

DEVELOPMENT OF A MODIFIED SOAVE-REDLICH-KWONG
EQUATION OF STATE

By

ENUMA DICKSON OZOKWELU

Bachelor of Science
University of Ife
Ile-Ife, Nigeria
1975

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1978

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
December, 1981

Thesis
1981D
099d



DEVELOPMENT OF A MODIFIED SOAVE-REDLICH-KWONG
EQUATION OF STATE

Thesis Approved:

Q. N. Maddox

Thesis Adviser

John H. Buley

Wesley J. Bell

Spencer

Norman N. Durham

Dean of the Graduate College

1110805

PREFACE

A better model for the α -term in the SRK equation of state has been proposed. Parameters for use in the new model have been obtained for thirty seven pure compounds. For easy application, these parameters have been accurately correlated as simple algebraic functions of acentric factor. The parameters in turn have been used to obtain interaction coefficients for several hydrocarbon-hydrocarbon and non-hydrocarbon-hydrocarbon binary mixtures. The model not only represents α correctly as a monotonically decreasing function of reduced temperature, but also very closely predicts vapor pressures of pure compounds.

The new modified SRK equation of state has been used to predict the K-values of several hydrocarbon-hydrocarbon and non-hydrocarbon-hydrocarbon binaries with reasonable accuracy. Pure component and mixture enthalpy departures of hydrocarbons and non-hydrocarbons have also been calculated with minimal errors, using the modified equation.

I wish to express my thanks to Dr. R.N. Maddox for his guidance and the special understanding he has shown me throughout the time he acted as my academic adviser. My special thanks also go to Dr. J.H. Erbar for his advice, immediate positive re-inforcement and encouragement during this research.

I want to take this opportunity to express my indebtedness to my initial sponsor to this country, Dr. Alex Ekwueme, now Vice President

of the Federal Republic of Nigeria. The same goes to Mr. Simon Okeke, Partner, Knight Frank & Rutley (Nig.) for acting as my second sponsor. Without the support from these two people, graduate study in this country may have been an unfulfilled dream for me.

I express my gratitude to the Nigerian Federal Government for their scholarship which although poorly administered, was nevertheless a great financial relief.

Special thanks go to my wife, Martha, for helping with most of the data punching, as well as her patience and encouragement during this research.

Finally, I continue to be grateful to my entire family in Nigeria for their patience, understanding and encouragement throughout my academic pursuit.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. LITERATURE SURVEY.	4
Original Redlich Kwong Equation of State.	4
Wilson's Modification	7
Barner, Pigford and Schreiner's Improvement	7
Cheuh and Prausnitz Proposal.	8
Joffe and Zudkevitch Proposal	11
Soave's Modification.	12
The Peng-Robinson Equation of State	15
Gray et al and Chaudron et al Approach.	17
Simonet-Behar and Graboski-Daubert Improvements	17
III. PROCEDURE.	19
Governing Equations	19
Development of $\Delta H'/RT$ Equation.	21
'MPMCGC' Program Modification	27
Fitting the Pure Component Parameters and Prediction of Pure Component Vapor Pressures.	28
Correlation of Pure Component Parameters as Functions of Acentric Factor, ω	29
Fitting the Binary Mixture Interaction Coef- ficients, k_{ij} , and Prediction of K-Values	34
Enthalpy Prediction	34
IV. RESULTS	35
V. DISCUSSION OF RESULTS	60
The New α -Model	60
Quality of Correlation Development for Pure Hydrocarbons	60
Quality of Vapor-Liquid Equilibrium Calculations.	61
Test of New Equation on Enthalpy Prediction	63

Chapter	Page
VI. CONCLUSIONS AND RECOMMENDATIONS	65
Conclusions.	65
Recommendations.	66
A SELECTED BIBLIOGRAPHY.	67
APPENDIX	73

LIST OF TABLES

Table	Page
I. Pure Component Parameters and Deviations in Vapor Pressure Predictions for Paraffin Hydrocarbons	37
II. Pure Component Parameters and Deviations in Vapor Pressure Predictions for Unsaturated Hydrocarbons.	40
III. Pure Component Parameters and Deviations in Vapor Pressure Predictions for Aromatic Hydrocarbons	41
IV. Pure Component Parameters and Deviations in Vapor Pressure Predictions for Non-Hydrocarbons.	42
V. CO ₂ Binary System Interaction Parameters and Deviations in K-value Predictions	44
VI. N ₂ Binary System Interaction Parameters and Deviations in K-value Predictions	48
VII. H ₂ S Binary System Interaction Parameters and Deviations in K-value Predictions	49
VIII. C ₁ Binary System Interaction Parameters and Deviations in K-value Predictions	51
IX. C ₂ Binary System Interaction Parameters and Deviations in K-value Predictions	53
X. C ₃ + Binary System Interaction Parameters and Deviations in K-value Predictions	54
XI. Pure Component Enthalpy Prediction Using the New Modified SRK Equation of State.	56
XII. Mixture Enthalpy Prediction Using the New Modified SRK Equation of State.	58

LIST OF FIGURES

Figure	Page
1. Plot of Pure Component Parameter, m , Versus Acentric Factor, ω	31
2. Plot of Product of Pure Component Parameters, m and n Versus Acentric Factor, ω	32
3. Plot of Pure Component Parameter, n , Versus Acentric Factor ω	33

NOMENCLATURE

MAJOR SYMBOLS

English Letters

P = Pressure , psia

V = Volume, $\text{ft}^3/\text{lb-mole}$

T = Temperature, $^{\circ}\text{F}$

R = Gas Constant, $\text{Btu}/\text{lb mole-}^{\circ}\text{R}$, equation (1-1)

K - Equilibrium ratio

x = Liquid mole fraction

y = Vapor mole fraction

Z = compressibility factor, equation (1-1)

a = RK parameter, equation (1-1)

b = RK parameter, equation (1-1)

H = Enthalpy, $\text{BTU}/\text{lb-mole}$

k = binary interaction parameter

Greek Letters

Σ = summation

α = Soave coefficient, equation (3-1)

ϵ = Tolerance limit

ω = Accentric factor

Ω = Chueh and Parusnitz parameter, equation (2-17)

Δ = Change in a property

ϕ = Fugacity coefficient

Subscripts

- i = component number
- j = component number
- m = mixture property
- mas. = maximum value
- min. = minimum value
- V,g = Vapor phase
- L,l = Liquid phase
- C,C_r = critical phase
- r = reduced property
- a = RK parameter, equation (2-14)
- b = RK parameter, equation (2-15)
- k = component number, equation (2-26)

Superscripts

- * = ideal gas property
- s = saturated phase
- L = Liquid phase
- v = vapor phase
- ' = Prime
- = average value

Abbreviations

- RK = Redlich-Kwong
- SRK = Soave-Redlich-Kwong
- H₂S = Hydrogen Sulfide
- CO₂ = Carbon Dioxide
- N₂ = Nitrogen
- ESDU = Engineering Sciences Data Unit
- API 44 = American Petroleum Institute Project Number 44

HC = Hydrocarbon

BUBPT = Bubble Point Temperature

C₁ = Methane

C₂ = Ethane

C₃ = Propane

C₃⁺ = Propane plus other hydrocarbons higher than C₃

BZ = Benzene

VLE = Vapor Liquid Equilibrium

CHAPTER I

INTRODUCTION

Phase-equilibrium predictions have become very important in all phases of the petroleum and chemical industries, including all kinds of petroleum production operations, gas-processing plants, enhanced oil recovery techniques such as CO_2 displacement, hydrocarbon solvent injection, et cetera. Knowledge of the properties and phase behavior of petroleum reservoir fluids used to be obtained experimentally, especially when made complex and complicated by the presence of such non-hydrocarbon gas mixtures as CO_2 , H_2S and nitrogen at high temperatures and pressures. With an accurate and reliable phase equilibrium prediction method, this information will be obtained with enormous savings of time and cost.

Previous studies by Yarborough (87) have shown that the Redlich-Kwong equation of state can be adapted for use in the calculation of typical hydrocarbon phase behavior relationships. Besides phase-equilibria predictions, the R-K equation can also predict reliable enthalpy departures and selected P-V-T relation calculations. The most widely accepted modification of the R-K equation is the one proposed by Soave (79) in 1972. The SRK equation is preferred to other equations with numerous constants, because it is not only simple to use, but also gives reasonably accurate results. According to Erbar and West (83), its only shortcoming is in the prediction of liquid densities, having been found accurate in

prediction of equilibrium coefficients, vapor densities, enthalpy and entropy departures.

Details of the Soave equation of state are given in the next chapter. Only an outline is given here for the purpose of illustration. The original form of R-K equation is:

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

Soave's form is :

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

Soave proposed that

$$b(T) = b(T_c) \quad (1-3)$$

$$a(T) = a(T_c) \left(\frac{T_r}{T} \right) \quad (1-4)$$

and that $\alpha_i^{1/2} = 1 + m_i (1 - T_{ri}^{1/2})$ (1-5)

This form of equation (1-5) predicts that α vanishes and then starts to increase again at high T_r . This is contrary to the observation of Heyen (27) that α is a monotonically decreasing function of T_r .

The primary objective of this study was to find a better model for α . Values of parameters from the new α model were to be computed by forcing the SRK equation of state to match experimental pure component vapor pressures from triple point to critical point. Vapor pressure and volumetric data to be used were to be those of N_2 , CO_2 , H_2S and light hydrocarbons including paraffins, alkenes and aromatics. The parameters obtained from the new α model were to be correlated as functions of the acentric factor, ω .

This work was then to be extended to binary mixtures of H_2S , CO_2 , N_2 and light hydrocarbons, where standard mixing rules were to be used to obtain optimal interaction parameters for these binaries.

An expression for pure component and mixture enthalpy departure which would reflect the new model was to be derived. This expression would then be used to test how good the new modified SRK equation of state would be in enthalpy departure predictions.

The main tool to be used for this study was to be Multiproperty and Multicomponent Fit Program "MPMCGC" for the PFGC Equation of State (20). MPMCGC was to be modified to handle SRK equation of state and the new α model.

CHAPTER II

LITERATURE SURVEY

The original Redlich-Kwong equation of state is:

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

where the constants a and b are related to the critical properties of the substance in question:

$$a = \frac{0.4278R^2 T_c^{2.5}}{P_c} \quad (2-2)$$

$$b = \frac{0.0867RT_c}{P_c} \quad (2-3)$$

For binary or multicomponent system, like in the case of a gas mixture, the following mixture rules are used:

$$b_m = \sum_i y_i b_i \quad (2-4)$$

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \quad (2-5)$$

In terms of the compressibility factor; equation (2-1) can be written as:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (2-6)$$

$$\text{where: } V = \frac{ZRT}{P} \quad (2-7)$$

$$A = \frac{aP}{R^2 T^{2.5}} \quad (2-8)$$

$$B = \frac{bP}{RT} \quad (2-9)$$

Equation (2-6) is a cubic equation which can be solved analytically to obtain three roots. The maximum root, Z_{\max} , is picked to determine the vapor mixture volume, while the minimum root, Z_{\min} , is picked to calculate the liquid mixture volume.

$$V = \frac{ZRT}{P} \quad (2-7)$$

For a one component system, the fugacity coefficient ϕ is obtained from the R-K equation as

$$\ln \phi = \ln \frac{RT}{P(V-b)} + \left(\frac{PV}{RT} - 1 \right) - \left(\frac{a}{RT^{3/2} b} \right) \ln \frac{V+b}{V} \quad (2-10)$$

For a component k in a multicomponent vapor mixture, the fugacity coefficient is given by

$$\begin{aligned} \ln \phi_k^V = & \ln \frac{V}{V-b} + \frac{b_k}{V-b} + \ln \frac{RT}{PV} - \frac{\sum_{i=1}^n y_i a_{ik}}{RT^{3/2} b} \ln \frac{V+b}{V} \\ & + \frac{ab_k}{RT^{3/2} b^2} \left[\ln \frac{V+b}{V} - \frac{b}{V+b} \right] \end{aligned} \quad (2-11)$$

The residual enthalpy for a gas mixture can also be computed from the following derived expression

$$\frac{\Delta H}{RT} = \frac{-1.5 a_m}{RT^{1.5} b_m} \cdot \ln \frac{\bar{V} + b_m}{\bar{V}} + \frac{P\bar{V}}{RT} - 1 \quad (2-12)$$

The R-K equation is widely accepted as the best generalized two-parameter equation of state available. Its greatest asset are its simplicity and its accuracy relative to other equations with numerous constants. It is easily applied in the calculation of P-V-T relations, enthalpy, and vapor-liquid equilibrium data, fugacity coefficients, compressibility factors, heat capacities, et cetera for single or multi-component systems. The shortcomings of the Redlich-Kwong equation include: its failure to give consistently good results for mixtures which Prausnitz et al (13) attributed to the inflexible mixing rules for the composition dependence to the equation-of-state constants and its inability to accurately describe the liquid phase volumetric properties. [The first inadequacy is most marked in the prediction of fugacity coefficient for components in the mixture. The R-K equation shows increasing errors as the acentric factor of the compound in question increases. In addition it predicts a value of one-third for the critical compressibility factor Z_c for all compounds, whereas Z_c varies from a value of 0.290 for compounds with spherical molecules down to a value of 0.260 for n-heptane.

Consequently, a barrage of publications has been published in the chemical engineering literature within the last two decades; all of these papers report attempts to modify the R-K equation of state to reduce the above-mentioned and other inadequacies. Only the highlights of these publications will be reviewed here. These modifications may be divided into four categories:

1. Improvement of the R-K mixing rules
2. Improvement of the R-K equation by changing the temperature dependence of the a term or a and b terms
3. Improvement of the R-K equation by changing the expression for determining the constants
4. Improvement of the R-K equation by adding a correction term to the original equation.

Wilson's Modification

The first paper was Wilson (85,86) in 1964 and 1966 who proposed temperature dependence for the a term in order to match the pure component vapor pressures. Wilson (86) proposed that the R-K equation be written as

$$\frac{PV}{RT} = \frac{V}{V-b} - f\left(\frac{T_c}{T}, \omega\right) \frac{b}{V+b} \quad (2-13)$$

$$\text{where } f\left(\frac{T_c}{T}, \omega\right) = 4.934 - 1 \left[+ (1.57 + 1.62\omega) \left(\frac{T_c}{T} - 1\right) \right] \quad (2-14)$$

For computing enthalpy, he derived the expression:

$$H = H^* + P\bar{V} - RT - 4.93R \left[\sum_i x_i (1.57 + 1.62\omega_i) \frac{T_{ci}}{T} \right] \ln \left(1 + \frac{b}{V} \right) \quad (2-15)$$

His modification had limited success, particularly at high pressures where deviations for vapor pressure predictions are very high.

Barner, Pigford and Schreiner's Improvement

Barner et al (6) tried to improve on Wilson's work by proposing another expression for $a/T^{1/2}$ in original equation (2-1):

$$\frac{a}{T^{1/2}} = 0.4275 \left(\frac{1 + 4.73 \omega^{3/2} T_r^{-3/2}}{1 + 4.73 \omega^{3/2}} \right) T_r^{-1/2} \quad (2-16)$$

The Barner modification gave improved estimates of enthalpy deviations for non-polar vapors and for vapor-phase mixtures of hydrocarbons, but was unsuitable for fugacity calculations.

Chueh and Prausnitz Proposal

Chueh and Prausnitz (13,14) proposed that equations (2-2) and (2-3) be written as

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \quad (2-17)$$

$$\text{and } b = \Omega_b \frac{RT_c}{P_c} \quad (2-18)$$

where the critical constraints on the R-K equation are relaxed and the parameters Ω_a and Ω_b are treated as empirical constants which are in turn determined separately for the liquid phase and for the vapor phase of a given substance. If the constants are solved by the classical method of van der Waals:

$$\left(\frac{\partial P}{\partial V} \right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \quad (2-19)$$

or by an alternate equivalent technique of using three equal volume roots at the critical point:

$$(V - V_c)^3 = 0 \quad (2-20)$$

the results are: $\Omega_a = 0.4278$

and $\Omega_b = 0.0867$ for all fluids as obtained by

Redlich and Kwong. Prausnitz (14) argued that adoption of these values is equivalent to fitting the equation of state to experimental results in the critical region, which although the most sensitive, does not provide the best fit over a wide range of conditions. Since, in vapor liquid equilibrium, we are interested in the volumetric behavior of saturated vapors over a relatively wide range of temperature, rather than in the critical region only, Prausnitz (13) proposed to evaluate Ω_a and Ω_b for each pure component by fitting equation (2-1) to the volumetric data of the saturated vapor, using the temperature range from the normal boiling point to the critical temperature. This he hoped, would enhance thermodynamic property predictions at high pressures. He also made changes in the mixing rules as follows.

$$b = \sum_{i=1}^n y_i b_i \quad (2-21)$$

where
$$b_i = \frac{\Omega_{bi} RT_{ci}}{P_{ci}} \quad (2-22)$$

and
$$a = \sum_{i=1}^n \sum_{j=1}^n y_i y_j a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii} a_{jj}}) \quad (2-23)$$

where
$$a_{ii} = \frac{\Omega_{ai} R^2 T_{ci}^{2.5}}{P_{ci}} \quad (2-24)$$

$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj}) R^2 T_{cij}^{2.5}}{2P_{cij}} \quad (2-25)$$

$$P_{cij} = \frac{Z_{cij} RT_{cij}}{V_{cij}} \quad (2-26)$$

$$V_{cij}^{1/3} = \frac{1}{2} (V_{ci}^{1/3} + V_{cj}^{1/3}) \quad (2-27)$$

$$Z_{cij} = 0.291 - 0.08 \left(\frac{\omega_i + \omega_j}{2} \right) \quad (2-28)$$

$$T_{cij} = T_{cij} T_{cij} (1 - k_{ij}) \quad (2-29)$$

where k_{ij} is a binary constant representing the deviation from geometric mean for T_{cij} and is approximately independent of temperature, density and composition.

Using equation (2-1) and his new mixing rules, he derived an expression for the fugacity coefficient of component k in the mixture as:

$$\ln \phi_k = \ln \frac{V}{V-b} + \frac{b_k}{V-b} - \left(\frac{\sum_{i=1}^n y_i a_{ik}}{RT^{3/2} b} \right) \ln \frac{V+b}{V} + \frac{ab_k}{RT^{3/2} b^2} \left[\ln \frac{V+b}{V} - \frac{b}{V+b} \right] - \ln \frac{PV}{RT} \quad (2-30)$$

One limitation of the Chueh and Prausnitz (13,14) modification is that with the change in the pre-multiplier, the condition at which $\left(\frac{\partial P}{\partial V} \right)_{T_C} = 0$ and $\left(\frac{\partial^2 P}{\partial V^2} \right)_{T_C} = 0$ no longer corresponds to the component critical temperature and pressure, thus introducing a slight inconsistency in the extent of the two-phase region. To be thermodynamically consistent, the same value of fugacity coefficient should be obtained for a pure component at same conditions of temperature and pressure irrespective of phase. Unfortunately, with the constants established by Chueh and Prausnitz (13,14), different coefficients are obtained using volumetric data on the different saturated phases, and therefore do not yield equal

fugacities, a fundamental requirement for phase equilibrium.

Joffe and Zudkevitch Proposal

The first proposals to make the Chueh and Prausnitz constants temperature dependent came from Joffe and Zudkevitch (89,90) and Chang and Lu (11) in 1970. Zudkevitch (90) used an additional

$$\text{constraint that } \phi_V^S = \phi_L^S \quad (2-31)$$

and equation (3-10) to obtain for a pure component:

$$\Omega_a = \Omega_b \left[\frac{\ln (V_g - b)/(V_L - b) - P(V_g - V_L)/RT}{(T_c/T)^{3/2} \ln V_g (V_L + b)/V_L (V_g + b)} \right] \quad (2-32)$$

Joffe, Zudkevitch and Schroeder (90) then solved equations (2-1), and (2-32) simultaneously at each temperature below the critical point by trial and error to yield values of Ω_a and Ω_b .

A trial and error procedure set up by them is outlined below:

- (1) Guess Ω_b and use experimental values of T, P and V_L , solve equation (2-1) for a and for Ω_a . This is Ω_a I.
- (2) Knowing a and b, solve equation (2-1) for V_g using Newton-Raphson method for largest root.
- (3) Substitute known values of V_g , V_L , P, T and Ω_b in equation (2-32) to obtain Ω_a . This is Ω_a II.
- (4) If $|\Omega_a \text{ I} - \Omega_a \text{ II}| \geq \epsilon$, go back to (1).
- (5) If $|\Omega_a \text{ I} - \Omega_a \text{ II}| < \epsilon$, convergence achieved and solution obtained.

This method gave one set of Ω_a and Ω_b for both liquid and vapor phases at each temperature point for a pure component and, therefore, solved the phase continuity problem inherent in the Chueh and Praus-

nitz work. Unfortunately, it was not widely adopted because of its complex nature.

Soave's Modification

In 1972, Soave (79, 80) presented an extremely simple temperature dependent expression for the a term, along the same line of thought as Wilson (85,86) and Barner et al (6). Much of the popularity of the R-K method stems from Soave's modification. Soave (79) replaced the term $a/T^{1/2}$ in equation (2-1) with a more general temperature dependent term:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (2-33)$$

Letting $V = \frac{ZRT}{P}$ (2-7)

$$A = \frac{aP}{R^2 T^2} \quad (2-34)$$

and $B = \frac{bP}{RT}$ (2-35)

equation (2-33) can be written in terms of compressibility factor Z as:

$$Z^3 - Z^2 + Z(A-B-B^2) - AB = 0 \quad (2-36)$$

For a pure component:

$$a_i(T_c) = \frac{0.42748R^2 T_{ci}^2}{P_{ci}} \quad (2-37)$$

$$A_i(T) = a_i(T_c) \cdot \alpha(T/T_{ci}) \quad (2-38)$$

where $\alpha_i^{\frac{1}{2}} = 1 + m_i (1 - T_{ri}^{\frac{1}{2}})$ (2-39)

and $m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$ (2-40)

$$b_i = \frac{0.08664RT_{ci}}{P_{ci}} \quad (2-41)$$

Thus $A = \frac{0.42748 a_i P_{ri}}{T_{ri}^2}$ (2-42)

and $B = \frac{0.8664 P_{ri}}{T_{ri}}$ (2-43)

The fugacity coefficient for a pure component is therefore given by

$$\ln \phi = Z - 1 - \ln(Z-b) - \frac{A}{B} \ln \frac{Z+B}{Z} \quad (2-44)$$

For mixtures, Soave (79) used the original mixing rules:

$$a = (\sum x_i a_i^{\frac{1}{2}})^2 \quad (2-45)$$

and $b = \sum x_i b_i$ (2-4)

which he claimed were adequate for non-polar mixtures. Using these rules, he obtained:

$$A = 0.42748 \frac{P}{T^2} \left(\sum x_i \frac{T_{ci} \alpha_i^{\frac{1}{2}}}{P_{ci}^{\frac{1}{2}}} \right)^2 \quad (2-46)$$

$$B = 0.8664 \frac{P}{T} \sum x_i \frac{T_{ci}}{P_{ci}} \quad (2-47)$$

and the fugacity coefficient of a component in a mixture as

$$\ln \phi_k = \int_{\infty}^V \left[\frac{1}{V} - \frac{1}{RT} \left(\frac{dP}{dn_i} \right)_{T, P, n_j} \right] dV - \ln Z \quad (2-48)$$

$$= \frac{b_k}{b} (Z-1) - \ln (A-B) - \frac{A}{B} \left\{ 2 \left(\frac{a_k}{a} \right)^{\frac{1}{2}} - \frac{b_k}{b} \right\} \ln \left(1 + \frac{B}{Z} \right) \quad (2-49)$$

The ratios a_k/a and b_k/b are given by

$$\left(\frac{a_k}{a} \right)^{\frac{1}{2}} = \frac{\alpha_k^{\frac{1}{2}} T_{ci}/P_{ci}^{\frac{1}{2}}}{\sum_i x_i \alpha_i^{\frac{1}{2}} T_{ci}/P_{ci}^{\frac{1}{2}}} \quad (2-50)$$

and

$$\frac{b_k}{b} = \frac{T_{ci}/P_{ci}}{\sum_i x_i T_{ci}/P_{ci}} \quad (2-51)$$

In order to improve the performance of his equation on polar compounds, Soave (80) made the following improvements on his work:

$$\alpha(T/T_c) = 1 + (1 - T/T_c)(m + n \frac{T_c}{T}) \quad (2-52)$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (2-53)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (2-54)$$

where $a_{ij} = (1 - C_{ij})(a_i + a_j)/2$ (2-55)

and $b_{ij} = (1 - D_{ij})(b_i + b_j)/2$ (2-56)

C_{ij} and D_{ij} are adjustable, empirically determined coefficients.

Fugacity coefficients ϕ_k^{ℓ} and ϕ_k^v are given by:

$$\begin{aligned} \ln \phi_k^L = & \left(\frac{PV}{RT} - 1 \right) \left(2 \frac{\sum_j x_j b_{kj}}{b} - 1 \right) - \ln \left[(V-b) \frac{P}{RT} \right] \\ & - \left(\frac{a}{RTb} \right) \ln \left(1 + \frac{b}{V} \right) \left(1 + 2 \frac{\sum_j a_{kj}}{a} - \frac{\sum_j x_j b_{kj}}{b} \right) \end{aligned} \quad (2-57)$$

and the same for ϕ_k^V , by replacing in equation (2-57) x_j with y_j .

The S-R-K equation gained acceptance by the hydrocarbon processing industry because of its relative simplicity as well as its capability for generating reasonably accurate equilibrium ratios in vapor-liquid equilibrium calculations. However its shortcoming lies in its failure to generate satisfactory density values for the liquid, even though the calculated vapor densities are generally acceptable.

The Peng-Robinson Equation of State

Peng and Robinson (39, 40, 41), (1967, 1977), published an equation that yields improved correlation for pure-component vapor pressures and better estimates of liquid densities. Peng-Robinson (39) proposed an R-K type equation of the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (2-58)$$

which can be written as

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2-59)$$

$$\text{where } A = \frac{aP}{R^2 T^2} \quad (2-34)$$

$$B = \frac{bP}{RT} \quad (2-35)$$

$$Z = \frac{PV}{RT} \quad (2-7)$$

In the two phase region, the maximum and minimum roots of equation (2-56) are the vapor and liquid compressibility factors, respectively.

$$\text{At critical, } a(T_c) = \frac{0.45724R^2T_c^2}{P_c} \quad (2-60)$$

$$b(T_c) = \frac{0.07780RT_c}{P_c} \quad (2-61)$$

$$\text{and } Z_c = 0.307 \quad (2-62)$$

Similar to SRK equation,

$$a_i(T) = a_i(T_c) \alpha_i(T_{ri}, \omega_i) \quad (2-38)$$

$$b_i(T) = b_i(T_c) \quad (2-41)$$

$$\alpha_i^{1/2} = 1 + m_i (1 - T_{ri}^{1/2}) \quad (2-34)$$

But correlation for m_i is different:

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (2-63)$$

The mixing rules used were

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (2-53)$$

$$\text{where } a_{ij} = (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \quad (2-64)$$

k_{ij} being an empirically determined binary interaction coefficient characterizing the binary formed by component i and component j .

$$b = \sum_i x_i b_i \quad (2-4)$$

Peng and Robinson derived the following expression for the fugacity coefficient of a pure component:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2 \cdot 2B} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (2-65)$$

and that of a component k in the mixture:

$$\ln \phi_k = \frac{b_k}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2 \cdot 2B} \left(2 \frac{\sum_i x_i a_{ik}}{a} - \frac{b_k}{b} \right) \cdot \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (2-66)$$

The enthalpy departure of a fluid that can be derived from the Peng-Robinson equation of state is given by

$$H - H^* = RT(Z - 1) + \frac{T \frac{da}{dT} - a}{2 \cdot 2b} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \quad (2-67)$$

Gray et al. and Chaudron et al. Approach

Gray et al. (26) (1970) and Chaudron et al. (12), (1973) modified the R-K equation by adding a deviation function to the compressibility factor of the original R-K equation to improve agreement with data. This deviation function Z_2 is made a function of temperature, pressure and acentric factor, ω .

$$Z = Z_{RK} + A_2 (T_r, P_r, \omega) \quad (2-68)$$

Simonet-Behar and Graboski-Daubert Improvements

One of the two latest RK equation modifications worth mentioning

in this review is the attempt by Simonet and Behar (78) in 1976 to find analytic functions for Ω_a and Ω_b previously computed by Zudkevitch and Joffe. The second is the improvement on SRK equation by Graboski and Daubert (20) in 1978. They used the following mixing rules:

$$\bar{\alpha} \bar{a} = \sum_{i=1}^n \sum_{j=1}^m x_i x_j \alpha_{ij} a_{ij} \quad (2-69)$$

and retained $\bar{b} = \sum_{j=1}^n x_j b_j$ from the original R-K equation where

$$\alpha_{ij} a_{ij} = (1 - C_{ij})(\alpha_i a_i \alpha_j a_j)^{\frac{1}{2}} \quad (2-70)$$

C_{ij} is a binary interaction coefficient which corrects for the effect of deviation from geometric mean combining rule for $\bar{\alpha} \bar{a}$ and is obtained by fitting binary mixture data. They retained the Soave original form for α :

$$\alpha^{\frac{1}{2}} = 1 + m (1 - T_r^{\frac{1}{2}}), \text{ but re-correlated the regression for } m \text{ as:}$$

$$m = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (2-71)$$

Their equation derived for the fugacity coefficient of component k in a mixture is:

$$\ln \phi_k = \frac{b_k}{b} (Z - 1) - \ln (Z - B) - \frac{A}{B} \left[\frac{2 \sum_{k=1}^n x_j \alpha_{kj} a_{kj}}{\bar{\alpha} \bar{a}} - \frac{b_i}{\bar{b}} \right] \ln \left(1 + \frac{B}{Z} \right) \quad (2-72)$$

CHAPTER III

PROCEDURE

Governing Equations

The governing equations used in this study were the original SRK equation of state, with standard mixing rules, but a new α model:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (2-33)$$

$$\text{Letting } V = \frac{ZRT}{P} \quad (2-7)$$

$$A = \frac{aP}{R^2T^2} \quad (2-34)$$

$$\text{and } B = \frac{bP}{RT} \quad (2-35)$$

equation (2-33) can be written in terms of compressibility factor as:

$$Z^3 - Z^2 + Z(A-B-B^2) - AB = 0 \quad (2-36)$$

$$\text{for pure substances, Let } \left(\frac{\partial P}{\partial V}\right) = \left(\frac{\partial^2 P}{\partial V^2}\right) = 0 \quad (2-19)$$

at critical point, then we obtain:

$$a_i(T_{ci}) = a_{ci} = \frac{0.4274R^2T_{ci}^2}{P_{ci}} \quad (2-37)$$

$$a_i(T) = a_{ci}\alpha_i(T) \quad (2-38)$$

where a new model for α was proposed as:

$$\alpha_i^{1/2} = \exp m_i (1 - T_{ri}^{n_i}) \quad (3.1)$$

m_i and n_i are empirical constants that were to be determined.

$$\text{Thus } A = \frac{a_i P}{R^2 T^2} = \frac{a_{ci} \alpha_i^P}{R^2 T^2} \quad (3-2)$$

$$B = \frac{b_i P}{RT}$$

the pure component fugacity coefficient remained as:

$$\ln \phi = (Z-1) - \ln(Z-B) - \frac{A}{B} \ln(1+B/Z) \quad (2-44)$$

For mixtures, the standard mixing rules used by Soave (78) were retained:

$$\bar{a} = \bar{a}_c \bar{\alpha} = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad (3-4)$$

where $a_{ij} = a_{cij} \alpha_{ij}$

$$\begin{aligned} &= (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \\ &= (1 - k_{ij}) (a_{ci} \alpha_i \cdot a_{cj} \alpha_j)^{1/2} \end{aligned} \quad (3-5)$$

k_{ij} is the binary interaction parameter to be determined empirically and characterizing the binary formed by components i and j .

$$\bar{b} = \sum_i^n x_i b_i \quad (2-4)$$

$$\text{thus } A = \frac{\bar{a} P}{R^2 T^2} = \frac{\bar{a}_c \bar{\alpha} P}{R^2 T^2} \quad (3-6)$$

$$B = \frac{\bar{b} P}{RT} \quad (3-7)$$

Hence the expression for the fugacity coefficient of a component i in the mixture remained as:

$$\ln \phi_i = \frac{b_i}{\bar{b}} (Z - 1) - \ln(Z - B) - \frac{A}{B} \left[\frac{2 \sum_{j=1}^n x_j a_{cij} \alpha_{ij}}{\bar{a}_c \bar{\alpha}} - \frac{b_i}{\bar{b}} \right] \cdot \ln(1 + B/Z) \quad (3-8a)$$

Equation (3-8a) is used to calculate K-values of components in a mixture:

$$K_i = \frac{\phi_i^L}{\phi_i^V} \quad (3-8b)$$

Development of $\Delta H^*/RT$ Equation

The expression for the residual enthalpy, which was to be used in the 'MPMCGC' program for prediction of enthalpy departures, was derived as follows:

Thermodynamic isothermal definition of enthalpy departure is given as:

$$\frac{H - H^0}{RT} = \frac{\Delta H^*}{RT} = 1 - Z + \frac{1}{RT} \int_{\infty}^V \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right] dv \quad (T \text{ const.}) \quad (3-9)$$

$$\text{or } \frac{\Delta H^*}{RT} = T \int_{\infty}^V \left(\frac{\partial Z}{\partial T} \right)_V \frac{dv}{v} - (Z - 1) \quad (T \text{ const.}) \quad (3-10)$$

Equation (3-9) is preferred here because it leads to easier and shorter calculations and reductions. An alternative derivation using equation (3-10) is shown in Appendix

Soave equation is given as:

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

$$a(T) = a_c \cdot \alpha(T) \quad (2-39)$$

$$\text{and } \alpha^{\frac{1}{2}} = \exp \left\{ m(1 - Tr^n) \right\} \quad (3-1)$$

Using the volume integral equation,

$$T \left(\frac{\partial P}{\partial T} \right)_V = \frac{RT}{V-b} - \frac{T}{V(V+b)} \cdot \frac{\partial a(T)}{\partial T}$$

$$\begin{aligned} \therefore P - T \left(\frac{\partial P}{\partial T} \right)_V &= \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} - \frac{RT}{V-b} + \frac{T}{V(V+b)} \cdot \frac{\partial a(T)}{\partial T} \\ &= \frac{1}{V(V+b)} \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \end{aligned}$$

$$\frac{1}{RT} \int_{\infty}^V \left[P - T \frac{\partial P}{\partial T} \right]_V dv = \frac{1}{RT} \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \cdot \int_{\infty}^V \frac{dv}{V(V+b)}; T \text{ const.}$$

$$\therefore \frac{\Delta H^*}{RT} = 1 - Z + \frac{1}{RT} \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \cdot \frac{1}{b} \cdot \ln \frac{V}{V+b} \Bigg|_{\infty}^V$$

$$= \int_{\infty}^V \frac{dv}{(V+b)^2 - b^2}$$

$$\lim_{V \rightarrow \infty} \ln \frac{V}{V+b} = \ln 1.0 = 0.0$$

$$\therefore \frac{\Delta H^*}{RT} = 1 - Z + \frac{1}{RTb} \ln \frac{V}{V+b} \cdot \left\{ T \cdot \frac{da(T)}{dT} - a(T) \right\} \quad (3-11)$$

$$\text{From equation (3-3), } b = \frac{BRT}{P}$$

$$\text{From equation (2-7), } V = \frac{ZRT}{P}$$

$$\text{Hence } \frac{V+b}{V} = \frac{ZRT/P + BRT/P}{ZRT/P}$$

$$= \frac{Z+B}{Z} = 1 + B/Z$$

$$\frac{1}{2b} \int_{\infty}^V \ln \frac{V+b \sqrt{1+b^2}}{V+b \sqrt{1-b^2}}$$

$$= \frac{1}{2b} \int_{\infty}^V \left(\ln \frac{V+b \sqrt{1+b^2}}{V+b \sqrt{1-b^2}} \right)$$

$$\lim_{V \rightarrow \infty} \ln \frac{V+b \sqrt{1+b^2}}{V+b \sqrt{1-b^2}} = \ln 1 = 0$$

$$\therefore \frac{\Delta H^*}{RT} = 1 - Z + \frac{a(T)}{RTb} \cdot \frac{1}{2b} \ln \left(\frac{V+b \sqrt{1+b^2}}{V+b \sqrt{1-b^2}} \right)$$

$$\ln \left(\frac{Z}{Z^0} \right) = \ln \left(\frac{2.2 \cdot 4.4^3}{2 \cdot 0.616} \right)$$

$$\therefore \frac{\Delta H'}{RT} = (1-Z) + \frac{1}{RTb} \ln (1+B/Z) \cdot \left\{ a(T) - T \cdot \frac{da(T)}{dT} \right\} \quad (3-12)$$

$$\text{Let } a(T) = a_c \alpha(T) \quad (2-37)$$

$$= a_c \cdot e^{2m(1-Tr^n)}$$

$$= a_c \cdot e^{2m} \cdot e^{-(2m/Tc^n) \cdot T^n}$$

$$\begin{aligned} \therefore \frac{\partial a(T)}{\partial T} &= a_c \cdot e^{2m} \cdot \frac{\partial}{\partial T} \left[e^{-(2m/Tc^n) \cdot T^n} \right] \\ &= a_c e^{2m} \cdot (-2m/Tc^n) \cdot e^{-(2m/Tc^n) \cdot T^n} \cdot nT^{n-1} \\ &= \frac{-2mna_c}{Tc} \cdot Tr^{n-1} \cdot e^{2m(1-Tr^n)} \end{aligned}$$

$$\frac{T \partial a(T)}{\partial T} = -2mnTr^n \cdot a_c \cdot \alpha(T)$$

$$\frac{\partial a(T)}{\partial T} = \frac{-2mnTr^{n-1}}{Tc} \cdot a(T) \quad (3-12)$$

This is the form for a_{ii} , hence for a pure substance, it becomes

$$\frac{\partial a(T)}{\partial T} = -2m_i n_i \frac{T_{ri}^{n_i-1}}{T_{ci}} a_i(T) = -2m_i n_i \frac{T_{ri}^{n_i-1}}{T_{ci}} a_{ci} \alpha_i(T)$$

Substituting (3-12) and (2-37) in (3-12):

$$\frac{\Delta H'}{RT} = (1-Z) + \frac{1}{RTb} \cdot \ln (1 + B/Z) \cdot \{ a(T) + 2mnTr^n a(T) \}$$

$$= (1-Z) + \frac{a(T)}{RTb} \cdot \ln(1 + B/Z) \cdot \{1 + 2mnTr^n\}$$

From equation (3-2), $a(T) = \frac{AR^2T^2}{P}$

From equation (3-3), $b = \frac{BRT}{P}$

hence $\frac{a(T)}{RTb} = \frac{AR^2T^2/P}{RT \cdot BRT/P}$

$$= A/B$$

$$\therefore \frac{\Delta H'}{RT} = (1-Z) + \frac{A}{B} \{1 + 2mnTr^n\} \cdot \ln(1 + B/Z) \quad (3-13)$$

Equation (3-13) could be used for calculation of enthalpy departure of a pure component.

For mixtures:

$$\bar{a} = \sum_i^n \sum_j^n x_i x_j a_{ij} ; \text{ where } a_{ij} = (1-k_{ij}) a_i^{1/2} a_j^{1/2}$$

Expanding for a binary,

$$\begin{aligned} \bar{a} &= x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \\ &= x_1^2 a_{11} + 2x_1 x_2 (1-k_{12}) a_{11}^{1/2} \cdot a_{22}^{1/2} + x_2^2 a_{22} \\ &= x_1^2 a_{c1} \alpha_1 + 2x_1 x_2 (1-k_{12}) a_{c1}^{1/2} \cdot a_{c2}^{1/2} \cdot \alpha_1^{1/2} \cdot \alpha_2^{1/2} + x_2^2 a_{c2} \cdot \alpha_2 \quad (3-14) \end{aligned}$$

Note that $a_{11} \equiv a_1$ and $a_{22} \equiv a_2$

$$\begin{aligned} \therefore \frac{\partial \bar{a}}{\partial T} &= x_1^2 a_{c_1} \frac{\partial \alpha_1}{\partial T} + 2x_1 x_2 a_{c_1}^{1/2} a_{c_2}^{1/2} (1-k_{12}) \cdot \frac{\partial}{\partial T} (\alpha_1^{1/2} \cdot \alpha_2^{1/2}) \\ &\quad + x_2^2 a_{c_2} \frac{\partial \alpha_2}{\partial T} \end{aligned} \quad (3-15)$$

From (3-12),

$$\frac{\partial a_i}{\partial T} = a_{c_i} \frac{\partial \alpha_i}{\partial T} = -\frac{2m_i n_i}{T_{c_i}} \cdot T_{r_i}^{n_i-1} \cdot a_{c_i} \alpha_i \quad (3-12)$$

$$\frac{\partial}{\partial T} (\alpha_1^{1/2} \cdot \alpha_2^{1/2}) = \alpha_2^{1/2} \cdot \frac{\partial \alpha_1^{1/2}}{\partial T} + \alpha_1^{1/2} \frac{\partial \alpha_2^{1/2}}{\partial T} \quad (3-17)$$

$$\text{Now } \alpha^{1/2} = e^{m(1-\text{Tr}^n)} = e^m \cdot e^{-(m/Tc^n)} \cdot T^n$$

$$\therefore \frac{\partial \alpha^{1/2}}{\partial T} = e^m \cdot (-m/Tc^n) \cdot e^{-(m/Tc^n)} \cdot T^n \cdot nT^{n-1}$$

$$\begin{aligned} \frac{\partial \alpha_i^{1/2}}{\partial T} &= -\frac{m_i n_i T_{r_i}^{n_i-1}}{T_{c_i}} \cdot e^{m_i(1-\text{Tri}^{n_i})} \\ &= -m_i n_i T_{r_i}^{n_i-1} \cdot \alpha_i^{1/2} \end{aligned} \quad (3-18)$$

Put (3-18), (3-17) and (3-13) in (3-15)

$$\begin{aligned} \frac{\partial \bar{a}}{\partial T} &= \frac{x_1^2 a_{c_1} \alpha_1}{T_{c_1}} \left(-2m_1 n_1 T_{r_1}^{n_1-1} \right) + \frac{x_2^2 a_{c_2} \alpha_2}{T_{c_2}} \left(-2m_2 n_2 T_{r_2}^{n_2-1} \right) \\ &\quad + 2x_1 x_2 a_{c_1}^{1/2} a_{c_2}^{1/2} (1-k_{12}) \left[\alpha_2^{1/2} \alpha_1 \frac{(-m_1 n_1 T_{r_1}^{n_1-1})}{T_{c_1}} \right. \\ &\quad \left. + \alpha_1^{1/2} \alpha_2 \frac{(-m_2 n_2 T_{r_2}^{n_2-1})}{T_{c_2}} \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{x_1^2 a_{c_1} \alpha_1}{Tc_1} (-2m_1 n_1 Tr_1^{n_1-1}) + 2 x_1 x_2 a_{c_1}^{1/2} a_{c_2}^{1/2} \alpha_1^{1/2} \alpha_2^{1/2} (1-k_{12}) \cdot \\
&\quad \left[\left(\frac{-m_1 n_1 Tr_1^{n_1-1}}{Tc_1} \right) + \left(\frac{-m_2 n_2 Tr_2^{n_2-1}}{Tc_2} \right) \right] \\
&+ \frac{x_2^2 a_{c_2} \alpha_2}{Tc_2} (-2m_2 n_2 Tr_2^{n_2-1}) \quad (3-18)
\end{aligned}$$

So in general, for a multicomponent mixture,

$$\begin{aligned}
\frac{\partial \bar{a}}{\partial T} &= \sum_i \sum_j x_i x_j a_{c_i}^{1/2} a_{c_j}^{1/2} \alpha_i^{1/2} \alpha_j^{1/2} (1-k_{ij}) \cdot \left\{ \frac{-m_i n_i Tr_i^{n_i-1}}{Tc_i} \right. \\
&\quad \left. - \frac{m_j n_j Tr_j^{n_j-1}}{Tc_j} \right\} \quad (3-19)
\end{aligned}$$

Check if (3-19) reduces to expression (3-12) for a pure component:

Expanding (3-10),

$$\begin{aligned}
\frac{\partial a_{11}}{\partial T} &= \cancel{x_1^2} a_{c_1}^{1/2} a_{c_1}^{1/2} \alpha_1^{1/2} \alpha_1^{1/2} (\cancel{1-k_{11}}) \cdot \left\{ \frac{-m_1 n_1 Tr_1^{n_1-1}}{Tc_1} - \frac{-m_1 n_1 Tr_1^{n_1-1}}{Tc_1} \right\} \\
&= \frac{-2m_1 n_1 Tr_1^{n_1-1}}{Tc_1} \cdot a_{c_1} \alpha_1 ; \text{ which is equation (3-12)}
\end{aligned}$$

So put (3-19) into equation 3-12:

$$\frac{\Delta H'}{RT} = (1 - Z) + \ln(1 + B/Z) \cdot \left\{ \frac{\bar{a}}{RT\bar{b}} - \frac{\partial a/\partial T}{Rb} \right\}$$

$$\frac{a}{RTb} = \frac{AR^2 T^2 / P}{RT BRT/P} = \frac{A}{B}$$

$$\therefore \frac{\Delta H'}{RT} = \left[\frac{A}{B} - \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j \gamma_{ij} (1-k_{ij})}{Rb} \right] \cdot \ln(1+B/Z) + (1-Z) \quad (3-20)$$

$$\text{where } \gamma_{ij} = a_{ci}^{1/2} \cdot a_{cj}^{1/2} \cdot \alpha_i^{1/2} \cdot \alpha_j^{1/2} \left\{ \frac{m_i n_i \text{Tr}_i^{n_i-1}}{Tc_i} + \frac{m_j n_j \text{Tr}_j^{n_j-1}}{Tc_j} \right\}$$

$$a_{ci}^{1/2} = \left(\frac{0.42747}{Pc_i} \right)^{1/2} \quad RTc_i = \frac{0.65381 RTc_i}{Pc_i^{0.5}}$$

$$\text{and } \alpha_i^{1/2} = e^{m_i (1 - \text{Tr}_i^{n_i-1})}$$

(3-20) is the required equation.

'MPMCGC' Program Modification

'MPMCGC' is a multiproperty and multicomponent fit program for the PFGC equation of state, about 4000 lines and consisting of 46 sub-programs. 'MPMCGC' is a very elaborate program and can be divided into five main functional parts: Input, Setting, Property Evaluation, Fitting, and Output. The Input program segments read in the data to be used in the program, while the Setting part is essentially a subroutine named 'SRKST' which transfers values from names used in the Input part into names that are used in the Property Evaluation and Fitting parts of the program. The Property Evaluation part of the program is comprised of a number of subprograms dealing with solution of the cubic equation of state in terms of compressibility factor Z; equilibrium calculations;

calculation of several thermodynamic properties and comparing calculated with experimental values. The Fitting part consists of several subprograms that handle the non-linear fitting process in the program; while the Output program segments at different points in the program write out both the input and computed results.

During the modification, the fitting, input and output parts remained unchanged. The setting part was slightly changed, while all the subprograms in the Property Evaluation part were completely changed, in order that the program could handle the SRK rather than PFGC equation of state.

Details of this 'MPMCGC' program can be found in Erbar (20).

Fitting the Pure Component Parameters and Prediction of Pure Component Vapor Pressures

Having modified the program 'MPMCGC' to handle the SRK equation of state with the new α expression, pure component vapor pressure and occasionally volumetric data were obtained. The complete set of pure component data used in the program included: critical temperature and pressure, acentric factor, and vapor pressures over a temperature range from the triple to the critical point. For some pure substances, volumetric data had to be supplied as well, at low pressures, in order to get the program to work. ESDU (91) vapor pressure data were used for paraffins ranging from C_1 to C_8 ; all the alkenes, and all the aromatics. Revised API-44 (95) vapor pressure data were used for the rest of the paraffins ranging from C_9 to C_{20} . The Steam Tables (92) was used for water, while the rest of the sources of vapor pressure data used for CO_2 , H_2S and N_2 are shown in Table IV.

Values of the fitted parameters m and n in equation (3-1) were obtained by fitting the SRK equation of state with the new α model, using non-linear regressions analysis. Summary of the results obtained from the program were final values of m and n , total number of points fitted, average percent deviation between experimental and predicted vapor pressures for a complete data set. The program each time selected the set of m and n that minimized this deviation. Also, for each point in the fit, the modified 'MEMCGC' gave experimental, predicted and percent deviation between experimental and predicted values for vapor pressures.

Very good estimates of m and n were required to obtain an optimal set of values. The criteria used to obtain the best set of fitted values for m and n was that the average deviation between the experimental and predicted vapor pressures for a complete set of data points must be less than or equal to one percent.

Correlation of Pure Component Parameters as Functions of Acentric Factor, ω

For applicaiton of correlation to components for which data are not available, the parameters m and n had to be correlated as functions of acentric factor, ω . First, m and n and different combination of m and n were plotted against ω , using the SAS PLOT program, in order to find out which plots best matched various algebraic functions. Figures 1 and 2 show the plots that were finally chosen.

m and n were fitted to the functions:

$$m = A + B\omega \quad (3-21)$$

$$n = \frac{1}{m} (A + B\omega) \quad (3-22)$$

The constants A and B in each equation were obtained using Chandler's (10) modified version of Marquardt's non-linear least squares fit program.

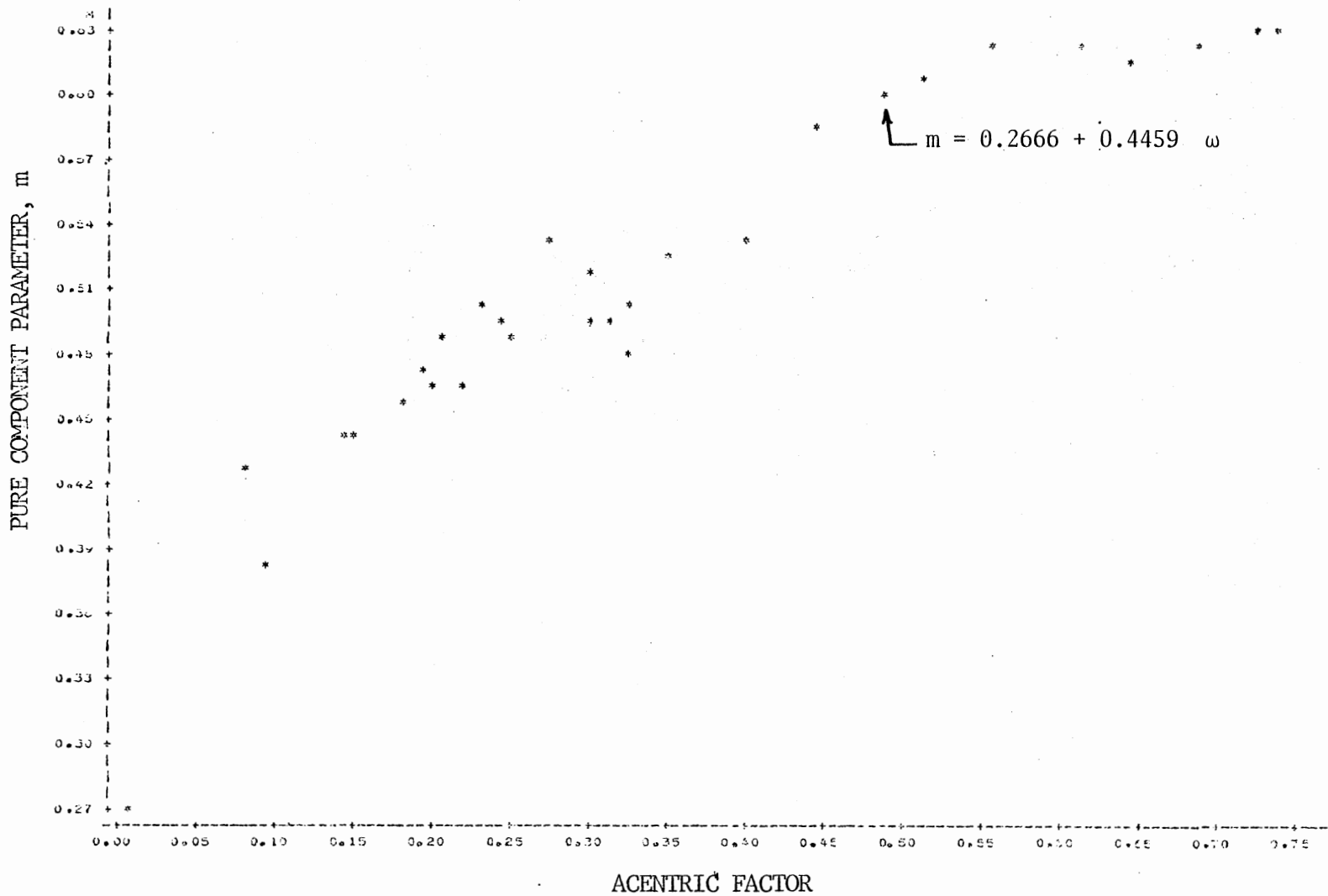


Figure 1. Plot of Pure Component Parameter m Versus Acentric Factor

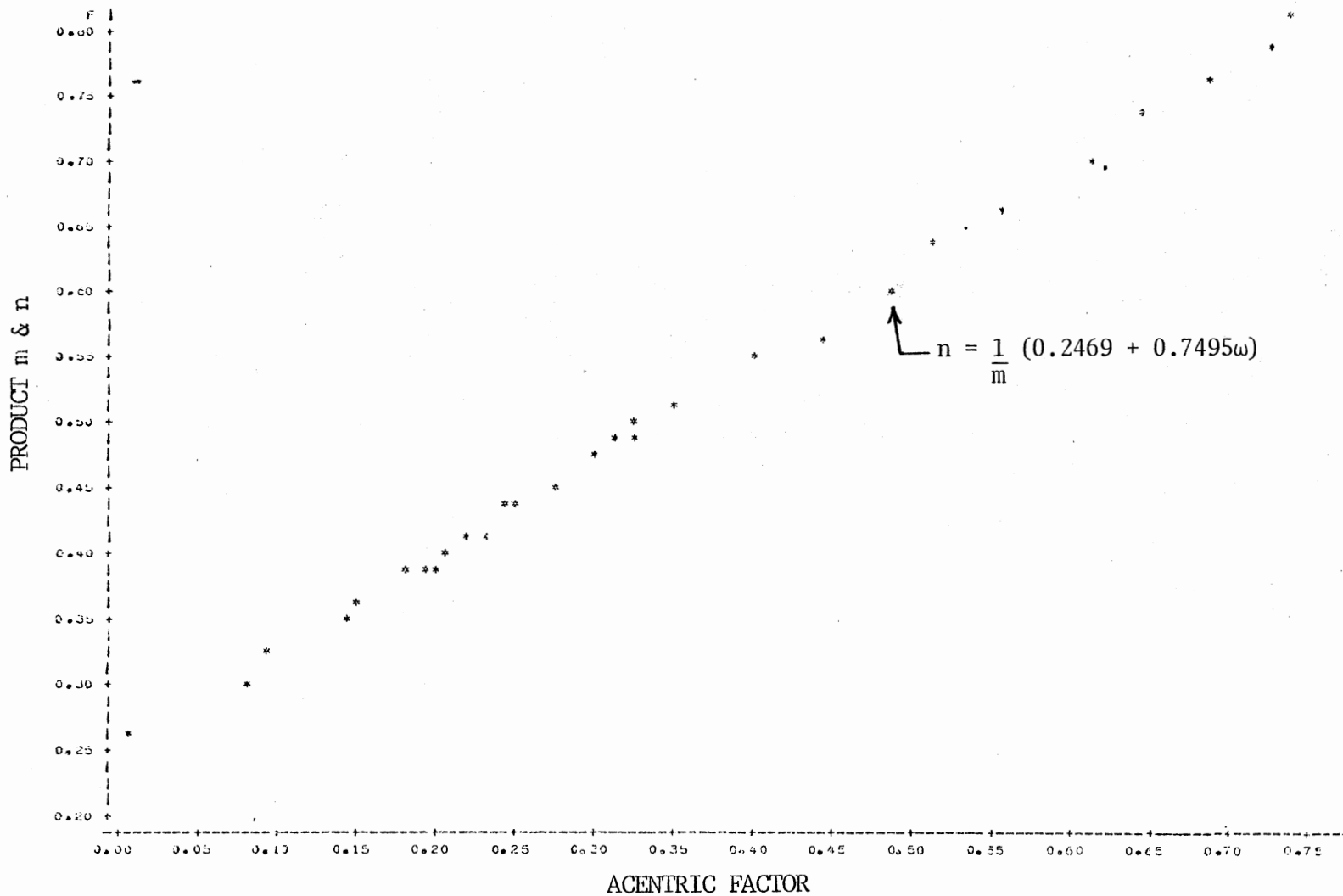


Figure 2. Plot of Product of Pure Component Parameters m and n Versus Acentric Factor ω

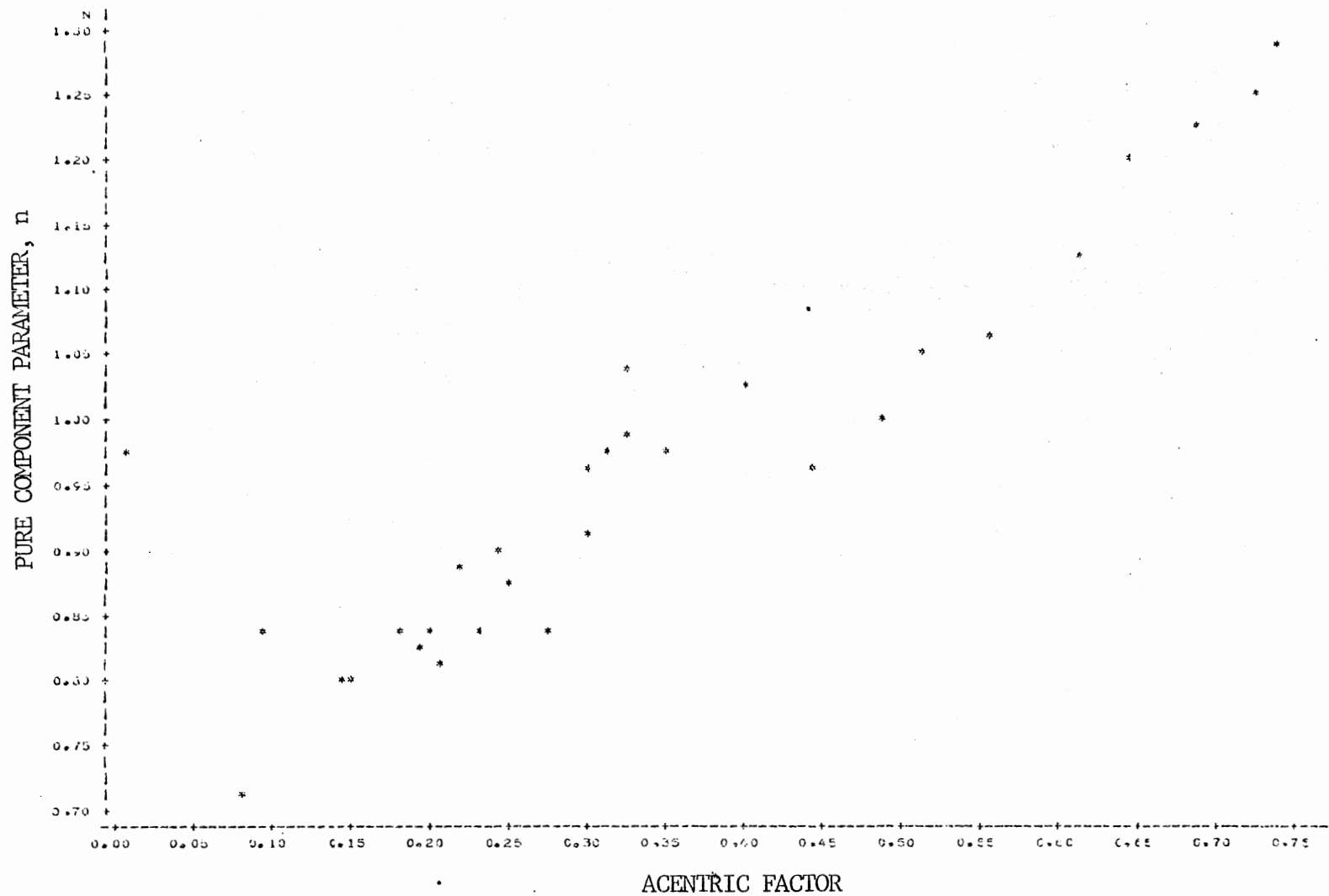


Figure 3. Plot of Pure Component Parameter n Versus Acentric Factor

Fitting the Binary Mixture Interaction

Coefficients, k_{ij} and Prediction of K-Values

Large numbers of experimental binary vapor-liquid equilibrium data were used to determine the interaction coefficients k_{ij} in equation (2-64). The value of the optimal k_{ij} obtained for each binary was the one that gave the minimum deviation between the predicted and experimental K-values. Most K-values were predicted via flash calculations. For cases where errors in calculating fraction of liquid in the feed, L/F , were high or flash calculations were unstable, the bubble point temperature calculation method was used. The sources of all the data used are listed in the tabulation of results in the next chapter.

Enthalpy Departure Prediction

Program inputs for this phase of the work were the fitted pure component parameters, fitted binary mixture k_{ij} s; temperature, pressure, composition, experimental enthalpy departures, BTU/lb-mole, and the option to calculate vapor or liquid enthalpy. Results obtained were total number of points, total points for vapor and liquid enthalpy calculations respectively, average deviations between experimental and predicted enthalpy departures in BTU/lb-mole for vapor phase, liquid phase, and for the entire set of points. Predicted enthalpy departures and deviations were also given for each point. Only the evaluation part of the program was used, since all the fitting required had been done.

CHAPTER IV

RESULTS

A new model was proposed for the α term in the SRK equation of state:

$$\alpha_i^{1/2} = \exp \left\{ m_i (1 - Tr_i^{n_i}) \right\} \quad (3-1)$$

where m_i and n_i are empirical constants to be determined for each pure component. Values of m and n determined for 37 pure compounds are presented in Tables I through IV. Values of m and n obtained are shown in Table I for paraffins ranging from C_1 to C_{20} , Table II for alkenes ranging from ethene to hex-1-ene, Table III for aromatics ranging from benzene to para-xylene, and Table IV for non-hydrocarbons CO_2 , N_2 , H_2S and water. Each of the tables, I through IV, also show the average percent deviation between predicted and experimental vapor pressures, the temperature and pressure ranges and number of points used in the fit. The regression equations obtained for m and n are:

$$m_i = 0.266 \text{ to } 0.4459 \sqrt{\omega_i} \quad (4-1)$$

$$n_i = \frac{1}{m_i} (0.2469 + 0.7495 \omega_i) \quad (4-2)$$

Tables V to X show the fitted values of binary interaction coefficients, k_{ij} s, obtained for CO_2 , N_2 , H_2S , C_1 , C_2 , C_3 and the other higher carbon number binary systems considered in this work, using values of m and n

obtained earlier and the proposed α model. Each table also gives the average percent deviations between predicted and experimental K-values and the number of points used in the fitting process; as well as the temperature and pressure ranges.

Tables XI and XII show the average percent deviations in calculation of pure and mixture enthalpies, using the new modified SRK equation of state. For each system considered, the average deviation in BTU per lb. is given for the vapor phase, the liquid phase and for the two phases combined. Results for each system are also directly compared with those obtained by Lee and Kessler using modified BWR equation of state.

TABLE I

PURE COMPONENT PARAMETERS AND DEVIATIONS IN VAPOR PRESSURE
PREDICTIONS FOR PARAFFIN HYDROCARBONS

COMPOUND NAME	T.P. °F	T _C °F	P _C PSIA	TEMP. RANGE °F	PRES. RANGE PSIA	ABS. AVG ERROR IN VAP. PRES.	No. OF POINTS	m	n
(DATA SOURCE)		(T _C °R)		(T _T RANGE)	(P _T RANGE)				
1 METHANE (ESDU)	-296.464	-116.7159 (342.9541°R)	666.5675	-279.4+117.4 (0.473+0.998)	1.56+655.429 (0.002+0.983)	0.62	21	0.275	0.9721
2 ETHANE (ESDU)	-297.868	90.0861 (549.7561°R)	707.7859	-234.4+89.6 (0.410+0.999)	0.101+701.263 (0.0001+0.991)	0.91	37	0.3842	0.8330
3 PROPANE (ESDU)	-305.878	206.3361 (666.0061°R)	616.51	-180.4+197.6 (0.419+0.987)	0.072+565.848 (0.0001+0.918)	0.97	43	0.4425	0.8058
4 N-BUTANE (ESDU)	-216.67	305.9841 (765.6541°R)	550.9561	-117.4+305.6 (0.447+1.0)	0.121+549.072 (0.0002+0.997)	0.94	47	0.4672	0.8410
5 ISO-BUTANE (ESDU)	-256.27	274.9821 (734.6521°R)	529.2971	-135.4+269.6 (0.441+0.993)	0.108+502.541 (0.0002+0.949)	0.98	46	0.4559	0.8395
6 N-PENTANE (ESDU)	-202.27	386.1921 (845.8621°R)	488.9099	-99.4+377.6 (0.426+0.990)	0.029+455.198 (0.00006+0.931)	0.91	54	0.4910	0.8788
7 ISO-PENTANE (ESDU)	-256.27	369.1039 (828.7739°R)	490.8252	-72.4+368.6 (0.467+0.999)	0.178+487.417 (0.0004+0.993)	1.0	50	0.4682	0.8931

TABLE I (Continued)

COMPOUND NAME (DATA SOURCE)	T.P. °F	T _c °F (T _c °R)	P _c PSIA	TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	ABS. AVG ERROR IN VAP. PRES.	No. OF POINTS	m	n
8 N-HEXANE (ESDU)	-139.27	454.55 (914.22°R)	439.8975	8.6-449.6 (0.512-0.995)	0.145-421.718 (0.0003-0.959)	0.98	50	0.4942	0.9573
9 N-HEPTANE (ESDU)	-132.07	512.5099 (972.1799°R)	396.8799	35.6-512.6 (0.509-1.0)	0.247-396.111 (0.0006-0.998)	0.99	54	0.5252	0.9689
10 N-OCTANE (ESDU)	-70.87	564.1879 (1023.8579°R)	360.9524	89.6-557.6 (0.537-0.994)	0.393-342.07 (0.001-0.948)	1.0	53	0.5339	1.0234
11 N-NOVANE (API-44)		610.43 (1.070.21°R)	331.8	100-360 (0.523-0.766)	0.180-31.52 (0.0005-0.095)	0.62	53	0.5874	0.9664
12 N-DECANE (API-44)		651.83 (1111.5°R)	305.0	135-405 (0.535-0.778)	0.189-31.81 (0.0006-0.104)	0.59	55	0.5992	1.003
13 N-C ₁₁ H ₂₄ (API-44)		690.04 (1149.171°R)	285.0	165-445 (0.543-0.787)	0.181-31.3 (0.0006-0.110)	0.71	57	0.6069	1.0464
14 N-C ₁₂ H ₂₆ (API-44)		725.13 (1184.8°R)	264.0	195-485 (0.553-0.797)	0.185-31.83 (0.0007-0.121)	0.65	59	0.6223	1.0623

TABLE I (Continued)

COMPOUND NAME (DATA SOURCE)	T.P. °F	T _c °F (T _c °R)	P _c PSIA	TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	ABS. AVG ERROR IN VAP. PRES.	No. OF POINTS	m	n
15 N-C ₁₃ H ₂₈ (API-44)		756.73 (1216.3999°R)	250.0	225+520 (0.563+0.805)	0.194+31.4 (0.0008+0.126)	0.80	60	0.6206	1.1269
16 N-C ₁₄ H ₃₀ (API-44)		785.53 (1245.2°R)	235.0	250+555 (0.570+0.815)	0.187+31.7 (0.0008+0.135)	0.97	62	0.6157	1.1941
17 N-C ₁₅ H ₃₂ (API-44)		812.53 (1272.2°R)	220.00	280+585 (0.581+0.821)	0.212+30.9 (0.001+0.140)	0.97	62	0.6209	1.2306
18 N-C ₁₆ H ₃₄ (API-44)		837.43 (1297.1001°R)	206.0	305+615 (0.509+0.829)	0.216+30.8 (0.001+0.150)	0.97	63	0.6323	1.2491
19 N-C ₁₇ H ₃₆ (API-44)		860.43 (1320.1°R)	191.0	330+645 (0.598+0.837)	0.237+31.1 (0.001+0.163)	1.0	64	0.6317	1.2817
20 N-C ₁₈ H ₃₈ (API-44)		881.8 (1341.4°R)	176.0	340+690 (0.596+0.842)	0.184+30.4 (0.001+0.173)	0.93	64	0.6576	1.2429
21 N-C ₁₉ H ₄₀ (API-44)		901.0 (1361.0°R)	162.0	360+690 (0.602+0.845)	0.181+28.4 (0.001+0.178)	0.68	66	1.1557	
22 N-C ₂₀ H ₄₂ (API-44)		921.0 (1381.0°R)	162.0	385+715 (0.612+0.851)	0.176+29.2 (0.001+0.180)	0.60	67	0.7186	1.2222

TABLE II

PURE COMPONENT PARAMETERS AND DEVIATIONS IN VAPOR PRESSURE
PREDICTIONS FOR UNSATURATED HYDROCARBONS

COMPOUND NAME	T.P. °F	T _c °F	P _c PSIA	TEMP. RANGE °F	PRES. RANGE PSIA	ABS. AVG ERROR IN	No. OF POINTS	m	n
(DATA SOURCE)		(T _c °R)		(T _r RANGE)	(P _r RANGE)	VAP. PRES.			
23 ETHENE (ESDU)	-272.524	48.92 (508.5901°R)	732.6399	-261.4+44.6 (0.390+0.992)	0.048+692.216 (0.00007+0.945)	0.95	34	0.4276	0.7079
24 PROPENE (ESDU)	-301.45	197.06 (656.73°R)	667.1741	-171.4+188.6 (0.439+0.987)	0.176+611.842 (0.0003+0.917)	0.94	41	0.4394	0.7983
25 BUT-1-ENE (ESDU)	-301.63	295.556 (755.226°R)	583.3206	-117.4+287.6 (0.453+0.99)	0.168+541.416 (0.0003+0.928)	0.99	46	0.4698	0.8236
26 PENT-1-ENE (ESDU)	-265.27	376.934 (836.604°R)	511.386	-108.4+368.6 (0.420+0.990)	0.027+476.717 (0.00005+0.932)	0.91	54	0.4988	0.8329
27 HEX-1-ENE (ESDU)	-220.27	447.5839 (907.2539°R)	451.7041	-72.4+440.6 (0.427+0.992)	0.020+426.619 (0.00004+0.945)	0.99	58	0.5342	0.8362

TABLE III

PURE COMPONENT PARAMETERS AND DEVIATIONS IN VAPOR PRESSURE
PREDICTIONS FOR AROMATIC HYDROCARBONS

COMPOUND NAME	T.P. °F	T _c °F	P _c PSIA	TEMP. RANGE °F	PRES. RANGE PSIA	ABS. AVG ERROR IN	No. OF POINTS	m	n
(DATA SOURCE)		(T _c °R)		(T _r RANGE)	(P _r RANGE)	VAP. PRES.			
28 BENZENE (ESDU)	41.954	552.2179 (1011.8879°R)	710.571	44.6-584.6 (0.498-0.996)	0.744-691.592 (0.001-0.973)	0.91	57	0.4906	0.8170
29 TOLUENE (ESDU)	-138.946	609.53 (1069.2°R)	590.0073	53.6-602.6 (0.48-0.994)	0.269-582.364 (0.00005-0.987)	1.0	62	0.4930	0.8988
30 ETHYL-BZ (ESDU)	-138.964	651.29 (1110.96°R)	522.3528	80.6-647.6 (0.486-0.997)	0.206-508.53 (0.0004-0.974)	1.0	64	0.5186	0.9069
31 O-XYLENE (ESDU)	-13.27	674.924 (1134.594°R)	541.1731	98.6-674.6 (0.492-0.9997)	0.252-538.805 (0.0005-0.996)	0.99	65	0.4949	0.9750
32 M-XYLENE (ESDU)	-54.67	651.0199 (1110.6899°R)	512.9141	80.6-647.6 (0.486-0.997)	0.179-500.119 (0.0004-0.975)	1.0	64	0.4991	0.9838
33 P-XYLENE (ESDU)	55	649.5441 (1109.2141°R)	509.3159	107.6-647.6 (0.511-0.998)	0.423-501.555 (0.0008-0.985)	0.98	61	0.4790	1.0333

TABLE IV
PURE COMPONENT PARAMETERS AND DEVIATIONS IN VAPOR PRESSURE
PREDICTIONS FOR NON-HYDROCARBONS

COMPOUND NAME (DATA SOURCE)	T.P. °F	T _c °F (T _c °R)	P _c PSIA	TEMP. RANGE °F (T _r RANGE)	PRES. RANGE PSIA (P _r RANGE)	ABS. AVG ERROR IN VAP. PRES.	No. OF POINTS	m	n
34 WATER (STEAM TABLES)	31.73	705.34 (1165.01°R)	3206.2	78-705.34 (0.462-1.0)	0.474-3206.2 (0.0002-1.0)	0.98	169	0.4501	1.1484
35 H ₂ S LANDOLT BORNSTEIN	-121.954	212.702 (672.1021°R)	1306.83	-121.954-212.702 (0.503-1.0)	3.292-1306.83 (0.0025-1.0)	0.83	38	0.3763	0.8665
36 CO ₂ (a) LANDOLT BORNSTEIN	-69.88	87.602 (547.272°R)	1070.895	-69.88-87.872 (0.712-1.0)	75.146-1070.895 (0.07-1.0)	0.64	20	0.5080	0.8038
36 CO ₂ (b) GULF PUB. CO. ASHRE	-69.9	87.93 (547.6°R)	1070.0	-69.9-87.8 (0.712-1.0)	75.1-1072.4 (0.07-1.0)	0.47	47	0.5060	0.8055
36 CO ₂ (c) GANJAR & MANNING	-69.9	87.93 (547.6°R)	1070.0	-69.9-87.0 (0.712-1.0)	75.146-1070.0 (0.07-1.0)	0.53	33	0.5077	0.8055
* 36 CO ₂ (d) NBS CIRC #564	-69.9	87.93 (547.6°R)	1070.0	-70.87-87.5 (0.71-0.999)	73.33-1066.25 (0.0685-0.9965)	0.26	89	0.4247	0.9828

* Used for parameter correlation

TABLE IV (Continued)

COMPOUND NAME	T.P. °F	T _c °F	P _c PSIA	TEMP. RANGE °F	PRES. RANGE PSIA	ABS. AVG ERROR IN	No. OF POINTS	m	n
(DATA SOURCE)		(T _c °R)		(T _r RANGE)	(P _r RANGE)	VAP. PRES.			
37 N ₂ (a) LANDBOLT BORNSTEIN	-345.982	-232.618 (227.052°R)	492.2954	-345.982+-232.618	2.1083+492.295 (0.5007-1.0) (0.004+1.0)	0.37	35	0.3168	0.8776
37 N ₂ (b) NBS CIRC #564	-345.989	-237.627 (227.043°R)	492.2	-347.17+-228.9	1.611+544.488 (0.496+1.016) (0.003+1.106)	0.38	41	0.3160	0.8804
* 37 N ₂ (c) NBS TECH. NOTE 129A	-345.989	-232.627 (227.043°R)	492.2	-346.0+-233.67	1.813+477.104 (0.5007+0.9954)(0.0037+0.9693)	0.51	58	0.3159	0.8787

* Used for parameter correlation.

TABLE V

CO₂ BINARY SYSTEM INTERACTION PARAMETERS AND DEVIATIONS
IN K-VALUE PREDICTIONS

SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k _{ij}	% ABS AVG ERRORS IN		
					K _{CO₂}	K _{2nd comp}	L/F or BUBBL'.
1 CO ₂ (2) - CH ₄ (1) (18, 17, 30)	26.33→50.00	515.683→1187.44	19	0.108295	1.27	4.47	5.21
	-9.67→8.00	293.92 →1175.68	21	0.091536	2.45	3.79	5.72
	-57.0→25.0	220.44 →1098.0	31	0.091238	5.06	4.63	2.89
	-100.0→65.0	651.0 →932.0	8	0.097174	10.36	3.52	8.69
	* -100.0→65.0	220.44 →1175.68	79	0.09255	4.21	5.03	4.89
2 CO ₂ (2) - C ₂ H ₆ (1) (23, 61, 74, 17, 38)	20.0 →68.0	355.5 →827.4	22	0.141282	3.04	1.62	24.40
	-20.0→14.0	209.18 →419.84	30	0.137269	3.59	3.29	20.6
	-60.0→-22.0	90.49 →237.54	18	0.135358	4.23	4.65	11.55
	* -60.0→68.0	90.49 →827.5	64	0.137929	3.20	3.45	15.91
3 CO ₂ (1) - C ₃ H ₈ (2) (46, 39, 38)	75 →160	200.0 →1002.5	43	0.144669	3.86	3.15	8.17
	32 →70	80.79 →800.0	30	0.128657	3.93	3.21	8.09
	-20 →20	66.1 →379.0	30	0.121933	5.08	3.35	7.47
	* -20 →160	66.1 →1002.5	103	0.133711	4.51	3.48	9.60

* All Points Together

TABLE V (Continued)

SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
					K_{CO_2}	$K_{2^{nd} \text{ comp}}$	L/F or BUBBL.
4 CO ₂ (1)-N-C ₄ H ₁₀ (2) (63, 43, 38)	160 → 280	150 → 1184.	41	0.157221	4.15	0.93	5.25
	50 → 150	51.9 → 1095.0	41	0.124212	4.59	3.56	4.65
	1.1 → 32.0	35.26 → 462.74	18	0.119923	3.74	8.76	2.73
	* 1.1 → 280.0	35.26 → 1184.0	100	0.136974	5.08	3.98	6.34
5 CO ₂ (1)-I-C ₄ H ₁₀ (2) (57, 38)	32 → 220	39.69 → 956.0	31	0.125262	5.05	4.58	5.19
6 CO ₂ (1)-N-C ₅ H ₁₂ (2) (58)	40.1 → 220.0	60.0 → 13.97.0	39	0.124252	5.06	5.49	3.34
7 CO ₂ (1)-I-C ₅ H ₁₂ (2) (60)	40.0 → 220.0	22.0 → 1290.0	33	0.126900	4.46	4.06	3.40
8 CO ₂ (1)-N-C ₆ H ₁₄ (2) (65)	104.0 → 248.0	1130 → 1593.0	35	0.127699	3.63	4.70	2.90

TABLE V (Continued)

	SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
						K_{CO_2}	K_{2nd} comp	L/F or BUBBL'PT.
9	CO ₂ (1)-N-C ₇ H ₁₆ (2) (63)	99.5 → 399.3	27 → 1746	47	0.133650	6.09	8.08	7.52
10	CO ₂ (1)-N-C ₁₀ H ₂₂ (2) (53, 76)	40.0 → 460.0	100 → 2000	52	0.119541	3.86	8.92	2.91
11	CO ₂ (1)-N-C ₁₆ H ₃₄ (2) (76)	373.82 → 735.08	291.06 → 737.94	13	0.140023	9.33	8.41	1.92
12	CO ₂ (1)-Toluene(2) (62)	100.6 → 399.0	54.6 → 2004.0	21	0.097340	4.93	8.99	4.98
13	CO ₂ (2)-C ₂ H ₄ (1) (38)	-42.88 → -.436	151.4 → 372.645	14	0.052550	0.81	1.47	0.10 **
14	CO ₂ (1)-C ₃ H ₆ (2) (38)	-4.36 → +32.0	116 → 485.1	16	0.096518	3.51	3.76	8.35

* All Points Together

** Percent Absolute Average Error in Bubble Point Temperature

TABLE V (Continued)

SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
					K_{CO_2}	$K_{2^{nd} \text{ comp}}$	L/F or BUBPT.
15 CO ₂ (1)-C ₄ H ₈ (2) (38)	32	45.57 → 463.05	8	0.068143	3.99	10.24	2.91
16 CO ₂ (2)-N ₂ (1) (31)	26.6	496.86 → 1603.476	24	0.000024	1.8	6.04	3.61
17 CO (2)-H ₂ S(1) (7)	3.2 → 176.0	294 → 1176	25	0.121827	3.43	1.22	0.26 **

** Percent Absolute Average Error in Bubble Point Temperature

TABLE VI
 N_2 BINARY SYSTEM INTERACTION PARAMETERS AND
 DEVIATIONS IN K-VALUE PREDICTIONS

	SYSTEM (REFERENCES)	TEMPERATURE RANGE ($^{\circ}$ F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN			
						K_{N_2}	$K_{2^{nd}}$ comp	L/F or BUBPT.	
1	$N_2(1)-H_2S(2)$ (MM)	-99 → -49	70 → 1993	12	0.162460	8.31	8.52	0.37	
2	$N_2(2)-CH_4(1)$ (81, 16)	-280 → -130	50 → 730	159	0.046562	5.48	2.57	9.87	
3	$N_2(1)-C_2H_4(2)$ (22)	-99 → 8.6	223.6 → 1028.85	8	0.079515	4.94	1.95	3.78	
4	$N_2(1)-C_2H_6(2)$ (82, 22)	-110 → +62.31	51 → 1283	37	0.038470	3.94	3.91	4.73	
5	$N_2(1)-I-C_4H_{10}(2)$ (55, 88)	50.1 → 240	82 → 1511	41	0.098963	7.03	4.10	1.86	
6	$N_2(1)-N-C_5H_{12}(2)$ (56)	40 → 220	36.3 → 2645	34	0.075677	4.72	5.45	1.77	
7	$N_2(1)-N-C_7H_{16}(2)$ (3, 8, 89)	90 → 435	1020 → 12,150	56	0.121826	5.84	26.69	3.51	
8	$N_2(1)-N-C_{10}H_{22}(2)$ (5)	100 → 280	100 → 4750	76	0.098535	4.58	10.16	1.53	

TABLE VII

H₂S BINARY SYSTEM INTERACTION PARAMETERS AND
DEVIATIONS IN K-VALUE PREDICTIONS

	SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k _{ij}	% ABS AVG ERRORS IN		
						K _{H₂S}	K _{2nd comp}	L/F or BUBPT.
1	H ₂ S(1)-CO ₂ (2) (mm)	3.2 → 176	294 → 1176	25	0.121827	1.22	3.43	0.26 *
2	H ₂ S(1)-C ₂ H ₆ (2) (55)	-99.8 → +50	31.6 → 442.7	25	0.094 046	5.44	3.93	49.93
3	H ₂ S(1)-C ₃ H ₆ (2) (107)	-22 → +59	44 → 239.6	12	0.036759	4.28	3.65	0.59 *
4	H ₂ S(1)-C ₃ H ₈ (2) (24)	-22 → 188	50 → 599	36	0.076951	3.02	3.67	0.89 *
5	H ₂ S(1)-N-C ₄ H ₁₀ (2) (mm)	100 → 250	69 → 1080	57	0.051550	3.31	5.51	0.50 *
6	H ₂ S(1)-I-C ₄ H ₁₀ (2) (59)	40 → 220	30 → 872	24	0.049 992	6.44	5.88	8.10
7	H ₂ S(1)-N-C ₅ H ₁₂ (2) (47)	100 → 340	100 → 1100	35	0.049 531	6.22	7.51	13.09
8	H ₂ S(1)-N-C ₇ H ₁₆ (2) (64)	100 → 400	23 → 1093	23	0.076 592	5.44	7.80	4.82
9	H ₂ S(1)-N-C ₁₀ H ₂₂ (2) (48)	100 → 340	100 → 1000	20	0.042 598	1.70	13.99	1.79

TABLE VII (Continued)

SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
					K_{H_2S}	$K_{2nd\ comp}$	L/F or BUBPT.
10 H ₂ S(1)- Toluene (64)	175 → 400	200 → 1679	12	0.007305	3.89	6.24	11.45

* Percent Absolute Average Error in Bubble Point Temperature

TABLE VIII

C₁ BINARY SYSTEM INTERACTION PARAMETERS AND
DEVIATIONS IN K-VALUE PREDICTIONS

	SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k _{ij}	% ABS AVG ERRORS IN		
						K _{C1}	K _{2nd comp}	L/F or BUBPT.
1	CH ₄ (1)-CO ₂ (2) (18, 17, 30)	-100.0 → +50.0	220.44 → 1175.68	79	0.092550	5.03	4.21	4.89
2	CH ₄ (1)-N ₂ (2) (81, 16)	-280 → -130	50 → 730	150	0.046562	2.57	5.48	9.87
3	CH ₄ (1)-H ₂ S(2) (33)	-100 → +160	400 → 1600	39	0.073000	5.56	5.98	1.47*
4	CH ₄ (1)-C ₂ H ₆ (2) (MM)	-225 → -99	25 → 740	80	0.004508	3.28	5.85	4.74
5	CH ₄ (1)-C ₃ H ₈ (2) (44, 2)	-109 → +190	100 → 1450	211	0.000053	4.09	4.18	6.16
6	CH ₄ (1)-N-C ₄ H ₁₀ (2) (67, 54, 28, 19)	-140 → +280	20 → 1652	206	0.000068	4.31	4.37	5.65
7	CH ₄ (1)-I-C ₄ H ₁₀ (2) (70)	100 → 220	80 → 1300	38	0.000076	4.67	2.47	5.79
8	CH ₄ (1)-N-C ₅ H ₁₂ (2) (69)	100 → 340	20 → 2455	52	0.000000	2.65	4.62	4.93

TABLE VIII (Continued)

	SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k _{ij}	% ABS AVG ERRORS IN		
						K _{c1}	K _{2nd comp}	L/F or BUBPT.
9	CH ₄ (1)-I-C ₅ H ₁₂ (2) (73)	160 → 340	500 → 1000	11	0.000003	8.02	4.43	7.95
10	CH ₄ (1)-N-C ₆ H ₁₄ (2) (77)	77 → 302	147 → 1470	41	0.009674	2.09	9.38	1.86
11	CH ₄ (1)-N-C ₇ H ₁₆ (2) (49)	40 → 460	200 → 2500	82	0.004911	2.76	5.90	3.18
12	CH ₄ (1)-N-C ₈ H ₁₈ (2) (32)	-58 → 302	147 → 3966	45	0.011940	4.73	11.10	0.43
13	CH ₄ (1)-N-C ₁₀ H ₂₂ (2) (42)	100 → 460	20 → 4750	134	0.024672	3.79	5.83	1.48
14	C-H ₄ (1)-Toluene(2) (35)	0.0 → 40	50 → 2000	24	0.021237	13.74	6.04	4.65

TABLE IX

C₂ BINARY SYSTEM INTERACTION PARAMETERS AND
DEVIATIONS IN K-VALUE PREDICTIONS

SYSTEM (REFERENCES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k _{ij}	% ABS AVG ERRORS IN			
					K _{C₂}	K _{2nd comp}	L/F or BUBPT.	
1 C ₂ H ₄ (1)-CO ₂ (2) (38)	-42.88 → -4.36	151.4 → 372.65	14	0.052550	1.47	0.81	0.10**	
2 C ₂ H ₄ (1)-C ₂ H ₆ (2) (21)	-155 → +60	7 → 714	28	0.009950	5.26	7.47	0.33**	
3 C ₂ H ₆ (1)-C ₃ H ₆ (2) (73)	100 → 150	250 → 705	11	0.000074	2.99	5.62	1.27**	
4 C ₂ H ₆ (1)-C ₃ H ₈ (2) (36)	0.0 → 200	50 → 750	53	0.005000	2.76	3.11	16.11	
5 C ₂ H ₆ (1)-N-C ₄ H ₁₀ (2) (MM)	0.0 → 250	100 → 600	19	0.005096	2.08	3.34	2.76	
6 C ₂ H ₆ (1)-I-C ₄ H ₁₀ (2) (MM)	100 → 219	207 → 779	27	0.005074	4.11	5.04	0.93**	
7 C ₂ H ₆ (1)-N-C ₅ H ₁₂ (2) (50)	40 → 340	50 → 900	52	0.013118	3.63	4.32	5.22	
8 C ₂ H ₆ (1)-N-C ₆ H ₁₄ (2) (MM)	150 → 250	200 → 800	12	0.007086	5.80	6.75	6.29	
9 C ₂ H ₆ (1)-N-C ₇ H ₁₆ (2) (MM)	40 → 450	100 → 800	19	0.004348	4.04	4.36	2.68	
10 C ₂ H ₆ (1)-N-C ₁₀ H ₂₂ (2) (51)	100 → 460	100 → 1640	43	0.019800	3.29	6.26	2.77	

** Percent Absolute Average Error in Bubble Point Temperature

TABLE X
 C_3^+ BINARY SYSTEM INTERACTION PARAMETERS AND
 DEVIATIONS IN K-VALUE PREDICTIONS

SYSTEM REFERENCES	TEMPERATURE RANGE ($^{\circ}F$)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
					K_1	K_2	L/F or BUBPT
1 $C_3H_6(1)-C_3H_8(2)$ (45)	100 → 190	197 → 603.5	13	0.000 002	7.85	8.14	0.87***
2 $C_3H_6(1)-C_4H_8(2)$ (72)	40 → 160	30 → 400	26	0.002 447	0.97	2.61	0.12***
3 $C_3H_8(1)-I-C_5H_{12}(2)$ (84)	32 → 356	14.7 → 632	73	0.010 323	5.12	5.42	17.57
4 $C_3H_8(1)-N-C_{10}H_{22}(2)$ (MM)	150 → 460	50 → 800	42	0.008 688	3.49	3.89	3.80
5 $C_3H_8(1)-BZ(2)$ (66)	100 → 400	40 → 867	64	0.015 991	2.56	3.10	5.77
6 $N-C_4H_{10}(1)-I-C_4H_{10}(2)$ (71)	100 → 280	52.5 → 484.5	16	0.000 099	4.44	4.98	0.78***
7 $N-C_4H_{10}(1)-N-C_7H_{16}(2)$ (MM)	200 → 440	100 → 400	15	0.000 000	1.33	1.39	3.51
8 $N-C_4H_{10}(1)-N-C_{10}H_{22}(2)$ (53)	100 → 460	25 → 714	109	0.023 533	2.85	4.74	6.27

*** Percent Absolute Average Error in Bubble Point Temperature

TABLE X (Continued)

SYSTEM (REFERNECES)	TEMPERATURE RANGE (°F)	PRESSURE RANGE (PSIA)	N ^o OF POINTS	OPTIMAL k_{ij}	% ABS AVG ERRORS IN		
					K_1	K_2	L/F or BUBPT
9 BZ(1)-N-C ₇ H ₁₆ (2) (MM)	103 → 206.1	3.5 → 14.7	33	0.006027	1.78	2.20	0.15**
10 BZ(1)-Toluene(2) (MM)	-180.1 → 536	14.7 → 560	22	0.005 258	2.39	2.59	0.18
11 BZ(1)-M-Xylene(2) (MM)	320 → 572	60 → 444.9	8	0.000 349	3.25	4.15	1.01**
12 ETHBZ(1)-N-C ₈ H ₁₈ (2) (88)	122 → 239	0.970 → 14.7	43	0.002 364	1.95	1.87	0.10**

** Percent Absolute Average Error in Bubble Point Temperature

TABLE XI
 PURE COMPONENT ENTHALPY PREDICTION USING THE NEW MODIFIED
 SRK EQUATION OF STATE

SYSTEM	COMPOSITION	TEMP RANGE (°F)	PRESSURE RANGE (PSIA)	NO. OF POINTS IN THE SYSTEM			ABS. AVG. DEVIATION (BTU/lb)			
				VAPOR PHASE	LIQUID PHASE	TOTAL	VAPOR PHASE	LIQUID PHASE	TOTAL	
1	N ₂	1.0	-250→+50	200→2000	43	6	49	0.563	0.415†	0.6
								0.387	0.422	0.4*
2	CO ₂	1.0	-60→+300	80→2000	34	20	54	0.594†	0.849	0.7†
								0.856	0.833	0.8*
3	H ₂ S	1.0	-110→+200	20→2000	15	33	48	1.294	3.038	2.5
								1.164	2.601	2.1*
4	CH ₄	1.0	-250→+50	250→2000	17	17	34	0.875	2.758	1.8
								0.296	1.577	0.9*
5	C ₂ H ₆	1.0	-240→+280	200→2000	26	43	69	0.124†	0.035†	0.1†
								1.029	1.063	1.1*
6	C ₃ H ₈	1.0	-250→+250	500→2000	4	39	43	2.778	2.743	2.8
								0.765	1.467	1.4*
7	N-C ₅ H ₁₂	1.0	75→700	200→1400	124	36	160	1.391†	1.591†	1.4†
								1.479	1.802	1.6*
8	N-C ₇ H ₁₂	1.0	50→600	50→2500	28	80	108	4.084	4.478	4.4
								2.817	4.688	4.2*

*Lee-Kessler Evaluation
 †Beat Lee-Kessler evaluation method.

TABLE XI (Continued)

SYSTEM	COMPOSITION	TEMP RANGE (°F)	PRESSURE RANGE (PSIA)	NO. OF POINTS IN THE SYSTEM			ABS. AVG DEVIATION (BTU/lb)			
				VAPOR PHASE	LIQUID PHASE	TOTAL	VAPOR PHASE	LIQUID PHASE	TOTAL	
9	N-C ₈ H ₁₈	1.0	75→600	200→1400	35	33	68	3.109	2.378	2.8
								2.289	0.851	1.6*
10	Toluene	1.0	50→650	50→2500	24	78	102	2.528†	4.475	4.0
								2.869	1.906	2.1*

* Lee-Kessler Evaluation

† Beat Lee-Kessler evaluation method

TABLE XII
MIXTURE ENTHALPY PREDICTION USING THE NEW
MODIFIED SRK EQUATION OF STATE

SYSTEM	COMPOSITION	TEMP RANGE (°F)	PRESSURE RANGE (PSIA)	NO. OF POINTS IN THE SYSTEM			ABS. AVG. DEVIATION (BTU/lb)			
				VAPOR PHASE	LIQUID PHASE	TOTAL	VAPOR PHASE	LIQUID PHASE	TOTAL	
1	CH ₄	0.50	-50→300	100→2000	39	7	46	1.378†	4.352†	1.8†
	CO ₂	0.50				5	44	1.454	8.924	2.3*
2	CH ₄	0.566	-250→+250	250→2000	45	9	54	0.809	0.626†	0.8†
	N ₂	0.434						0.678	4.017	1.2*
3	CH ₄	0.50	-110→+200	20→2000	25	6	31	1.761†	7.589†	2.9†
	H ₂ S	0.50						2.559	11.686	4.3*
4	CH ₄	0.948	-250→+250	250→2000	30	17	47	0.766	3.425	1.7
	C ₃ H ₈	0.766						0.518	1.678	0.9*
5	CH ₄	0.494	-250→+250	250→2000	8	37	45	1.464	2.383	2.2
	C ₃ H ₈	0.766						0.893	1.764	1.6*
6	CH ₄	0.494	-250→+250	250→2000	16	29	45	1.584†	1.990†	1.9†
	C ₃ H ₈	0.506						2.163	3.270	2.9*
7	CH ₄	0.720	-250→+250	250→2000	23	22	45	0.729†	1.725†	1.2†
	C ₃ H ₈	0.280						1.496	2.321	1.9*
8	CH ₄	0.883	-250→+250	250→2000	28	19	47	0.598†	1.632†	1.0†
	C ₃ H ₈	0.117						0.765	1.502	1.1*

*Lee Kessler Evaluation

†Beat Lee Kessler evaluation method

TABLE XII (Continued)

SYSTEM	COMPOSITION	TEMP RANGE (°F)	PRESSURE RANGE (PSIA)	NO. OF POINTS IN THE SYSTEM			ABS. AVG. DEVIATION (BUT/lb)			
				VAPOR PHASE	LIQUID PHASE	TOTAL	VAPOR PHASE	LIQUID PHASE	TOTAL	
9	CH ₄	0.951	150→600	50→2500	79	1	80	2.328↑	3.663↑	2.3↑
	C ₇ H ₁₆							0.049	2.347	4.185
10	CH ₄	0.491	50→600	50→2500	39	4	43	2.591↑	1.030↑	2.5↑
	C ₇ H ₁₆							0.509	3.791	4.914
11	CH ₄	0.249	50→600	60→2500	36	22	58	3.185	2.429	2.9
	C ₇ H ₁₆							0.751	3.008	1.101
12	CH ₄	0.500	50→600	60→2500	33	1	34	1.714↑	5.637↑	1.8↑
	Toluene							0.500	3.039	14.12
13	C ₂ H ₆	0.276	-240→+240	500→2000	6	12	18	1.519↑	2.243	2.0
	C ₃ H ₈							0.724	2.928	0.846
14	C ₂ H ₆	0.763	-240→+240	250→2000	12	18	30	1.741	2.069	1.9
	C ₃ H ₈							0.237	0.810	1.093
15	C ₂ H ₆	0.498	-240→+240	250→2000	11	18	29	1.663	2.077	1.9
	C ₃ H ₈							0.502	0.519	0.873

* Lee-Kessler Evaluation

↑ Beat Lee-Kessler Evaluation method

CHAPTER V

DISCUSSION OF RESULTS

The New α -model

The proposed expression for α appears to be a better representation of α as a function of T_r than the Soave (79) expression. The new model correctly portrays α as a monotonically decreasing function of reduced temperature, T_r , rather than Soave's model which incorrectly suggests that α decreases at low values of T_r , then goes to zero and finally increases at high values of T_r . With the new α model, the modified SRK equation closely reproduces the vapor pressures of pure components.

Quality of Correlation Development for Pure Hydrocarbons

Accurate correlation of vapor pressure would enable the new modified equation of state to accurately predict fluid fugacities and consequently the phase equilibrium behavior. Soave (1972) used the Antoine expressions reported by API Project 44 (95) as experimental vapor pressures. Also Soave (1972) used the critical point and acentric factors for a number of compounds to determine the function required to correlate vapor pressures. Graboski and Daubert (25) in an attempt to avoid anchoring the equation at $T_r = 0.7$, used hydrocarbon vapor pressure data compiled by the Penn State API research staff. In the current work, the ESDU (91) data which has the wider temperature ranges (triple point to the critical point) were used for all the hydrocarbons, except of C_9 to C_{20} whose ESDU

data were not available. Graboski-Daubert's modified SRK equation yields vapor pressures with large errors at reduced temperatures below 0.45. The new modified SRK equation can predict vapor pressures of most pure substances down to reduced pressures of 0.41, with reasonable accuracy. The fitting of the pure component parameters to very simple two constant straight-line form algebraic functions of acentric factor, instead of the usual quadratic form used by previous investigators, makes this correlation much more attractive to use.

Quality of Vapor-Liquid Equilibrium Calculations

For correlation testing and development, good binary VLE data are very valuable. Availability of such data helps to evaluate the model in terms of the effect of different families and molecular sizes on equilibrium predictions. It also permits determination of binary interaction parameters, k_{ij} 's, which are used for scaling up to multi-component systems based on the assumption of pairwise mixing. In this work, a total of 3,329 data points were used in fitting the k_{ij} 's. This is considered a large number of data points when compared with previous investigators in this area. For example, Graboski and Daubert (25) had a total of 1966 data points available in the Penn State Binary Vapor-Liquid Equilibrium Data Set and this included those points that were not used in the final fit. Use of more data points often improves the quality of the fit, hence the k_{ij} 's obtained in this work should be highly reliable.

All the interaction coefficients obtained are between the order of 0.0 to 0.2. In agreement with previous authors, hydrocarbon-non-hydrocarbon

k_{ij} s were larger than hydrocarbon-hydrocarbon k_{ij} s. This can be explained by the greater molecular interactions in the non-hydrocarbon-hydrocarbon binaries. For most hydrocarbon-hydrocarbon binaries, where molecular similarities are very high, the k_{ij} s obtained were zero or nearly so. Previous authors had recommended a value of zero for all hydrocarbon-hydrocarbon binary k_{ij} s. This ought to be done with some caution. A look at Table V shows that k_{ij} s for C_1 - n - C_8 , C_1 - n - C_{10} and C_1 -Toluene are significantly higher in order of magnitude than for the rest of the binaries in the same table, and cannot be approximated to zero in cases where very accurate work is required. The guideline recommended here therefore is that for HC-HC binaries which belong to the same family, for example paraffin-paraffin or aromatic-aromatic and having a carbon content difference of not more than five, a value of zero can be assumed for the k_{ij} value. Otherwise the real k_{ij} value should be determined and used.

According to previous authors (14, 15, 79, 80, 39, 40), k_{ij} was assumed a universal constant for a given binary pair and was therefore independent of temperature and pressure. In this work, this assumption may hold for most HC-HC binaries, but for non-HC-HC or non-HC-non-HC pairs, k_{ij} s were found to be temperature dependent. Thus, whenever a large amount of data was available at different temperature, the data were fitted separately in narrow temperature ranges and the weighted average of the results of these separate fittings used as guess for the total fitting. This was the approach used to obtain k_{ij} s for the binaries of CO_2 and C_1 , C_2 , C_3 , n - C_4 in Table V. For very accurate work, k_{ij} s for systems of this kind should be determined at temperatures and

pressures where they will find the most usage. Meanwhile, accurate correlation of k_{ij} s as functions of temperature have become very necessary.

The equilibrium ratios (K-values) predicted by the modified SRK equation of state are also very reliable. The percent absolute average deviation between predicted and experimental K-values for 55 out of 72 binary systems used in this study be between 1 and about 6 percent. High errors in K-value prediction were more frequent with the N_2 systems, in particular binaries of N_2 with heavier hydrocarbons. Nitrogen is mostly in supercritical state at normal conditions, resulting in almost all the nitrogen being in gaseous phase in most of its mixtures with hydrocarbons. Hence the results obtained were reasonable in view of the circumstances. Robinson et al., (65) used the Soave (.79) equation of state to correlate their CO_2 -Hexane data and had average absolute errors in predicted K-values of 4% and 13% for CO_2 and n-hexane respectively. When the same data were correlated using the new modified SRK equation, absolute average errors were 3.63% and 4.70% for CO_2 and n-hexane respectively. However, the k_{ij} value obtained for the CO_2 -n-hexane system by Robinson et al., agree with the one from this study to two decimal places. (See Table V.)

Test of the New Equation on Enthalpy Prediction

The modified SRK equation, coupled with the pure component parameters and the fitted k_{ij} s, was tested on enthalpy departure prediction. The errors in predicted enthalpy departures stayed within 0.1 to 4.4

BTU/lb. and 0.8 to 2.9 BTU/lb. for the pure components and mixtures used respectively. This is the same degree of error reported in Lee and Kessler's evaluation for the same systems. (See Tables XI and XII.)

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A new modified SRK equation of state has been obtained by proposing a new model which more correctly represents the α term in the original SRK equation as a monotonically decreasing function of reduced temperature, T_r . The new equation is capable of reproducing the vapor pressures of pure components very closely. Values of the parameters m and n in the new α expression have been obtained for thirty seven different compounds including water, N_2 , H_2S , CO_2 , and paraffin, alkene and aromatic hydrocarbons. Simple generalized correlations of these parameters as algebraic functions of acentric factor have been provided.

With the use of the same mixing rules as originally used by Soave, the new equation was successfully used to predict binary VLE computations, for mixtures of N_2 , H_2S , CO_2 and light paraffin, alkene, and aromatic hydrocarbons. Binary interaction coefficients were fitted for seventy-two systems and K -values were also predicted with reasonable accuracies for the same systems.

The equation was also found to be good in both pure component and mixture enthalpy departure predictions. By proper characterization, the new equation can be used to treat petroleum fractions.

Recommendations

For future work, further modification of the mixing rules is suggested, with the hope of improving the VLE mixture calculations.

The a term should be retained as in this work:

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})$$

while the b term changes from $b = \sum_i x_i b_i$ to

$$b = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - l_{ij}) (b_i + b_j) / 2.0$$

Attempt should be made to correlate binary interaction coefficients, k_{ij} s as functions of temperature for different binary systems.

Finally, the correlation should be tested on multi-component vapor-liquid equilibrium data, including such components as hydrogen, water, sulfur and nitrogen oxides.

The present correlation is based heavily on data of light hydrocarbons, hence caution should be exercised when trying to extrapolate its use to mixtures containing heavier components. Efforts in experimental research should be geared towards providing more accurate experimental VLE data on these heavier components, in particular aromatic, naphthene and alkene systems, because data on these systems are essential to further improve the generalized equation of state for better equilibrium calculations.

SELECTED BIBLIOGRAPHY

1. Akers, W.W., Attwell, L.L. and Robinson, J.A., Ind. Eng. Chem., 46 (12) (1954).
2. Akers, W.W., Burns, J.F. and Fairchild, W.R., Ind. Eng. Chem., 46 (12) (1954).
3. Akers, W.W., Kehn, D.M. and Kilgore, C.H., Ind. Eng. Chem., 46(12) (1954).
4. Amick, E.H., Johnson, W.B. and Dodge, B.F., Chem. Eng. Symposium Series, 48(2) (1956).
5. Azarnoosh, A. and McKetta, J.J., J. Chem. Eng. Data, 8(4)(1963).
6. Barner, H.E., Pigford, R.L. and Schriener, W.C., Paper presented at 31st Midyear API Meeting, Houston (1966).
7. Bierlein, J.A. and Kay, W.B., Ind. Eng. Chem., 45(3) (1953).
8. Brunner, G., Peter, S. and Wenzel, H., Chem. Eng. J., Vol. 7, 99-104 (1974).
9. Canjar, L. and Manning, F., Thermodynamic Properties and Reduced Correlations for Gases, Gulf Pub. Corp. Houston, Texas, (1966).
10. Chandler, J.P. and Leon, L.W., Modification of Marquardt's Non-Linear Fit Program, Department of Computing and Information Sciences, Oklahoma State University, Stillwater, Oklahoma (1978).
11. Chang, S.D. and Lu, B. C. -Y., Can. J. Chem. Eng., 48, 261 (1970).
12. Chaudron, J., Asselineau, L. and Renon, H., Chem. Eng. Sci., 28, 839 (1973).
13. Chueh, P.L. and Prausnitz, J.M., Ind. Eng. Chem. Fundam., 6(4), 491 (1967).
14. Chueh, P.L. and Prausnitz, J.M., AIChE J., 13, 1099 (1967).
15. Chueh, P.L. and Prausnitz, J.M., Ind. Eng. Chem. Fundam., 6, 492 (1967).
16. Cines, M.R., Roach, J.T., Hogan, R.J. and Roland, C.H., Chem. Eng. Symposium Series No. 6, Vol. 49 (1956).

17. Davalos, J., Anderson, W., Phelps, R.E. and Kidnay, A.J., J. Chem. Eng. Data, 21(1) (1976).
18. Donnelly, H.G. and Katz, D.L., Ind. Eng. Chem., 46(3) (1954).
19. Elliot, D.G., Vrhorn, R.F.F., Chappellear, P.S. and Kobayashi, R., J. Chem. Eng. Data, March 23, (1973).
20. Erbar, J.H., Comments on the Multiproperty and Multicomponent Fit Program "MPMCGC" for the PFGC Equation of State, LINDE AG, Munich, West Germany (1980).
21. Fredenslund, A. and Mollerup, J., Off-Print from J. of Chem. Soc., Faraday Transactions I, (1974).
22. Fredenslund, A., Mollerup, J. and Hall, K.R., Off-Print from J. of Chem. Soc., Faraday Transactions I (1975).
23. Fredenslund, A., Mollerup, J. and Gausq, L., Institutte for Kemiteknik, Tech. Univ. of Denmark, Paper Presented at the Centinneial ACS Meeting in New York (1976).
24. Gilliland, E.R. and Scheeline, H.W., Ind. Eng. Chem., 32(1) (1940).
25. Graboski, M.S. and Daubert, T.W., Ind. Eng. Chem. Process Des. Dev., 17, 443 (1978).
26. Gray, R.D., Jr., Rent, N.H., and Zudkevitch, D., AIChE J., 16, 991 (1970).
27. Heyen, G., Liquid and Vapor Properties from a Cubic Equation of State, University of Liege, Belgium (1976).
28. Kahre, LeRoy C., Phillips Pet. Co., Bartlesville, Oklahoma, R & D Report 6581 - 73 (1977).
29. Kalra, H., Ng, Heng-Joo, Miranda, R.D. and Robinson, D.B., J. Chem. Data, 23(4) p. 321 (1978).
30. Kaminishi, G., Arai, Y., Saito, S. and Maeda, S., J. Chem. Eng. of Japan, 1(2) (1968).
31. Kidnay, A.J. and Fahad, S., J. Chem. Eng. Data, 23(4) (1978).
32. Kohn, J.P. and Bradish, W.F., J. Chem. Eng. Data, 9(1) (1964).
33. Kohn, J.P. and Kurata, R., AIChE J., 4(2) (1958).
34. Legeret, D., Richon, D. and Renon, H., AIChE J., 27(2) (1981).
35. Lin, Y.-N., Hwang, S.-C. and Kobayashi, R., J. Chem. Eng. Data, 23(3) p 231 (1978).

36. Matschke, D.E. and Thodos, G., J. Chem. Eng. Data, 7(2)(1962).
37. Miller, P., Dodge, B.F., Ind. Eng. Chem., 32(3)(1940).
38. Nagahama, K., Konish, H., Hoshino, D. and Hirata, M., J. of Chem. Eng. of Japan, 7(5)(1974)
39. Peng, K.-Y., Robinson, D.B., Ind. Eng. Chem. Fundam., 15, 59 (1967).
40. Peng, D.-Y., Robinson, D.B., Can. J. Chem. Eng., 54, 595 (1976).
41. Peng, D.-Y., Robinson, D.B., AIChE J., 23, 137 (1977).
42. Reamer, H.H., Sage, B.H., Lacey, W.N. and Seelck, F.T., Ind. and Eng. Chem., 34(12)(1942).
43. Reamer, H.H., Sage, B.H., Lacey, W.N. and Olds, R.H., Ind. and Eng. Chem., 41(3)(1949).
44. Reamer, H.H., Sage, B.H., and Lacey, W.N., Ind. Eng. Chem., 42(3)(1950).
45. Reamer, H.H., and Sage, B.H., Ind. and Eng. Chem., 43(7)(1951).
46. Reamer, H.H., Sage, B.H. and Lacey, W.N., Ind. Eng. Chem., 43(11) (1951).
47. Reamer, H.H., Sage, B.H. and Lacey, W.N., Ind. Eng. Chem., 45(8) (1953).
48. Reamer, H.H., Sage, B.H., Lacey, W.N. and Selleck, F.T., Ind. and Eng. Chem., 45(8) (1953).
49. Reamer, H.H., Sage, B.H. and Lacey, W.N., Ind. Eng. Chem., 1(1) (1956).
50. Reamer, H.H., Sage, B.H. and Lacey, W.N., J. Chem. Eng. Data, 5(11) (1960).
51. Reamer, H.H., Sage, B.H., J. Chem. Eng. Data, 7(2) (1962).
52. Reamer, H.H., Sage, B.H., J. Chem. Eng. Data, 8(4) (1963).
53. Reamer, H.H., Sage, B.H., J. Chem. Eng. Data, 9(1) (1964).
54. Roberts, L.R., Wang, R.H., Zamoosh, A.A. and McKetta, J.J., J. Chem. Eng. Data, 17, (1962).
55. Robinson, D.B., Karla, H., Krishnan, T. and Miranda, R.D., The Phase Behavior of Selected Hydrocarbon-non-hydrocarbon binary Systems, Dept. of Chem., Univ. of Alberta, Edmonton, Alberta, Canada. (1973).

56. Robinson, D.B., Equilibrium Phase Props of the n-Pentane-Nitrogen Systems, A Progress Report Submitted to the Canadian Natural Gas Processing Association, 1973.
57. Robinson, D.B. and Besserer, G.J., J. Chem. Eng. Data, 18(3)(1973).
58. Robinson, D.B. and Besserer, G.J., J. Chem. Eng. Data, 18(4)(1973).
59. Robinson, D.B. and Besserer, G.J., J. Chem. Eng. Data, 8(1)(1975).
60. Robinson, D.B. and Besserer, G.J., J. Chem. Eng. Data, 20(1)(1975).
61. Robinson, D.B. and Kalra, H., J. Chem. Eng. Data, 21(2)(1976).
62. Robinson, D.B. and Ng, Heng-Joo, J. Chem. Eng. Data, 23(4)(1978).
63. Robinson, D.B., Kalra, H., Kubota, H. and Ng, Heng-Joo, J. Chem. Eng. Data, 23(4)(1978).
64. Robinson, D.B., Kalra, H., Kubota, H. and Ng, Heng-Joo, J. Chem. Eng. Data, 25(1), 51-55, (1980).
65. Robinson, R.L., Jr., Li, Y. and Killard, K., J. Chem. Eng. Data, 26(53) (1981).
66. Sage, B.H., Lacey, W.N., Reamer, H.H. and McKay, R.A., Ind. and Eng. Chem., 43(9)(1951).
67. Sage, B.H., Lacey, W.N. and Hicks, B.L., Ind. and Eng. Chem., 32(8)(1940).
68. Sage, B.H. and Lacey, W.N., Ind. and Eng. Chem., 32(7)(1940).
69. Sage, B.H., Reamer, H.H., Olds, R.H. and Lacey, W.N., Ind. and Eng. Chem., 34(9) (1942).
70. Sage, B.H., Lacey, W.N. and Olds, R.H., Ind. and Eng. Chem., 34(8) (1942).
71. Sage, B.H. and Lacey, W.N., Ind. Eng. Chem., 40(7)(1948).
72. Sage, G.H., Goff, B.H., Farrington, P.S., Ind. Eng. Chem., 42(4) (1950).
73. Sage, B.H., Lacey, W.N., Reamer, H.H. and McKay, R.A., Ind. and Eng. Chem., 43(9)(1951).
74. Salah, E.M.H. and Benjamin, C.-Y. Lu, Can. J. Chem. Eng., 52, (1974).
75. Salah, E.M.H. and Benjamin, C.-Y. Lu, J. Chem. Eng. Data, 21(2)(1976).
76. Sebastin, H.M., Simnick, J.J., Lin, H. and Chao, K., J. Chem. Eng. Data, 25(2), 138-140, (1980).
77. Shim, Joosup and Kohn, J.P., J. Chem. Eng. Data, 7(1)(1962).

78. Simonet, R. and Behar, E., Chem. Eng. Sci., 31, 37 (1976).
79. Soave, G., Chem. Eng. Sci., 27, 1197 (1972).
80. Soave, G., I. Chem. E. Symposium Series No. 56. (1973).
81. Stryjek, Roman, P.S. Chappellear and Kobayashi, R., J. of Chem. Eng. Data, 19(4) (1974).
82. Stryjek, Roman, Chappellear, P.S. and Kobayashi, R., J. Chem. Eng. Data, 19(4) (1974).
83. West, E.H. and Erbar, J.H., An Evaluation of Four Methods of Predicting the Thermodynamic Properties of Light Hydrocarbon Systems, pp 50-60. Proc. of NGPA, Tulsa, Oklahoma (1973).
84. William, E.V. and Collins, F.C., Ind. Eng. Chem., 34(7) (1942).
85. Wilson, G.M., Adv. Cryog. Eng., 9, 168 (1964).
86. Wilson, G.M., Adv. Cryog. Eng., 11, 392 (1964).
87. Yarbrough, Lyman: "Application of a Generalized Equation of State to Petroleum Reservoir Fluids," in: Equations of State in Engineering, Advances in Chemical, 182, K.C. Chao and Robert L. Robinson, ed, American Chemical Society Washington, D.C., 385-435 (1979).
88. Young, C.P. and Van Winkle, M., Ind. Eng. Chem., 47(2) (1955).
89. Zudkevitch, K. and Joffe, J., AIChE J., 16(1), 112 (1970).
90. Zudkevitch, K., Joffe, J. and Schroeder, G.M., AIChE J., 16(3), 496 (1970).
91. Engineering Sciences Data Unit, Chemical Engineering Series, Physical Data, Volume 5, 251-259 Regent Street London W1R 7AD, August (1975).
92. Steam Tables, Properties of Saturated and Superheated Steam from 0.08865 to 15,500 psia, Values Reprinted from 1967 ASME Steam Tables by the American Society of Mechanical Engineers, 4th Printing. (1976).
93. Tables of Thermal Physical Properties, NBS Circular 564, Nov. (1955).
94. The Thermodynamic Properties of Nitrogen from 114 to 540^oR between 1.0 and 3000 psia, NBS Tech. Note. 129A, Feb.(1963).
95. Selected Values of Properties of Hydrocarbons and Related Compounds, API Research Project 44. Texas A & M University, Updated (1979).

APPENDIX

ALTERNATIVE METHOD OF DERIVING $\Delta H'/RT$ EQUATION

Thermodynamic isothermal enthalpy departure definition is given by equation (3-10) as

$$\frac{\Delta H'}{RT} = -T \int_{\infty}^V \left(\frac{\partial Z}{\partial T} \right)_V \frac{dV}{V} - (Z - 1) \quad (T \text{ const.}) \quad (3-10)$$

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

$$a(T) = a_c \alpha(T) \quad (2-37)$$

$$\text{and } \alpha^{1/2} = \exp \left\{ m(1 - Tr^n) \right\} \quad (3-1)$$

Equation (3-10) can be re-written as

$$\frac{PV}{RT} = \frac{V}{V-b} - \frac{a(T)}{RT(V+b)}$$

$$\text{i.e. } Z = \frac{V}{V-b} - \frac{a(T)}{RT(V+b)} \quad (A-1)$$

$$\begin{aligned} \text{Then } \left(\frac{\partial Z}{\partial T} \right)_V &= 0 - \frac{\left\{ RT(V+b) \cdot \frac{\partial a(T)}{\partial T} - a(T) \cdot R(V+b) \right\}}{R^2 T^2 (V+b)^2} \\ &= \frac{a(T) - T \frac{\partial a(T)}{\partial T}}{RT^2 (V+b)} \end{aligned}$$

$$\therefore -T \int_{\infty}^V \left(\frac{\partial Z}{\partial T} \right)_V \cdot \frac{dV}{V} = -T \int_{\infty}^V \left\{ \frac{a(T) - T \frac{\partial a(T)}{\partial T}}{RT^2 (V+b)} \right\} \frac{dV}{V}$$

$$\begin{aligned}
&= \frac{-1}{RT} \left(a(T) - T \frac{\partial a(T)}{\partial T} \right) \int_{\infty}^{V^-} \frac{dV}{V(V+b)} \\
\therefore \frac{\Delta H'}{RT} &= -T \int_{\infty}^{V^-} \left(\frac{\partial Z}{\partial T} \right)_V \cdot \frac{dV}{V} - (Z - 1) \quad (T \text{ const.}) \quad (3-10) \\
&= \frac{1}{RT} \left\{ T \frac{\partial a(T)}{\partial T} - a(T) \right\} \int_{\infty}^{V^-} \frac{dV}{V(V+b)} - (Z - 1) \\
&= \frac{1}{RT} \left\{ T \frac{\partial a(T)}{\partial T} - a(T) \right\} \frac{1}{b} \ln \frac{V}{V+b} - (Z - 1) \\
&= (1 - Z) + \frac{1}{RTb} \cdot \ln \frac{V}{V+b} \cdot \left\{ T \frac{\partial a(T)}{\partial T} - a(T) \right\} \quad (A-2)
\end{aligned}$$

Equation (A-2) is the same as equation (3-11) on page 22, hence the rest of the derivation follows as in the text.

VITA ²

Enuma Dickson Ozokwelu

Candidate for the Degree of

Doctor of Philosophy

Thesis: DEVELOPMENT OF A MODIFIED SOAVE-REDLICH-KWONG EQUATION
OF STATE

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Amichi, Anambra State, Nigeria
April 28, 1946, to Beniah O. and Victoria N. Ozokwelu.
Married to Martha N. Ekedum, January 9, 1979.

Education: Attended Elementary School in Amichi and passed
first school leaving certificate examination in 1959
with distinction; graduated from Dennis Memorial Grammar
School Onitsha in 1964 with a division one pass in West
Africa School Certificate examination; received the Bachelor
of Science Degree in Chemical Engineering from University
of Ife, Nigeria, June, 1975; received the Master of Science
Degree in Chemical Engineering from Oklahoma State University
in May, 1978; completed requirements for the Doctor of
Philosophy degree at Oklahoma State University in December, 1981.

Membership in Scholarly or Professional Societies: Omega Chi
Epsilon, honorary Chemical Engineering fraternity.
Associate Member American Institute of Chemical Engineers,
Certified as Engineer-in-Training by Oklahoma Board of
Registration of Engineers, Architects and Land Surveyors.

Professional Experience: Instructor, Langston University, Langston,
Oklahoma, September, 1979 to June, 1981; Employed as Quality
Control Analyst by Mortell Company, Wichita Kansas, Summer,
1978; Graduate Teaching Assistant, School of Chemical Engineering
September, 1976 to December, 1979; Employed as Assistant
Shift Engineer by Gombe Oil Seed Processors Limited, Nigeria,
September, 1975 to July, 1976; Summer Intern, 1974 with
Lever Bros (Nigeria) Ltd., Lagos; Summer Intern with APAPA

Chemical Industries (Nigeria) Ltd., Benin; 1973 and
Summer Intern with Nigerian Petroleum Refining Company
Port Harcourt, Nigeria, 1972.