP}-\text{Calc})/\text{Exp}]|}{\text{NPTS}} \times 100$$

The selected pure components can be divided into five main groups; paraffins, olefins, cycloparaffins, aromatics, and inorganic materials. For the paraffins ranging from C₇ to C₈, ESDU (103) and Kobayashi et al., (102) data were used. Kobayashi reports vapor pressure data at very low pressures. These data were used to confirm the utility of the new proposed model for very low temperature conditions. For C₉ and C₁₀ Revised API-rr (104) and Kobayashi et al. (10), vapor pressure data were used. For iso-butane, iso-pentane, 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane, ESDU data were used. For the rest of the selected pure components for paraffin hydrocarbons including n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, and 2,2-dimethylbutane, Revised API-44 and extrapolated data up to the critical point of the component were used in order to test the capability of the modified Heyen equation of state from the triple point to the critical point. The deviations between the predicted and experimental vapor pressures for the pure components are presented in Table I.

ESDU (103), API-44 (104), or IUPAC (106) vapor pressure data were used for olefins based on the availability of the data. The results are given in Table II. In order to check the accuracy of the predicted

TABLE I
PURE COMPONENT DEVIATION IN VAPOR PRESSURE
PREDICTIONS FOR PARAFFINE HYDROCARBONS

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRESS	ABS. AVG. ERROR IN VAP. PRESS	NO. OF POINTS
NAME	REFERENCE					
Methane	103	-297.4 → -117.4 (0.473 → 0.998)	1.56 → 655.429 (0.00234 → 0.982)	-0.03	0.07	21
Ethane	102 103	-291.01 → 89.33 (0.307 → 1.00)	0.0004 → 701.447 (0.0000006 → 0.9913)	-0.05	0.84	48
Propane	102 103	-270.4 → 179.33 (0.4118 → 0.960)	0.000016 → 517.234 (0.0000000259 → 0.839)	0.11	1.61	50
iso-Butane	103	-162.670 → 269.33 (0.404 → 0.993)	0.023 → 502.672 (0.0000435 → 0.95)	0.02	1.19	49
n-Butane	102 103	-211.76 → 305.33 (0.324 → 1.0)	0.00016 → 549.215 (0.0000003 → 0.997)	-0.14	1.17	58
iso-Pentane	103	-108.67 → 368.33 (351.0 → 0.999)	0.032 → 487.545 (0.000065 → 0.994)	-0.01	0.2	54
n-Pentane	102 103	-188.75 → 377.30 (0.320 → 0.990)	0.00004 → 455.318 (0.0000000818 → 0.9315)	0.19	1.38	60
n-Hexane	102 103	-119.18 → 449.33 (0.372 → 0.994)	0.001 → 421.829 (0.0000023 → 0.9592)	0.02	0.57	64
n-Heptane	102 103	-126.13 → 512.3 0.343 → 1.0	0.00004 → 396.157 (0.0000001 → 0.9984)	0.07	1.55	68

TABLE I (Continued)

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRESS	ABS. AVG. ERROR IN VAP. PRESS	NO. OF POINTS
NAME	REFERENCE					
n-Octane	102 103	-69.79 → 557.33 (0.3808 → 0.9931)	0.00035 → 342.159 (0.000001 → 0.0947)	0.05	1.39	69
n-Nonane	102 104	-56.92 → 353.210 (0.376 → 0.760)	0.00012 → 29.005 (0.0000004 → 0.0874)	0.04	1.25	32
n-Decane	102 104	-7.31 → 397.180 (0.407 → 0.77)	0.0005 → 29.005 (0.0000016 → 0.0951)	0.15	1.95	32
n-Undecane	104 105	167.18 → 653.0 (0.545 → 0.968)	0.193 → 223.82 (0.000677 → 0.7855)	-0.00	0.79	37
n-Dodecane	104 105	196.65 → 690.0 (0.554 → 0.970)	0.193 → 199.526 (0.00073 → 0.756)	0.02	0.79	37
n-Tridecane	104 105	224.96 → 756.4 (0.563 → 1.0)	0.193 → 250.0 (0.00077 → 1.0)	0.10	0.95	36
n-Tetradecane	104 105	251.240 → 748.0 (0.571 → 0.970)	0.193 → 158.48 (0.00082 → 0.574)	-0.17	1.15	36
n-Pentadecane	104 105	276.44 → 765.00 (0.579 → 0.963)	0.193 → 158.0 (0.000877 → 0.718)	0.14	1.70	35
n-Hexadecane	104 105	300.52 → 802.0 (0.5860 → 0.973)	0.193 → 158.48 (0.000937 → 0.769)	0.16	2.12	34

TABLE I (Continued)

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRESS	ABS. AVG. ERROR IN VAP. PRESS	NO. OF POINTS
NAME	REFERENCE					
n-Heptadecane	104	321.620 → 830.0 (0.2436 → 0.6287)	0.193 → 158.480 (0.00101 → 0.8297)	0.17	0.91	36
	105					
2-Methylpentane	103	-0.570 → 431.330 (0.5119 → 0.481)	0.479 → 420.740 (0.0011 → 0.955)	-0.01	0.21	49
3-Methylpentane	103	-54.67 → 440.33 (0.446 → 0.9912)	0.052 → 425.367 (0.0001148 → 0.939)	0.00	0.10	56
2,2 Dimethyl - butane	104	-42.7 → 152.93 (0.4454 → 0.5911)	0.193 → 29.005 (0.000432 → 0.0549)	0.00	0.11	26
2,3 Dimethyl - butane	103	-72.67 → 440.33 (0.4297 → 0.9994)	0.033 → 453.33 (0.0000725 → 0.995)	0.01	0.14	57

TABLE II
 PURE COMPONENT DEVIATION IN VAPOR PRESSURE
 PREDICTIONS FOR UNSATURATED HYDROCARBONS

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRES.	ABS. AVG. ERROR IN VAP. PRES.	NO. OF POINTS
NAME	REFERENCE					
Ethylene	103	-251.670 → 44.330 (0.390 → 0.991)	0.048 → 692.395 (0.0000655 → 0.945)	0.03	0.23	34
Propylene	106	-301.458 → 188.33 (0.241 → 0.9857)	0.0000001384 → 512.089 (0.00000021 → 0.917)	0.05	2.03	59
1-Butene	103	-144.570 → 287.33 (0.417 → 0.989)	0.040 → 541.557 (0.0000586 → 0.928)	0.00	0.20	44
cis-2-Butene	103	-135.57 → 323.33 (0.413 → 0.999)	0.031 → 503.241 (0.000051 → 0.991)	-0.01	0.19	52
trans-2-Butene	103	-135.670 → 305.33 (0.420 → 0.992)	0.042 → 546.096 (0.0000727 → 0.945)	0.00	0.15	50
iso-Butene	103	-153.670 → 287.33 (0.407 → 0.993)	0.025 → 553.507 (0.0000448 → 0.955)	-0.01	0.18	50
1,3-Butadiene	104	-115.0 → 50.0 (0.451 → 0.679)	0.156 → 30.10 (0.000264 → 0.0479)	0.00	0.13	36
1-Pentene	103	-99.67 → 368.30 (0.430 → 0.990)	0.043 → 475.840 (0.0000841 → 0.9322)	0.01	0.18	52
cis-2-Pentene	103	-99.57 → 395.33 (0.421 → 1.0)	0.025 → 532.782 (0.0000468 → 1.0)	0.52	0.52	56

TABLE II (Continued)

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRES.	ABS. AVG. ERROR IN VAP. PRES.	NO. OF POINTS
NAME	REFERENCE					
trans-2-Pentene	103	-108.57 → 386.33 (0.414 → 0.999)	0.015 → 502.975 (0.0000315 → 0.985)	0.01	0.58	55
2-Methyl-1-Butene	103	-99.57 → 385.3 (0.425 → 1.0)	0.038 → 558.294 (0.0000584 → 1.0)	0.01	0.17	55
3-Methyl-1-Butene	103	-117.67 → 350.330 (0.419 → 0.993)	0.034 → 492.04 (0.000055 → 0.955)	0.01	0.07	53
2-Methyl-1-Butene	103	-90.57 → 404.33 (0.425 → 0.998)	0.037 → 559.149 (0.0000552 → 0.985)	0.04	0.19	56
1-Hexane	103	-53.0 → 440.0 (0.437 → 0.992)	0.032 → 426.730 (0.000071 → 0.945)	0.02	0.08	57
1-Heptene	104	20.0 → 245.0 (0.495 → 0.729)	0.186 → 28.92 (0.00045 → 0.071)	-0.00	0.14	46
Propadiene	104	-145.0 → 0.0 (0.445 → 0.65)	0.210 → 25.9 (0.00026 → 0.034)	0.15	1.81	31
1,2 Butadiene	104	-90.0 → 90.0 (0.453 → 0.588)	0.210 → 30.90 (0.00032 → 0.0474)	0.00	0.28	38

vapor pressure values using the modified Heyen equation of state for cyclo-paraffin and aromatic hydrocarbons, pure component vapor pressure data from API-44 (104), ESDU (103) and Canjar and Manning (107) were used. The percent average and absolute average deviations are given in Tables III and IV, respectively.

The procedure was also tested for its ability to predict vapor pressures for a number of non-hydrocarbons, including N_2 , CO , CO_2 , O_2 , H_2S , and SO_2 . The results are given in Table V.

Besides the above numerical comparison, a graphical presentation of experimental and predicted vapor pressure for a number of selected pure components are presented in Figures 3 and 4.

The values of the fitted parameters n , m , $k/2$, θ , $Z_{c,cal}$, and R in Equations (3-17), (3-18), (3-9) and (3-38) which yield the lowest percent absolute average deviations for vapor pressure are presented in Tables VI through X.

The pure component vapor pressure values predicted by the modified Heyen equation of state were compared to the values obtained from the original Heyen Equation of state in order to evaluate the accuracy of the new model. The evaluation is based on 53 pure components including normal and branched paraffins and olefins, cyclic and aromatic hydrocarbons, and inorganic compounds. Percent errors in the calculated vapor pressure and the range of experimental temperature and pressure used for the 53 pure components are presented in Tables XI through XV.

Since the average errors and/or average absolute errors do not provide information on the distribution of errors, the error distributions for methane which are typical of those obtained for all components, for both original and modified Heyen EOS, are presented in Figure 5.

TABLE III
 PURE COMPONENT DEVIATION IN VAPOR PRESSURE
 PREDICTIONS FOR CYCLOPARAFFIN
 HYDROCARBONS

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRES.	ABS. AVG. ERROR IN VAP. PRES.	NO OF POINTS
NAME	REFERENCES					
Cyclopentane	104	-40.0 → 165.0 (0.456 → 0.5782)	0.2 → 30.90 (0.00031 → 0.047)	0.00	0.16	42
Methylcyclopentane	104	-10.0 → 205.0 (0.455 → 0.574)	0.20 → 29.30 (0.000364 → 0.053)	0.06	0.37	44
Cyclohexane	104	45.0 → 225.0 (0.507 → 0.587)	0.796 → 30.5 (0.00135 → 0.052)	0.00	0.06	37
Methyl-cyclohexane	104	25.00 → 265.0 (0.471 → 0.704)	0.185 → 30.7 (0.0003674 → 0.061)	0.00	0.22	49
Ethyl-cyclopentane	104	31.838 → 264.740 (0.480 → 0.707)	0.193 → 29.005 (0.00092 → 0.0589)	0.0	0.10	27
Ethyl-cyclohexane	104	59.08 → 319.10 (0.482 → 0.710)	0.193 → 29.005 (0.000438 → 0.066)	0.0	0.09	27

TABLE IV
 PURE COMPONENT DEVIATION IN VAPOR PRESSURE
 PREDICTIONS FOR AROMATIC HYDROCARBONS

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRES.	ABS. AVG. IN VAPOR PRES.	NO. OF POINTS
NAME	REFERENCE					
Benzene	107	700.0 → 540.0 (0.553 → 0.988)	3.22 → 654.0 (0.0045 → 0.921)	0.02	0.24	46
Toluene	103	62.330 → 602.33 (0.490 → 0.997)	0.357 → 582 (0.0006 → 0.977)	-0.01	0.25	61
o-Xylene	103	35.33 → 665.330 (0.436 → 0.9915)	0.029 → 508.314 (0.0000535 → 0.9385)	-0.02	0.31	70
m-Xylene	103	17.33 → 647.0 (0.429 → 0.996)	0.017 → 500.0 (0.0000331 → 0.975)	0.03	0.98	70
p-Xylene	103	62.33 → 547.33 (0.471 → 0.998)	0.105 → 501.685 (0.00021 → 0.985)	-0.00	0.31	65
Ethylbenzene	104	91.576 → 325.254 (0.496 → 0.707)	0.29 → 29.008 (0.000554 → 0.055)	0.01	0.07	27

TABLE V
 PURE COMPONENT DEVIATION IN VAPOR PRESSURE
 PREDICTIONS FOR NON-HYDROCARBONS

COMPONENT		TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	AVG. ERROR IN VAP. PRES.	ABS. AVG. IN VAP. PRES.	NO. OF POINTS
NAME	REFERENCES					
N ₂	112 113	-345.945 → 235.56 (0.5004 → 0.985)	1.823 → 454.350 (0.00368 → 0.9187)	0.09	0.12	20
O ₂	107	-351.67 → 185.0 (0.388 → 0.987)	0.105 → 677.0 (0.000435 → 0.225)	0.02	0.15	31
CO	107	-337.010 → 225.0 (0.513 → 0.981)	2.225 → 445.10 (0.003 → 0.608)	-0.09	0.30	24
CO ₂	110	-69.83 → 80.33 (0.712 → 0.986)	75.13 → 973.132 (0.0702 → 0.910)	0.05	0.10	21
H ₂ S	108	-76.4 → 190.0 (0.570 → 0.966)	14.697 → 1077.16 (0.0112 → 0.824)	0.96	1.67	27
SO ₂	107	0.00 → 309.0 (0.592 → 0.991)	10.26 → 1078.0 (0.0090 → 0.943)	0.02	0.12	35

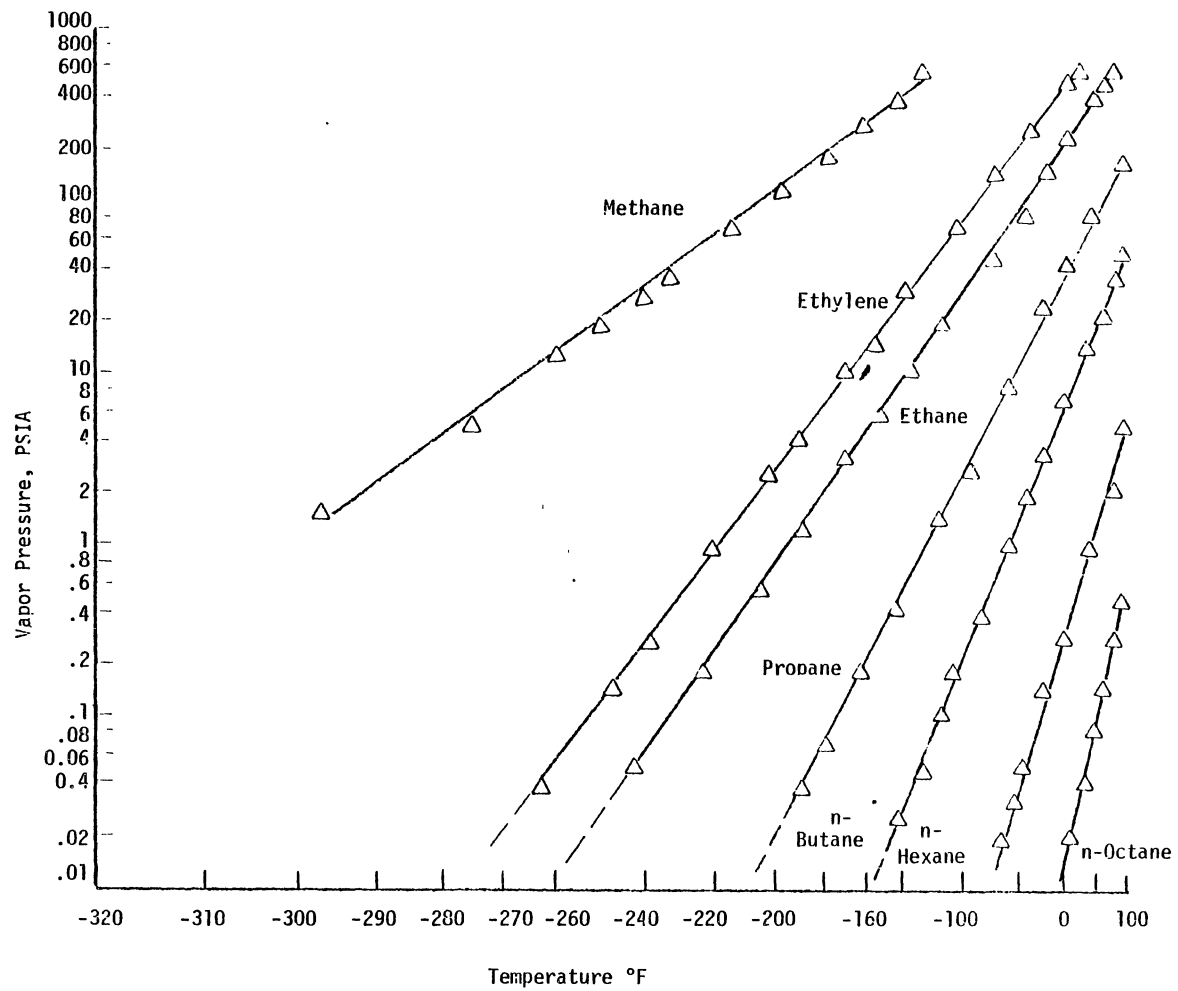


Figure 3. Comparison of Predicted and Experimental Vapor Pressure Data for Selected Hydrocarbons

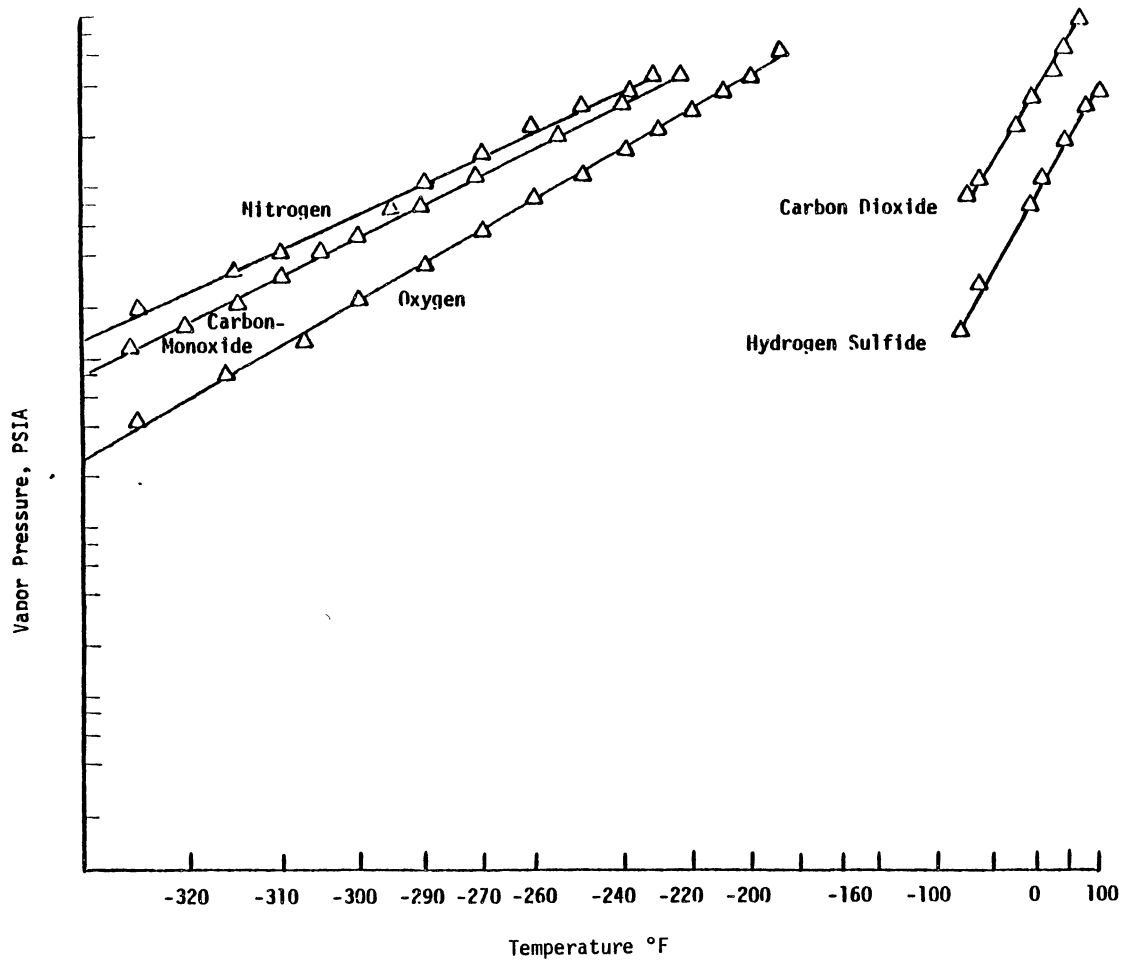


Figure 4. Comparison of Predicted and Experimental Vapor Pressure Data for Selected Hydrocarbons

TABLE VI
 PURE COMPONENT PARAMETERS IN VAPOR PRESSURE
 PREDICTIONS FOR PARAFFIN HYDROCARBONS

COMPONENT	PARAMETERS						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
Methane	1.224	0.2585	0.3043	4.9796	0.8603	0.2895	343.08	667.800
Ethane	0.6985	0.0576	0.3291	7.0059	0.2608	0.2698	548.756	707.596
Propane	1.6981	0.6470	0.4098	6.5201	0.9143	0.2698	665.676	616.4116
Iso-Butane	1.3070	0.8395	0.5677	4.8487	0.8646	0.2782	734.63	529.100
n-Butane	1.1042	0.1923	0.2871	7.3591	0.4922	0.2772	765.324	550.811
Iso-Pentane	1.3751	0.1360	0.3065	10.3707	0.3190	0.2697	828.7	490.40
n-Pentane	0.3136	0.0074	0.7712	35.4418	0.00000375	0.2546	845.532	488.778
n-Hexane	0.8587	0.2528	0.5244	6.9629	0.5853	0.2565	914.22	439.784
n-Heptane	0.8138	0.1590	0.5131	9.0885	0.4091	0.2508	972.18	396.78
n-Octane	0.5350	0.1234	0.7286	8.4374	0.3676	0.2470	1023.858	360.8695
n-Nonane	2.0170	0.9006	0.5158	8.4224	0.8136	0.2451	1070.208	331.835

TABLE VI (Continued)

COMPONENT	PARAMETERS						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
n-Decane	0.5690	0.1516	0.7466	10.0589	0.3393	0.2324	1111.5	305.1
n-Undecane	1.8282	0.3632	0.4030	15.9910	0.5228	0.2347	1149.71	285.0
n-Dodecane	1.3692	0.3412	0.4877	9.7284	0.3559	0.2336	1184.8	264.0
n-Tridecane	1.7407	0.3499	0.4037	17.0169	0.1476	0.2185	1216.398	250.0
n-Tetradecane	1.9169	0.4443	0.4235	14.6716	0.2208	0.2185	1245.20	235.0
n-Pentadecane	2.2446	0.4760	0.4445	16.6474	0.4410	0.2349	1272.2	220.0
n-Hexadecane	2.2597	0.5614	0.4434	17.3481	0.3166	0.2194	1297.100	206.0
n-Heptadecane	1.6403	0.3238	0.4786	13.7488	0.1048	0.2248	1320.1	191.0
2-MT-C ₅	1.6512	0.2576	0.3456	9.7644	0.5403	0.2681	896.58	440.1613
3-MT-C ₅	1.5680	0.2544	0.3591	9.1378	0.6317	0.2707	907.92	453.07
2,2 DMTC ₄	1.2789	0.2761	0.3790	9.8743	0.4754	0.2746	897.71	446.80
2,3 DMTC ₄	1.5898	0.2599	0.3363	9.1660	0.5674	0.2665	900.54	455.448

TABLE VII

PURE COMPONENT PARAMETERS IN VAPOR PRESSURE
PREDICTIONS FOR UNSATURATED HYDROCARBONS

COMPONENT	PARAMETER						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
Ethylene	1.1568	0.2260	0.3193	6.6470	0.5916	0.2780	508.59	732.44
Propylene	1.1849	0.2228	0.3368	6.4897	0.4767	0.2740	656.73	667.32
1-Butene	1.1778	0.1959	0.3627	7.5158	0.4979	0.2748	755.23	583.47
cis-2-Butene	1.9120	0.2424	0.2879	10.3989	0.4246	0.2740	784.04	608.695
trans-2-Butene	1.5374	0.2066	0.3626	9.7776	0.5490	0.2676	771.53	577.95
iso-Butene	1.8964	0.2345	0.2831	10.4731	0.5275	0.2735	752.22	579.85
1,3 Butadiene	1.3620	0.2221	0.3336	7.0906	0.4850	0.2726	765.0	628.
1-Pentene	1.9457	0.2512	0.2965	10.9499	0.4898	0.2708	836.604	511.52
cis-2-Pentene	1.2513	0.3267	0.4256	7.1417	0.7120	0.2662	855.00	533.74
trans-2-Pentene	1.2219	0.0935	0.2978	13.7728	0.0747	0.2560	847.8	510.53
2MT-1-Butene	1.9186	0.2582	0.2872	10.7381	0.4629	0.2625	846.0	558.25

TABLE VII (Continued)

COMPONENT	PARAMETER						T_c °R	P_c PSIA
	n	m	n/2	θ	R	Z_c		
3-MT-1-Butene	1.4162	0.1949	0.3432	8.4745	0.5822	0.2812	815.41	514.74
2-MT-2-Butene	1.3822	0.2593	0.3570	8.3300	0.6312	0.2621	865.8	567.389
1-Hexene	1.3222	0.2288	0.3768	8.9895	0.5189	0.2634	907.00	451.82
1-Heptene	1.4042	0.2971	0.4084	8.6708	0.5852	0.2591	967.122	410.458
Propadiene	4.4649	3.9651	0.6928	5.5712	0.000000508	0.2947	707.4	793.58
1,2 Butadiene	1.5836	0.1195	0.2875	10.5217	0.7017	0.2744	798.659	652.5

TABLE VIII
 PURE COMPONENT PARAMETERS IN VAPOR PRESSURE
 PREDICTIONS FOR CYCLOPARAFFIN
 HYDROCARBONS

COMPONENT	PARAMETER						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
Cyclopentane	1.8435	0.2275	0.2860	9.9431	0.4304	0.2747	921.0	653.8
Methylcyclopentane	1.8218	0.2567	0.2898	52.0767	0.1408	0.2788	996.2	591.6
Cyclohexane	1.4345	0.2427	0.3571	8.3189	0.5308	0.2772	985.91	548.9
Methyl-cyclohexane	1.7436	0.2589	0.3449	8.9382	0.5549	0.2834	1029.82	503.50
Ethylbenzene	1.9661	0.2480	0.3084	13.5814	0.3749	0.2625	1110.96	523.0
Ethyl-cyclopentane	1.9446	0.2448	0.3055	12.0152	0.4025	0.2679	1025.0	492.8
Ethyl-cyclohexane	1.6852	0.2599	0.3305	13.9320	0.3654	0.2654	1097.0	441.0

TABLE IX
 PURE COMPONENT PARAMETERS IN VAPOR PRESSURE
 PREDICTIONS FOR AROMATIC HYDROCARBONS

COMPONENT	PARAMETERS						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
Benzen	1.8626	0.2319	0.2783	10.3994	0.1321	0.2668	1011.89	710.4
Toluene	1.9016	0.2376	0.3017	11.0561	0.3671	0.2677	1065.254	595.5
o-Xylene	1.9695	0.2532	0.311	11.6789	0.3752	0.2623	1134.59	541.60
m-Xylene	1.9496	0.2615	0.3069	11.5919	0.2022	0.2554	1110.69	512.9
p-Xylene	1.9666	0.2605	0.3119	11.6136	0.3871	0.2592	1109.21	509.2

TABLE X

PURE COMPONENT PARAMETERS IN VAPOR PRESSURE
PREDICTION FOR NON-HYDROCARBONS

COMPONENT	PARAMETERS						T _c °R	P _c PSIA
	n	m	n/2	θ	R	Z _c		
N ₂	1.2990	0.1649	0.2670	6.8389	0.7165	0.2938	227.268	494.58
O ₂	1.6166	0.2393	0.2455	6.9901	0.8195	0.2888	278.28	731.861
CO	1.6501	0.2820	0.2778	7.3040	0.7503	0.2886	239.22	507.012
CO ₂	1.3741	0.2697	0.3857	8.0646	0.7387	0.2761	547.4286	1069.699
H ₂ S	1.7281	0.2241	0.2778	7.9463	0.3889	0.2908	672.37	1306.8
SO ₂	1.5342	0.2831	0.3526	9.0999	1.0290	0.2620	775.44	1143.349

TABLE XI
 ERRORS IN PURE COMPONENT VAPOR
 PRESSURES--PARAFFIN
 HYDROCARBONS

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				% ERRORS IN CALCULATED VAPOR PRES.				No. of Points
		PRESSURE		TEMPERATURE T_r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave. Abs.	Ave.	Ave. Abs.	
Methane	103	1.56	655.6	0.473	0.998	-0.01	0.05	1.29	1.32	21
Ethane	102 103	0.0004	701.5	0.307	1.00	-0.05	0.84	0.35	4.56	48
Propane	102 103	0.000016	517.234	0.4118	0.960	0.11	1.61	1.26	5.90	50
iso-Butane	103	0.023	502.672	0.404	0.993	0.02	0.19	13.34	15.42	49
n-Butane	102 103	0.00016	549.215	0.324	1.00	-0.14	1.17	2.24	5.66	58
iso-Pentane	103	0.032	487.55	0.424	1.00	-0.0	0.19	16.78	16.80	54
n-Pentane	102 103	0.00004	455.32	0.320	0.990	0.19	1.38	-1.57	8.59	60
n-Hexane	102 103	0.001	421.829	0.372	0.994	0.02	0.57	-4.68	7.43	64
n-Heptane	102 103	0.00004	396.2	0.343	1.00	0.08	0.74	2.07	7.51	68

TABLE XI (Continued)

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				% ERRORS IN CALCULATED VAPOR PRES.				NO. of Points
		PRESSURE		TEMPERATURE T_r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave. Abs.	Ave.	Ave. Abs.	
n-Octane	102 103	0.00035	342.16	0.381	0.993	0.05	1.39	3.93	8.10	69
n-Nonane	102 104	0.00012	29.005	0.376	0.760	0.00	0.13	7.64	14.64	27
n-Decane	102 104	0.0005	29.005	0.407	0.77	0.00	0.09	8.14	15.24	32
n-Undecane	104 105	0.193	223.83	0.545	0.968	0.00	0.79	-0.12	1.43	37
n-Dodecane	104 105	0.193	199.526	0.554	0.970	0.02	0.79	-0.23	1.83	37
n-Tridecane	104 105	0.193	250.0	0.563	1.00	0.10	0.95	0.06	2.06	36
n-Tetradecane	104 105	0.193	158.48	0.571	0.970	-0.17	1.15	-0.61	2.62	36
n-Pentadecane	104 105	0.193	158.0	0.579	0.963	0.14	1.70	-6.61	8.74	27+8
n-Hexadecane	104 105	0.193	158.48	0.586	0.973	0.16	2.12	-13.26	13.72	27+7
n-Heptadecane	104 105	0.193	158.48	0.2436	0.6287	0.17	0.91	-10.08	11.05	37+9
2-Methylpentane	103	0.479	420.74	-0.520	0.994	-0.01	0.21	15.91	16.43	49
3-Methylpentane	103	0.052	425.34	0.446	0.9912	0.0	0.10	13.65	15.06	56
2,3-Dimethyl- butane	103	0.033	453.33	0.430	1.00	0.01	0.14	14.55	14.62	57

TABLE XII
 ERRORS IN CALCULATED PURE COMPONENT
 VAPOR PRESSURES--UNSATURATED
 HYDROCARBONS

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				% ERRORS IN CALCULATED VAPOR PRES.				NO. of Points
		PRESSURE		TEMPERATURE T_r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave. Abs.	Ave.	Ave. Abs.	
Ethylene	-	-	-	-	-	-	-	-	-	-
Propylene	106	0.009	612.089	0.241	0.987	0.05	2.03	14.86	14.96	59
1-Butene	-	-	-	-	-	-	-	-	-	-
cis-2-Butene	103	0.031	603.24	0.413	0.999	-0.01	0.19	15.89	16.23	52
trans-2-Butene	103	0.042	546.096	0.42	0.945	0.00	0.16	14.94	15.27	50
iso-Butene	103	0.026	553.5	0.407	0.993	-0.01	0.18	15.88	15.93	50
1,3 - Butadiene	104	0.166	30.1	0.451	0.679	0.00	0.13	11.70	12.01	36
1-Pentene	103	0.043	476.84	0.430	0.990	0.01	0.18	15.23	15.61	52
cis-2-Pentene	103	0.025	532.78	0.421	1.00	0.52	0.52	16.95	16.95	56
trans-2-Pentene	103	0.016	502.98	0.414	0.999	0.01	0.68	16.26	16.41	55
2-Methyl-1-Butene	103	0.038	558.294	0.426	1.0	0.01	0.17	14.32	14.23	55

TABLE XII (Continued)

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				% ERRORS IN CALCULATED VAPOR PRES.				No. of Points
		PRESSURE		TEMPERATURE T_r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave. Abs.	Ave.	Ave. Abs.	
3-Methyl-1-Butene	103	0.034	492.04	0.419	0.993	0.01	0.07	13.76	14.17	54
2-Methyl-2-Butene	103	0.037	559.149	0.425	0.998	0.04	0.19	14.38	14.39	56
1-Hexane	103	0.032	426.730	0.437	0.992	0.02	0.08	16.54	16.54	58
1-Heptene	103	0.186	28.92	0.496	0.729	-0.00	0.14	16.22	16.22	46
Propadiene	104	0.210	26.9	0.445	0.65	0.15	1.81	18.17	18.17	31
1,2 Butadiene	104	0.210	30.9	0.463	0.688	0.00	0.28	8.36	8.46	38

TABLE XIII
 ERRORS IN CALCULATED PURE COMPONENT VAPOR
 PRESSURES--CYCLOPARAFFIN
 HYDROCARBONS

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				% ERROR IN CALCULATED VAPOR PRES.				NO. of Points
		PRESSURE PSIA		TEMPERATURE T _r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave.Abs	Ave.	Ave.Abs.	
Cyclopentane	104	0.200	30.9	0.456	0.678	0.00	0.16	12.03	12.44	42
Methylcyclopentane	104	0.200	29.9	0.456	0.674	0.06	0.37	16.45	16.45	44
Cyclohexane	104	0.796	30.6	0.507	0.687	0.00	0.06	7.65	8.22	37
Methylcyclohexane	104	0.185	30.7	0.471	0.704	0.00	0.22	12.60	13.03	49

TABLE XIV
 ERROR IN CALCULATED PURE COMPONENT VAPOR
 PRESSURES--AROMATIC
 HYDROCARBONS

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				ERRORS IN CALCULATED VAPOR PRESSURE				NO. of Points
		PRESSURE PSIA		TEMPERATURE T _r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave.Abs.	Ave.	Ave. Abs.	
Benzene	107	3.22	654.0	0.553	0.988	0.02	0.24	-2.31	2.71	46
Tolvene	103	0.357	582.0	0.490	0.997	-0.01	0.25	4.24	5.21	61
Ortho-Xylene	103	0.029	508.314	0.436	0.9915	-0.02	0.31	15.23	15.82	70
Meta-Xylene	103	0.017	500.00	0.429	0.996	0.03	0.98	15.36	16.33	70
Para-Xylene	103	0.105	501.685	0.471	0.998	-0.00	0.31	8.20	9.20	66

TABLE XV
 ERRORS IN CALCULATED PURE COMPONENT VAPOR
 PRESSURES--NON-HYDROCARBONS

COMPONENT	REF.	RANGE OF EXPERIMENTAL DATA				ERRORS IN CALCULATED VAPOR PRESSURE				NO. of Points
		PRESSURE PSIA		TEMPERATURE T_r		THIS WORK		HEYEN		
		Min.	Max.	Min.	Max.	Ave.	Ave.Abs.	Ave.	Ave.Abs.	
Nitrogen	112 113	1.823	454.350	0.5004	0.985	0.09	0.12	0.26	0.73	20
Oxygen	107	0.105	677.0	0.388	0.987	0.02	0.15	4.18	4.27	31
Carbon Monoxide	107	2.226	445.1	0.514	0.981	-0.09	0.30	0.0	1.84	24
Carbon Dioxide	110	15.14	973.14	0.712	0.986	0.05	0.10	-0.44	0.64	28
Hydrogen Sulfide	108	14.697	1077.16	0.570	0.966	0.96	1.67	-0.57	1.11	27
Sulfur Dioxide	107	10.26	1078.0	0.592	0.991	0.02	0.12	-1.23	1.23	35

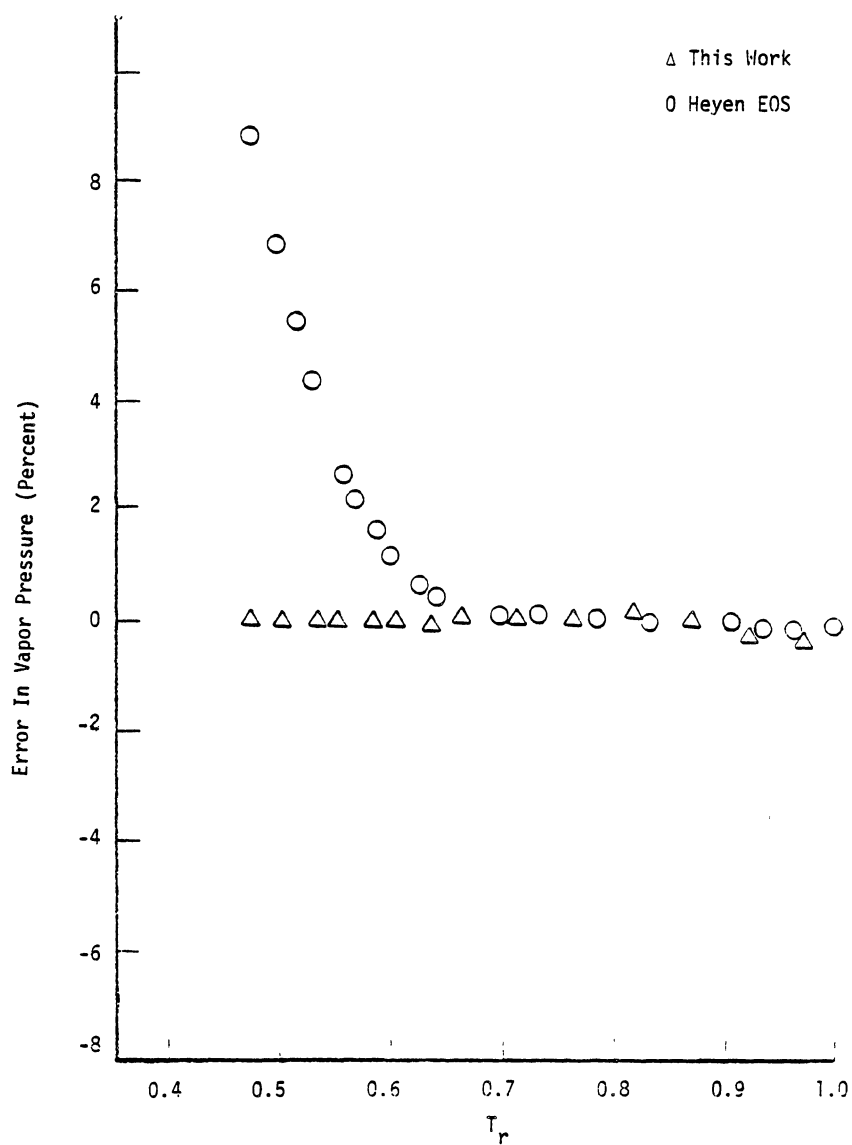


Figure 5. Comparison of Vapor Pressure Error Distribution of Methane for This Work and Heyen EOS

Error distributions for ethane, propane, butane, ethylene, hydrogen sulfide, carbon monoxide, and sulfur dioxide are presented numerically in Tables XVI through XXII.

Vapor Liquid Equilibrium of Binary Mixtures (K-Values Prediction)

The best parameters obtained were used for a selected number of binary mixtures to predict the equilibrium ratios (K-values) which play a very important role in practical engineering design. Selected binary mixtures are divided into four systems: (1) Methane Systems, (2) Ethane Systems, (3) C_3^+ Systems, and (4) Benzene Systems. The C_3^+ systems include binary systems of propane, butane, hexane, heptane and octane. The components of each mixture, temperature and pressure ranges, number of points evaluated, absolute average percent and average percent deviations in predicted equilibrium ratios, liquid/feed ratios, and the references for each mixture are presented in Tables XXIII through XXVI. The calculated K-value error distributions, and calculated K-values are compared with the predicted values from the modified Heyen, SRK and PFGC equations of state. Results are tabulated in Tables XXVII through XXXII and Table XXXIII respectively.

TABLE XVI
 VAPOR PRESSURE ERROR DISTRIBUTION
 FOR ETHANE

TEMPERATURE °F	T_r	P_{exp} , PSIA	P_{cal} , PSIA	% AVE. ERROR	POINT NO.
80.33	0.98	631.62	638.90	-1.15	1
44.33	0.92	406.77	409.33	-0.63	5
-0.67	0.835	217.40	217.00	0.18	10
-45.67	0.75	101.77	101.42	0.35	15
-90.67	0.67	39.29	39.37	-0.21	20
-135.67	0.59	11.43	11.98	-0.47	25
-180.67	0.51	2.14	2.14	0.42	30
-225.67	0.43	0.188	0.186	1.40	35
-269.59	0.35	0.0048	0.0052	-1.99	40
-295.26	0.299	0.0002	0.0002	-1.87	45

TABLE XVII
 VAPOR PRESSURE ERROR DISTRIBUTION
 FOR PROPANE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO.
197.33	0.99	565.99	564.84	0.20	1
161.33	0.93	390.09	388.23	0.48	5
116.33	0.87	232.05	231.82	0.10	10
71.33	0.80	127.16	127.65	-0.39	15
26.33	0.73	62.29	62.75	-0.75	20
-18.65	0.66	26.12	26.39	-1.01	25
-72.67	0.58	6.83	6.84	-0.14	30
-117.67	0.51	1.53	1.52	1.19	35
-162.67	0.45	0.201	0.198	1.49	90
-189.67	0.41	0.0410	0.040	1.27	45
-270.4	0.28	0.0002	0.00023	-14.30	48

TABLE XVIII
 VAPOR PRESSURE ERROR DISTRIBUTION
 FOR n-BUTANE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO
305.33	1.00	549.33	549.33	0.0	1
287.33	0.98	466.5	467.50	-0.21	5
251.33	0.93	331.75	333.39	-0.50	10
209.33	0.87	208.19	209.66	-0.71	15
161.33	0.81	122.65	123.74	-0.89	20
116.33	0.75	66.31	67.06	-1.13	25
71.33	0.70	32.00	32.48	-1.50	30
26.33	0.64	13.27	13.50	-1.63	35
-18.67	0.58	4.48	4.52	-1.07	40
-63.67	0.52	1.13	1.13	0.07	45
-108.67	0.46	0.186	0.184	1.16	50
-144.67	0.41	0.0027	0.0026	4.67	55
-209.6	0.33	0.0002	0.00019	2.27	60

TABLE XIX
VAPOR PRESSURE ERROR DISTRIBUTION
FOR ETHYLENE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO.
44.33	0.99	692.40	692.32	0.01	1
8.33	0.90	435.27	434.42	0.2	5
-36.67	0.83	222.72	222.20	0.23	10
-63.67	0.78	138.93	138.75	0.13	15
-81.67	0.74	97.12	66.23	-0.16	20
-135.67	0.64	26.34	26.49	-0.41	25
-153.67	0.60	15.24	15.30	-0.36	30
-198.67	0.51	2.655	2.652	0.11	35
-261.67	0.39	0.048	0.0482	-0.43	40

TABLE XX
VAPOR PRESSURE ERROR DISTRIBUTION
FOR HYDROGEN SULFIDE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO.
-76.4	0.57	14.695	14.228	3.18	1
-60.0	0.59	22.043	22.293	-1.13	2
-40.0	0.62	36.74	36.475	0.72	4
0.0	0.68	82.293	84.148	-2.25	8
40.0	0.74	167.525	167.14	0.23	12
80.0	0.80	305.66	299.74	1.94	16
120.0	0/86	509.92	496.58	2.62	20
160.0	0.92	796.48	774.379	2.77	24
190.0	0.97	1077.16	1049.81	2.54	27

TABLE XXI
VAPOR PRESSURE ERROR DISTRIBUTION
FOR CARBON MONOXIDE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO.
-337.01	0.5	2.226	2.35	-0.40	1
-335.0	0.52	2.716	2.695	0.76	2
-325.0	0.56	6.245	6.241	0.06	4
-305.0	0.65	23.34	23.410	-0.30	8
-285.0	0.73	63.26	63.10	0.26	12
-265.0	0.81	137.70	137.98	-0.21	16
-245.0	0.9	262.0	261.60	0.15	20
-225.0	0.98	445.1	445.489	-1.44	24

TABLE XXII
VAPOR PRESSURE ERROR DISTRIBUTION
FOR SULFUR DIOXIDE

TEMPERATURE °F	T_r	P_{exp}	P_{cal}	% AVE. ERROR	POINT NO.
0.0	0.59	10.26	10.27	0.12	1
40.0	0.64	26.60	26.63	-0.12	5
90.0	0.71	71.00	70.76	0.33	10
140.0	0.77	157.7	157.66	0.02	15
200.0	0.85	347.00	347.38	-0.11	20
250.0	0.92	604.0	603.92	0.01	30
295.0	0.97	940.0	940.95	-0.10	35
309.0	0.99	1078.00	1073.40	0.42	40

TABLE XXIII

C₁ BINARY SYSTEM DEVIATIONS IN K-VALUE
PREDICTIONS

SYSTEM NAME (REFERENCE)	TEMPERATURE RANGE °F		PRESSURE RANGE (PSIA)		% ERRORS						NO. of POINTS
					AVERAGE IN			ABSOLUTE AVERAGE IN			
					K _{1st}	K _{2nd}	L/F or BUBPT	K _{1st}	K _{2nd}	L/F or BUBPT	
CH ₄ (1)/C ₂ H ₆ (2) (119)	-240.0	50.0	17.88	1000.0	-2.54	-1.15	-4.64	3.62	5.75	14.75	195
CH ₄ (1)/C ₃ H ₈ (2) (120,121)	-254	190.0	13.00	1450.0	15.18	-8.63	-7.26	15.20	12.05	17.9	312
CH ₄ (1)/I-C ₄ H ₁₀ (2) (122)	100	220.0	80.0	1600.0	7.37	-10.16	6.22*	7.37	10.16	6.23	137
CH ₄ (1)/n-C ₄ H ₁₀ (2)(123,124)	-200.0	220.0	20.0	1850.0	5.21	4.7	-2.92	8.58	8.37	6.63	237
CH ₄ (1)/I-C ₅ H ₁₂ (2) (125)	160.	350.0	400.	1922.0	5.85*	-3.93*	-13.16*	6.81*	7.32*	17.97*	42
CH ₄ (1)/n-C ₅ H ₁₂ (2)(126,127)	-47.960	340.0	20.00	2250.0	6.02	6.31*	-7.24	11.81	11.91	12.72	179
CH ₄ (1)/n-C ₆ H ₁₄ (2)(138,129)	-116.770	302.0	19.9	2300.00	-2.87*	7.50	0.79	15.00*	12.32	5.76	124
CH ₄ (1)/n-C ₇ H ₁₆ (2) (130,131)	-110.00	460.00	100.00	300.00	-17.96	14.55	6.53	21.72	17.85	9.39	100

TABLE XXIII (Continued)

SYSTEM NAME (REFERENCE)	TEMPERATURE RANGE °F		PRESSURE RANGE (PSIA)		% ERRORS						No. of POINTS
					AVERAGE IN			ABSOLUTE AVERAGE IN			
					K _{1st}	K _{2nd}	L/F or BUBPT	K _{1st}	K _{2nd}	L/F or BUBPT	
CH ₄ (1)/n-C ₈ H ₁₈ (2) (132)	77.0	302.	146.96	1028.720	-26.55	3.33	2.04*	25.61	3.35	2.11	35
CH ₄ (1)/n-C ₉ H ₂₀ (2) (133)	-58.0	302.0	146.96	4114.88	9.43	-18.40	-5.90	7.00	21.28	6.85	30
CH ₄ (1)/n-C ₁₀ H ₂₂ (2)(134)	100.0	589.820	735.53	3000.00	-27.59	12.35	0.19**	27.59	12.35	2.08**	33
CH ₄ (1)/Benzene (2) (135,136)	150.0	442.400	100.0	4400.0	-6.53	6.79	-1.79	12.15	18.25	4.15	30
CH ₄ (1)/Tolvene (2) (136,137)	150.0	518	292.450	5200.00	0.70	10.90	0.14*	5.94	22.24	3.34	26

* Percent average and absolute average error in bubble point temperature.

TABLE XXIV
 C_2 BINARY SYSTEM DEVIATIONS IN
 K-VALUE PREDICTIONS

SYSTEMS REFERENCE	TEMPERATURE RANGE °F	PRESSURE RANGE (PSIA)	% ERRORS						NO. OF POINTS
			AVERAGE IN			ABSOLUTE AVERAGE IN			
			K_{1st}	K_{2nd}	L/F or BUBPT	K_{1st}	K_{2nd}	L/F or BUBPT	
$C_2H_6(1)/C_3H_8(2)$ (138)	10.0 → 160.	100. → 705.	2.80	-0.00	-1.3*	3.69	6.70	1.31	25
$C_2H_6(1)/I-C_4H_{10}$ (139)	100.60 → 249.	155.0 → 779.	13.37	-12.47	-1.37	13.37	12.48	16.51	33
$C_2H_6(1)/N-C_5H_{12}$ (2) (140)	40.0 → 340.0	50.0 → 900.0	1.96	-2.74	3.38	3.12	6.62	6.88	65
$C_2H_6(1)/N-C_6H_{14}$ (2) (141)	150.0 → 350.0	50.0 → 950.	2.56	-3.76	1.53	11.52	4.71	1.53	27
$C_2H_6(1)/N-C_7H_{16}$ (2) (142)	150.0 → 350.0	455.0 → 975.0	1.69	-29.06	7.71	3.05	29.06	7.71	18
$C_2H_6(1)/N-C_{10}H_{22}$ (2) (143)	50.0 → 460.	100.0 → 1000.0	-5.26	1.39	1.73	5.87	3.58	2.05	48
$C_2H_6(1)/C_2H_4(2)$ (144, 145)	-100.0 → 68.0	35.9 → 614.0	-1.62	3.05	-0.35	2.28	3.13	0.35	48

* Percent average and absolute average error in bubble point temperature.

TABLE XXV
 C_3^+ BINARY SYSTEM DEVIATIONS IN K-VALUE
PREDICTIONS

SYSTEMS NAME (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	% AVERAGE ERROR IN			% ABS AVERAGE ERROR IN			NO. OF PTS.
			K_{1st}	K_{2nd}	L/F or BUBPT	K_{1st}	K_{2nd}	L/F or BUBPT	
$C_3H_8(1)/I-C_5H_{12}(2)$ (146)	32.0 → 356.0	7.35 → 646.0	3.44	-4.87	-4.05	4.58	5.79	15.28	88
$C_3H_8(1)/n-C_5H_{12}(2)$ (147)	160.0 → 340.0	60.0 → 600.0	3.89	-4.13	0.51*	4.12	4.49	0.59*	56
$C_3H_8(1)/n-C_{10}H_{22}(2)$ (148)	100.0 → 460.0	50.0 → 1000.0	-16.10	5.37	0.47**	16.37	6.97	0.79*	50
$C_3H_8(1)/C_3H_6(2)$ (149, 150)	-20.0 → 190.	14.400 → 546.0	-0.55	1.02	-2.28* ^p	0.93	1.10	3.85* ^p	306
$n-C_4H_{10}/n-C_{10}H_{22}(2)$ (151)	340.0 → 460.	300.0 → 600.0	-3.76	-14.46	-13.37	4.65	14.69	13.68	27
$n-C_5H_{12}(1)/Cyclo-$ $hexane(2)$ (152)	102.2 → 170.96	14.7	8.74	-0.7	-7.04	8.74	4.20	15.40	26
$n-C_5(1)/MT-Cyc-C_5$ (2) (152)	97.0 → 158.72	14.7	0.96	3.70	-0.4*	1.97	5.01	0.40*	44
$n-C(1)/MT-Cyc-C_5(2)$ (152)	156.02 → 161.15	14.7	1.63	-1.12	0.06*	1.67	1.20	0.06*	29

TABLE XXV (Continued)

SYSTEMS NAME (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	% AVERAGE ERROR IN			% ABS AVERAGE ERROR IN			NO. OF PTS.
			K _{1st}	K _{2nd}	L/F or BUBPT	K _{1st}	K _{2nd}	L/F or BUBPT	
n-C ₆ (1)/MT-Cyc-C ₆ (2) (152)	158.99 → 212.00	14.7	2.03	0.09	-6.14	2.23	1.08	6.37	33
n-C ₇ (1)/Cyc-C ₆ (2) (152)	102.20 → 170.96	14.7	6.20	-9.65	-0.34*	6.32	6.81	0.34*	26
n-C ₇ (1)/MT-Cyc-C ₆ (2) (153)	209.516 → 213.134	14.7	-0.19	-1.17	0.06*	0.90	1.40	0.06	11
n-C ₈ (1)/2-MT-C ₅ (2) (154)	50.0 → 104.0	0.230 → 6.10	2.57	0.35	0.99	2.77	1.50	1.50	98
n-C ₈ (1)/3-MT-C ₅ (2) (154)	50.0 → 104.0	0.31 → 6.010	-13.54	11.55	-7.80*	13.57	11.55	7.80*	48
n-C ₈ (1)/ET-Benzene (2) (155)	122.00 → 275.180	0.97 → 14.70	3.34	-0.60	-0.18	3.68	3.05	0.18	46

*Percent average and/or absolute average error in bubble point temperature

TABLE XXVI

BENZENE BINARY SYSTEM DEVIATIONS IN
K-VALUE PREDICTIONS

SYSTEMS NAME (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	% AVERAGE ERROR IN			% ABS AVERAGE ERROR IN			NO. OF PTS.
			K 1st	K 2nd	L/F or BUBPT	K 1st	K 2nd	L/F or BUBPT	
Benzene(1)/n-C ₃ H ₈ (2) (156)	100.0 → 400.00	40.0 → 850.0	-0.26	10.93	-12.71	6.47	13.34	13.53	56
Benzene(1)/n-C ₇ H ₁₆ (2) (153)	103.64 → 203.78	3.480 → 14.70	1.26	1.30	0.30*	1.79	3.76	0.64*	52
Benzene(1)/n-C ₈ H ₁₈ (2) (153)	179.780 → 238.73	14.7	4.60	-6.26	2.99	9.60	6.26	6.08	20

* Percent average and absolute average error in bubble point temperature.

TABLE XXVII

K-VALUE ERROR DISTRIBUTIONS FOR ETHANE AND
NORMAL PENTANE IN ETHANE-PENTANE SYSTEM

EXPERIMENTAL DATA		ETHANE			NORMAL-PENTANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
40.	50.0	6.395	6.474	-1.23	0.098	0.0999	-1.66
40.	100.	3.287	3.300	-0.40	0.069	0.058	15.97
40.	150.	2.238	2.292	-0.20	0.060	0.047	22.34
40.	200	1.725	1.719	0.65	0.055	0.043	21.96
40.	250	1.916	1.400	1.10	0.053	0.093	19.10
40.	300	1.216	1.197	1.59	0.053	0.047	10.82
40.	350	1.079	1.064	1.36	0.052	0.058	-11.33
100	50	10.910	10.905	0.04	0.340	0.339	0.33
100	100	5.562	5.565	-0.06	0.183	0.191	-4.47
100	150	3.752	3.781	-0.76	0.145	0.144	0.28
100	200	2.853	2.889	-1.23	0.127	0.123	3.41
100	250	2.320	2.359	-1.45	0.1194	0.1128	5.52
100	300	1.967	1.998	-1.57	0.117	0.109	7.07
100	350	1.719	1.744	-1.48	0.118	0.109	7.96
100	400	1.535	1.556	-1.31	0.120	0.1130	5.63
100	450	1.397	1.410	-0.95	0.125	0.121	3.52
100	500	1.296	1.296	-0.02	0.129	0.134	-3.94
100	600	1.150	1.133	1.51	0.146	0.188	-29.22
160	100	7.755	8.001	-3.31	0.448	0.976	-6.13

TABLE XXVII (Continued)

EXPERIMENTAL DATA		ETHANE			NORMAL-PENTANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
160	150	5.305	5.440	-2.55	0.344	0.350	-1.92
160	200	4.048	4.146	-2.41	0.285	0.290	-1.88
160	250	3.316	3.368	-1.57	0.251	0.257	-2.32
160	300	2.814	2.848	-1.20	0.229	0.238	-3.90
160	350	2.455	2.475	-0.83	0.217	0.228	-5.15
160	400	2.185	2.196	-0.48	0.213	0.223	-5.07
160	450	1.973	1.978	-0.25	0.213	0.224	-5.07
160	500	1.803	1.800	0.21	0.216	0.228	-5.75
160	600	1.556	1.541	0.96	0.231	0.251	-8.61
160	700	1.381	1.352	2.19	0.266	0.297	-11.64
160	800	1.247	1.203	3.54	0.333	0.391	-17.48
220	100	9.625	10.000	-3.90	0.958	0.853	0.56
220	150	6.621	6.839	-3.29	0.700	0.698	0.33
220	200	5.080	5.219	-2.58	0.572	0.572	-0.07
220	250	4.168	4.232	-1.54	0.498	0.499	-0.11
220	300	3.590	3.569	-0.81	0.444	0.454	-2.19
220	350	3.089	3.091	-0.04	0.406	0.925	-4.61
220	400	2.733	2.730	0.13	0.382	0.407	-6.70
220	450	2.459	2.446	0.51	0.365	0.397	-8.83
220	500	2.235	2.218	0.7	0.356	0.394	-10.64
220	600	1.895	1.870	1.36	0.355	0.403	-13.65
220	700	1.638	1.612	1.56	0.391	0.434	-11.21
220	800	1.440	1.406	2.40	0.447	0.496	-11.07

TABLE XXVII (Continued)

EXPERIMENTAL DATA		ETHANE			NORMAL-PENTANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
220	900	1.277	1.218	4.58	0.540	0.624	-15.55
280	200	5.726	5.657	1.21	0.960	0.950	1.09
280	250	4.683	4.605	1.69	0.832	0.827	0.58
280	300	3.967	3.883	2.11	0.735	0.748	-1.85
280	350	3.456	3.354	2.91	0.674	0.695	-3.19
280	400	3.034	2.950	2.76	0.635	0.660	-3.89
280	450	2.714	2.630	3.13	0.609	0.637	-9.74
280	500	2.459	2.367	3.73	0.589	0.624	-5.95
280	600	2.067	1.959	5.23	0.576	0.622	-7.96
280	700	1.783	1.644	7.78	0.592	0.651	-9.97
280	800	1.546	1.371	11.34	0.638	0.725	-13.66
280	900	1.306	1.215	6.96	0.729	0.794	-8.98
340	350	2.917	2.976	2.02	0.974	0.963	-0.05
340	400	2.825	2.595	8.13	0.914	0.926	-1.39
340	450	2.706	2.83	15.63	0.859	0.895	-4.10
340	500	2.522	2.018	19.97	0.818	0.876	-7.14
340	600	2.054	1.566	23.74	0.798	0.879	-9.88
340	700	1.516	1.145	24.43	0.853	0.948	-11.17

TABLE XXVIII

K-VALUE ERROR DISTRIBUTIONS FOR PENTANE
AND METHYLCYCLOHEXANE IN PENTANE-
METHYLCYCLOHEXANE SYSTEM

EXPERIMENTAL DATA		PENTANE			ETHYLCYCLOHEXANE		
Temper- ature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
213.139	14.7	1.072	1.081	-3.28	0.986	0.985	0.31
212.630	14.7	1.056	1.067	-0.86	0.982	0.972	0.81
212.968	14.7	1.047	1.055	-1.05	0.978	0.974	0.35
211.982	14.7	1.047	1.096	-0.8	0.971	0.971	0.41
211.73	14.7	1.040	1.036	0.02	0.964	0.968	-0.02
211.28	14.7	1.033	1.028	0.40	0.960	0.966	-0.39
211.01	14.7	1.024	1.021	0.46	0.959	0.964	-0.60
210.614	14.7	1.0196	1.0145	0.29	0.951	0.964	-0.54
210.308	14.7	1.0287	1.010	0.50	0.895	0.964	-1.35
209.822	14.7	1.008	1.004	1.83	0.9321	0.9654	-7.68
209.516	14.7	1.032	1.026	0.41	0.9451	0.9759	-3.57

TABLE XXIX
 K-VALUE ERROR DISTRIBUTIONS FOR BENZENE AND
 NORMAL OCTANE IN BENZENE-OCTANE SYSTEM

EXPERIMENTAL DATA		BENZENE			OCTANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Errors	K _{exp}	K _{cal}	% Ave. Errors
238.73	14.7	3.345	2.902	13.24	0.701	0.746	-6.42
238.69	14.7	3.239	2.899	10.52	0.703	0.745	-5.96
236.75	14.7	3.139	2.826	10.00	0.703	0.723	-2.95
235.76	14.7	3.120	2.787	10.67	0.675	0.712	-5.56
224.78	14.7	2.550	2.384	6.51	0.568	0.598	-5.26
222.8	14.7	2.551	2.315	9.24	0.550	0.579	-5.30
222.89	14.7	2.500	2.318	7.26	0.557	0.586	-4.07
208.22	14.7	1.910	1.836	3.87	0.444	0.457	-2.88
207.23	14.7	1.856	1.806	2.71	0.4387	0.450	-2.59
206.33	14.7	1.852	1.778	3.99	0.434	0.444	-2.19
206.96	14.7	1.827	1.797	1.63	0.437	0.448	-2.57
198.32	14.7	1.590	1.591	3.05	0.381	0.393	-3.21
197.78	14.7	1.563	1.526	2.37	0.380	0.390	-2.67
197.51	14.7	1.553	1.518	2.22	0.377	0.389	-3.29
191.12	14.7	1.357	1.342	1.08	0.337	0.360	-6.69
190.67	14.7	1.344	1.330	1.05	0.334	0.358	-7.11
185.63	14.7	1.214	1.201	1.06	0.318	0.346	-8.72
185.36	14.7	1.211	1.195	1.32	0.318	0.345	-8.67
180.14	14.7	1.075	1.075	0.01	0.299	0.351	-17.29
179.78	14.7	1.07	1.068	0.29	0.289	0.352	-21.85

TABLE XXX

K VALUE ERROR DISTRIBUTIONS FOR HEXANE AND
METHYLCYCLOHEXANE IN HEXANE-
METHYLCYCLOHEXANE SYSTEM

EXPERIMENTAL DATA		HEXANE			METHYLCYCLOHEXANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
212	14.7	2.833	2.336	17.54	0.972	0.977	-0.50
209.84	14.7	2.497	2.269	7.26	0.942	0.946	-0.32
207.41	14.7	2.305	2.196	4.74	0.900	0.912	-0.35
204.62	14.7	2.167	2.113	2.49	0.872	0.874	-0.15
201.29	14.7	2.179	2.018	7.4	0.817	0.83	-1.52
197.60	14.7	1.984	1.915	3.45	0.778	0.784	-0.69
193.91	14.7	1.885	1.816	3.64	0.729	0.739	-1.41
190.04	14.7	1.741	1.716	1.42	0.695	0.695	0.04
187.79	14.7	1.607	1.66	1.61	0.672	0.670	0.30
185.18	14.7	-	-	-	-	-	-
182.48	14.7	1.997	1.533	-2.34	0.644	0.614	4.60
177.08	14.7	1.429	1.411	1.28	0.554	0.562	-1.33
175.12	14.7	1.369	1.369	-0.05	0.549	0.544	0.82
171.77	14.7	1.3034	1.298	0.4	0.519	0.514	1.03
168.62	14.7	1.228	1.234	0.54	0.501	0.487	2.69
161.78	14.7	1.109	1.105	0.36	0.439	0.434	1.13
158.99	14.7	1.058	1.056	0.21	0.404	0.413	-2.22

TABLE XXXI
 K-VALUE ERROR DISTRIBUTIONS FOR n-OCTANE
 AND ETHYLBENZENE IN OCTANE-
 ETHYLBENZENE SYSTEM

EXPERIMENTAL DATA		OCTANE			ETHYLBENZENE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
275.18	14.7	1.551	1.419	8.47	0.971	0.978	-0.70
270.32	14.7	1.383	1.294	6.41	0.904	0.926	-2.17
265.46	14.7	1.199	1.169	2.41	0.857	0.878	-2.92
260.42	14.7	1.053	1.061	-0.75	0.864	0.843	2.35
258.44	14.7	1.005	1.007	-0.22	0.884	0.834	5.66
246.20	9.67	1.558	1.400	10.08	0.941	0.958	-1.75
240.98	9.67	1.305	1.234	5.45	0.860	0.893	-3.78
235.58	9.67	1.093	1.093	0.0	0.845	0.845	-0.00
232.70	9.67	1.012	1.017	-0.49	0.879	0.829	5.62
194.72	3.87	1.699	1.448	14.74	0.928	0.954	-2.77
190.04	3.87	1.336	1.253	6.21	0.843	0.882	-4.59
185.9	3.87	1.112	1.102	0.89	0.820	0.836	-1.95
183.2	3.87	1.013	1.018	-0.96	0.868	0.821	5.39
132.44	0.97	1.807	1.503	16.8	0.922	0.951	-3.18
128.48	0.97	1.386	1.286	7.26	0.83	0.876	-5.26
125.42	0.97	1.186	1.152	2.83	0.802	0.837	-4.47
122.	0.97	1.013	1.018	-0.48	0.866	0.817	5.68

TABLE XXXII

K-VALUE ERROR DISTRIBUTIONS FOR BENZENE AND
n-HEPTANE FOR BENZENE-HEPTANE SYSTEM

EXPERIMENTAL DATA		BENZENE			HEPTANE		
Temperature °F	Pressure Psia	K _{exp}	K _{cal}	% Ave. Error	K _{exp}	K _{cal}	% Ave. Error
203.774	14.7	1.909	1.826	4.38	0.912	0.92	-0.88
200.03	14.7	1.763	1.712	2.88	0.863	0.872	-1.05
196.88	14.7	1.685	1.631	3.19	0.8256	0.839	-1.66
190.184	14.7	1.45	1.929	1.92	0.754	0.765	-1.49
186.314	14.7	1.322	1.318	0.29	0.729	0.732	-0.44
180.122	14.7	1.116	1.125	-0.83	0.732	0.710	2.94
176.216	14.7	1.002	1.004	-0.16	0.9000	0.819	8.96
124.7	3.98	2.450	2.08	15.02	0.839	0.880	-4.87
118.94	3.48	2.02	1.83	9.39	0.745	0.792	-6.36
114.62	3.48	1.72	1.63	5.16	0.691	0.729	-5.50
109.09	3.48	1.344	1.341	0.19	0.656	0.658	-0.39
105.62	3.48	1.129	1.150	-1.90	0.7000	0.650	7.14
103.64	3.48	1.016	1.032	-1.61	0.86	0.713	17.13
165.02	7.730	2.18	1.928	11.56	0.860	0.897	-3.22
158.90	7.73	1.865	1.724	7.55	0.784	0.819	-4.49
154.4	7.73	1.633	1.558	4.63	0.729	0.761	-4.45
150.8	7.73	1.458	1.421	2.53	0.695	0.720	-3.53
145.94	7.73	1.212	1.213	-0.15	0.683	0.68	0.40
141.44	7.73	1.018	1.029	-1.06	0.84	0.743	11.54
140.00	4.190	1.0	1.0	-0.0	-	-	-
140	5.16	1.0	1.0	-0.0	-	-	-
140	6.100	1.0	1.0	-0.0	-	-	-
140	7.08	7.0	7.0	-0.0	-	-	-
140	7.57	1.021	1.004	1.68	0.000	0.799	0.0

TABLE XXXIII
COMPARISON OF CALCULATED K-VALUE ERRORS
FOR SEVERAL HYDROCARBONS FOR
DIFFERENT BINARY MIXTURES

SYSTEM	REF. NO.	RANGE OF EXPERIMENTAL DATA				PERCENT ABS. AVG. ERROR IN						NO. of Points
		PRESSURE PSIA		TEMPERATURE °F		THIS WORK		MODIFIED SRK		PFGC		
		Min.	Max.	Min.	Max.	K _{1st}	K _{2nd}	K _{1st}	K _{2nd}	K _{1st}	K _{2nd}	
CH ₄ (1)-C ₂ H ₆ (2)	119	17.88	1000.0	-240.0	50.0	3.62	5.75	3.28	5.85	4.98	10.05	195
CH ₄ (1)-nC ₄ H ₁₀ (2)	123 124	20.0	1850.0	+200.0	220.0	8.58	8.37	-	-	8.33	22.42	237
CH ₄ (1)-iC ₄ H ₁₀ (20)	122	80.0	1600.0	100.0	220.0	7.37	6.22	-	-	8.92	9.76	137
CH ₄ (1)-nC ₅ H ₁₂ (2)	125 127	20.0	2250.0	-47.96	340.0	11.81	1.91	-	-	6.42	17.63	174
CH ₄ (1)-iC ₅ H ₁₀ (2)	125	400.0	1922.0	160.0	350.0	6.81	7.32	-	-	12.02	9.72	42
CH ₄ (1)-nC ₆ H ₁₄ (2)	128 129	19.9	2300.0	-116.77	302.0	15.00	.32	-	-	7.07	27.13	124
C ₂ H ₆ (1)-C ₂ H ₄ (2)	144 145	35.9	614.0	-100.0	68.0	3.13	0.35	-	-	3.72	9.05	48
C ₂ H ₆ (1)-nC ₅ H ₁₀ (2)	140	50.0	900.0	40.0	340.0	3.12	6.62	3.36	4.32	7.92	21.99	65
C ₃ H ₈ (1)-C ₃ H ₆ (2)	149 150	14.44	546.0	-20.0	190.0	0.93	1.10	8.14	1.85	5.86	8.98	306
C ₃ H ₈ (1)-iC ₅ H ₁₂ (2)	146	7.35	646.0	32.0	356.0	4.58	5.79	5.12	5.42	5.42	4.16	88

-: Data is not available.

TABLE XXXIII (Continued)

SYSTEM	REF. NO.	RANGE OF EXPERIMENTAL DATA				PERCENT ABS. AVG. ERRORS IN						NO. of Points
		PRESSURE PSIA		TEMPERATURE °F		THIS WORK		MODIFI. SRK		PFGC		
		Min.	Max.	Min.	Max.	n _{1st}	n _{2nd}	n _{1st}	n _{2nd}	n _{1st}	n _{2nd}	
C ₃ H ₈ (1)-nC ₅ H ₁₂ (2)	151	600.0	600.0	160.00	340.0	4.65	14.69	-	-	4.23	19.89	56
nC ₅ H ₁₂ (1)-Methylcyclopentane	152	14.7	14.7	97.0	158.72	2.78	4.29	-	-	9.82	5.85	44
nC ₅ H ₁₂ (1)-Cyclohexane	152	14.7	14.7	102.2	170.96	6.21	6.71	-	-	22.78	19.20	26
nC ₆ H ₁₄ (1)-Methylcyclopentane	152	14.7	14.7	156.02	161.15	1.67	1.20	-	-	5.88	4.64	29
nC ₆ H ₁₄ (1)-Methylcyclohexane (2)	152	14.7	14.7	158.99	212.0	2.23	1.08	-	-	7.73	8.21	1
nC ₇ H ₁₆ (1)-Methylcyclohexane (2)	153	14.7	14.7	209.516	213.134	0.9	1.40	-	-	7.14	7.79	11
nC ₈ H ₁₈ (1)-2-Methylpentane (2)	154	0.230	6.10	50.0	104.0	2.77	1.50	-	-	4.23	7.71	98
nC ₈ H ₁₈ (1)-Ethylbenzene (2)	155	0.97	14.7	122.0	275.18	3.68	3.05	-	-	24.49	19.51	96
Benzene (1)-nC ₇ H ₁₆ (2)	153	3.48	14.7	103.64	203.78	1.79	3.76	-	-	6.49	5.40	52
Benzene (1)-nC ₈ H ₁₈ (2)	153	14.7	14.7	179.78	238.73	4.60	6.26	-	-	9.84	8.71	20

-: Data is not available.

CHAPTER V
DISCUSSION AND ANALYSIS OF RESULTS

The new α model for low T_r , which incorporates the best features of both Soave's and Heyen's models was developed. The steps outlined earlier in this report were used to determine the values of parameters which led to reliable predictions of thermodynamic properties. The modified Heyen equation of state was evaluated over the entire range of temperature and pressure. A multiproperty, multicomponent fit program "MPCGC" for the PFGC (Parameter for Group Contribution) (115) was used to assist in the fitting of the data for obtaining reliable parameters. The set of parameters that yields the lowest percentage average error in some pure component vapor pressure predictions was selected. Using these pure component parameters, vapor liquid equilibrium data of binary mixtures were determined by way of a flash and/or bubble point temperature calculation.

Calculated vapor pressures obtained by the modified Heyen equation of state and original Heyen EOS for selected pure components were compared with experimental data and also with each other. Results indicate that the objective of this research has been fulfilled. On the whole, with the new α model the Heyen EOS is better in accuracy compared to the original Heyen EOS method.

Accuracy of Pure Component Property Prediction

Accurate prediction of thermodynamic properties for a wide variety of components is very important in the development of any equation of state. The modified Heyen equation of state reliably predicts the vapor pressure for the vapor and liquid phases for paraffins, olefins, cycloparaffins, aromatics, and some inorganics.

In order to severely test suitability of the modified Heyen's EOS over a wide range of temperature and pressure, 56 pure components, including compounds having a wide range of molecular weights, were chosen. The selected pure components can be divided into five main groups: (1) Paraffins, (2) Olefins, (3) Cycloparaffins, (4) Aromatics, and (5) Inorganic materials.

From the results reported in Table I it can be seen that the percent average deviation from experimental values rarely exceeds 0.14% for vapor pressure predictions for paraffin hydrocarbons. This indicates that the ability of the modified Heyen equation of state to predict pure component properties for paraffin hydrocarbons is indeed remarkable. For C_1 to C_8 paraffins, ESDU (103), and Kobayashi et al. (102) data were used. Kobayashi reports vapor pressure data at very low pressure. This data was used to confirm the utility of the new proposed model for very low pressure conditions, and results shown for these components in Table I are excellent. Also, good results have been obtained for C_9 and C_{10} with revised API-44 (104) and Kobayashi et al. (10) vapor pressure data. From the results reported in Table I for iso-butane, iso-pentane, 2-methylpentane, 3-methylpentane and

2,3-dimethylbutane with ESDU data, a very good agreement is obtained between experimental and predicted vapor pressures.

The capability of the modified Heyen EOS for predicting vapor pressures for the rest of the paraffin hydrocarbons including; n-decane, n-hexadecane, n-heptadecane, and 2,2-dimethylbutane using re-decane, n-hendecane, n-heptadecane, and 2,2-dimethylbutane using revised API-44 data up to the critical point was tested. The components where such extensive data were unavailable, an attempt was made to extend existing data using extrapolation techniques. As shown in Table I, the results obtained are in very good agreement with experimental data, and the average percent deviations between experimental and predicted vapor pressures do not exceed 0.17%.

For olefins, results from Table II demonstrate the predictive power of the modified Heyen EOS. The average percent error in calculated vapor pressure for all components (except Cis-2 pentane and propadiene which are 0.52 and 0.15 respectively), are below 0.05%.

From Table III the predicted vapor pressures for cycloparaffin hydrocarbons indicate that the results match very well with experimental data. From Table IV the same conclusion is obtained for aromatic hydrocarbons.

The modified Heyen EOS was also tested for its ability to predict the vapor pressures for a number of non-hydrocarbons, including nitrogen, carbon monoxide, carbon dioxide, oxygen, hydrogen sulfide, and sulfur dioxide. From the results presented in Table V it appears that they are in excellent agreement with experimental data. Besides the above numerical comparison, a graphical presentation of experimental and predicted vapor-pressure for a number of selected pure components

is presented in Figures 3 and 4. The agreement between experimental and predicted vapor pressure by the proposed modified Heyen equation of state is exceptionally good.

Values of parameters which yield the lowest percent average absolute deviations were obtained for the modified Heyen equation of state and are reported in Tables VI through X. The values of these parameters were used to predict K-values for different binary systems.

Tables XI through XV represent the results obtained by this work compared to the original Heyen EOS for 53 selected pure components, including normal and branched paraffins and olefins, cyclic and aromatic hydrocarbons, and inorganic compounds. The results obtained for every pure component indicate the superiority in reliability and accuracy of the proposed model over the original one. It can be seen that the vapor pressure deviation from experimental values for the modified version of all 53 pure component rarely exceed 0.19%. However, the original model often deviates more than 14%.

Since the average errors and/or average absolute error do not provide information on the distribution of errors, the error distributions for methane, which is typical of those obtained for all 53 pure components, using both original and modified Heyen equations of state presented in Figure 5. As can be seen from Figure 5, in the reduced temperature range from approximately 0.7 to 1.0 percent, errors in both methods are relatively small. Below reduced temperatures of 0.6 to 0.7, errors in calculated vapor pressure tend to increase unproportionally for the Heyen EOS as the temperature decreases. However, that is not the case for the modified version, which for the same reduced temperature range maintains minimal error. For more support of the conclusion

we have reached so far, Tables XVI through XXII clearly illustrate the error distributions for the whole range of conditions for several selected pure components.

According to these findings, the modified version of Heyen EOS is superior in reliability and accuracy to the Heyen EOS in prediction of pure component vapor pressure. Based on the literature review performed for this work through which the superiority of the Heyen EOS was established over the SRK and PR EOS in predicting pure component vapor pressure. It can also be concluded that the modified version of Heyen's EOS is superior, not only to the SRK and the PR equations of state, but to many other existing cubic equations of state as well.

The results reported in Table XVI through XXII, indicate that, on the whole, the performance of the proposed modified Heyen EOS is excellent over the whole range of conditions. However, it is noteworthy that using this method errors in the predicted vapor pressures for some components increase with decreasing temperatures lower than 0.4. This observation implies two possibilities; first, this discrepancy in predicting vapor pressure for some specific points could be traced to disputable data which has been referred to as major problems in other research (163); second, there might exist a possibility for further improvement for T_r 's lower than 0.4 with a more refined expression for $\alpha(T)$. Along the way, several difficulties were encountered in fitting the modified version of Heyen EOS to pure component data. The most important ones were the following:

1. Because of experimental difficulties, few measurements have been reported for the vapor pressures of heavy hydrocarbons. Further, the limited measurements that have been made are primarily for normal

paraffins. For heavy hydrocarbons where molecules contain highly branched chains or saturated molecules including paraffins heavier than octane, olefins, cycloparaffins, and aromatics there are few high temperature vapor pressure data available.

2. Very close to or at the critical point, there were some convergence difficulties in finding compressibility factors for the liquid and vapor phases.

3. For some of the Kobayashi et al. data, the percent error in predicted vapor pressure was so high that they were omitted.

Accuracy of Vapor-Liquid Equilibrium Predictions for Mixtures

To derive fitting parameters for the mixtures requires the application of mixing rules. It actually appears that such rules are more important for computing equilibria than the equation of state itself (13).

It should be emphasized that the proposed mixing rule, due to the interaction parameters K_{ij} , provides a satisfactory correlation among a great many systems, as shown by Goyal et al. (160).

The interaction parameter, K_{ij} , is the empirical constant which corrects the energy of interaction between two different molecules to optimize the prediction of phase equilibrium. The interaction coefficient increases with molecular size and compatibility differences. It is assumed generally to be constant for a given binary pair and, therefore, is independent of temperature, pressure, density, and composition. Realistically, that is not always true.

Using the pure component parameters and extensive vapor-liquid equilibrium literature data on mixtures, binary component interaction parameters are derived which minimize the average and absolute average error in equilibrium K-values of the mixtures over the given pressure and temperature range. However, for hydrocarbon--hydrocarbon binary mixtures, values of K_{ij} were found to be approximately zero. In this work, the assumption of $K_{ij}=0$ is reasonable. Then, the best fit of parameters tabulated in Tables VI through X were used for a selected number of binary mixtures to predict the equilibrium ratios (K-values) which play a very important role in practical engineering design. Selected binary mixtures used were divided into four systems: (1) Methane, (2) Ethane, (3) C_3^+ , and (4) Benzene systems. The C_3^+ binaries include propane, butane, hexane, heptane, and octane. The results are tabulated in Tables XXIII through XXVI.

A look at the results shows that errors in K-values predicted for $CH_4-C_2H_6$, $C_2H_6-C_3H_8$, and $C_2H_6-C_2H_4$ systems, where the molecular similarities are great, are notably low. This result can be explained by lesser molecular interactions. Justifiably, our approximation that $K_{ij}=0$ is reasonable. However, for binary mixtures such as $CH_4-C_{10}H_{22}$, $CH_4-C_8H_{18}$ and CH_4 -tolene, the errors in predicted K-values are high due to the greater molecular interactions. Therefore, in these cases where very accurate K-values are required, the K_{ij} cannot be approximated as zero. A guideline which might be followed in this case is that for those binaries that belong to the same family and have carbon content differences of not more than five, the assumption of $K_{ij}=0$ is reasonable. Otherwise, for more accurate results, K_{ij} should be calculated.

The equilibrium K-value data for binary mixtures are dispersed over a wide range of pressure and temperatures. Therefore, it is not proper to draw a general conclusion on the ability of the modified version of the Heyen EOS in predicting K-values solely based on the percent average error or percent absolute average deviations. As mentioned earlier, the percent average and/or percent absolute average errors are only one of the several criterion necessary for prediction of equilibrium K-values. It is important to tabulate the experimental, calculated, and average percent errors for equilibrium K-values for as many points as possible. Based on the distribution of errors, temperature and pressure conditions, molecular weights of individual components, and the reliability of the data source, a qualitative evaluation can be made. While the percent average and/or percent absolute average errors in equilibrium K-values were considered an important criteria for the error minimization method, K-value error distributions for binary mixtures are presented in Tables XXVII through XXXII for quantitative evaluation.

As a whole, the binary mixtures were selected so that they would provide a rigorous test of the ability of the modified Heyen equation of state to predict equilibrium K-values over a wide range of temperature and pressure, and specifically to evaluate predicted K-values when $T_r \leq 0.7$. Tabulated results show that the values predicted by this work agree well with experimental data.

The final test of credibility, accuracy, and ability of the modified Heyen EOS was the comparison of calculated K-values with respect to the related ones obtained using the original Heyen EOS or other well-known equations.

The predicted pure component vapor pressures obtained by the modified version were compared with values obtained using the original Heyen EOS by Wagner (158). Since the unacceptable errors in equilibrium vapor pressures at low pressure for pure components would also be encountered in multicomponent phase equilibrium calculations at low partial pressures, the original Heyen EOS was judged to be unsuitable for use in K-value calculations. Thus, the predicted K-values by this work were compared with the other available values, namely, the modified SRK (162) and the PFGC equations of state (163, 164, 165, 166). Certainly, this comparison at this stage makes more sense, since the results obtained by the modified Heyen EOS have already been subjected to error distribution analysis and have come out successfully. That is, the percent errors for the whole range of predicted vapor pressure have been almost uniform. Results reported in Table XXXIII for 20 selected binary mixtures indicate that the modified Heyen equation of state is superior in accuracy to modified SRK and PFGC in evaluation of equilibrium K-values.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

Conclusions

A new modified Heyen equation of state has been obtained by developing a better model for the temperature dependence of attractive term α , when reduced temperature is less than or equal to 0.7. For a wide range of temperatures and pressures, many pure component vapor pressures and several binary mixture equilibrium K-values were calculated using Heyen equation coupled with the proposed α model. Results were compared with experimental data, calculated values using the original Heyen equation of state, a modified SRK equation of state, and a PFGC equation of state. Consequently, the following conclusions were arrived at as a result of this study.

1. The Heyen equation of state with the proposed α model has demonstrated the capability to reliably calculate the pure component vapor pressures for paraffins, olefins, cycloparaffins, aromatics, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulfide, and sulfur dioxide.

2. The predicted vapor pressure for every pure component indicated that the objective of this work was achieved. On the whole, with the new α model, the Heyen equation of state is superior in reliability and accuracy compared to the original Heyen equation of state.

3. The Heyen equation of state coupled to the new α model made it suitable as a generalized equation of state for use in equilibrium K-values prediction for binary systems.

4. Calculated equilibrium K-values indicated the superiority of the modified Heyen equation of state compared to modified SRK (163) and PFGC (164) equations of state.

5. The assumption of $k_{ij} = 0$ for those binary mixtures in which both components belong to the same family and also have a carbon number difference of not more than five is justified. Otherwise, k_{ij} 's should be obtained for more accurate results.

Recommendations

For further improvement and investigation of the work the following recommendations are made:

1. For more efficient use of the program the term "R" should be accurately correlated as simple algebraic function of acentric factor.

2. For the hydrocarbon-hydrocarbon binary mixture in which both components do not belong to the same family or do have a carbon number difference more than five, hydrocarbon-hydrocarbon K_{ij} 's should be obtained and used in equilibrium K-values calculations.

3. As new data on thermodynamic properties for pure components become available, the parameters in the modified Heyen equation of state should be evaluated and improved.

4. Mixing rules play a very important part in equilibrium K-values calculations. They should be modified, particularly, for hydrocarbon-non-hydrocarbon binary mixtures.

5. The suggested approach should be applied to other similar equations, in order to overcome their deficiencies.

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APPENDIXES

APPENDIX A

DERIVATION OF THE DIMENSIONLESS FORM OF
HEYEN EQUATION OF STATE

The Heyen equation of State is defined as:

$$P = \frac{RT}{V-e} - \frac{a}{V^2 + (b+e)V-be} \quad (A-1)$$

Substituting $V = \frac{ZRT}{P}$ gives

$$P = \frac{RT}{\frac{ZRT}{P} - e} - \frac{a}{\frac{Z^2 R^2 T^2}{P^2} + (b+e) \frac{RT}{P} - be} \quad (A-2)$$

dividing both sides of equal sign by P, gives

$$1 = \frac{RT}{ZRT - eP} - \frac{aP}{Z^2 R^2 T^2 + (b+e)ZRT - beP^2} \quad (A-3)$$

Multiplying the denominator and the numerator of the second term of the right hand side by P, yields

$$P = \frac{RTP}{ZRT - eP} - \frac{aP^2}{Z^2 R^2 T^2 + (b+e)ZRT - beP^2} \quad (A-4)$$

dividing the numerator and denominator of the first and the second terms on the right hand side by RT and $R^2 T^2$, respectively, yields

$$1 = \frac{1}{Z - \frac{eP}{RT}} - \frac{aP/R^2T^2}{Z^2 + (b+e)\frac{P}{RT}Z - \frac{beP^2}{R^2T^2}}$$

Substituting $A = \frac{aP}{R^2T^2}$, $B = \frac{bP}{RT}$, and $E = \frac{eP}{RT}$ in the above equation

leads to

$$1 = \frac{1}{Z-E} - \frac{A}{Z^2+Z(B+E) - EB} \quad (A-6)$$

Rearranging

$$Z^3 + Z^2 B - Z^2 - 2BEZ - BZ - EZ + AZ + BE^2 - BE - AE = 0 \quad (A-7)$$

Finally,

$$Z^3 + (B-1)Z^2 + (A-B-E-2BE-E^2)Z + (BE-AE) = 0 \quad (A-8)$$

Deriving the expressions for A_c , B_c and E_c ,

Starting from Heyen equation defined as:

$$P = \frac{RT}{V-e} - \frac{a}{V^2 + (b+e)V-be} \quad (A-1)$$

and rearranging yields,

$$P = \frac{RTV^2 + RT(b+e)V - RT be - aV + ae}{(V-e) [V^2 + (b+e)V - be]} \quad (A-9)$$

$$\begin{aligned} \frac{RTV^2}{P} + \frac{RT}{P} (b+e)V - \frac{RTbe}{P} - \frac{a}{P} V + \frac{ae}{P} - V^3 + (b+e)V^2 - be V \\ - eV^2 - e(b+e)V + be^2 \end{aligned} \quad (A-10)$$

$$\frac{RT}{P} V^2 + \left[\frac{RT}{P} (b+e) - \frac{a}{P} \right] V + \frac{ae-RTbe}{P} = V^3 + bV^2 - (2be + e^2) V + be^2 \quad (A-11)$$

$$\begin{aligned} V^3 + \left(b - \frac{RT}{P} \right) V^2 - \left[\frac{RT}{P} (b+e) - \frac{a}{P} + e(2b+e) \right] V + e \left[be + \frac{RTb}{P} \right. \\ \left. - \frac{a}{P} \right] = 0 \end{aligned} \quad (A-12)$$

At the critical point with three equal roots:

$$(V-V_c)^3 = 0$$

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad (A-13)$$

Comparing the Equations (A-12) and (A-13), result in,

$$b - \frac{RT_c}{P_c} = -3V_c \quad b = \frac{RT_c}{P_c} - 3V_c$$

Multiplying all the Terms by $\frac{P_c}{RT_c}$,

$$b \frac{P_c}{RT_c} = 1 - \frac{3V_c P_c}{RT_c} \quad B_c = 1 - 3Z_c \quad (A-14)$$

$$- \left[\frac{RT}{P} (b+e) - \frac{a}{P} + e(2b + e) \right] = 3V_c^2$$

$$\frac{RT}{P} (b+e) - \frac{a}{P} + (2eb + e^2) = -3V_c^2$$

Assuming critical condition and multiplying all the terms by $\frac{P_c^2}{R^2 T_c^2}$, the following relation is obtained:

$$\frac{P_c}{RT_c} b + \frac{P_c}{RT_c} e - \frac{aP_c}{R^2 T_c^2} + \frac{P_c^2}{R^2 T_c^2} (2eb + e^2) = -3 \frac{V_c^2 P_c^2}{R^2 T_c^2}$$

Substituting $b \frac{P_c}{RT_c} = B_c$, $e \frac{P_c}{RT_c} = E_c$ and $\frac{aP_c}{R^2 T_c^2} = A_c$,

$$B_c + E_c - A_c + 2 E_c B_c + E_c^2 = -3 Z_c^2$$

$$A_c = B_c + E_c + 2B_c E_c + E_c^2 + 3Z_c^2 \quad (A-15)$$

$$e [be + RT \frac{b}{P} - \frac{a}{P}] = -V_c^3$$

$$be^2 + RT \frac{be}{P} - \frac{ae}{P} = V_c^3$$

Similarly, assuming critical condition and multiplying all the terms by

$\frac{P_c^2}{R^3 T_c^3}$ leads to

$$be^2 \frac{P_c^3}{R^3 T_c^3} + \frac{P_c^2}{R^2 T_c^2} be - ae \frac{P_c^2}{R^3 T_c^3} = - \frac{V_c^3 P_c^3}{R^3 T_c^3}$$

$$B_c E_c^2 + B_c E_c - A_c E_c = -Z_c^3$$

$$(1-3Z_c) E_c^2 + (1 - 3Z_c) E_c - [1-3Z_c + E_c + (2-6Z_c)E_c + E_c^2 + 3Z_c^2]$$

$$E_c + Z_c^3 = 0$$

$$(1 - 3Z_c)E_c^2 + (1-3Z_c) E_c + (-1 + 3Z_c - 3Z_c^2)E_c + (-3 + 6 Z_c)$$

$$E_c^2 - E_c^3 + Z_c^3 = 0$$

$$- E_c^3 + (1 - 3Z_c - 3 + 6Z_c)E_c^2 + (1 - 3Z_c - 1 + 3Z_c - 3Z_c^2)E_c^2 + Z_c^3 = 0$$

Rearranging and multiplying both sides by (-1) finally gives

$$E_c^3 + (2-3Z_c)E_c^2 + 3Z_c^2 E_c - Z_c^3 = 0 \quad (A-10)$$

APPENDIX B

DERIVATION OF FUGACITY COEFFICIENT FOR
THE HEYEN EQUATION OF STATE

$$p = \frac{RT}{V-e} - \frac{a}{V^2 + (b+e)V-be} \quad (B-1)$$

Substitute $v = \frac{V}{n_T}$

$$P = \frac{n_T RT}{V-n_T e} - \frac{n_T^2 a}{V^2 + n_T(b+e)V-n_T^2 be} \quad (B-2)$$

Taking derivative of pressure with respect to the number of moles of component i in the mixture while volume, temperature and the number of moles of other components are constant:

$$\begin{aligned} \frac{\partial P}{\partial n_i} \bigg|_{V,T,n_j} &= \frac{RT}{V-n_T e} \frac{\partial n_T}{\partial n_i} + \frac{n_T RT}{(V-n_T e)^2} \frac{\partial (n_T e)}{\partial n_i} \\ &\quad - \frac{\partial (n_T^2 a)}{\partial n_i} \frac{1}{V^2 + n_T(b+e)V-n_T^2 be} \\ &\quad + \frac{n_T^2 a \left[\left(\frac{\partial (n_T b)}{\partial n_i} + \frac{\partial (n_T e)}{\partial n_i} \right) V - \left(n_T b \frac{\partial (n_T e)}{\partial n_i} + n_T e \frac{\partial (n_T b)}{\partial n_i} \right) \right]}{(V^2 + n_T(b+e)V - n_T^2 be)^2} \end{aligned}$$

Mixing Rules:

$$b = \sum x_i b_i$$

$$e = \sum x_i e_i$$

$$a = \sum x_i \sum x_j \sqrt{a_i a_j} (1 - \delta_{ij})$$

$$b = \sum \frac{n_i}{n_T} b_i \qquad e = \sum \frac{n_i}{n_T} e_i$$

$$n_T b = \sum n_i b_i \qquad n_T e = \sum n_i e_i$$

$$\frac{\partial (n_i b)}{\partial n_i} = b_i \qquad \frac{\partial (n_i e)}{\partial n_i} = e_i$$

The fugacity coefficient of component i in the mixtures can be derived by applying to equation (B-1) the following general thermodynamic relationship:

$$\begin{aligned} RT \ln \phi_i &= \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{V,T,n_j} - \frac{RT}{V} \right] dV - RT \ln Z & (B-4) \\ &= \int_V^{\infty} \left(\frac{RT}{V - n_T e} - \frac{RT}{V} \right) dV + \int_V^{\infty} \frac{n_T RT e_i}{(V - n_T e)^2} dV \\ &\quad - \frac{\partial (n_T^2 a)}{\partial n_i} \int_V^{\infty} \frac{dV}{V^2 + n_T (b + e)V - n_T^2 be} \\ &\quad + n_T^2 a (b_i + e_i) \int_V^{\infty} \frac{V dV}{(V^2 + n_T (b + e)V - n_T^2 be)^2} \end{aligned}$$

$$- n_T^2 a n_T (b e_i + e b_i) \int_V^\infty \frac{dV}{(V^2 + n_T(b+e)V - n_T^2 be)^2}$$

$$- RT \ln Z$$

(B-5)

$$\begin{aligned} RT \ln \phi_i &= -RT \ln \frac{V - n_T e}{V} + \frac{n_T R T e_i}{V - n_T e} \\ &+ \frac{\partial(n_T^2 a)}{\partial n_i} \frac{1}{\sqrt{-q}} \ln \frac{2V + n_T(b+e) - \sqrt{-q}}{2V + n_T(b+e) + \sqrt{-q}} \\ &- n_T^2 a (b_i + e_i) \left\{ - \frac{n_T(b+e)V - 2n_T^2 be}{q(V^2 + n_T(b+e)V - n_T^2 be)} \right. \\ &\left. - \frac{n_T(b+e)}{q} \frac{1}{\sqrt{-q}} \ln \frac{2V + n_T(b+e) - \sqrt{-q}}{(b+e) + \sqrt{-q}} \right\} \\ &+ n_T^2 a n_T (b e_i + e b_i) \left\{ \frac{2V + n_T(b+e)}{q(V^2 + n_T(b+e)V - n_T^2 be)} \right. \\ &\left. + \frac{2}{q} \frac{1}{\sqrt{-q}} \ln \frac{2V + n_T(b+e) - \sqrt{-q}}{2V + n_T(b+e) + \sqrt{-q}} \right\} \end{aligned}$$

(B-6)

$$- RT \ln Z$$

where

$$q = -4n_T^2 be - n_T^2 (b+e)^2$$

(B-7)

Substituting $v = \frac{V}{n_T}$ and rearranging slightly,

$$\begin{aligned}
 RT \ln \phi_i &= RT \ln \frac{v-e}{v} + RT \frac{e_i}{-e} - RT \ln Z \\
 &+ \frac{a(n_T^2 a)}{a n_i} \frac{1}{\sqrt{-q}} \ln \frac{2v + b + e - \sqrt{-q}/n_T}{2v + b + e + \sqrt{-q}/n_T} + \frac{a(b_i + e_i)}{q/n_T^2} \\
 &\left\{ \frac{(b+e)v - 2be}{v^2 + (b+e)v - be} + (b+e) \frac{1}{\sqrt{-q}/n_T} \right. \\
 &\left. \ln \frac{2v + b + e - \sqrt{-q}/n_T}{2v + b + e + \sqrt{-q}/n_T} \right\} + \frac{a(b e_i + e b_i)}{q/n_T^2} \quad (B-8) \\
 &\left\{ \frac{2v + (b+e)}{v^2 + (b+e)v - be} + \frac{2}{\sqrt{-q}/n_T} \ln \frac{2v + b + e - \sqrt{-q}/n_T}{2v + b + e + \sqrt{-q}/n_T} \right\}
 \end{aligned}$$

Collecting Coefficients,

$$\begin{aligned}
 RT \ln \phi_i &= RT \ln \frac{v}{v-e} - RT \ln Z + RT \frac{e_i}{v-e} \\
 &+ \left\{ \frac{a(n_T^2 a)}{a n_i} \frac{1}{\sqrt{-q}} + \frac{a}{\sqrt{-q}/n_T} \left[\frac{(b_i + e_i)(b+e) + 2(b e_i + e b_i)}{q/n_T^2} \right] \right\} \\
 &\left\{ \ln \frac{2v + b + e - \sqrt{-q}/n_T}{2v + b + e + \sqrt{-q}/n_T} \right\} + a \left[\frac{(b_i + e_i)(b+e) + 2(b e_i + e b_i)}{q/n_T^2} \right] \\
 &\frac{v}{v^2 + (b+e)v - be} + a \left[\frac{-(b_i + e_i)2be + (b e_i + e b_i)(b+e)}{q/n_T^2} \right] \\
 &\frac{1}{v^2 + (b+e)v - be} \quad (B-9)
 \end{aligned}$$

$$\begin{aligned}
\text{Now } v &= \frac{ZRT}{P} \\
RT \ln \phi_i &= RT \frac{Z}{Z - eP/RT} - RT \ln Z + RT \frac{e_i P/RT}{Z - eP/RT} \\
&+ \left\{ \frac{\partial (n_T^2 a)}{\partial n_i} \frac{1}{\sqrt{-q}} + \frac{a}{\sqrt{-q}/n_T} \left[\frac{(b_i + e_i)(b + e) + 2(be_i + eb_i)}{q/n_T^2} \right] \right\} \\
&\left\{ \ln \frac{2Z + bP/RT + eP/RT - (\sqrt{-q}/n_T)P/RT}{2Z + bP/RT + eP/RT - (\sqrt{-q}/n_T)P/RT} \right\} \\
&+ a \left[\frac{(b_i + e_i)(b + e) + 2(be_i + eb_i)}{q/n_T^2} \right] \\
&\left(\frac{Z(P/RT)}{Z^2 + (bP/RT + eP/RT) - (bP/RT)(eP/RT)} \right) \\
&+ a \left[\frac{-2be(b_i + e_i) + (be_i + eb_i)(b + e)}{q/n_T^2} \right] \\
&\left(\frac{(P/RT)^2}{Z^2 + (bP/RT + eP/RT)Z - (bP/RT)(eP/RT)} \right)
\end{aligned} \tag{B-10}$$

Define the following variables:

$$B = \frac{bP}{RT}; \quad B_i = \frac{b_i P}{RT}; \quad E = \frac{eP}{RT}; \quad E_i = \frac{e_i P}{RT}; \quad A = \frac{aP}{R^2 T^2}$$

$$W = \frac{\sqrt{-q}}{n_T} \frac{P}{RT}$$

$$W = \sqrt{\frac{-q p^2}{n_T^2 R^2 T^2}} = \sqrt{(b^2 + 6be + e^2) \frac{p^2}{R^2 T^2}}$$

$$W = \sqrt{B^2 + 6BE + E^2}$$

$$\delta = \frac{2Z + B + E + W}{2Z + B + E - W} \quad \text{Note Sign on W terms}$$

$$\ln \phi_i = -\ln(Z-E) + \frac{E_i}{Z-E}$$

$$+ \left\{ \frac{1}{RT} \frac{1}{\sqrt{-q}} \frac{\partial (n_T^2 a)}{\partial n_i} \right.$$

$$+ \frac{1}{RT} \frac{a}{\sqrt{-q}/n_T} \frac{(P/RT)}{(P/RT)} \left[\frac{(b_i + e_i)(b + e) + 2(be_i + eb_i)}{q/n_T^2} \right]$$

$$\left. \frac{p^2/(R^2 T^2)}{p^2/(R^2 T^2)} \right\} \left\{ -\ln \delta \right\}$$

(B-11)

$$+ \frac{a}{RT} \left[\frac{(b_i + e_i)(b + e) + 2(be_i + eb_i)}{q/n_T^2} \right] \frac{p^2/(R^2 T^2)}{p^2/(R^2 T^2)} \frac{P}{RT}$$

$$\left(\frac{Z}{Z^2 + (B + E) Z - BE} \right)$$

$$+ \frac{a}{RT} \left[\frac{-2be(b_i + e_i) + (be_i + eb_i)(b + e)}{q/n_T^2} \right] \frac{P^2/(R^2T^2)}{P^2/(R^2T^2)}$$

$$\left(\frac{P}{RT} \right)^2 \left(\frac{1}{Z^2 + (B + e)Z - BE} \right)$$

$$\ln \phi_i = \ln(Z - E) + \frac{E_i}{Z - E}$$

$$- \left\{ \frac{1}{RT \sqrt{-q}} \frac{2(n_T^2 a)}{2n_i} + \frac{A}{W} \left[\frac{E_i(E + 3B) + B_i(B + 3E)}{-W^2} \right] \right\} \ln \delta$$

(B-12)

$$+ A \left[\frac{E_i(E + 3B) + B_i(E + 3B)}{-W^2} \right] \frac{Z}{Z^2 + (B + E)Z - BE}$$

$$+ A \left[\frac{-2BE(B_i + E_i) + (BE_i + EB_i)(B + E)}{-W^2} \right]$$

$$\frac{1}{Z^2 + (B + E)Z - BE}$$

$$\text{Let } Q_i = \frac{E_i(E + 3B) + B_i(B + 3E)}{2W}$$

$$\text{Note: } \frac{q}{n_T^2} = - (b^2 + 6be + e^2)$$

$$\frac{q}{n_T^2} \frac{P^2}{R^2T^2} = - (B^2 + 6BE + E^2) = -W^2$$

Now

$$\begin{aligned}
 a &= \sum_{i=1}^m x_i \sum_{j=1}^m x_j a_i a_j (1-\delta_{ij}) \\
 n_T a &= \sum_{i=1}^m n_i \sum_{j=1}^m x_j a_i a_j (1-\delta_{ij}) \\
 \left(\frac{\partial [n_T (n_T a)]}{\partial n_i} \right)_{V,T,n_j} &= n_T \frac{\partial (n_T a)}{2n_i} + n_T a \frac{2n_T}{2n_i} \\
 &= n_T \sum_{j=1}^m x_j \sqrt{a_i a_j} (1-\delta_{ij}) \\
 &\quad + \sum_{i=1}^m n_i \sum_{j=1}^m x_j \sqrt{a_i a_j} (1-\delta_{ij}) \\
 &= n_T 2 \sum_{j=1}^m x_j \sqrt{a_i a_j} (1-\delta_{ij}) \\
 \frac{1}{RT \sqrt{-q}} \frac{\partial (n_T^2 a)}{\partial n_i} &= \frac{1}{RT \sqrt{-q/n_T}} 2 \sum_{j=1}^m x_j \sqrt{a_i a_j} (1-\delta_{ij})
 \end{aligned}$$

Multiply numerator and denominator by $\frac{aP}{RT}$ yields

$$\frac{1}{RT \sqrt{-q}} \frac{(n_T^2 a)}{2n_i} = \frac{aP}{R^2 T^2} \frac{\frac{2}{a} \sum N_j a_i a_j (1-\delta_{ij})}{(\sqrt{-q}/n_T)(P/RT)}$$

Let $r_i = \frac{2}{a} \sum \alpha_j \sqrt{a_i a_j} (1-\delta_{ij})$

$$\frac{A}{Z^2 + (B + E)Z - BE} = \frac{\frac{aP}{R^2T^2}}{Z^2 + \left(\frac{bp}{RT}\right) + \left(\frac{ep}{RT}\right)Z - \left(\frac{bp}{RT}\right)\left(\frac{ep}{RT}\right)}$$

$$= \frac{1}{P} \frac{a}{v^2 + (b+e)v - be}$$

Rearranging the Heyen equation of state gives

$$\frac{a}{v^2 + (b+e)v - be} = \frac{RT}{v-e} - p$$

Substituting for the values of a, b, and e, results in

$$\frac{A}{Z^2 + (B + E)Z - BE} = \frac{1}{P} \left[\frac{RT}{v-e} - p \right]$$

$$= \frac{1}{Z-E} - 1$$

$$\ln \phi_i = -\ln(Z-E) + \frac{E_i}{Z-E} - \frac{A}{W} (r_i - Q_i) \ln \delta$$

$$+ \left(\frac{1}{Z-E} - 1 \right) \left[\frac{2BE(B_i + E_i) - (BE_i + EB_i)(B+E)}{W^2} - Q_i Z \right] \quad (B-13)$$

$$\ln \phi_i = -\ln(Z-E) + \frac{E_i}{Z-E} - \frac{A}{W} (r_i - Q_i) \ln \delta$$

$$\left(+ \frac{1}{Z-E} - 1 \right) \left[\frac{B(EB_i - BE_i) + E(BE_i - EB_i)}{W^2} - Q_i Z \right]$$

Which after some manipulation, and rearrangement results in

$$\ln \phi_i = -\ln(Z-E) + \frac{E_i}{Z-E} - \frac{A}{W} (r_i - Q_i) \ln \delta$$

$$+ \left(\frac{1}{Z-E} - 1 \right) \left\{ \frac{1}{2} \left[E_i + B_i - (E + B)Q_i - Q_i Z \right] \right\} \quad (B-14)$$

NOTE: The only difference between two derivations is that r_i is equal to $\frac{r_k}{a}$ in the original equation derived by Heyen.

VITA 2

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Doctor of Philosophy

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