EVALUATION OF THE MODIFIED PARK-GASEM-ROBINSON EQUATION OF STATE AND CALCULATION OF CALORIMETRIC PROPERTIES USING EQUATIONS OF STATE

By

KYOUNG HO ROW

Bachelor of Science
Yonsei University
Seoul, Korea
1987

Master of Science
Florida Institute of Technology
Melbourne, Florida
1991

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
May, 1998

EVALUATION OF THE MODIFIED PARK-GASEM-ROBINSON EQUATION OF STATE AND CALCULATION OF CALORIMETRIC PROPERTIES USING EQUATIONS OF STATE

Thesis Approved:

K.A.M. Gasem

Thesis Advisor

Robert L Robinson Jr.

Arland H. Johannes

Wayne B Powell

Dean of the Graduate College

PREFACE

The Park-Gasem-Robinson (PGR) equation of state has been modified to improve its volumetric and equilibrium predictions. Specifically, the attractive term of the PGR equation was modified and a new expression was developed for the temperature dependence of the attractive term in this segment-segment interactions model. In addition, Elliott's expression for the repulsive term was further refined to approximate the Carnahan and Starling repulsive term more accurately. The predictive capabilities of the modified PGR equation were compared to those of the Peng-Robinson (PR), the simplified-perturbed-hard-chain theory (SPHCT) and the original PGR equations of state. Pure fluid vapor pressures, saturated liquid and vapor densities of selected compounds were used in such comparisons. Simple one-fluid mixing rules with one interaction parameter were used to apply the modified equation to mixtures. Several case studies were performed to evaluate the model representation of binary mixtures involving ethane, carbon dioxide or hydrogen with normal paraffins. The calculated bubble point pressures were compared to those of the PR, the SPHCT and the original PGR equations of state.

The predictive abilities of the equations of state for calorimetric properties were also evaluated. Specifically, the accuracy of enthalpy and entropy predictions using the original and the modified SPHCT and the modified PGR equations of state were compared with those of the widely used PR equation of state. The evaluations were conducted for six pure fluids of varying chemical structure and covering the two-phase and single-phase regions.

I would like to express my sincere gratitude to my advisor, Dr. Khaled A. M. Gasem for his intelligent guidance, encouragement, and invaluable assistance. I also appreciate the advice and encouragement received from Dr. Robert L. Robinson, Jr. I extend my sincere thanks to him and to the other members of my graduate committee, Drs. Arland H. Johannes and John N. Veenstra.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

a	Energy parameter in the SRK or PR equation of state
A	Helmholtz energy
b	Molecular size parameter in the SRK or PR equation of state
B	Second virial coefficient
c	Degree of freedom parameter
C_{ij}, D_{ij}	Binary interaction parameters
g	Radial distribution function; molar Gibbs free energy
G	Gibbs free energy
H	Enthalpy
k	Boltzmann constant
K	Ratio of square-well width from hard sphere center to hard sphere radius
n	Number of data points; number of moles
N	Number of components in mixture; total number of molecules
p	Pressure
q	External molecular surface area
Q	Canonical partition function; equation of state constant
r	Radial distance from center molecule
R	Gas constant
SS	Objective function

T	Temperature
T^*	Characteristic temperature parameter
$\tilde{T}$	Reduced temperature (T/T^*)
u	Potential energy between molecules; equation of state constant
U	Internal energy
v	Molar volume
v^*	Characteristic volume parameter
V	Total system volume
w	Equation of state constant
x	Liquid phase mole fraction
X	Any calorimetric property
y	Vapor phase mole fraction
Y	Temperature-dependent function in the new equation of state at low density limit
z	Mole fraction
Z	Compressibility factor

Greek letters

α	Temperature-dependent parameter in cubic equation of state, temperature correction function
β_1, β_2	Constants in repulsive term of the new equation of state
$\Delta(\rho)$	Density dependent function in the attractive term of the new equation of state
ε	Square-well potential energy between segments
ϕ	Intermolecular potential energy

η	Reduced density ($\tau v^{*}/v$)
κ	Acentric factor dependent parameter in cubic equation of state; equation of state constant
Λ	de Broglie wave length
$\Theta(T)$	Temperature correction function on square-well potential width
σ	Radius of hard sphere
τ	Geometrical constant (0.74048)
ω	Acentric factor

Subscripts

c	Critical state
calc	Calculated
exp	Experimental
f	Free
i, j	Component or data point identification number
l	Liquid
min	Minimum
r	Reduced property
v	Vapor

Superscripts

att	Attractive
rep	Repulsive
o	Ideal gas
*	Characteristic parameter

CHAPTER 1

INTRODUCTION

Most chemical processes involve near equilibrium conditions of vapor and liquid fluid phases; thus, accurate predictions of thermodynamic properties are essential in designing and optimizing these processes. Practical phase equilibrium calculations are performed by means of an equation-of-state model or the activity coefficient method, where the activity coefficients are used to represent the nonideality of the liquid phase while fugacity coefficients are used to describe the vapor phase nonideality. This method is accurate for equilibria at low and moderate pressures and can be applied to a wide variety of mixtures. However, its application to supercritical systems is rather demanding.

In the equation-of-state approach, a single equation is used to represent all fluid phases over a wide range of temperature and pressure. An equation of state (EOS) has long been considered the most convenient form for representating equilibrium phase behavior as well as volumetric and calorimetric properties for process design and optimization calculations. An equation of state is an analytical expression relating pressure, volume, temperature, and composition. The expression is used to describe volumetric behavior, multi-phase equilibria, and the thermal properties of pure substances and mixtures.

Numerous equations of state have been proposed since van der Waals first introduced his expression in 1873. Among these, the most commonly used equations of state are the cubic van der Waals-type equations such as the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK) equations (1, 2). While these equations (and cubic equations in general) are used frequently in industry for vapor-liquid equilibrium (VLE) calculations, they suffer from several shortcomings including poor density predictions, the inability to describe mixtures containing molecules with large variation in size, the inability to describe adequately mixtures of polar and associating molecules, the inability to handle proper mixtures of polymeric compounds, and the restricted range of use due to improper limiting behavior at high temperatures (3, 4).

In order to overcome some of these drawbacks, attention has been focused increasingly on equations of state with improved theoretical bases. The perturbed-hard-chain theory (PHCT) of Beret and Prausnitz (5) and Donohue and Prausnitz (6) has formed the basis of several successful equations of state (7-17). A feature of the PHCT is the factoring of the partition function into external and internal contributions. This theoretically-based PHCT equation of state helps to narrow the gap between conventional equations of state representing both liquid and vapor and those used for representation of polymeric liquids. However, a shortcoming of the equation of state derived from the PHCT partition function is its complexity, especially for mixtures.

Since the development of the original PHCT equation of state, a number of equations based on the same theoretical structure have been proposed and tested (10-16, 20-22). A widely used model, the simplified-perturbed-hard-chain theory (SPHCT) equation of state, was proposed by Kim, et al. (9). The attraction term of the PHCT equation was replaced with the local composition model of Lee et al. (23). The SPHCT equation has a comparable predictive capability to the SRK and PR equations in representing the phase behavior of simple molecules, and it has a better capability for handling some asymmetric mixtures (24, 25). However, the SPHCT equation suffers from the several shortcomings. First, the SPHCT equation of state often fails to generate accurately the vapor-liquid phase envelope for pure fluids. Second, it fails to predict adequately pure fluid vapor pressures below 0.007 bar (24, 26). Third, it yields worse vapor density predictions than the PR equation of state (25, 26). A modified SPHCT equation of state was introduced by Shaver to improve the SPHCT equation of state prediction capabilities (25). Although the modified SPHCT equation of state is better than the original SPHCT equation of state in representing equilibrium and volumetric properties for a variety of pure fluids, its algorithms for the critical constraints and volume translation require additional computational time.

Another new equation of state was introduced by Park (26). The PGR equation of state is capable of representing the phase behavior of simple, normal, and asymmetric mixtures involving molecules of diverse molecular sizes. It is theoretically based and its parameters are evaluated from various equilibrium and volumetric properties of pure fluids. The PGR equation of state was derived from the generalized van der Waals partition function for chain-like molecules proposed by Donohue and Prausnitz (6). The equation has a simple repulsive term proposed by Elliott and coworkers (27) which performs similar to the Carnahan and Starling equation (18). Since the attractive term of the generalized cubic equation of state under-predicts compressibility factors of fluids, a correction term was added to the attractive term of the generalized cubic equation. Like the original and modified SPHCT equations of state, the PGR equation has three substance-specific parameters for each pure fluid.

The PGR equation of state is more accurate than Shaver's modified SPHCT equation of state (25) in predicting fluid phase equilibrium and volumetric properties of pure fluids from the triple point to near the critical point, as well as for mixture properties over a wide range of conditions (25). However, the PGR equation of state is not as accurate as the PR equation of state (2) in predicting the vapor pressure of pure fluids and the bubble point pressures of binary mixtures.

In this work, the attractive term of the PGR equation of state has been modified to improve its predictive capabilities. Case studies similar to those performed by Shaver and coworkers (25) were applied to determine an improved temperature-dependent expression in the attractive term. Also, a more generalized form of the attractive term was introduced. Two repulsive terms, Carnahan and Starling (18) and Elliott et al. (27), were used as a basis to produce a simple and accurate repulsive term.

Detailed modification and derivation of the equation is shown in Chapter 2 along with a brief literature review on equations of state. Chapter 3 presents the equation-of-state parameter evaluations and assessment of pure fluid property predictions. The predictive capability of the new equation is compared to that of the PR, SPHCT, and original PGR equations. For this purpose, predictions of the vapor pressure and saturated vapor and liquid densities for a variety of pure fluids are compared to those of the other equations. Bubble point pressure calculations for binary mixtures of ethane + n-paraffins, carbon dioxide + n-paraffins and hydrogen + n-paraffins with the new equation are shown in Chapter 4. Comparisons are also undertaken with the PR, SPHCT, and original PGR equations.

CHAPTER 2

A MODIFICATION OF THE PGR EQUATION OF STATE

Abstract

The Park-Gasem-Robinson (PGR) equation of state has been modified to improve its volumetric and equilibrium predictions. Specifically, (a) a new expression was developed for the temperature dependence of the attractive term in this segment-segment interactions model, (b) the second attractive term of the original PGR equation was modified to enhance the flexibility of the model, and (c) Elliott's expression for the repulsive term was further refined to approximate the Carnahan and Starling repulsive compressibilities more accurately. Case studies similar to those of Shaver and coworkers were used to evaluate the optimal temperature-dependent expression in the attractive term of the equation.

Introduction

An equation of state is commonly applied to many chemical engineering problems. In particular, it is well suited for phase equilibria calculations because the pressure, temperature, volume, and composition (in case of mixtures), of all coexisting phases can be simultaneously determined. A quantitative description of vapor-liquid equilibria (VLE) is required in mass transfer calculations and separation operations such as distillation and absorption. VLE information is also significant in the design of chemical reactors. Therefore, there has been continuous demand from industry for accurate thermodynamic models.

There are two common approaches in the VLE calculations. One is the equation of state approach and the other is the activity coefficient model approach. Activity coefficient models such as the Wilson (28), NRTL (29) and UNIFAC (30) models are very convenient in the calculation of vapor-liquid equilibrium or distribution coefficients of highly nonideal systems. On the other hand, application of these models to high pressure systems containing supercritical components is rather difficult (31).

Despite their long history, equations of state have continued to be an important research subject in applied thermodynamics. Since its first appearance more than a hundred years ago, van der Waals equation of state has been a basis for several equations of state, which provide both volumetric and equilibrium properties. Among these equations of state, the SRK (1) and PR (2) equations are widely used in industry. Although these equations are essentially empirical, their predictive capabilities for the equilibrium properties of mixtures containing simple and normal fluids are good. However, since both equations are based on molecule-molecule interactions, application of either equation to asymmetric mixtures produces poor predictions.

Recent interest in asymmetric mixtures has generated new requirements for thermodynamic models for systems containing small molecules and heavy solvents. Also the development of fast computers makes it possible to perform Monte Carlo simulations and molecular dynamics simulations to delineate molecular interactions. These simulation results have stimulated the development of theoretically-based equations of state. Park (26) introduced a new simple equation of state (PGR) for chain-like molecules by utilizing an existing free volume expression and a new expression for the attractive term. The structure of the equation is, in part, similar to both the Peng-Robinson (2) and SPHCT (9) equations of state. In this work, the PGR equation of state is modified to obtain more accurate volumetric, equilibrium and calorimetric predictions.

Literature Review

The first equation of state that represented reasonably both vapor and liquid phases was proposed by van der Waals in 1873

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2-1}$$

or

$$Z = \frac{pV}{RT} = \frac{V}{(V - b)} - \frac{a}{RTV} \tag{2-2}$$

where b is a co-volume parameter and a/v^2 is an expression for the internal pressure (32). The currently used van der Waals-type equations of state resemble their common predecessor in that all of them contain a repulsion term, Z^{rep}, and an attractive term, Z^{att}

$$Z = Z^{rep} + Z^{att} \tag{2-3}$$

Among this type of equation of state, cubic equations proved to be preferable due to their simplicity, short computation time and reliability. A cubic equation is the simplest polynomial form capable of satisfying the ideal gas limit and of representing both vapor and liquid phases. The most general form of a cubic equation of state contains five parameters and takes the form (33)

$$p = \frac{RT}{v - b} - \frac{\theta(v - \eta)}{(v - b)(v^2 + \delta v + \varepsilon)} \tag{2-4}$$

where the adjustable parameters b, θ, η, δ and ε are, in general, functions of temperature.

Redlich and Kwong (RK) proposed the first cubic equation of state that was widely accepted as a tool for routine engineering calculations (33). The equation was proposed to satisfy the boundary conditions in the low and high density limits (34). The temperature-dependent part of the attractive term in the RK equation was investigated by several researchers (1, 35-36). Soave proposed the first widely used method (SRK equation of state) for expressing the temperature dependence, which was both more accurate and simple (1).

While an appropriate temperature-dependent part of the attractive term is sufficient for representing the vapor pressure, modification of the pressure-volume functional dependence is necessary to improve the prediction of the volumetric properties. Peng and Robinson (2) recognized that the critical compressibility factor of the RK equation of state ($Z_c = 0.333$) is overestimated, thus impairing liquid volume calculations. They postulated an equation reducing the critical compressibility factor to 0.307.

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{2-5}$$

This form improved the representation of liquid density relative to the SRK equation of state (2). These two-parameter cubic equations of state predict a constant critical compressibility factor for all components. Therefore, a third parameter has been used by several researchers to introduce a component-dependent critical compressibility factor and thus to enhance the flexibility (37-40).

In general, these cubic equations of state can be treated as convenient engineering tools due their simplicity and reliability. Such equations with generalized parameters provide reasonable predictions of thermodynamic properties. However, extrapolation of the equations beyond the range of the properties and conditions for which they are designed may be unreliable. Also, these empirical equations are intrinsically limited in their ability to describe mixtures containing molecules of diverse molecular sizes and polar species.

Equations of state such as the perturbed-hard-chain theory (PHCT) equation (5, 6), the chain-of-rotators (COR) equation (13), the simplified-perturbed-hard-chain theory (SPHCT) equation (9) and the cubic chain-of-rotators (CCOR) equation (41, 42), which originated from statistical mechanics, have proved useful in predicting fluid phase equilibria of industrially important mixtures.

The COR equation has a rotational term in the compressibility factor along with the repulsive and attractive terms. The equation is given as

$$Z = 1 + Z^{rep} + cZ^{rot} + \left(1 + cf(T)\right)Z^{att} \tag{2-6}$$

The repulsive term of the COR equation is that of the Carnahan and Starling equation, and the rotational term is from the hard-dumbbell equation provided by Boublik and Nezbeda (43). The basic assumption in the rotational term is that a chain molecule consists of a series of hard dumbbell molecules. Each dumbbell has three translational degrees of motion and two rotational degrees of motion. The attractive term of the COR equation is given by Alder and coworkers (19). The equation shows reasonable performance in predicting vapor pressures and saturated liquid and vapor densities of some paraffins and aromatics (13). However, the COR equation is considered more complex than most other equations of state. Thus, Lin et al. (41) simplified the COR equation using a simple correlation for the repulsive term and the rotational term along with two empirical expressions in the attractive term. One of these expressions is similar to that of the SRK equation. Evaluations of the simplified COR equation using two binary interaction parameters for some hydrogen binary mixtures were conducted (41, 42), and the results were compared to those of the SRK equation using one interaction parameter. The simplified COR equation showed better precision than the SRK equation for the systems considered. However, no evaluation of the equation with one interaction parameter is available in the literature.

The perturbed-hard-chain theory equation of state is one of the accurate equations for representing vapor-liquid equilibrium properties of chain-like hydrocarbons. Similar to most van der Waals type equations of state, this equation of state consists of repulsive and attractive terms.

$$Z = 1 + c\left(Z^{\text{rep}} + Z^{\text{att}}\right) \qquad (2\text{-}7)$$

where c is the degrees of freedom parameter and Z^{rep} and Z^{att} are repulsive and attractive contributions, respectively, given in terms of compressibility factors. The repulsive model of Carnahan and Starling (CS) is used in this equation (18). The attractive term is based on molecular simulation results for molecules having a square-well potential (19). The resultant equation contains as many as 24 terms. Consequently, when applied to mixtures, its application in practical systems becomes fairly complicated.

Kim and coworkers (9) introduced a simplified version of the PHCT (SPHCT) equation of state. The double summation form of the attractive term of PHCT equation of state is replaced with single term of the Lee-Lombardo-Sandler (LLS) local composition model (23). The predictive capability of this modified equation is comparable to the SRK equation, which is commonly used in industry (24). Furthermore, the SPHCT equation of state shows better performance than the SRK equation in the prediction of phase properties of heavy hydrocarbons. However, the SPHCT equation of state requires more computation time than a cubic equation of state such as the SRK equation for calculating thermodynamic properties in the two-phase region. This is because the SPHCT equation of state requires more computation time to identify a proper liquid root of the equation in each iteration of the equilibrium calculations.

A number of researchers have assessed the predictive ability of the SPHCT equation of state for various mixtures (8, 44-47). Its ability to predict the critical points was demonstrated on four oil reservoir fluid systems containing up to forty-eight components by Garcia-Sanchez et al. (47). The SPHCT equation has successfully converged to all the critical points in few iterations without any difficulty.

Shaver and coworkers (25) introduced a modified version of the SPHCT (MSPHCT) equation of state. In the SPHCT, the molecular attraction is expressed as a ratio of the potential energy of a molecule to its kinetic energy. Shaver replaced this term with a four-term polynomial function of temperature (25). The critical constraints were applied to both the SPHCT and MSPHCT equations to improve near-critical property predictions. Vapor pressures and phase densities of twenty-three pure components and of bubble point pressures of a number of binary mixtures comprised of ethane + n-paraffins and CO_2 + hydrocarbons were calculated and compared with the original SPHCT and the PR equations of state.

Wang and Guo (48) modified the SPHCT equation of state by reformulating the attractive portion of the canonical partition function for mixtures and replacing the repulsive portion by a simple simulated expression. The evaluation of this equation of state was made on pure fluids, binary/multi-component mixtures and reservoir fluids. This cubic SPHCT (CSPHC) equation of state showed significant improvements over the SPHCT in predicting VLE and liquid phase density of mixtures of CO_2 + heavy hydrocarbons.

Park introduced a new equation of state (PGR) based on the generalized van der Waals partition function for chain-like molecules (26). This equation of state utilized an existing expression for the free volume of hard spheres in the repulsive term and augmented the generalized cubic equation of state attractive term. A square-well potential was used to describe the attractive energy between segments of molecules, and temperature and density correction functions were introduced to amend the low-density radial distribution function. The predictive ability of this equation of state was demonstrated through vapor-liquid equilibrium predictions involving pure fluids and n-paraffin binary mixtures containing ethane, carbon dioxide, and hydrogen.

The PGR Equation of State

The following is a brief review on the PGR equation of state and a detailed derivation of its repulsive and attractive terms.

A well defined interaction energy between molecules and the free volume of a system, along with the aid of the statistical mechanics, are very important in calculating thermodynamic properties accurately. A typical example of the statistical mechanical connection between the behavior of particles and bulk thermodynamic properties is the canonical partition function. The necessary equations for relating the canonical partition function of statistical thermodynamics to classical thermodynamics are as follows (49)

$$A = -kT\ln(Q) \tag{2-8}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln(Q)}{\partial V}\right)_{T,N} \tag{2-9}$$

$$U = kT^2\left(\frac{\partial \ln(Q)}{\partial T}\right)_{N,V} \tag{2-10}$$

where Q is the canonical partition function, A is the Helmoltz energy, k is Boltzmann's constant, T is absolute temperature, V is total volume, N is the number of molecules, p is pressure and U is internal energy. The partition function can be written as a sum over all possible energy states for a collection of N molecules as

$$Q(N,V,T) = \sum_{i} e^{-E_i(N,V)/kT} \tag{2-11}$$

Once a partition function is established, thermodynamic properties can be derived. Among the expressions for partition functions, the generalized van der Waals partition function has been the starting point for developing equations of state having repulsive and attractive terms. This generalized van der Waals partition function requires a free volume expression and intermolecular potential energy to account for dispersion effects or attractive interactions between molecules (50).

The extended van der Waals partition function to chain-like molecules using the degree of freedom parameter, c, was introduced by Donohue and Prausnitz (6). The kinetic energy of a chain-like molecule is assumed to be affected by the translational, rotational and vibrational degrees of freedom. Consequently, the total degrees of freedom for a chain-like molecule is assumed to be 3c instead of 3 in the generalized van der Waals partition function. The partition function for chain-like molecules is (6)

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \left(\frac{V_f}{V}\exp\left(\frac{-\phi}{2ckT}\right)\right)^{Nc} \tag{2-12}$$

where V_f is the free volume of hard-spheres and Λ is the de Broglie wave length given by

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} \tag{2-13}$$

For simple molecules, such as methane and argon, the degree of freedom parameter c is one and the partition function of Equation (2-12) becomes the generalized van der Waals partition function. The relationships between system pressure and the partition function is given as

$$\frac{p}{kT} = \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \tag{2-14}$$

By taking the logarithm of Equation (2-12) and applying Stirling Approximation, lnN! = Nln N - N, the following equation is obtained

$$\ln Q = -N \ln N + N + N \ln V - N \ln \Lambda^3 + Nc\left(\ln V_f - \ln V - \frac{\phi}{2ckT}\right) \tag{2-15}$$

Application of the expression of Q of Equation (2-15) to Equation (2-14) becomes

$$\frac{pV}{NkT} = 1 + c\left(\frac{V}{V_f}\frac{\partial V_f}{\partial V} - 1 - \frac{V}{2ckT}\frac{\partial \phi}{\partial V}\right) \tag{2-16}$$

When Equation (2-16) is rewritten on a molar basis using the definition of the molar volume, $v = V(N_A/N)$.

$$\frac{pv}{RT} = 1 + c\left(\frac{v}{v_f}\frac{\partial v_f}{\partial v} - 1 - \frac{v}{2ckT}\frac{\partial \phi}{\partial v}\right) \tag{2-17}$$

where N_A is Avogadro's number, and N is the total number of molecules in a system. An equation of state for chain-like molecules can be obtained from Equation (2-17) when the free volume expression and the potential energy for a given system are specified.

The free-volume expression given by Elliott and coworkers (27) was used, which leads to

$$\frac{v}{v_f}\frac{\partial v_f}{\partial v}-1=\frac{4\eta}{1-1.9\eta}$$

$$=\frac{4\tau}{v_r-1.9\tau} \tag{2-18}$$

where $\eta=\frac{\tau v^*}{v}$, $v_r=\frac{v}{v^*}$, and τ=0.7405

The attractive term in the partition function of the PGR equation of state was expressed in terms of the segment number within the interaction range by Kim and coworkers as follows (9)

$$\frac{-\phi}{2ckT}=\frac{1}{2}\int_{1/\tilde{T}=0}^{1/\tilde{T}} N_c(\rho,T)\,d\left(1/\tilde{T}\right) \tag{2-19}$$

where $\tilde{T}=\frac{T}{T^*}=\frac{ckT}{\varepsilon q}$

The coordination number, N_c, is the number of segments within the interaction range of a center molecule, and ε is the potential energy between segments. Applying the square-well potential between two segments, the coordination number, N_c, becomes

$$N_c=\frac{N}{V}\int_{\sigma}^{K\sigma} g(r;\rho,T)\; s\;\left(4\pi r^2\right)\,dr \tag{2-20}$$

where the lower limit, σ, is the radius of a hard-sphere; the upper limit, Kσ, is the potential well width from σ; s is the number of segments in the center molecule; and g(r;ρ ,T) is the radial distribution function.

At the low density limit, the radial distribution function is given as (51)

$$\lim_{\rho\to 0} g(r;\rho,T) = \exp\left(\frac{-u(r)}{kT}\right) \tag{2-21}$$

where u(r) is the potential energy between molecules. The degree of freedom parameter, c, which represents the ratio of the total system energy (translational, rotational and vibrational energy) to the translational energy, was introduced into the attraction energy term in the partition function of chain-like molecules. It was also introduced in the potential energy term of the radial distribution function of Equation (2-21).

$$\lim_{\rho\to 0} g(r;\rho,T) = \exp\left(\frac{-u(r)}{ckT}\right) \tag{2-22}$$

Integration of Equation (2-20) for a square-well potential fluid leads to

$$\lim_{\rho\to 0} N_c = \frac{N}{V}\frac{4\pi}{3}\sigma^3\left(K^3-1\right)s\exp\left(\frac{\varepsilon q}{ckT}\right) \tag{2-23}$$

where ε is the intermolecular potential energy per unit external surface area and q is the external surface area of a molecule. The term εq represents the total square well potential energy of a center molecule. From Equation (2-19), the attraction term at the low density limit becomes

$$\lim_{\rho\to 0}\frac{-\phi}{2ckT}=\lim_{\rho\to 0}\left[\frac{1}{2}\int_{1/\tilde{T}=0}^{1/\tilde{T}}N_c(\rho,T)\,d(1/\tilde{T})\right]$$

$$=\frac{1}{2}\int_{1/\tilde{T}=0}^{1/\tilde{T}}\left[\lim_{\rho\to 0}\{N_c(\rho,T)\}\right]d(1/\tilde{T}) \tag{2-24}$$

Substitution of Equation (2-23) into Equation (2-24) gives

$$\lim_{\rho\to 0}\frac{-\phi}{2ckT}=\left(\frac{K^3-1}{2}\right)\left(\frac{v^*}{v}\right)\int_{1/\tilde{T}=0}^{1/\tilde{T}}\exp\left(\frac{1}{\tilde{T}}\right)d(1/\tilde{T}) \tag{2-25}$$

where $T^*=\frac{\varepsilon q}{ck}$ and $\tilde{T}=\frac{T}{T^*}$

The following potential energy expression at the low density limit can be obtained by eliminating the integral in Equation (2-25).

$$\lim_{\rho\to 0}\frac{-\phi}{2ckT}=\alpha_0\left(\frac{v^*}{v}\right)\left(\exp\left(\frac{1}{\tilde{T}}\right)-1\right) \tag{2-26}$$

where $\alpha_0 = (K^3-1)/2$

Even though the potential energy expression in Equation (2-26) is a function of temperature, Park (26) added two empirical functions, which are dependent on density and temperature, to amend the limiting definition of the radial distribution function.

$$\frac{-\phi}{2ckT}=\alpha_0 h(T)\Delta(\rho)\left(\frac{v^*}{v}\right)\left(\exp\left(\frac{1}{\tilde{T}}\right)-1\right) \tag{2-27}$$

By taking a partial derivative of molar volume to Equation (2-27) the attractive term of the equation of state becomes

$$\begin{aligned}\frac{-v}{2ckT}\left(\frac{\partial\phi}{\partial v}\right)_{N,T} &= \alpha_0 h(T)\left(\exp\left(\frac{1}{\tilde{\tilde{T}}}\right)-1\right)v^*\left(\frac{\partial\Delta(\rho)}{\partial v}-\frac{\Delta(\rho)}{v}\right) \\ &= \alpha_0 h(T)\left(\exp\left(\frac{1}{\tilde{\tilde{T}}}\right)-1\right)\left(\frac{\partial\Delta(\rho)}{\partial v_r}-\frac{\Delta(\rho)}{v_r}\right)\end{aligned} \tag{2-28}$$

The PGR equation of state used an augmented generalized cubic equation of state attractive term. The following expression for the density-dependent function $\Delta(\rho)$ was used as the attractive term of the PGR equation of state.

$$\frac{\partial\Delta(\rho)}{\partial v_r}-\frac{\Delta(\rho)}{v_r}=-\frac{v_r}{v_r^2+uv_r+w}-\frac{Q}{v_r+1} \tag{2-29}$$

The actual form of the density correction function, $\Delta(\rho)$, is given by integrating Equation (2-28) from $v_r = \infty$ to $v_r = 0$

$$\Delta(\rho)=\frac{-v_r}{\sqrt{u^2-4w}}\ln\frac{2v_r+u-\sqrt{u^2-4w}}{2v_r+u+\sqrt{u^2-4w}}+Qv_r\ln\frac{v_r+1}{v_r} \tag{2-30}$$

if $u^2 > 4w$ or

$$\Delta(\rho)=\frac{-2v_r}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right)+Qv_r\ln\frac{v_r+1}{v_r} \tag{2-31}$$

if $u^2 < 4w$

The final form of the PGR equation of state can be obtained from Equations (2-17), (2-18), (2-28) and (2-29).

$$Z = 1 + c\left(\frac{4\tau}{v_r - 1.9\tau} - \frac{\alpha Y v_r}{v_r^2 + uv_r + w} - \frac{Q\alpha Y}{v_r + 1}\right) \tag{2-32}$$

$$\alpha = \alpha_0 h(T) \tag{2-33}$$

and

$$Y = \exp\left(\frac{1}{\widetilde{T}}\right) - 1 \tag{2-34}$$

An empirical expression for h(T) is

$$h(T) = 1 + \kappa_1 \widetilde{T}^{1/2} + \kappa_2 \widetilde{T} + \kappa_3 \widetilde{T}^2 + \kappa_4 \widetilde{T}^{-1} \tag{2-35}$$

where κ_1, κ_2, κ_3 and κ_4 are the original PGR equation of state constants.

Modification of the PGR Equation of State

The Repulsive Term

The repulsive term of an equation of state is often used to describe hard-sphere, hard-disc, or hard-chain interactions without attraction energy between molecules. Monte Carlo or molecular dynamic simulation results are available in the literature for the repulsive contribution to the fluid compressibility for different densities (52, 53). Among the equations of state for hard-spheres, Carnahan and Starling (18) provided one of the better known and more accurate expressions. Their expression is a simple correlation of the virial type analytical derivation for the hard-sphere compressibility factor (54).

$$Z^{rep} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$$

$$= 1 + \frac{4\eta - 2\eta^2}{(1-\eta)^3} \qquad (2\text{-}36)$$

where $\eta = \frac{1}{6}\left(\pi\sqrt{2}\right)\left(\frac{v^*}{v}\right)$ and v^* is molar close packed volume for hard spheres. Several equations of state with the Carnahan and Starling repulsive term have been proposed in the literature (55-57). In general, these equations showed better or comparable performance to the PR and SRK equations in calculating fluid phase equilibrium properties of simple mixtures. Recently, an empirical expression for hard spheres was proposed by Elliott and coworkers (27).

$$Z^{rep} = 1 + \frac{\beta_1 \eta}{1-\beta_2 \eta} \qquad (2\text{-}37)$$

where $\beta_1 = 4$ and $\beta_2 = 1.9$.

The models of Carnahan and Starling and Elliott et al. have a limiting value of η. The limiting value of η is 1 for the Carnahan and Starling model and 0.53 for the Elliott et al. model. The repulsive model of Carnahan and Starling is more accurate than that of Elliott et al. (26) when the expressions for the repulsive compressibility factors (Equations (2-36) and (2-37)) are compared to the molecular dynamics calculations of Erpenbeck and Wood (52). Furthermore, as shown in Figure 1, the Elliott expression produced repulsive compressibilities which varied from the Carnahan-Starling values by

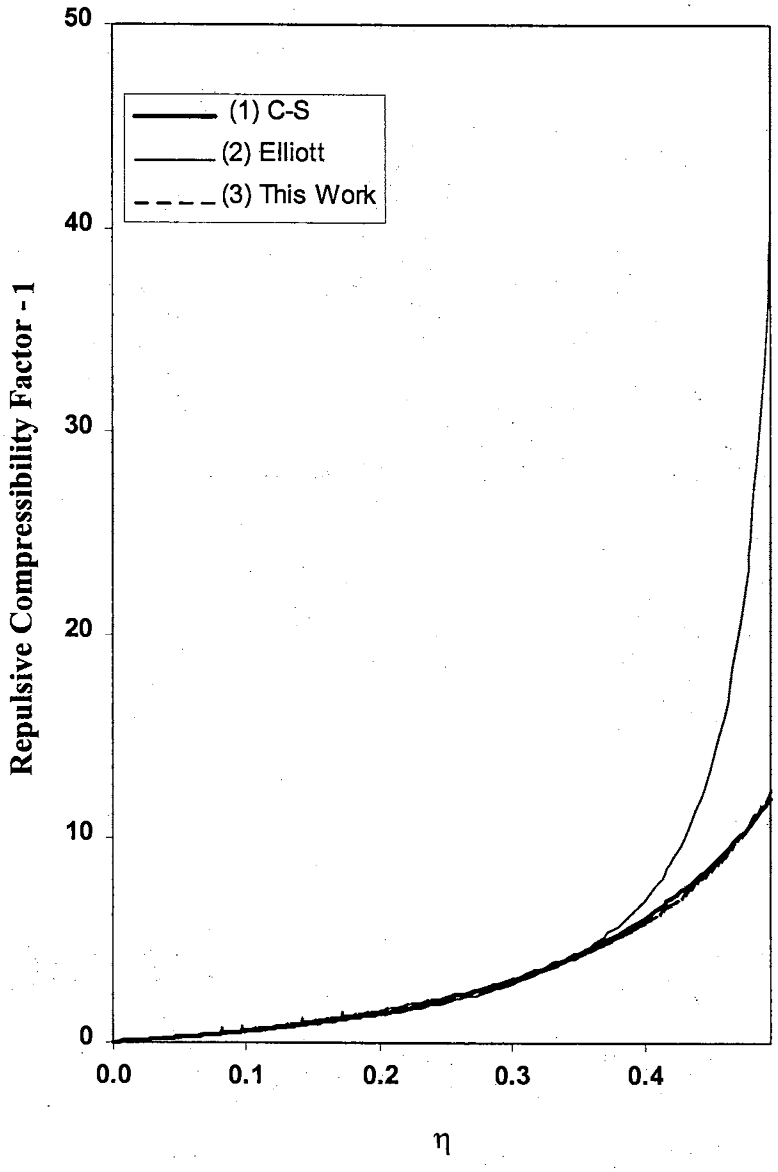

Figure 1. Comparison of Repulsive Compressibility Factor Expressions. (1) Carnahan and Starling; (2) Elliott et al.; (3) This Work

as much as 200% when the reduced density exceeded 0.38. To retain the simplicity of the Elliott repulsive expression and to produce Carnahan-Starling repulsive compressibilities more accurately, the model parameters in the Elliott equation were re-optimized. This new expression for the repulsive compressibility is given as

$$Z^{rep} = 1 + \frac{\gamma_1 \eta}{1 - \gamma_2 \eta} \tag{2-38}$$

where $\gamma_1 = 5.34$ and $\gamma_2 = 1.57$. As shown in Figure 1, this expression compares favorably with the Carnahan-Starling model. However, the pure-fluid results of the Elliott model are better; thus, the model was retained in the current work.

Modification of the Attractive Term

The attractive term of most equations of state, such as the SPHCT equation, contains several assumptions which simplify its temperature and density dependence. Thus, improvements in equation of state predictions can be achieved by modifying the temperature and/or structural dependence of the attractive term (24, 25, 58-60).

The attractive term of the PGR equation of state is an augmented generalized cubic equation of state. The attractive term of the generalized cubic equation of state such as SRK equation under-predicts compressibility factors compared to molecular simulation results (27, 31). The additional term is expected to eliminate one of the deficiencies of the cubic equation of state attractive term. The two attractive terms are

$$Z^{I}_{att} = -\frac{\alpha Y v_r}{v_r^2 + u v_r + w} \qquad (2\text{-}39)$$

$$Z^{II}_{att} = -\frac{Q\alpha Y}{v_r + 1} \qquad (2\text{-}40)$$

In this study, a more general expression is suggested for the attractive term, which gives the equation added flexibility when applied to chain-like molecules

$$Z^{II}_{att} = -\frac{Q_1\alpha Y}{v_r + Q_2} \qquad (2\text{-}41)$$

where Q, Q_1, and Q_2 are all equation constants. The fact, along with the high sensitivity of calculated properties to T^* discussed by Shaver and coworkers (25), suggest that improvement in equation of state predictions can be achieved by modifying the temperature dependence of the attractive term. A modified form for the radial distribution function of Equations (2-39) and (2-40) are

$$\alpha Y = Z_M \alpha \left[\exp(F_t) - 1\right] \qquad (2\text{-}42)$$

where

$$\alpha = 1 + \kappa_1 \tilde{T}^{1/2} + \kappa_2 \tilde{T} + \kappa_3 \tilde{T}^2 + \kappa_4 \tilde{T}^{-1} \qquad (2\text{-}43)$$

$$F_t = \omega_1\left(\frac{1}{2\tilde{T}}\right)^{1/2} + \omega_2\left(\frac{1}{2\tilde{T}}\right) + \omega_3\left(\frac{1}{2\tilde{T}}\right)^{3/2} + \omega_4\left(\frac{1}{2\tilde{T}}\right)^2 \qquad (2\text{-}44)$$

and Z_M, κ_1, κ_2, κ_3, κ_4, ω_1, ω_2, ω_3, and ω_4 are constants.

Combinations of three repulsive equations (Equations (2-36) to (2-38)) and several functions for the attractive term (Equations (2-41) to (2-44)) were studied using vapor pressure data for the pure paraffins methane, propane, n-decane, and n-tetradecane. The predictive abilities of each combination was evaluated by optimizing the function parameters and equation of state parameters simultaneously.

Table I presents a summary of results for several cases studied attempting to identify a more accurate equation of state. Using the Elliott repulsive model and the F_t function provides the best results (average absolute % deviation of 1.0). Using α in addition to F_t does not provide any improvement in vapor pressure predictions over the use of F_t alone. Therefore, the present work is restricted to the use of only F_t. The optimized coefficients for F_t are given in Table II. The new repulsive expression of Equation (2-38) and Carnahan and Starling model predicts close to molecular simulation results. Nevertheless, the evaluation results in Table I indicate that the Elliott model performs better than the other two repulsive expressions.

By combining Equation (2-37), (2-39), (2-41), (2-42), and (2-44), the final form of the modified PGR equation of state can be written as

$$Z = 1 + c\left(\frac{\beta_1\tau}{v_r - \beta_2\tau} - \frac{\alpha Y v_r}{v_r^2 + u v_r + w} - \frac{Q_1 \alpha Y}{v_r + Q_2}\right) \tag{2-45}$$

where

$$\alpha Y = Z_M\left[\exp(F_t) - 1\right] \tag{2-46}$$

and function F_t is defined in Equation (2-44).

TABLE I

EVALUATION OF MODIFYING FUNCTIONS FOR THE REPULSIVE AND ATTRACTIVE PORTION OF THE PGR EQUATION

Function Included	Number of Constants	% AAD*** For Vapor Pressure Predictions		
		Carnahan and Starling	Elliott et al.	This Work
α*	4	6.3	2.0	5.6
F_t**	4	5.9	1.0	2.0
α and F_t	8	5.7	1.0	1.5

* Equation (2-42)
** Equation (2-43)
*** average absolute % deviation

TABLE II

COEFFICIENTS FOR THE MODIFYING FUNCTION F_t FOR THE PGR EQUATION OF STATE

Coefficient	Value
ω_1	0.07635
ω_2	2.01240
ω_3	-0.22322
ω_4	-0.70301

Characteristics of the Modified PGR Equation

The limiting behavior of this equation follows that of the other equations of state. As the molar volume approaches infinity at any temperature, the repulsive term of the equation becomes unity, and the attractive term becomes zero. Similarly, the equation of state can be simplified to the ideal gas law as the system molar volume approaches infinity. At the highly compressed state, the molar volume can be calculated from the denominator of the repulsive term

$$v_{\min} = \beta_1 \tau v^* \tag{2-47}$$

This molar volume of Equation (2-47) is the smallest possible molar volume. The initial guess for Z can be obtained from this molar volume to find the liquid root in the equilibrium calculation

$$Z_{\min} = \frac{\beta_1 \tau p v^*}{RT} \tag{2-48}$$

As the temperature approaches infinity, the attractive term becomes negligible because (αY) in the attractive term converges to zero, as shown in Figure 2. Moreover, when the molecular size (characteristic volume, v^*) is zero and the temperature goes to infinity, the equation also satisfies the ideal gas law.

The effect of introducing the modified function of (αY) with F_t of the attractive term can be seen in Figure 2. The original and the modified PGR equation show similar behaviors. However, the temperature derivative of (αY) of the modified PGR equation

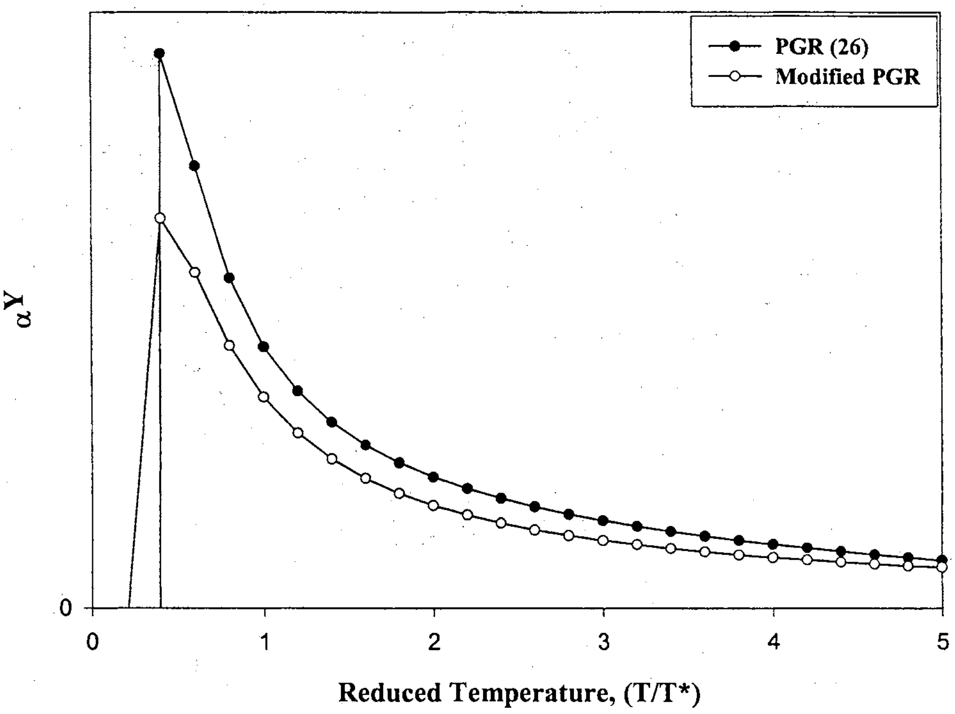

Figure 2. The Temperature Dependence of the Attractive Term.

is smoother near the break point where the reduced temperature value is 0.4. The stability of this derivative plays an important role in calorimetric property calculations. Below this point the values of (αY) are less steep than those of the original PGR equation. In Figure 3, the values of (αY) from the original and modified PGR equations of state are shown relative to the values obtained from individual regressions of experimental data for methane. The values of (αY) obtained from the original PGR equation show considerable deviation from the regressed values while those obtained using the modified PGR equation show good agreement. Detailed evaluations of this modified PGR equation for both pure fluid and mixture calculations are included in the following chapters.

The sensitivity of calculated properties (vapor pressures and saturated liquid and vapor densities) to each of the three parameters was determined from the triple point to the critical point for methane. The parameter sensitivity is defined as

$$\frac{A}{C}\left(\frac{\partial C}{\partial A}\right) \tag{2-49}$$

where C is the calculated property (vapor pressure and vapor and liquid density) and A is one of the equation parameters (25). The parameter sensitivity may be viewed as the percentage change in the calculated property, C, caused by a 1% change in the equation parameter, A. Figures 4 through 6 show the sensitivity of calculated vapor pressure, saturated liquid and saturated vapor densities, respectively. These figures show that the effect of v^* is nearly constant over the entire temperature range for all calculations. Vapor pressure and liquid density are least sensitive to the parameter v^*. All property

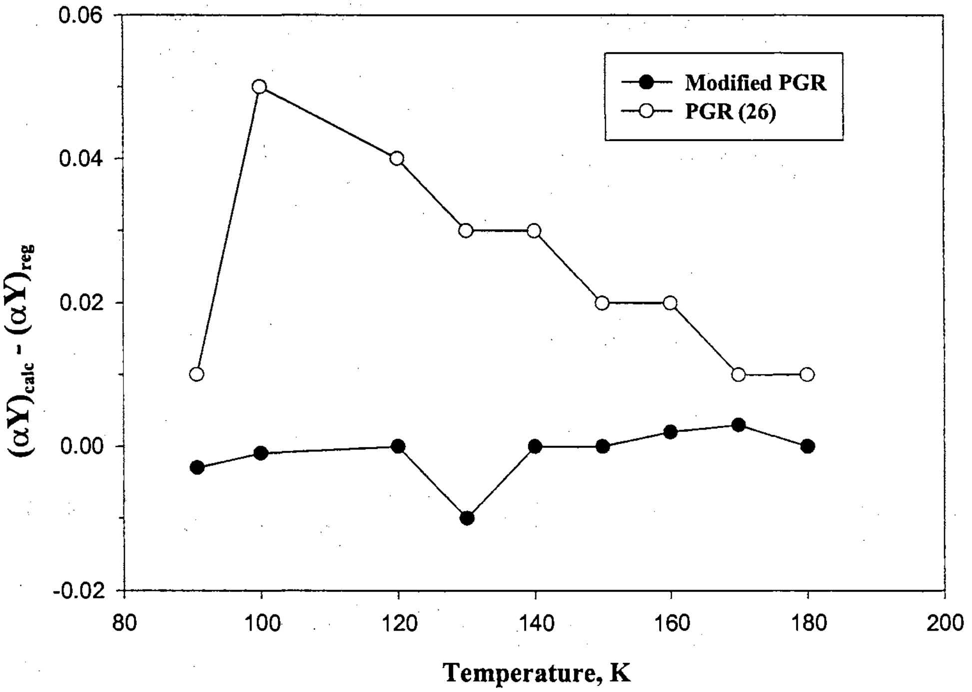

Figure 3. Comparison of Calculated and Regressed Values of (αY) for Methane.

calculations are more sensitive to T^*, which may indicate some remaining deficiency in the attractive term. The effects of T^* and c on vapor pressure and vapor density calculations are similar and both have greater impact at low temperatures. Since the property calculations and parameter generalization routine use the same objective function with even-weight-distribution, better predictions on vapor pressure and vapor density were expected according to the sensitivity study result.

Summary

The original Park-Gasem-Robinson (PGR) equation was modified to enhance its volumetric and equilibrium predictive capabilities. The two temperature-dependent terms in the attractive part of the equation were replaced with a new simpler term, which was tested for its efficacy and numerical stability. The universal equation of state constants and the pure component parameters for selected compounds were obtained for the modified version of the PGR equation of state. A study of the modified PGR equation parameters (T^*, v^*, c) was performed to gain insight into the sensitivity of calculated properties to the equation parameters and to investigate the behavior of the parameters required to produced accurate vapor-liquid equilibrium calculations. The characteristic temperature, T^*, showed stronger dependence on temperature in vapor pressure and saturated phase density calculations. As such, a possible deficiency in the attractive portion of the equation of state may still exist.

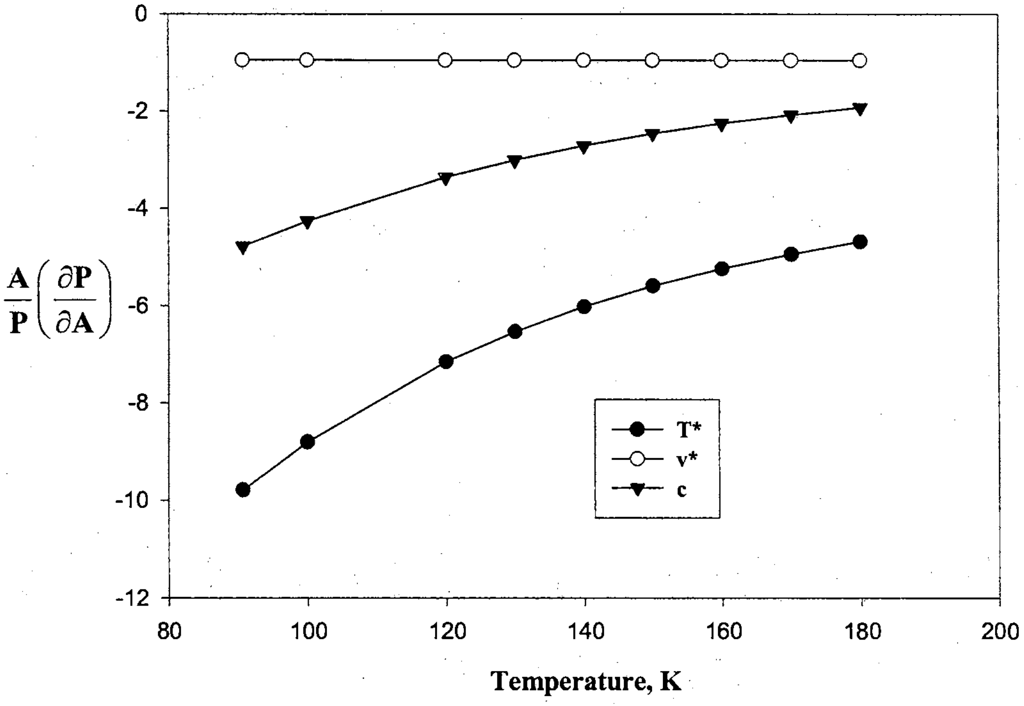

Figure 4. Effect of Reduced Temperature on Vapor Pressure Sensitivity for Saturated Methane.

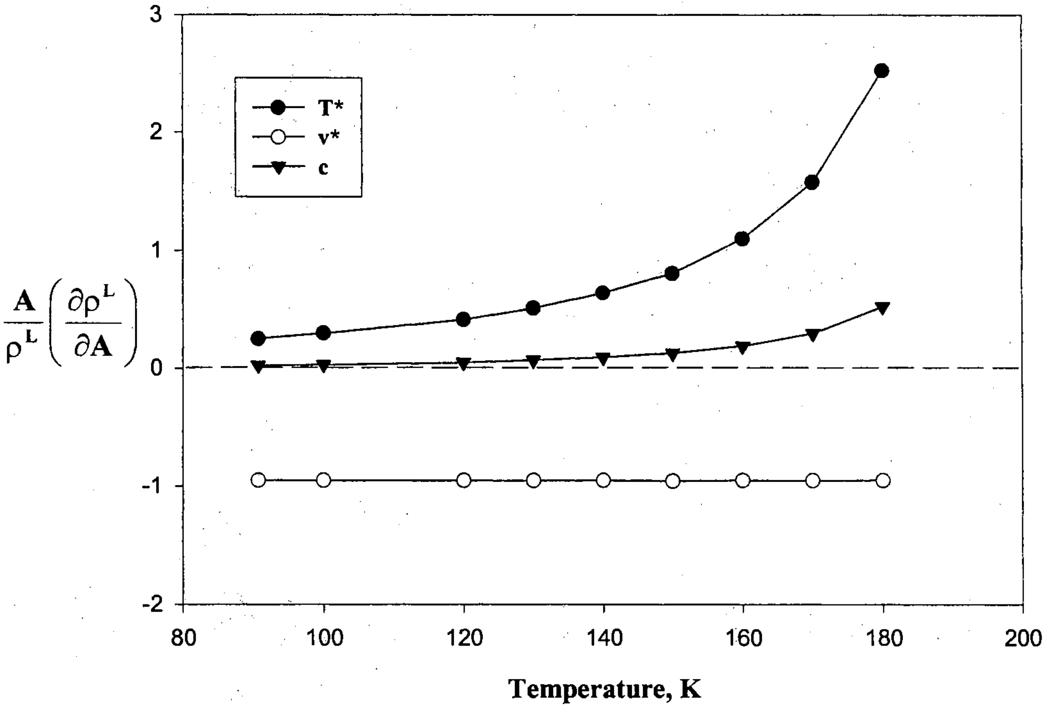

Figure 5. Effect of Reduced Temperature on Liquid Density Sensitivity for Saturated Methane.

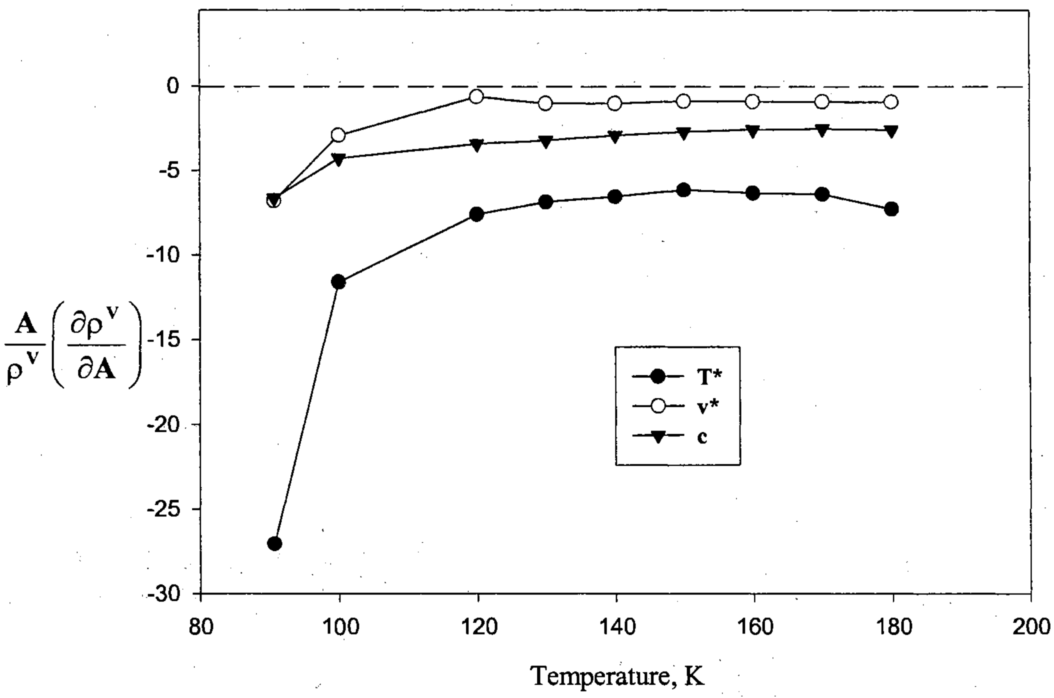

Figure 6. Effect of Reduced Temperature on Vapor Density Sensitivity for Saturated Methane.

CHAPTER 3

EVALUATION OF THE MODIFIED PGR EQUATION OF STATE FOR SELECTED PURE COMPOUNDS

Abstract

The equation of state modification discussed in the previous chapter was investigated. The predictive capability of the modified PGR equation of state for vapor pressure, and saturated liquid and vapor densities was evaluated for selected normal paraffins, normal alkenes, cyclo-paraffins, light aromatics, argon, carbon dioxide and water. The generalized equation of state constants and substance-specific characteristic parameters in the modified PGR equation of state were obtained from the pure component vapor pressures, and saturated liquid and vapor molar volumes. The calculated phase properties were compared to those of the Peng-Robinson (PR) equation (2), the simplified-perturbed-hard-chain theory (SPHCT) equation (9) and the original Park-Gasem-Robinson (PGR) equation (26). Generally, the performance of the proposed equation of state (%AAD of 1.3, 2.8 and 3.7 for vapor pressure, saturated liquid and vapor densities, respectively) was better than the PR, SPHCT and original PGR equations in predicting the pure fluid properties.

Introduction

Accuracy, simplicity, and generality have been most desired characteristics of an equation of state. Even though a large number of equations have been introduced and analyzed, most have satisfied these requirements only partially. To develop a useful equation of state, one has to begin with theory and some sound approximations for the physical reality. However, such attempts typically evoke a lack of fit with experimental data. Therefore, adjustable substance-specific model parameters of the equation are utilized to fit pure fluid experimental data and render the equation useful for practical applications. Such parameters are then generalized and mixing rules are introduced to handle mixtures.

The equation of state constants and the component-specific parameters of an equation of state can be determined from the vapor-liquid equilibrium phase properties. In vapor-liquid equilibrium, a pure component has one degree of freedom. Thus, any experimental data set containing more than one thermodynamic intensive property can be used to evaluate constants and parameters. Temperature, pressure, and saturated liquid and vapor densities (or molar volumes) are the commonly used thermodynamic properties in the development and evaluation of pure-fluid equations of state.

The purpose of this study is to demonstrate the usefulness of the changes to the original PGR equation of state through the prediction of pure fluid saturation properties.

The Equation of State

The pressure explicit form of the modified PGR equation of state derived in the previous chapter may be written as

$$\frac{pv}{RT} = 1 + c\left(\frac{\beta_1\tau}{v_r - \beta_2\tau} - \frac{Z_M Y v_r}{v_r^2 + uv_r + w} - \frac{Q_1 Z_M Y}{v_r + Q_2}\right) \tag{3-1}$$

where

$$Y = \exp\left(F_t\right) - 1 \tag{3-2}$$

$$F_t = \omega_1\left(\frac{1}{2\tilde{T}}\right)^{1/2} + \omega_2\left(\frac{1}{2\tilde{T}}\right) + \omega_3\left(\frac{1}{2\tilde{T}}\right)^{3/2} + \omega_4\left(\frac{1}{2\tilde{T}}\right)^2 \tag{3-3}$$

and

$$\tilde{T} = \frac{T}{T^*} \quad \text{and} \quad v_r = \frac{v}{v^*}$$

The universal constants in this equation are shown in Table III. These equation of state constants, including u, w, Z_M, Q_1, Q_2 and ω_1 - ω_4 are regressed from pure fluid experimental data.

The modified equation of state shown in the Equation (3-1) is fifth order in volume (or in compressibility factor). This equation can be expanded in terms of the compressibility factor, Z, as

$$Z^5 + AZ^4 + BZ^3 + CZ^2 + DZ + E = 0 \tag{3-4}$$

TABLE III

UNIVERSAL CONSTANTS FOR THE MODIFIED PGR EQUATION OF STATE

Constant	Value
τ	0.74048
u	-2.8969
w	2.6944
Q_1	10.5121
Q_2	1.0226
Z_M	1.4264
ω_1	0.076354
ω_2	2.0124
ω_3	-0.22322
ω_4	-0.70301

A, B, C, D and E are constants for a given temperature and pressure. This expanded form of the equation of state (Equation (3-4)) and definitions for the coefficients are presented in Appendix A. During equilibrium calculations, Equation (3-4) is solved to identify liquid and vapor roots of Z.

Fugacity coefficients are required in multi-phase equilibrium calculations. The fugacity coefficient of a pure fluid can be derived as follows (32)

$$\ln\phi = -\frac{1}{RT}\int_{\infty}^{v}\left(p-\frac{RT}{v}\right)dv + Z - 1 - \ln Z \tag{3-5}$$

For the modified PGR equation of state given in Equation (3-1), the following expression is obtained for the fugacity coefficient.

$$\begin{aligned}\ln\phi = &-c\frac{\beta_1}{\beta_2}\ln\frac{v_r-\beta_2\tau}{v_r}\\ &+cZ_MY\left[\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right)-\frac{Q_1}{Q_2}\ln\frac{v_r+Q_2}{v_r}\right]\\ &+\frac{c\beta_1\tau}{v_r-\beta_2\tau}-\frac{cZ_MYv_r}{v_r^2+uv_r+w}-\frac{cZ_MYQ_1}{v_r+Q_2}\end{aligned} \tag{3-6}$$

Detailed derivation of this fugacity coefficient is given in Appendix B.

Methods

The modified PGR equation of state proposed in this work has a set of universal constants for all compounds (u, w, Q_1, Q_2, and ω_1 - ω_4) and substance-specific pure component parameters (T^*, v^* and c). Experimental vapor pressure data along with liquid and vapor phase densities at different temperatures were used to evaluate the universal constants and component parameters. The various data sets used in this work contain T-p-ρ_l-ρ_v, T-p-ρ_l, T-p, or T-ρ_l, as shown in the next section. The parameters for the original form of the PGR equation of state (T^*, v^*, and c) were regressed to minimize the following objective function for both vapor pressures and phase densities

$$SS = \sum_{i=1}^{N} \left(\left(\frac{p_{exp} - p_{calc}}{p_{exp}} \right)_i^2 + \left(\frac{\rho_{exp}^L - \rho_{calc}^L}{\rho_{exp}^L} \right)_i^2 + \left(\frac{\rho_{exp}^V - \rho_{calc}^V}{\rho_{exp}^V} \right)_i^2 \right) \qquad (3\text{-}7)$$

The form of this objective function can be changed according to the availability of the information in the database. For the compounds with no available vapor densities, the three equation parameters were fit only to vapor pressures and liquid densities. When neither phase density data was available, the last two terms of Equation (3-7) were omitted from the objective function and the three equation parameters were fit only to vapor pressures. The calculated values of vapor pressure and phase densities in the objective function were obtained using the equation of state.

Multiple nonlinear regressions were used to regress the constants and the pure-component parameters (T^*, v^* and c) in the equation. The constants in the equation (u, w, Z_M, Q_1, Q_2 and ω_1 - ω_4) were obtained mainly with the methane, ethane, propane, and butane saturation data. More information on the equilibrium calculation method and the regression technique used in this work are given by Gasem (61).

In calculating vapor pressures and saturated phase densities, a reliable solution algorithm is essential in determining the compressibility factors for the equation of state. As mentioned in the previous section, both the original and modified PGR equations of state are fifth order in terms of the compressibility factor. To solve this equation efficiently, an initializing routine was implemented. This equation-solver algorithm, which is similar to Park's (26) approach, is as follows. First, the lower limit value of the compressibility factor in Equation (2-47) was taken as the initial value of compressibility factor, Z^L, for a liquid phase. The right-hand side of Equation (3-4) was calculated, starting with this initial value until its sign changed from negative to positive upon increasing Z^L in 2% increments. When the change of sign occurred, the Z^L value becomes a new initial value, and the simple Newton-Raphson Method was then used to locate the correct root. The initial value of the compressibility factor, Z^v, for a vapor phase was set to three. This value was decreased by 2% until the sign of the right hand side of Equation (3-4) changed from positive to negative. Then, the same Newton-Raphson Method was applied with the updated Z^v as an initial guess. When the relative change of compressibility factor with a previous iteration was smaller than 1.0×10^{-8}, the system converges and the iteration terminates. This solution algorithm is more adequate than that introduced by Shaver and coworkers (25).

The Pure Fluid Database

A database of 20 pure compounds described previously by Shaver and coworkers (25) and Park (26) was used in this work. The database covers almost the entire vapor-

TABLE IV

SOURCES AND RANGES OF PURE FLUID SATURATION DATA

Compound (# of pts)	Temperature Range, K	Pressure Range, bar	Liquid Density Range, g/cm^3	Vapor Density Range, g/cm^3	Source
Methane (9)	90.68 - 188.0	0.1172 - 42.412	0.2299 - 0.4512	2.514×10^{-4} - 0.0986	62
Ethane (9)	90.348 - 295.0	1.131×10^{-5} - 39.16	0.3309 - 0.6519	4.557×10^{-8} - 0.0925	63
Propane (26)	85.47 - 360.0	3.0×10^{-9} - 35.55	0.3453 - 0.6574	2.72×10^{-5} - 0.1054	64
n-Butane (12)	134.86 - 420.0	6.736×10^{-6} - 34.83	0.3281 - 0.7353	3.492×10^{-8} - 0.1335	65
n-Octane (8)	243.15 - 553.15	3.16×10^{-4} - 19.97	0.3818 - 0.7102	0.0003 - 0.09873	66
n-Decane (12)	330.85 - 613.15	0.01333 - 20.366	0.324 - 0.6996	*	67
n-Tetradecane (11)	394.26 - 573.15	0.0129 - 2.605	0.6685**	*	67
Ethene (12)	103.986 - 276.0	0.0012 - 43.73	0.3242 - 0.6549	4.01×10^{-6} - 0.1115	68
Propene (11)	87.89 - 360.0	9.54×10^{-9} - 42.202	0.3292 - 0.7688	5.49×10^{-11} - 0.1338	69
1-Butene (12)	119.95 - 413.15	5.0×10^{-7} - 36.18	0.345 - 0.618	*	67
1-Hexene (12)	156.15 - 493.15	5.0×10^{-7} - 26.86	*	*	67
Cyclopropane (12)	171.85 - 393.15	0.01333 - 51.252	*	*	67
Cyclobutane (13)	204.95 - 453.15	0.01333 - 45.191	*	*	67
Cyclohexane (15)	279.82 - 543.15	0.05328 - 35.889	0.3130 - 0.7102	*	67

TABLE IV (Continued)

Compound	Temperature Range, K	Pressure Range, bar	Liquid Density Range, g/cm^3	Vapor Density Range, g/cm^3	Source
Cyclooctane (17)	308.45 - 633.15	0.01333 - 31.309	*	*	67
trans-Decalin (9)	334.06 - 492.03	0.01333 - 1.9998	0.7726 - 0.8355	*	67
Benzene (10)	278.68 - 555.0	0.0478 - 44.8502	0.4355 - 0.8965	$1.62x10^{-4}$ - 0.1750	70
Toluene (12)	270.0 - 580.0	0.0076 - 35.56	0.2914 - 0.8873	$2.87x10^{-5}$ - 0.1318	71
Argon (8)	84.0 - 146.0	0.7052 - 49.05	0.8296 - 1.413	0.004194 - 0.2680	68
Carbon Dioxide (17)	216.55 - 298.15	5.179 - 64.356	0.7138 - 1.1778	0.0138 - 0.2424	72
Water (14)	273.16 - 633.15	0.006117 - 186.55	0.5281 - 0.9998	$4.855x10^{-6}$ - 0.1437	73
n-Eicosane (5)	473.15 - 623.15	0.01533- 1.110	0.5903 - 0.6668	*	67
n-Octacosane (5)	323.15 - 704.45	$7.0x10^{-9}$ - 1.0133	0.6226 - 0.7876	*	67
n-Hexatriacontane (6)	373.15 - 769.15	$6.9x10^{-8}$ - 1.0133	0.6399 - 0.7667	*	67
n-Tetratetracontane (5)	373.15 - 818.15	$6.9x10^{-8}$ - 1.0133	0.7450 - 0.7760	*	67

* Saturated density data for these compounds was not available.

** Only one saturated liquid density value was available for n-tetradecane.

liquid saturated region from the triple point to a reduced temperature of about 0.95. For several compounds, only limited saturated liquid density data are available, and for six compounds only vapor pressures are used. Specific ranges of saturated data used for pure fluids and their sources are given in Table IV. Additional data for heavy normal hydrocarbons (n-C_{20}, n-C_{28}, n-C_{36} and n-C_{44}) and hydrogen were also used to evaluate the pure component parameters of the equation for those compounds. The temperature, pressure and saturated density ranges for these heavy normal hydrocarbons and hydrogen with their sources are shown in Table IV. The critical properties, required in the PR equation, and the pure component parameters for the SPHCT and PGR equations are provided by Park (26) as shown in Tables V to VII.

Results and Discussion

The PGR equation of state modifications discussed in Chapter 2 were evaluated. Errors in predicted vapor pressures for 20 selected compounds are shown in Table VIII, along with those of the PR, SPHCT and PGR equations. The errors are expressed using the root-mean-squared error (RMSE) and the absolute-average-percentage deviation (%AAD). The RMSE and %AAD are defined as,

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N}\left(Y_{calc,i} - Y_{exp,i}\right)^2}{N}} \tag{3-8}$$

and

TABLE V

CRITICAL PROPERTIES USED IN THE PR EQUATION OF STATE

Compound	T_c (K)	p_c (bar)	ω	Source
Methane	190.56	45.95	0.0110	62
Ethane	305.41	48.20	0.0990	63
Propane	369.80	42.42	0.1530	63
n-Butane	425.16	37.96	0.1990	63
n-Octane	569.35	24.96	0.3980	24
n-Decane	617.50	20.97	0.4890	24
n-Tetradecane	691.58	15.62	0.6442	61
n-Eicosane	766.60	10.69	0.8791	64
n-Octacosane	845.40	8.30	1.1070	61
n-Hexatriacontane	901.10	6.80	1.2850	61
n-Tetratetracontane	944.30	6.00	1.4180	61
Ethene	282.34	50.40	0.0910	65
Propene	365.57	46.65	0.1440	65
1-Butene	419.95	40.43	0.1910	63
1-Hexene	504.03	31.43	0.2850	63
Cyclopropane	398.25	55.75	0.1300	63
Cyclobutane	460.00	49.85	0.1810	63
Cyclohexane	553.50	40.74	0.2100	63
Cyclooctane	647.20	35.67	0.2360	63
trans-Decalin	687.10	31.40	0.2700	63
Benzene	561.75	48.76	0.2120	63
Toluene	591.80	41.04	0.2630	63
Argon	150.86	49.05	0.0010	65
Carbon Dioxide	304.20	73.76	0.2390	63
Water	647.13	220.55	0.3440	66

TABLE VI

PURE FLUID PARAMETERS FOR THE SPHCT EQUATION OF STATE (25)

Compound	T* (K)	v* (cm^3/mol)	c
Methane	80.050	18.889	1.0298
Ethane	120.73	26.988	1.2485
Propane	136.94	35.876	1.5015
n-Butane	151.73	43.922	1.6867
n-Octane	177.91	74.084	2.6453
n-Decane	186.03	93.130	3.0697
n-Tetradecane	196.70	127.416	3.9218
n-Eicosane	205.98	181.657	5.1600
Ethene	111.58	24.684	1.2379
Propene	133.85	31.881	1.5267
1-Butene	157.89	40.457	1.5212
1-Hexene	255.90	26.597	1.0854
Cyclopropane	252.76	13.699	0.6646
Cyclobutane	312.12	13.976	0.6413
Cyclohexane	199.49	49.825	1.7077
Cyclooctane	212.41	69.815	2.1068
trans-Decalin	381.13	29.826	0.9682
Benzene	192.59	41.457	1.8866
Toluene	205.78	52.971	1.8921
Argon	63.250	14.275	1.0270
Carbon Dioxide	104.32	14.486	1.9258
Water	225.08	9.0710	2.0233

TABLE VII

PURE FLUID PARAMETERS FOR THE PGR EQUATION OF STATE (26)

Compound	T* (K)	v* (cm^3/mol)	c
Methane	81.287	23.180	1.0000
Ethane	121.46	30.817	1.2545
Propane	143.01	40.915	1.3990
n-Butane	157.04	50.202	1.5973
n-Octane	189.10	84.736	2.3581
n-Decane	201.84	105.16	2.5979
n-Tetradecane	206.31	155.95	3.5223
n-Eicosane	208.53	204.99	5.2086
n-Octacosane	218.51	286.38	6.5399
n-Hexatriacontane	230.91	395.89	7.0828
n-Tetratetracontane	234.06	491.49	8.1107
Ethene	112.58	27.566	1.2402
Propene	138.78	36.804	1.4365
1-Butene	158.68	47.191	1.5180
1-Hexene	170.35	73.850	2.0271
Cyclopropane	156.97	33.757	1.3242
Cyclobutane	177.17	41.313	1.4512
Cyclohexane	205.40	59.327	1.6119
Cyclooctane	227.67	77.828	1.8601
trans-Decalin	203.89	161.70	2.4709
Benzene	205.02	48.701	1.6738
Toluene	212.37	60.107	1.7995
Argon	64.055	16.928	1.0000
Carbon Dioxide	111.31	18.052	1.6565
Water	231.08	10.352	1.9365
Hydrogen	20.555	18.434	0.38545

TABLE VIII

EVALUATION OF PURE FLUID VAPOR PRESSURE PREDICTIONS

Component	Peng-Robinson		SPHCT		PGR		This Work	
	RMSE bar	%AAD	RMSE bar	%AAD	RMSE bar	%AAD	RMSE bar	%AAD
Methane	0.162	1.6	0.444	3.8	0.383	1.6	0.032	0.5
Ethane	0.075	3.5	0.721	4.4	0.685	2.5	0.536	2.2
Propane	0.074	5.8	0.721	3.7	0.053	0.0	0.203	0.8
n-Butane	0.094	1.7	0.764	4.5	0.311	1.7	0.100	0.5
n-Octane	0.050	2.0	0.408	4.2	0.259	2.5	0.258	2.1
n-Decane	0.063	3.9	0.489	3.6	0.551	2.2	0.424	2.7
n-Tetradecane	0.030	7.3	0.021	1.3	0.036	1.8	0.014	0.7
Ethene	0.056	2.8	0.923	4.1	0.719	2.1	0.077	2.6
Propene	0.053	1.2	0.655	4.0	0.710	2.3	0.203	1.1
1-Butene	0.052	10.3	0.685	3.3	0.271	0.8	0.247	0.9
1-Hexene	0.039	1.1	0.227	0.9	0.171	1.6	0.158	0.8
Cyclopropane	0.072	1.6	0.384	1.0	0.150	0.5	0.086	0.5
Cyclobutane	0.061	0.5	0.378	1.2	0.411	0.9	0.286	1.1
Cyclohexane	0.029	2.1	0.668	2.2	0.284	1.0	0.283	0.7
Cyclooctane	0.176	7.3	1.029	4.0	0.182	1.0	0.207	1.2
trans-Decalin	0.049	11.9	0.009	0.8	0.002	0.1	0.004	0.3
Benzene	0.082	2.1	0.447	3.8	0.963	2.7	0.522	2.1
Toluene	0.056	1.8	1.105	4.1	0.162	1.0	0.145	1.0
Argon	0.110	0.4	0.338	2.3	1.012	2.7	0.609	1.8
Carbon Dioxide	0.344	2.2	0.651	3.0	0.582	2.3	0.384	0.5
Water	0.829	4.7	3.763	7.0	4.824	6.5	1.792	4.1
Overall	0.243	3.8	1.094	3.3	1.268	1.7	0.207	1.3

$$\%\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Y_{\mathrm{calc},i} - Y_{\exp,i}}{Y_{\exp,i}}\right| \times 100 \ , \tag{3-9}$$

respectively. In both equations, Y stands for a property being evaluated.

Table VIII shows the results of the vapor pressure predictions for the modified PGR equation of state along with the results obtained from the PR, original SPHCT and original PGR equations. The comparisons shown in Table VIII are based on vapor pressures greater than 0.007 bar (0.1psia) and reduced temperatures less than 0.95. The SPHCT and PGR equations showed poor vapor pressure prediction below 0.007 bar (24, 25, 26). The overall RSME and %AAD are defined, respectively, as

$$(\mathrm{RMSE})_{\mathrm{overall}} = \sqrt{\frac{\sum_{j=1}^{M}\sum_{i=1}^{N_j}\left(Y_{\mathrm{calc},i} - Y_{\exp,i}\right)^2}{\sum_{j=1}^{M} N_j}} \tag{3-10}$$

and

$$(\%\mathrm{AAD})_{\mathrm{overall}} = \frac{\sum_{j=1}^{M}\sum_{i=1}^{N_j}\left|\frac{Y_{\mathrm{calc},i} - Y_{\exp,i}}{Y_{\exp,i}}\right| \times 100}{\sum_{j=1}^{M} N_j} = \frac{\sum_{j=1}^{M}\left(N_j\,(\%\mathrm{AAD})_j\right)}{\sum_{j=1}^{M} N_j} \ , \tag{3-11}$$

M indicates the total number of pure components analyzed and N_j is the number of data points of the *j*th component. For vapor pressures, the overall RSME is 0.2 bar and the overall %AAD is 1.3. The overall %AAD for the modified PGR equation is less than half of those for the PR and SPHCT equations and 20% less than that for the original PGR equation. The overall RSME of the modified PGR equation is less than the original

PGR equation and one third of that of the original SPHCT equation. However, a slightly higher overall RSME value than the PR equation indicates that the modified PGR equation produced less evenly distributed errors. Among these equations considered, the modified PGR equation of state showed the best vapor pressure predictions.

In the prediction of vapor pressures for argon, cyclobutane, and n-octane, the modified PGR equation performed worse than the PR equation while the modified PGR equation performed mostly better than the original SPHCT and the original PGR equations. Otherwise, the modified PGR equations gave better predictions than the PR equation, which implies the superiority of the segment-segment interactions model to that of molecule-molecule interactions model in predicting the vapor pressure for heavy as well as light compounds. In comparison, for vapor pressures of carbon dioxide and a highly polar fluid, such as water, the original SPHCT and original PGR equations of state yielded worse results than the PR. This drawback is shown to be lessened using the modified PGR equation (%AAD of 0.5 and 4.1, respectively), albeit the RSME values of the modified PGR equation are higher than that of the PR. Accordingly, the performance of the modified PGR equation is generally better than the PR, the original SPHCT and the original PGR equations of state in predicting vapor pressures of pure fluids over the full saturation range.

Tables IX and X show the results for saturated liquid and vapor density predictions of the PR, original SPHCT, original PGR, and modified PGR equations. For saturated liquid densities, the overall RMSE of 0.02 g/cm^3 and %AAD of 2.8 are obtained. In spite of its larger vapor pressure errors for argon, the modified PGR equation shows much better results for the liquid density of this component. Like the PR

TABLE IX

EVALUATION OF PURE FLUID LIQUID DENSITY PREDICTIONS

Component	Peng-Robinson		SPHCT		PGR		This Work	
	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD
Methane	0.036	8.8	0.028	7.0	0.017	4.6	0.004	1.1
Ethane	0.030	5.5	0.045	7.8	0.010	2.1	0.013	2.8
Propane	0.032	5.6	0.047	7.8	0.014	2.7	0.012	2.1
n-Butane	0.029	5.0	1.049	7.9	0.022	4.3	0.017	2.8
n-Octane	0.030	5.2	0.062	9.9	0.042	7.7	0.042	7.1
n-Decane	0.043	7.2	0.068	11.5	0.028	4.9	0.008	0.9
n-Tetradecane	0.079	8.8	0.002	0.3	0.020	2.9	0.000	0.2
Ethene	0.041	7.1	0.037	7.4	0.011	2.2	0.016	2.7
Propene	0.041	6.6	0.039	7.6	0.022	4.2	0.020	3.6
1-Butene	0.024	3.9	0.024	3.7	0.017	2.9	0.020	2.9
Cyclohexane	0.018	2.6	0.029	4.1	0.022	3.9	0.017	2.0
Benzene	0.038	5.6	0.072	9.3	0.043	6.2	0.042	6.1
Toluene	0.027	2.9	0.060	7.2	0.033	4.8	0.027	3.3
Argon	0.145	10.0	0.077	5.9	0.018	1.4	0.014	1.0
Carbon Dioxide	0.047	4.4	0.051	4.5	0.047	4.5	0.048	4.3
Water	0.156	19.5	0.077	8.3	0.032	3.6	0.041	3.4
Overall	0.062	6.8	0.052	6.9	0.028	3.8	0.017	2.8

TABLE X

EVALUATION OF PURE FLUID VAPOR DENSITY PREDICTIONS

Component	Peng-Robinson		SPHCT		PGR		This work	
	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD
Methane	0.002	3.1	0.007	6.6	0.006	5.0	0.002	3.4
Ethane	0.001	4.0	0.006	7.1	0.002	2.0	0.003	2.2
Propane	0.001	6.1	0.006	5.3	0.004	3.6	0.003	2.7
n-Butane	0.001	2.1	0.010	6.5	0.005	2.2	0.002	2.6
n-Octane	0.001	2.3	0.009	8.1	0.005	4.1	0.006	4.4
Ethene	0.001	2.9	0.008	6.5	0.002	1.7	0.003	3.9
Propene	0.000	1.6	0.009	6.1	0.003	1.5	0.005	2.5
Benzene	0.002	2.8	0.014	7.1	0.008	3.0	0.009	3.4
Toluene	0.004	4.0	0.009	5.1	0.003	2.2	0.001	1.8
Argon	0.003	1.4	0.014	4.0	0.003	1.4	0.007	1.6
Carbon Dioxide	0.001	2.7	0.015	4.6	0.007	2.3	0.012	5.3
Water	0.003	6.0	0.017	11.3	0.010	6.6	0.015	8.6
Overall	0.002	3.6	0.011	6.4	0.006	3.1	0.007	3.7

equation of state, the modified PGR is observed to be less accurate than the original PGR equation for ethane. However, the overall performance for pure fluid liquid density predictions of the modified PGR equation of state exceeds those of the PR, the original SPHCT, and the original PGR equations of state.

For saturated vapor densities, an overall RMSE of 0.007 g/cm^3 and %AAD of 3.7 are obtained. The overall RSME and %AAD of the modified equation are higher than those of the original PGR equation which are 0.005 g/cm^3 and 3.1%, respectively. The results show that the vapor density predictive capability of the modified equation exceeds that of the original SPHCT equation of state and is comparable to that of the PR equation.

The modified equation is better than the PR, original SPHCT and original PGR equations in representing both vapor pressure and saturated liquid densities of pure fluids. While the PR and original PGR equations show comparable performance in predicting the saturated vapor densities of pure fluids (%AAD of 3.6 and 3.1, respectively), the SPHCT equation showed the worst results for saturated vapor density predictions (%AAD of 6.4).

Figures 7 to 9 show the experimental and calculated phase envelopes for methane, ethane, and propane. The calculated properties are obtained from the vapor-liquid equilibrium calculations at selected temperatures. As shown in Figures 7 and 9, the proposed equation provides accurate saturated liquid density predictions while larger deviations occur in calculating the saturated vapor densities near the critical points. The phase envelope plot for ethane in Figure 8 shows a relatively constant deviation from the experimental values on the saturated vapor side and larger deviations near the critical point on the saturated liquid side.

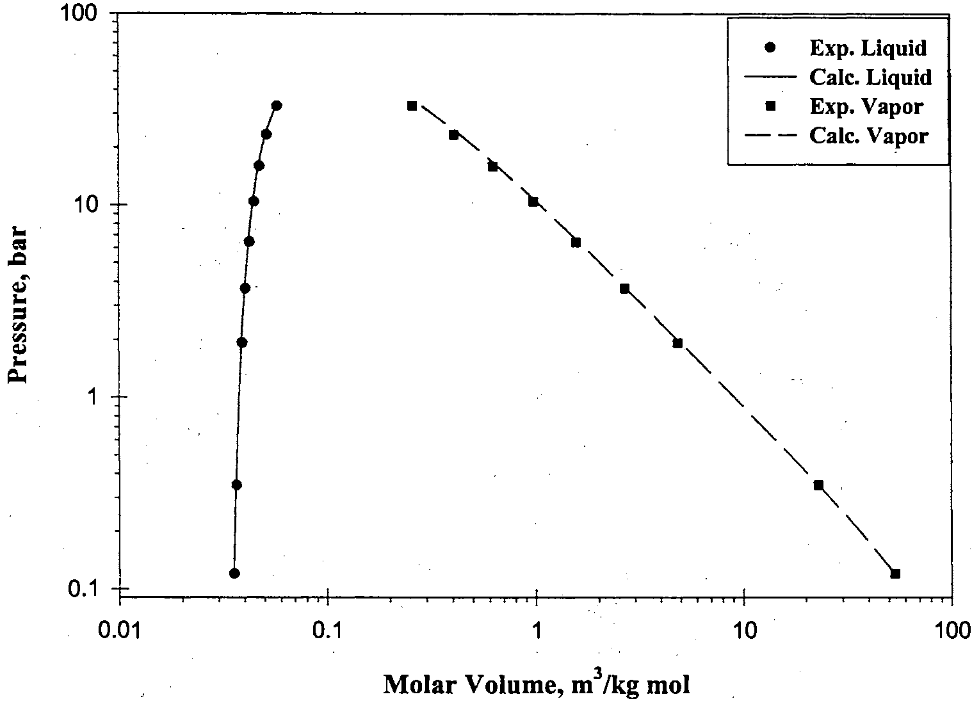

Figure 7. Experimental and Calculated Vapor Pressures and Phase Molar Volumes for Methane.

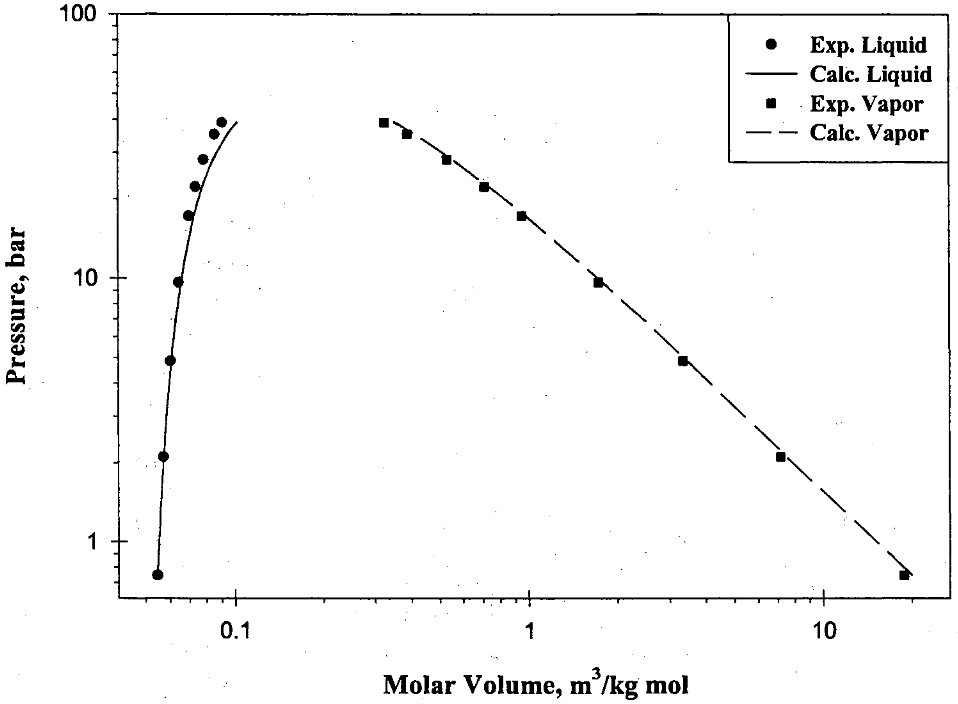

Figure 8. Experimental and Calculated Vapor Pressures and Phase Molar Volumes for Ethane.

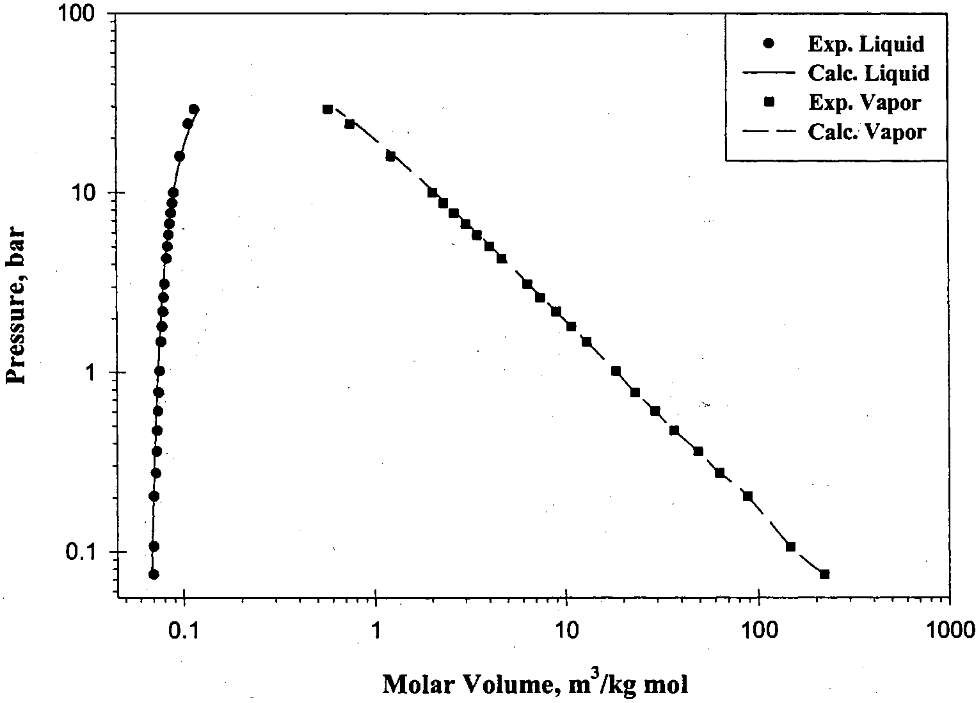

Figure 9. Experimental and Calculated Vapor Pressures and Phase Molar Volumes for Propane.

Table XI presents the pure-component parameters of the modified PGR equation of state. The parameters follow the general behavior of those of the SPHCT and PGR equations. The characteristic temperature, T^*, is proportional to the normal boiling point of the compound. The characteristic volume, v^*, increases as the molecular size of the n-paraffin increases. The trend for the degree of freedom parameter, c, is similar to the characteristic volume. Figures 10 to 12 show the pure-component parameters of several normal paraffins as a function of their carbon number. In Figure 10, the characteristic temperature shows an asymptotic behavior as the carbon number increases; n-octane deviates slightly from the trend of the other paraffins. The characteristic volume and the degree of freedom parameter are almost linear relative to the carbon number of the compound. For heavier n-paraffins such as n-C_{20}, n-C_{28}, n-C_{36}, and n-C_{44}, accurate pure component parameter determinations were not easy due to the scarcity of available saturation data. For these components, both pure component and binary mixture data were used simultaneously to obtain accurate parameters. The resulting trends of the pure-component parameters are similar to those of the original SPHCT, modified SPHCT (26), and original PGR (25) equations of state.

Conclusions and Recommendations

The universal constants and the substance-specific characteristic parameters of the modified Park-Gasem-Robinson (PGR) equation of state for selected pure components were obtained from the pure component vapor pressures and saturated phase densities.

TABLE XI

PURE FLUID PARAMETERS FOR THE MODIFIED PGR EQUATION OF STATE

Compound	T* (K)	v* (cm^3/mol)	c
Methane	81.217	20.413	1.0000
Ethane	116.67	27.809	1.3459
Propane	137.74	37.752	1.4821
n-Butane	151.59	46.941	1.6862
n-Octane	180.89	79.449	2.5204
n-Decane	191.32	90.444	2.8887
n-Tetradecane	199.87	137.78	3.7097
n-Eicosane	213.75	180.99	4.6851
n-Octacosane	212.96	249.00	6.6735
n-Hexatriacontane	208.07	307.01	9.4587
n-Tetratetracontane	212.25	345.81	10.889
Ethene	107.38	25.880	1.3452
Propene	133.45	34.359	1.5260
1-Butene	150.31	44.345	1.6533
1-Hexene	169.65	63.663	2.0272
Cyclopropane	140.11	37.070	1.5685
Cyclobutane	180.86	32.561	1.4232
Cyclohexane	197.62	53.480	1.7204
Cyclooctane	231.08	61.238	1.8287
trans-Decalin	207.06	123.79	2.4176
Benzene	196.03	44.800	1.8007
Toluene	203.28	55.991	1.9281
Argon	62.793	15.451	1.0269
Carbon Dioxide	106.02	16.096	1.8331
Water	228.95	9.4878	1.9452
Hydrogen	20.556	18.434	0.38545

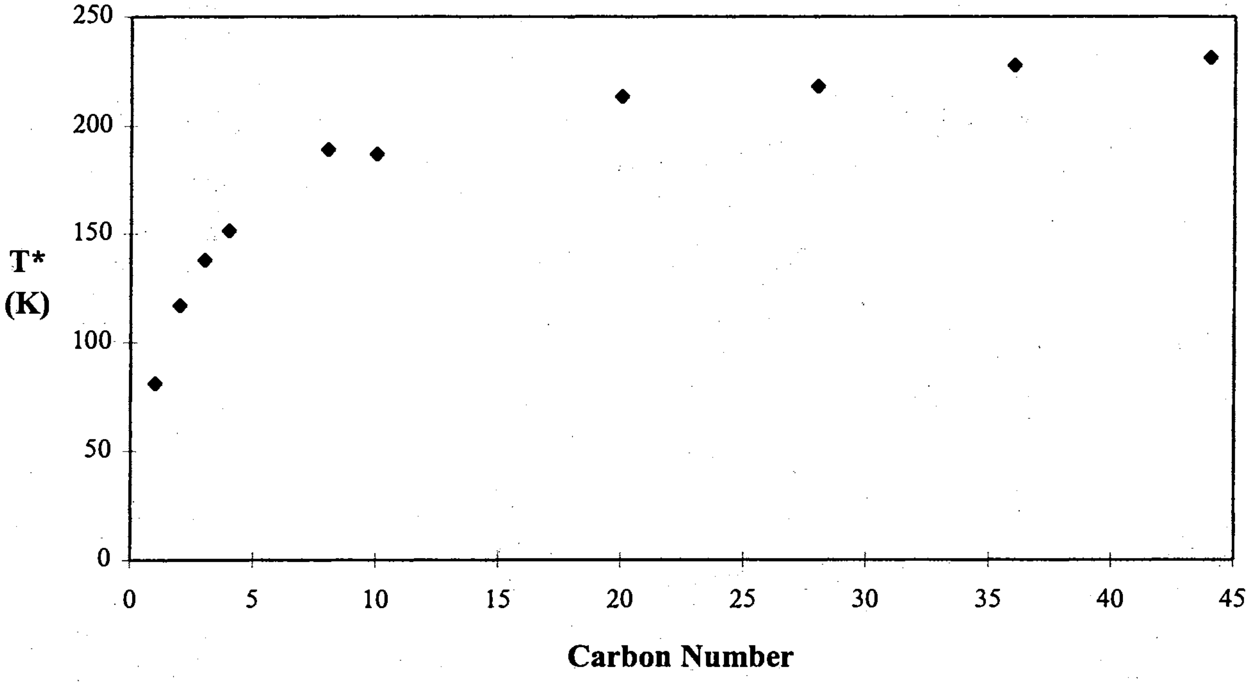

Figure 10. Characteristic Temperature, T^*, of Normal Paraffins.

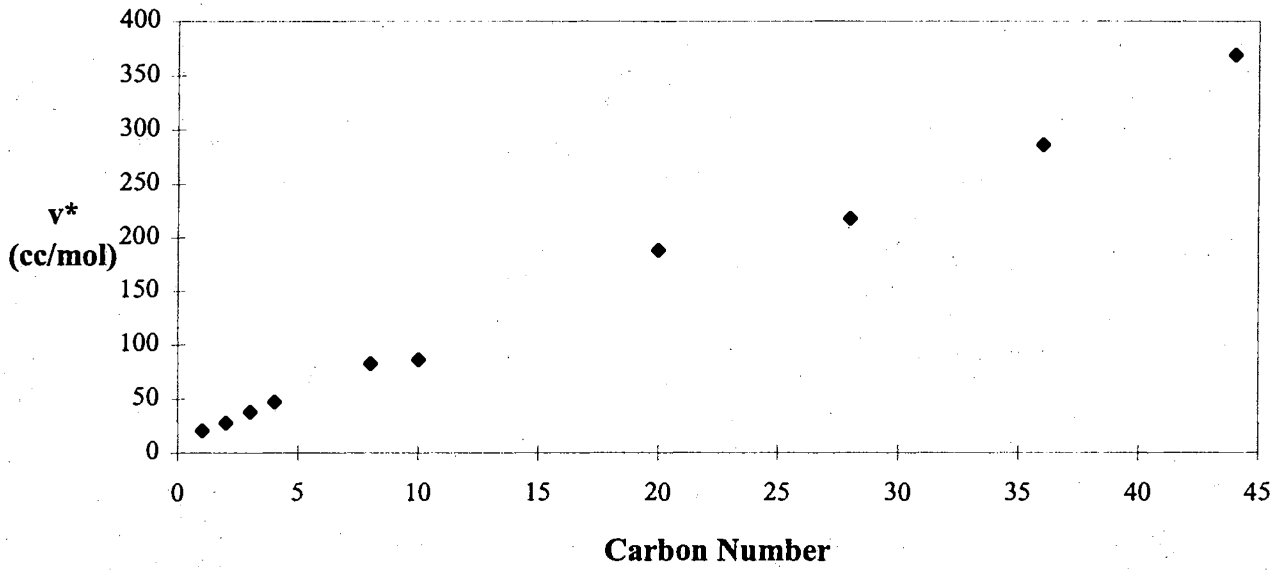

Figure 11. Characteristic Volume, v*, of Normal Paraffins.

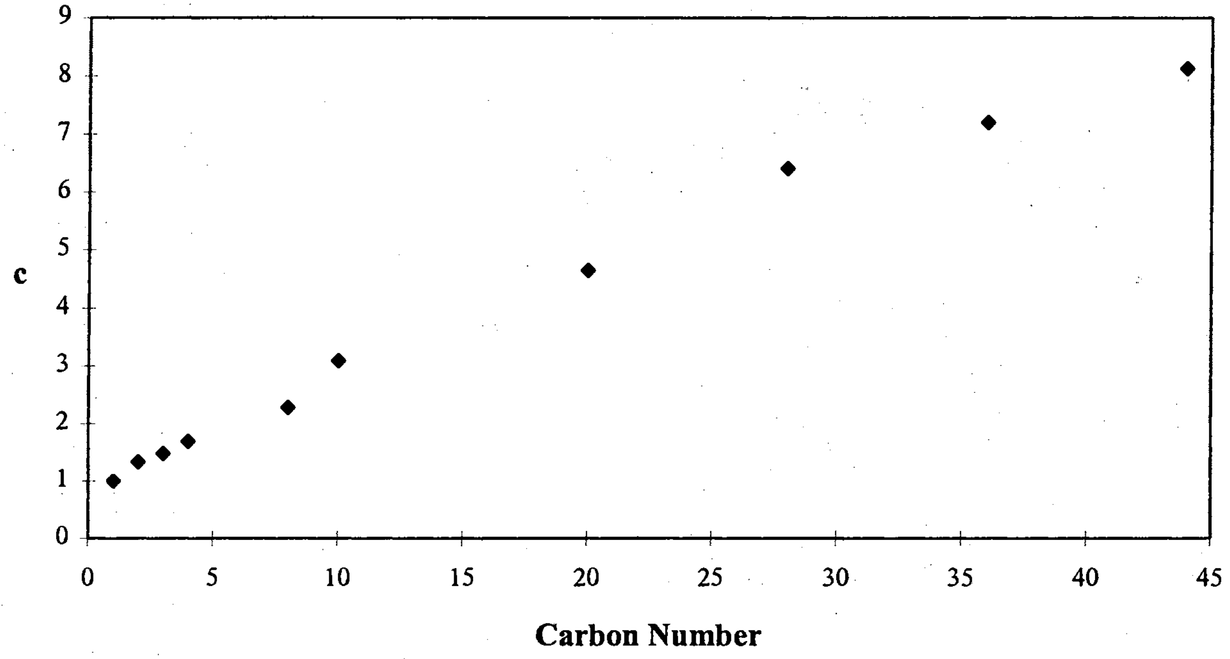

Figure 12. Degree of Freedom Parameter, c, of Normal Paraffins.

According to the comparison results, the modified PGR equation of state is superior to the PR, original SPHCT, and original PGR equations of state in the prediction of vapor pressure and saturated liquid density. The saturated vapor densities from the modified PGR equation (%AAD of 3.7%) are better than the original SPHCT equation, while the other equations (the PR and original PGR equations) are comparable. The original PGR equation is the best among the equations considered in representing saturated vapor densities (%AAD of 3.1%). The modification reduces %AAD of the vapor pressure calculation from 1.7% to 1.3% (23% improvement) and of the saturated liquid density calculation from 3.8% to 2.8% (26% improvement). However, the modification worsened the saturated vapor density prediction capability from %AAD of 3.1% to that of 3.7% (19% increase).

For most of the systems, the modified equations performed better than the PR, SPHCT and original PGR equations in representing vapor pressures and saturated phase densities. However, the modified PGR equation of state produces larger deviations in the saturated vapor densities near the critical region. Like the other equations of state, the pure-component parameters of the modified PGR equation exhibit a systematic trend with carbon number. This distinct behavior of the pure component parameters indicates that the pure component parameters can be generalized easily.

Based on the present work, the following future investigations are recommended.

1. The equation of state constants and the pure component parameters of the equation should be obtained from data covering the entire p-v-T surface, including volumetric properties in the single-phase region.

2. Evaluations of the equation with the parameters obtained by including critical-point constraints should be pursued.
3. Evaluation and implementation of a volume translation strategy should be performed.
4. Generalization of the pure component parameters for n-paraffins should be undertaken to expand the applicability of the equation of state.

CHAPTER 4

EVALUATION OF THE MODIFIED PGR EQUATION OF STATE FOR SELECTED BINARY MIXTURES

Abstract

The Park-Gasem-Robinson (PGR) equation of state modifications discussed in Chapter 2 were investigated in applications to selected binary mixture systems. A set of mixing rules was proposed for the modified equation of state to extend its predictive capabilities to mixtures. The predictive capability of the modified PGR equation of state for bubble point pressures was evaluated for selected carbon dioxide + normal paraffins, ethane + normal paraffins, and hydrogen + normal paraffins.

Three case studies for the use of an interaction parameter (C_{ij}) were performed for the binary mixtures considered. For a given solute, the cases are (1) predictions without any interaction parameter, (2) with one interaction parameter for each solvent, and (3) with one interaction parameter for each isotherm of each solvent. The predicted bubble point pressures for the ethane + n-paraffin and carbon dioxide + n-paraffin binaries were compared to those of the Peng-Robinson (PR), simplified-perturbed-hard-chain theory (SPHCT) and original PGR equations of state for each case studied. For the hydrogen binaries, comparisons were limited to the PR and original PGR equations using a system-dependent (Case 2) or temperature-dependent (Case 3) interaction parameter. The

predictive capability of the proposed equation is better or comparable to the PR, SPHCT and original PGR equations of state for the ethane binaries (%AAD of 1.9) and the carbon dioxide binaries (%AAD of 2.0). For the hydrogen binaries, the modified PGR equation showed much better performance (%AAD of 1.7) than the original PGR equation and very comparable to the PR equation.

Introduction

Accurate knowledge of equilibrium properties is one of the key factors in most calculations for chemical processes such as separation and purification. Equations of state are widely used for mixtures of nonpolar and slightly polar substances. The present chapter describes tests of the proposed equation of state for vapor-liquid equilibrium predictions of selected asymmetric mixtures.

The one-fluid approach, introduced by van der Waals, is the most commonly used method for extending equations of state to nonpolar mixtures (74). This one-fluid approach assumes that the properties of a mixture are equivalent to those of a hypothetical pure component at the same temperature and pressure with the characteristic constants properly averaged over the composition (74). The averaging function of the one-fluid mixing approach is quadratic in mole fraction and expressed as

$$p = \sum \sum x_i x_j p_{ij} \tag{4-1}$$

On the right hand side of Equation (4-1), p_{ii} is an equation of state constant for pure component i and p_{ij} ($i \neq j$) is obtained by an appropriate combining rule with or without binary interaction parameters. The standard method for introducing a binary parameter, C_{ij}, into the mixing rule is to assume a corrected geometric mean rule for the energetic interaction parameter such as 'a' in the cubic equation of state

$$a_{ij} \equiv (a_i a_j)^{1/2} (1 - C_{ij}) \tag{4-2}$$

This classical one-fluid method is very simple and reliable, primarily for nonpolar mixtures. However, compared to the other mixing rules, more computational difficulties were reported with Benedict-Webb-Rubin (BWR) type equations (31).

The van der Waals mixing rules fail to give satisfactory results for complex mixtures at extreme conditions of pressure or density; this has led to the development of new mixing rules. Mixing rules used in conjunction with a "shape factor" approach are proposed by several researchers. Lee et al. (76) extended the van der Waals one-fluid mixing rule by using an additional corresponding-states parameter. Johnson and Rowley (77) employed mixing rules based on a three-parameter principle of corresponding states (PCS) proposed by Wong et al. (78) for their extension of the Lee-Kesler method (ELK) to polar mixtures. The mixing rules in explicit corresponding-states format require one binary parameter employed and the computation time differs according to the reference equation of state. Applicability of these mixing rules is limited primarily to nonpolar and weakly polar mixtures (74-76).

Huron and Vidal claimed that any mixing model that gives a finite excess Gibbs free energy at infinite pressure can be used to construct a mixing rule (79) for the SRK equation. Their mixing rules are

$$\langle b \rangle = \sum_i z_i b_{ii} \tag{4-3}$$

and

$$\langle a \rangle = \langle b \rangle \left(\sum_i z_i \frac{a_{ii}}{b_{ii}} - \frac{G^{ex}(T, x_i)}{C^*} \right) \tag{4-4}$$

where values of C* for SRK and PR are 0.6931 and -0.6232, respectively. Since Huron and Vidal developed the basic idea of excess Gibbs free energy mixing rules, similar models have been proposed. Vidal derived the infinite-pressure limit of the excess Gibbs energy calculated from the Redlich-Kwong equation with quadratic mixing rules (80). The local composition models of Wilson (28) and NRTL (29) are typical examples of the excess Gibbs energy models. Wong and Sandler introduced a similar mixing rule (Wong-Sandler mixing rule) that is also based on the idea of equating free energies at infinite pressure (81). However, the Wang-Sandler mixing rule makes use of the excess Helmholtz free energy of mixing rather than the Gibbs free energy. This mixing rule is simpler than the mixing rules that use the excess Gibbs free energy.

Mansoori and Lerand (82) introduced density-dependent mixing rules. They postulated that for mixtures of molecules differing in size, better results can be obtained by allowing the mixture parameters to be a function of composition and density.

The lack of fit of an equation of state in representing equilibrium properties of mixtures may be due to inherent deficiencies in the equation and/or the mixing rules applied. Normally, binary interaction parameters are required to improve the predictive capability of an equation of state. These binary interaction parameters (characterizing interaction between different species in the mixture) are commonly obtained from a small amount of experimental data. The parameters thus obtained can be generalized to expand the capability of the equation of state.

In the present work, the one-fluid mixing rules of van der Waals with one binary interaction parameter are introduced to improve the VLE prediction capability. These interaction parameters are evaluated for ethane, carbon dioxide and hydrogen binary mixtures with n-paraffins.

Literature Review

Chemical process design for separation processes, such as distillation and flash separations require thermodynamic models for phase equilibrium calculations. Accurate predictive methods are of great importance for efficient design of separation units.

Numerous equations of state have been presented in the literature for calculating vapor-liquid equilibria and thermodynamic properties of mixtures. A comprehensive comparison of mixing rules was presented for nonpolar and weakly polar binary mixtures (83). These included the one- and two-fluid conventional mixing rules, the pressure- and density-dependent mixing rules, and two mixing rules based on the excess Gibbs free energy. The two-fluid mixing rules were reported to give the best results and the density-dependent mixing rules gave poor predictions for systems where one component is highly supercritical.

Marrucho et al. (84) modified the extended corresponding-states mixing rules to obtain theoretically-correct composition dependence for the second virial coefficient.

The modified mixing rules were applied to analyze selected binary mixtures of natural gas. Clarke et al. (85) applied their modified version of extended corresponding-states mixing rules to binary and ternary mixtures. The model represented single-phase and VLE properties well over a wide range of compositions. However, in these studies, no comparisons with the other mixing rules were made.

Li and Huang (86) applied the density-dependent mixing rules to polar and strongly nonideal fluid systems. The augmented hard sphere equation of state was used to evaluate the capability of the mixing rules. The model was compared with the van der Waals one-fluid mixing rules (VDW) and proved to be comparable to the VDW for polar systems and superior to the VDW for strongly nonideal systems. Alvarado and Eubank (87) examined the density-dependent mixing rules and the van der Waals one-fluid mixing rules with the Redlich-Kwong equation of state. The density-dependent mixing rules produced better results than the one-fluid mixing rules without interaction parameters. They concluded that the density-dependent mixing rules are highly complex for every equation of state except the van der Waals equation of state.

Recently, numerous mixing rules based on the excess Gibbs free energy (79, 88-92), Helmholtz energy (81, 88), and enthalpy (93, 94) have been studied by various researchers. Studies by Kalospiros and Tassios (89) and Kalospiros et al. (90) showed that two modified Huron-Vidal mixing rules (MHV1 and MHV2) can be directly and easily applied to the prediction of VLE in polymer solutions. Orbey and Sandler (88) pointed out the drawbacks generated by replacing the original mixing rules based on the excess Gibbs free energy with the convenient mixing rules based on the excess Helmholtz energy. Fliho and Costa (95) studied the influence of the three mixing rules that incorporate excess Gibbs energy models. The SRK equation was applied to several liquid-liquid binary mixtures. According to their work, the Wong-Sandler mixing rules were superior to the others for weakly polar- and strongly polar-nonpolar and strongly polar-strongly polar binary systems. Huang et al. (96) showed that an extended PR equation of state and the Wong-Sandler mixing rules can correlate hydrogen + hydrocarbon systems successfully. The results were compared to van der Waals one-fluid mixing rules. Their work concluded that the three parameters of the Wong-Sandler mixing rules can be generalized in terms of temperature and the acentric factor of the hydrocarbon. Furthermore, the extrapolation of the parameters, which is one of problems in mixing rules, was reported to be solved. Other extensive comparisons of selective excess Gibbs free energy mixing rules in the prediction of vapor-liquid equilibria in asymmetric binary (97) and ternary (98) systems were presented. For both asymmetric binary and selected ternary systems, unlike the results by Huang et al. (96), the Wong-Sandler mixing rules showed poor performances.

The Equation of State for Mixtures

Mixing rules are required to extend the applicability of an equation of state to mixtures. The assumption inherent in mixing rules is that the same equation of state used for pure fluids can be used for mixtures with a satisfactory way of obtaining the mixture parameters. The mixing rules employed by Park (26) are used in this study after appropriate modification is made for the temperature-dependent part in the attractive term.

For pure fluids, the second virial coefficient of the modified equation of state is

$$B = c\left[\beta_1\tau - (1+Q_1)Z_M Y\right]v^* \tag{4-5}$$

In order to satisfy the quadratic combining rules of van der Waals for a mixture, the following relationships must be satisfied

$$c\left[\beta_1\tau - (1+Q_1)Z_M Y\right]v^* = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j \left(\beta_1\tau c v^* - c(1+Q_1)Z_M Y v^*\right)_{ij} \tag{4-6}$$

where N is the total number of components in the system.

In the cross-terms, the geometric average for energy parameter (ε_{ij}) and the arithmetic average for volume parameter (σ_{ij}) were selected for use. The mixing rules adopted in this study are similar to those of the SPHCT equation of state

$$\left\langle cv^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j c_i v_{ji}^* \tag{4-7}$$

$$\left\langle v^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j v_{ij}^* \tag{4-8}$$

where

$$v_{ij}^* = \frac{s_i \sigma_{ij}^3}{\sqrt{2}} \tag{4-9}$$

and z_i and z_j are the mole fractions of component i and j, respectively. Equations (4-7) and (4-8) are the same as those of the original PGR equation of state. When the employed mixing rules are applied to the modified temperature-dependent term, the resulting expression is

$$\langle cYv^* \rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j c_i \left(\exp(F_t)_{ij} - 1\right) v_{ji}^* \tag{4-10}$$

where

$$(F_t)_{ij} = \omega_1 \left(\frac{T_{ij}^*}{2T}\right)^{1/2} + \omega_2 \left(\frac{T_{ij}^*}{2T}\right) + \omega_3 \left(\frac{T_{ij}^*}{2T}\right)^{3/2} + \omega_4 \left(\frac{T_{ij}^*}{2T}\right)^2 \tag{4-11}$$

$$T_{ij}^* = \frac{\varepsilon_{ij} q_i}{c_i k} \tag{4-12}$$

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right)\left(1 + D_{ij}\right) \tag{4-13}$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\left(1 - C_{ij}\right) \tag{4-14}$$

The properties in angular brackets, $\langle\ \rangle$, are for the mixture. The D_{ij} and C_{ij} in Equations (4-13) and (4-14) are the co-volume and energetic interaction parameters, respectively. In this study, the co-volume interaction parameter was set to zero and the energetic interaction parameter was the only concern.

According to the expressions shown above, the modified version of the PGR equation of state for mixture systems becomes

$$Z = 1 + \frac{\beta_1 \tau \langle cv^* \rangle}{v - \beta_2 \tau \langle v^* \rangle} - \frac{Z_M \langle cYv^* \rangle v}{v^2 + u\langle v^* \rangle v + w\langle v^* \rangle^2} - \frac{Q_1 Z_M \langle cYv^* \rangle}{v + Q_2 \langle v^* \rangle} \tag{4-15}$$

When the hard core radii, σ_{ij}, in Equation (4-13) are the same and the co-volume interaction parameter, D_{ij}, is set to zero for all components in a mixture, v_{ij}^* may be expressed as

$$\begin{aligned} v^*_{ij} &= v^*_{ii} \\ v^*_{ji} &= v^*_{jj} \end{aligned} \qquad (4\text{-}16)$$

For ethane binary mixtures, Equation (4-16) is applied in calculating v^*_{ij}. For carbon dioxide binary systems, Park (26) performed preliminary calculations of the hard sphere radius, σ, of carbon dioxide and normal paraffins and found that they are almost equivalent. Thus, Equation (4-16) is also used for carbon dioxide + normal paraffins binary systems. Due to a scarcity of information about the hard sphere radius for hydrogen, the same assumption which was used by Park is used in this work. This assumption along with a zero value for D_{ij} leads to the linear mixing rule for the characteristic volume of a mixture, as shown in Equation (4-16). These assumptions simplify the mixture version of the equation of state. Another reason for this simplification is to avoid the use of multiple interaction parameters.

As suggested in several previous works (9, 24-26), a constant characteristic energy term in Equation (4-12) is used throughout the evaluation of the modified equation of state for the binary mixtures considered in this study. As a consequence, the expression for T^*_{ij} can be written as

$$\begin{aligned} T^*_{ij} &= T^*_{ii}\left(1 - C_{ij}\right) \\ T^*_{ji} &= T^*_{jj}\left(1 - C_{ij}\right) \end{aligned} \qquad (4\text{-}17)$$

The Binary Mixture Database

The databases used in evaluating the modified equation of state for mixtures are the same as those used by Park (26) for ethane, carbon dioxide and hydrogen binaries with n-paraffins. The ethane + n-paraffin binary database consists of bubble point pressures (p at fixed x) or, equivalently, ethane solubilities (x at fixed p) at different temperatures. The database covers solvent molecular sizes extending from n-butane (C_4) to n-tetratetracontane (C_{44}), temperatures from 310.9 to 423 K and pressures to 82.4 bar. In the present work, the normal paraffin solvents selected are n-butane, n-octane, n-decane, n-eicosane, n-octacosane, n-hexatriacontane and n-tetratetracontane. The normal paraffin solvents selected for the evaluation of carbon dioxide binaries are n-butane, n-decane, n-eicosane, n-octacosane, n-hexatriacontane and n-tetratetracontane. The carbon dioxide binary database covers temperatures from 310.9 to 510.9 K and pressures to 172.4 bar. The database for hydrogen + n-paraffins covers solvent molecular size variations from n-butane to n-hexatriacontane, temperatures from 323.2 to 573.3 K and pressures up to 173.9 bar. Ranges of temperature, pressure and mole fraction considered in the ethane, carbon dioxide and hydrogen binary mixture database are shown in Tables XII to XIV.

Results and Discussion

Bubble point pressure predictions were performed at various temperatures and liquid phase compositions using the modified PGR equation of state. The equation was evaluated using the binary mixtures of ethane, carbon dioxide and hydrogen with normal

TABLE XII

ETHANE + N-PARAFFIN SYSTEMS USED IN MODIFIED EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Source (# of pts)
n-C_4	338.7 - 394.3	32.4 - 50.3	0.118 - 0.753	99 (19)
n-C_8	323.2 - 373.2	4.1 - 52.7	0.047 - 0.863	100 (33)
n-C_{10}	310.9 - 410.9	4.2 - 82.4	0.105 - 0.638	101 (30)
n-C_{20}	323.2 - 423.2	5.0 - 76.9	0.118 - 0.653	102 (19)
n-C_{28}	348.2 - 423.2	5.6 - 51.8	0.102 - 0.520	103 (24)
n-C_{36}	373.2 - 423.2	3.7 - 47.6	0.087 - 0.531	102 (13)
n-C_{44}	373.2 - 423.2	3.9 - 31.7	0.099 - 0.516	102 (16)

TABLE XIII

CARBON DIOXIDE + N-PARAFFIN SYSTEMS USED IN MODIFIED EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Source (# of pts)
n-C_4	310.9 - 410.9	5.5 - 75.4	0.002 - 0.908	104 (52)
n-C_{10}	310.9 - 510.9	3.5 - 172.4	0.045 - 0.864	105 (70)
n-C_{20}	323.2 - 373.2	6.2 - 67.6	0.073 - 0.501	106 (22)
n-C_{28}	323.2 - 423.2	8.1 - 96.0	0.070 - 0.617	106 (23)
n-C_{36}	373.2 - 423.2	5.2 - 86.5	0.062 - 0.502	106 (18)
n-C_{44}	373.2 - 423.2	5.8 - 70.8	0.082 - 0.502	106 (14)

TABLE XIV

HYDROGEN + N-PARAFFIN SYSTEMS USED IN MODIFIED EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Source (# of pts)
n-C_4	327.7 - 394.3	27.78 - 168.8	0.0190 - 0.2660	107 (60)
n-C_{10}	344.3 - 423.2	37.07 - 173.9	0.0369 - 0.1288	26 (21)
n-C_{20}	323.2 - 573.3	9.940 - 118.2	0.0113 - 0.1289	26, 108 (37)
n-C_{28}	348.2 - 573.2	9.859 - 131.0	0.0206 - 0.1728	26, 108 (35)
n-C_{36}	373.2 - 573.2	10.22 - 167.5	0.0154 - 0.2272	26, 108 (27)

paraffins. Results were generated for three cases involving the use of interaction parameters, as described in Table XV. Case 1 with no interaction parameter ($C_{ij} = 0$) represents the raw predictive ability of the equation to predict bubble point pressures. Case 2 is the most commonly used representation of the interaction parameter in literature, in which a separate C_{ij} is used for each binary mixture system. In Case 3, a separate C_{ij} is used for each isotherm of each binary system. Similar evaluations were conducted using the PR, SPHCT and original PGR equations for ethane and carbon dioxide binary mixtures. For hydrogen binaries, evaluations were undertaken only with the original PGR equation and the PR equation for Cases 2 and 3. The SPHCT equation was not evaluated for hydrogen binaries because pure component parameters for the equation are not available.

The following objective function was used in all model evaluations to obtain the optimum interaction parameters

$$SS = \sum_{i=1}^{N} \left(\frac{p_{calc} - p_{exp}}{p_{exp}} \right)_i^2 \tag{4-18}$$

where p_{exp} is the experimental bubble point pressure and p_{calc} is the calculated bubble point pressure. The regressed parameters through the above objective function leads to the minimum value of average absolute percentage deviation (%AAD) in bubble point pressure. The same regression and calculation methods used for the original PGR equation of state evaluation were applied in this study. Details on the regression technique and bubble point calculation method used in this work are described by Gasem (61).

TABLE XV

CASE STUDIES USED IN EVALUATING THE MODIFIED PGR EQUATION OF STATE

Case	Interaction Parameter	Description
1	$C_{ij} = 0$	A simple mixing rule with no interaction parameter.
2	$C_{ij}(CN^*)$	A separate value of C_{ij} is determined for each binary mixture. The value of C_{ij} is dependent only on the normal paraffin carbon number for a given solute.
3	$C_{ij}(CN^*, T)$	A separate value of C_{ij} is determined for each binary mixture at each temperature. The value of C_{ij} is dependent only on the normal paraffin carbon number and system temperature for a given solute.

* Carbon number of the specific n-paraffin

The required fugacity coefficient expression for component i in a mixture was derived for the modified PGR equation of state

$$
\begin{aligned}
\ln\phi_i = {} & -\frac{\beta_1}{\beta_2}\left(\frac{1}{\langle v^*\rangle}\frac{1}{n}\frac{\partial n^2\langle cv^*\rangle}{\partial n_i}-\frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\ln\frac{v_r-\beta_2\tau}{v_r} \\
& +\left(\beta_1\tau\frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{1}{v_r-\beta_2\tau}-\left(\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Z_M v_r}{v_r^2+uv_r+w} \\
& +\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_1}-\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right) \\
& -\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_1}-\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{Q_2}\ln\frac{v_r+Q_2}{v_r} \\
& -\left(\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{v_r+Q_2}-\ln Z
\end{aligned}
\tag{4-19}
$$

where

$$\frac{\partial n\langle cYv^*\rangle}{\partial n_i}=\sum_{j=1}^{N}z_j\left(c_iY_{ij}v_{ji}^*+c_jY_{ji}v_{ij}^*\right)-\langle cYv^*\rangle \tag{4-20}$$

$$\frac{\partial n\langle v^*\rangle}{\partial n_i}=\sum_{j=1}^{N}z_j\left(v_{ij}^*+v_{ji}^*\right)-\langle v^*\rangle \tag{4-21}$$

and

$$Y_{ij}=\exp\left[\omega_1\left(\frac{T_{ij}^*}{2T}\right)^{1/2}+\omega_2\left(\frac{T_{ij}^*}{2T}\right)+\omega_3\left(\frac{T_{ij}^*}{2T}\right)^{3/2}+\omega_4\left(\frac{T_{ij}^*}{2T}\right)^2\right]-1 \tag{4-22}$$

Detailed derivation of the fugacity coefficient expression for components in a mixture is given in Appendix C.

Results for the modified PGR, the original PGR, the original SPHCT and the PR equations of state for the three cases studied are discussed below.

Ethane + n-Paraffin Systems

Bubble point pressure calculations for the three evaluation cases described above were performed for the selected equations of state. A summary of the results is presented in Table XVI. Detailed tables containing the complete statistics for each isotherm of each case are shown in Appendix D. The modified version of the PGR equation showed the best results in Case 1 (RSME of 1.55 bar and %AAD of 5.0) while the SPHCT equation was the worst (RSME of 4.83 bar and %AAD of 16.6). This implies that the modified PGR equation is the most accurate among the equations considered in predicting bubble point pressures without any interaction parameter. With the introduction of interaction parameters (Cases 2 and 3), the modified PGR equation was still the best among the equations considered. When the interaction parameters are considered to be independent of system temperature (Case 2), the prediction capability of the modified equation exceed that of the other equations (RSME of 1.19 bar and %AAD of 2.8). In Case 3, the modified equation was shown to be compatible to the original SPHCT equation, which showed the best results. The quality of fit for Case 3 is 4.1%, 1.6%, 2.8% and 1.9% for the PR, the SPHCT, the original PGR and the modified PGR equations, respectively.

TABLE XVI

SUMMARY OF RESULTS FOR CALCULATION OF BUBBLE POINT PRESSURES FOR ETHANE + N-PARAFFIN SYSTEMS

	Peng-Robinson		SPHCT		Original PGR		This Work	
Case Number	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	2.06	9.5	4.83	16.6	3.95	7.7	1.55	5.0
2	1.79	4.4	1.29	3.2	2.47	5.1	1.19	2.8
3	1.77	4.1	0.78	1.6	1.34	2.8	0.68	1.9

The modified PGR equation performed much better than the PR and original PGR equations.

Figure 13 shows the effect of the solvent molecular size on the optimum interaction parameter for Case 2. For systems whose solvents are lighter than C_{20}, the optimum interaction parameters obtained from the modified PGR equation are close to the arithmetic mean of those from the SPHCT and the original PGR equations. Both the original and modified PGR equations require smaller values for the interaction parameters than the original SPHCT equations. The figure indicates that both the SPHCT and modified PGR equations result in fairly constant interaction parameters with increasing carbon number as compared to those of the PR equation of state. This is one of the typical characteristics of an equation of state based on segment-segment interactions (25).

The effect of temperature on the optimum interaction parameters is shown in Figures 14 to 17, in which the C_{ij}'s of Case 3 are plotted for the modified PGR equation, the original PGR equation, the SPHCT equation and the PR equation, respectively. As can be seen from these figures, the modified PGR equation has interaction parameters that are less sensitive to temperature than the other equations selected. This weak temperature dependence of the interaction parameters may indicate the adequacy of the mixing rules used. The C_{ij}'s of the original and modified PGR equations behave like those of the cubic equation of state. The values decrease as the temperature increases while the interaction parameters of the SPHCT equation exhibit the opposite trend. Comparison of Figures 14 and 15 indicate that interaction parameters from both

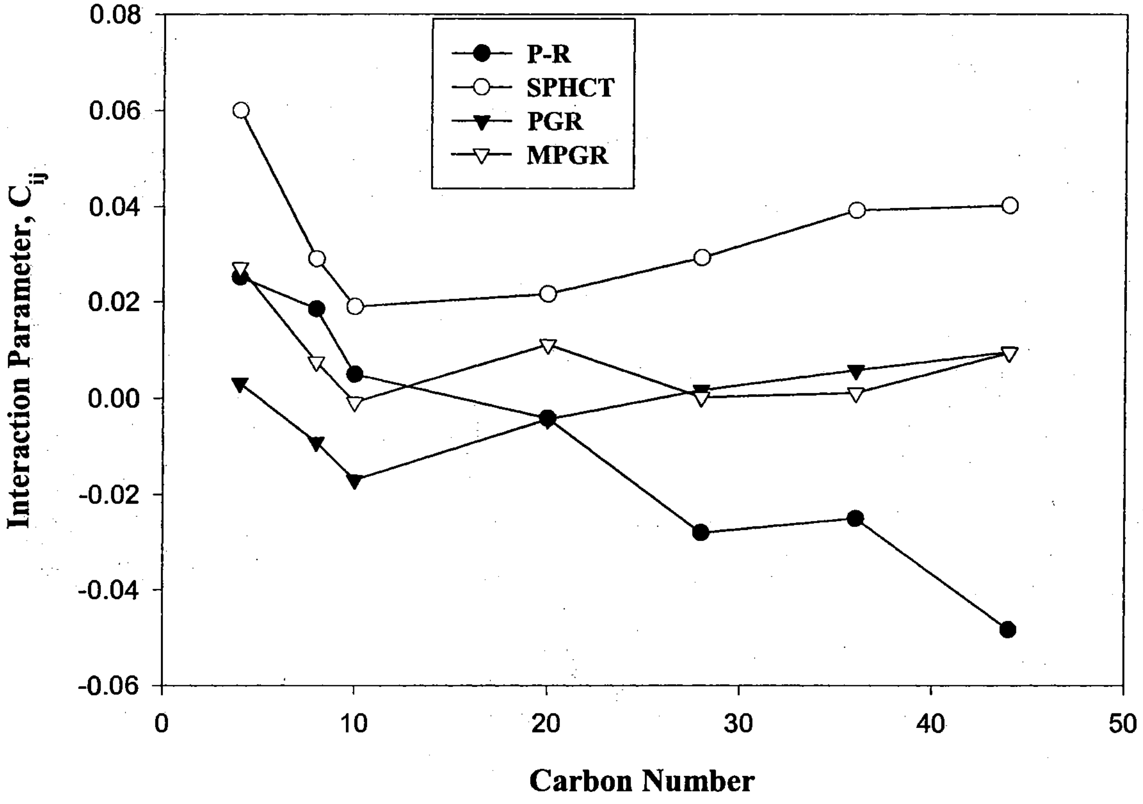

Figure 13. Equation of State Interaction Parameters, C_{ij}, for the Ethane + n-Paraffin Systems.

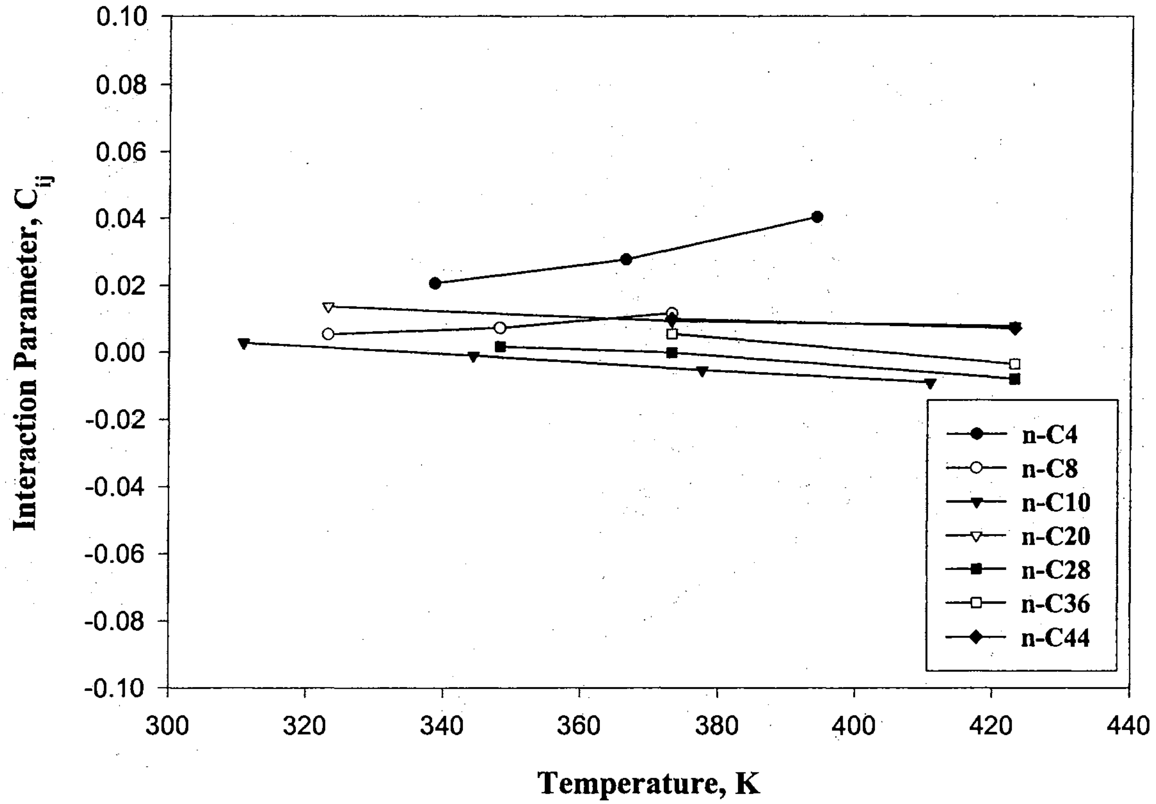

Figure 14. Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.

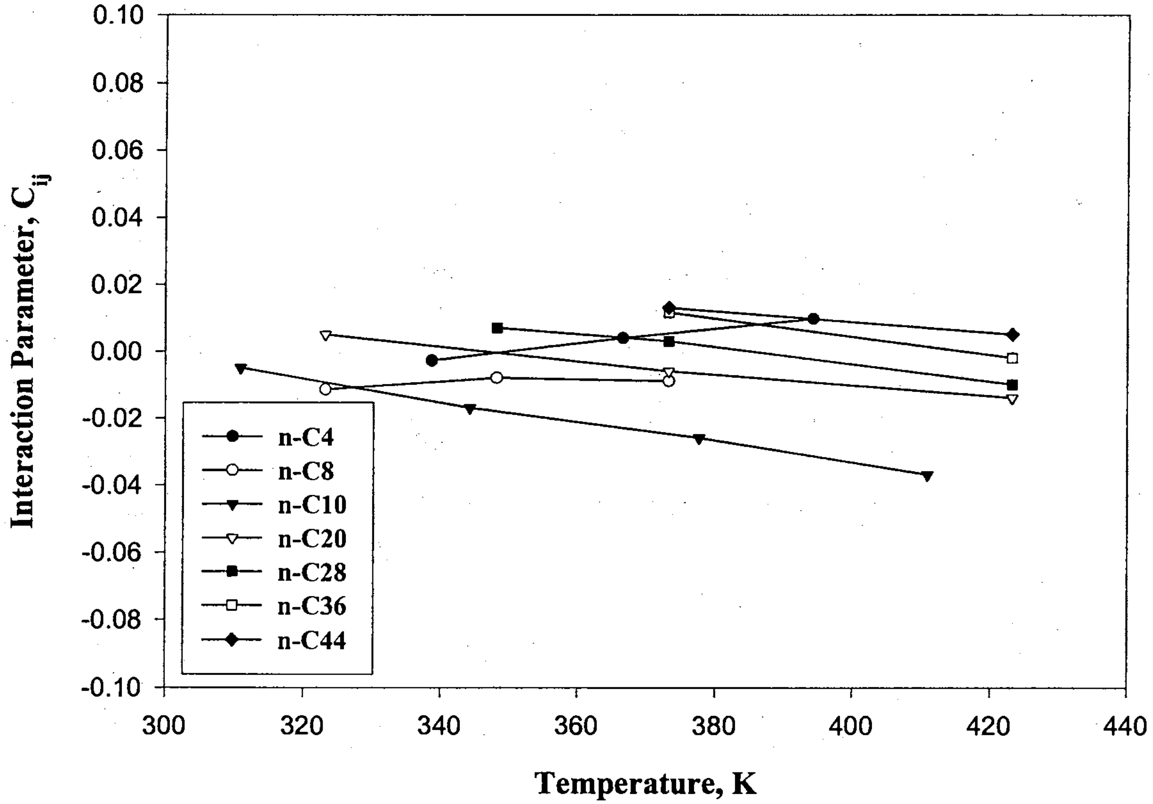

Figure 15. PGR equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.

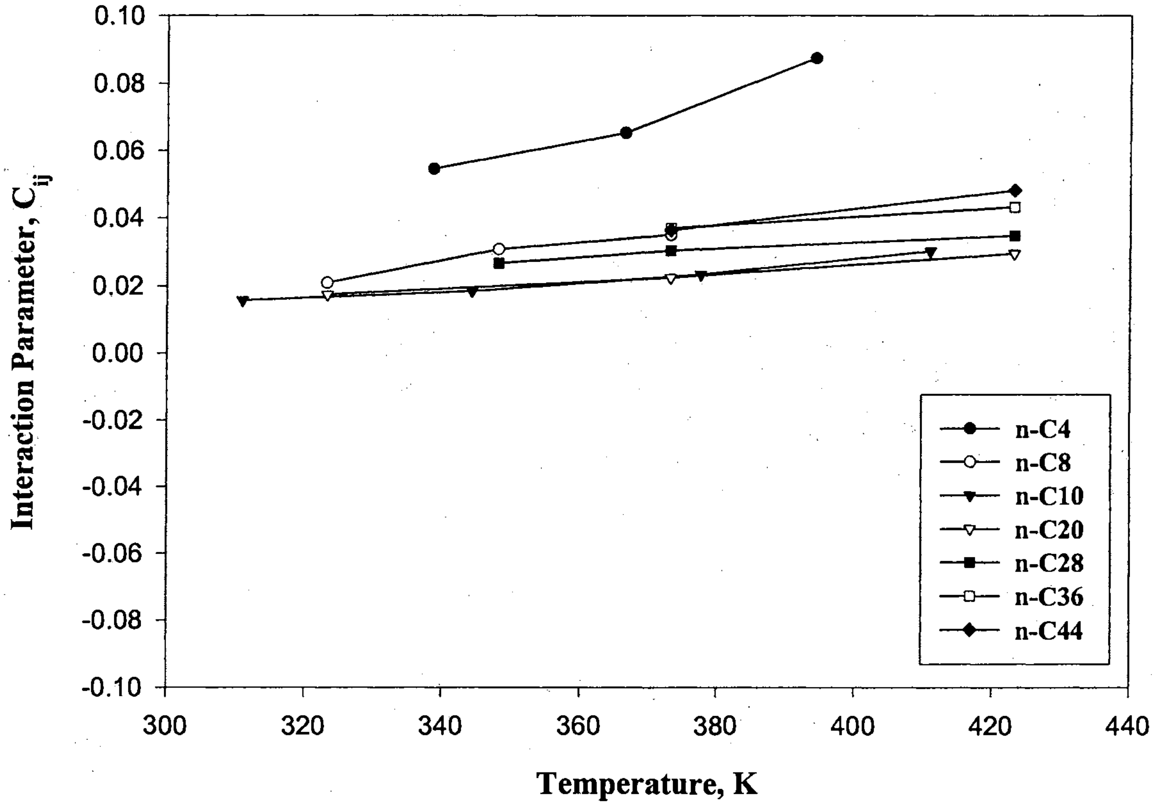

Figure 16. SPHCT Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.

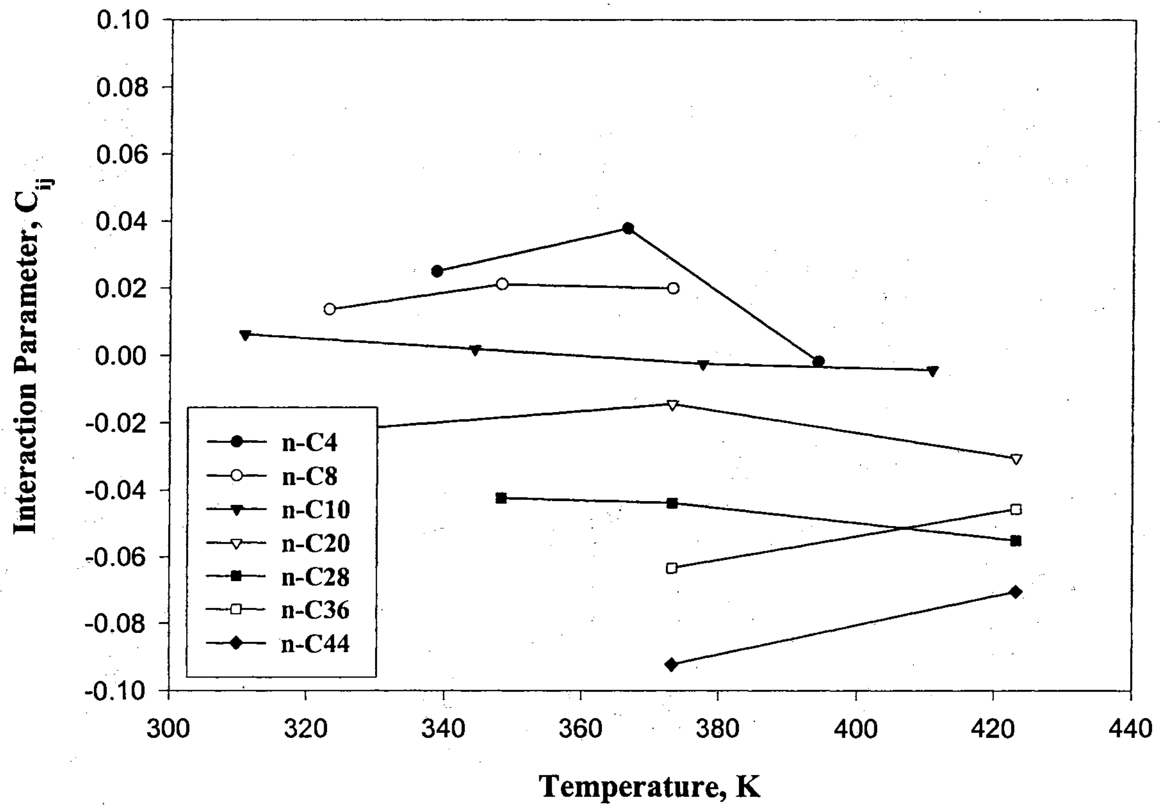

Figure 17. PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.

equations exhibit similar trends. Also a compactness in the parameter dispersion is observed.

Carbon Dioxide + n-Paraffin Binaries

A summary of the bubble point pressure calculations of carbon dioxide + n-paraffin binary mixtures for three cases described in Table XV is presented in Table XVII. Detailed calculation results are shown in Appendix D. For the zero interaction parameter case (Case 1), the modified PGR equation showed the best results among the equations considered. Convergence problems were observed with the SPHCT equation for the high pressure data points. This can be mainly because the SPHCT equation of state was derived for nonpolar compounds. The original PGR equation performed the worst for all cases. The original PGR equation and the modified PGR equation were less sensitive to the introduction of the interaction parameters than the PR equation and the SPHCT equation, which showed great improvements in the RSME and %AAD. Once the interaction parameters were introduced, both the original and modified PGR equations gave larger errors than the PR and SPHCT equations.

The relatively poor predictions of the modified PGR equations for Case 2 may be caused by the character of the partition function of the PGR and modified PGR equations. The partition function of the PGR equation of state did not explicitly account for polar effects (26). If the polar effects were considered in the partition function for the segment-segment interaction models, better performances of the model would be expected. Assumptions used in the simple one-fluid mixing rules may be another factor for these

TABLE XVII

SUMMARY OF RESULTS FOR CALCULATION OF BUBBLE POINT PRESSURES FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS

	Peng-Robinson		SPHCT		Original PGR		This Work	
Case Number	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	13.45	19.9	14.77*	26.8*	8.83	17.9	7.87	14.3
2	2.76	3.3	2.73	4.6	5.95	10.0	3.26	7.0
3	2.17	2.5	2.10	1.9	2.36	2.1	0.86	2.0

* Approximately 1/4 of the higher pressure data points were predicted as being single phase.

poor results. Like in the case of the original PGR and SPHCT equations, a common value of the hard core radius (σ) and the square-well potential depth (ε) are used for all compounds. Actually, the hard core radius for the carbon dioxide molecule is different from that of a segment in normal paraffins. Similarly, the attractive energy between the carbon dioxide molecule and a segment in normal paraffins is expected to be different. It is likely that this assumption limits the capability of the equation.

For Case 3, the predictive capability of the modified PGR equation (%AAD of 2.0) is almost identical to that of the SPHCT (%AAD of 1.9) and original PGR (%AAD of 2.1) equations. However, the RMSE of the modified PGR equation (RMSE of 0.86 bar) was much smaller than that of the other equations considered (RMSE of 2.17 bar, 2.10 bar and 2.36 bar for the PR, SPHCT and PGR equations, respectively) which implies that the errors of the modified equation are more evenly distributed throughout the isotherms. For all equations of state studied, temperature-dependent interaction parameters (Case 3) are needed to obtain accurate predictions.

Figure 18 shows the effect of carbon number on the optimum interaction parameter of Case 2 for all the equations considered. As with the ethane systems, the modified PGR equation requires smaller interaction parameters than the PR, SPHCT, and original PGR equations. The interaction parameter values of the modified PGR and SPHCT equations are less scattered than those of the other equations. The parameter values for the modified PGR and SPHCT equations are relatively constant (0.02 and 0.06, respectively) with increase in solvent molecular size. This makes extrapolations to heavier molecular weight compounds for the CO_2 systems more reliable.

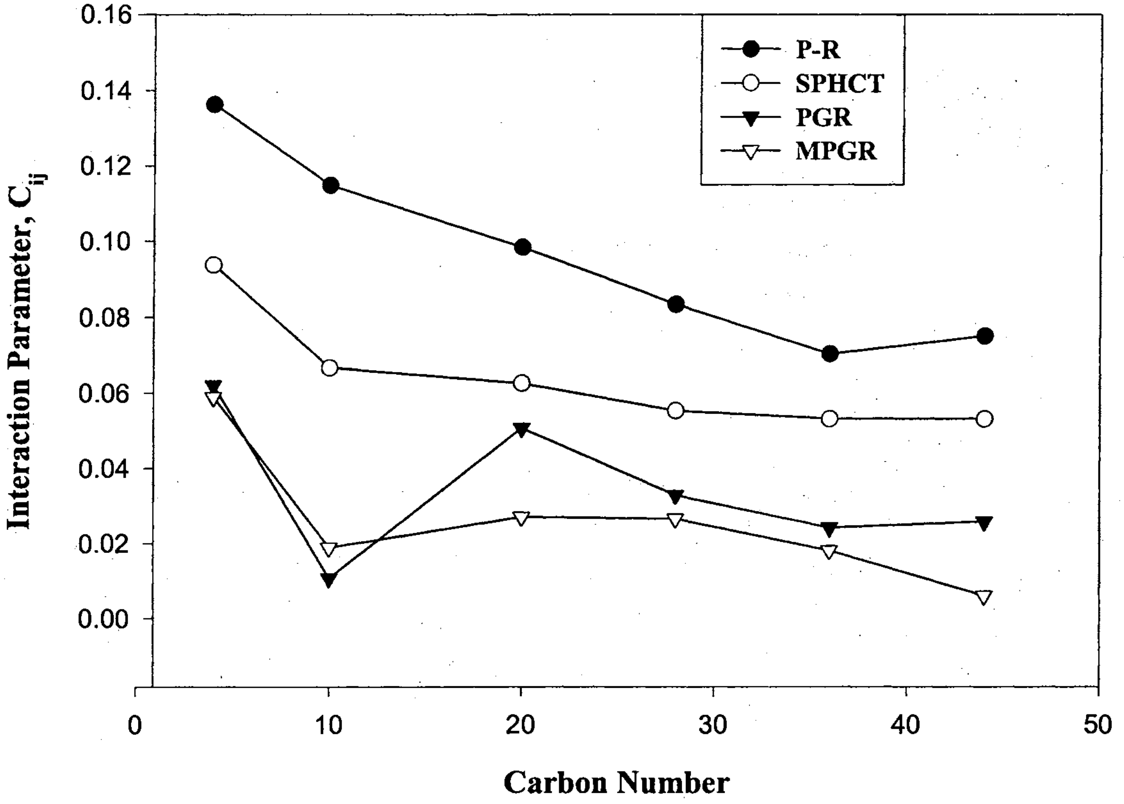

Figure 18. Equation of State Interaction Parameters, C_{ij}, for the Carbon Dioxide + n-Paraffin Systems.

The effect of temperature on the interaction parameters can be seen in Figures 19 to 22. Unlike the ethane + n-paraffin systems, Figure 19 shows a very strong temperature dependence for the binaries containing heavy components. The figures indicate that the interaction parameters are more sensitive to temperature than to the solvent molecular weight. The magnitude of the temperature dependence for the modified PGR equation is greater than that of the SPHCT equation and less than the PR and original PGR equations. This observation matches the results for Case 3 in Table XVII.

Hydrogen + n-Paraffin Binaries

A summary of the bubble point pressure calculations of hydrogen + n-paraffin binary mixtures for selected cases are presented in Table XVIII. Detailed calculation results are shown in Appendix D. Since all equations showed convergence problems for the zero interaction parameter case (Case 1), evaluations and comparisons were made only for Cases 2 and 3.

The modified PGR equation performed worse than the PR equation in Case 2 (%AAD of 5.8 and 4.5, respectively) while the RSME values of the modified PGR were lower than that of the PR equation (RSME of 4.06 bar and 5.23 bar, respectively). The original PGR equation showed considerable errors in Case 2. The modified PGR equation appeared preferable to the PR and original PGR equations when the temperature-dependent interaction parameters were introduced (%AAD of 1.7, 2.0 and 2.7 and RSME of 1.09 bar, 3.22 bar and 3.35 bar, respectively). Overall, the

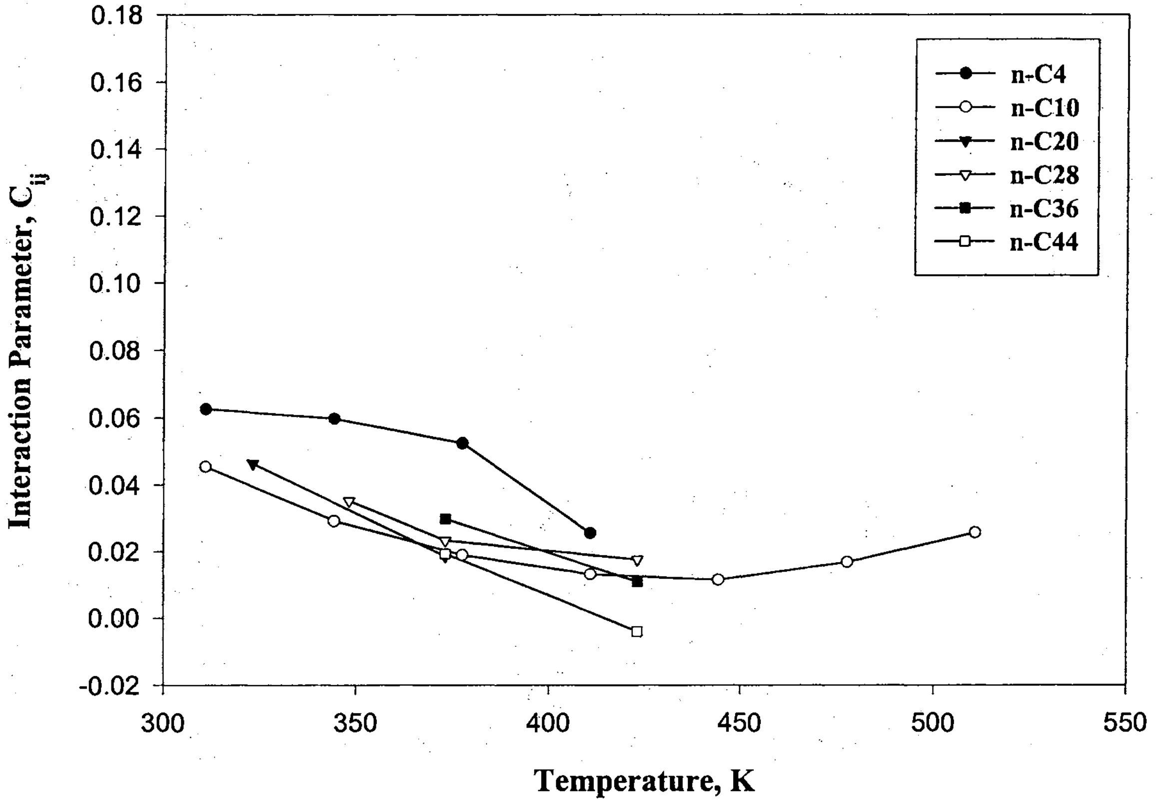

Figure 19. Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

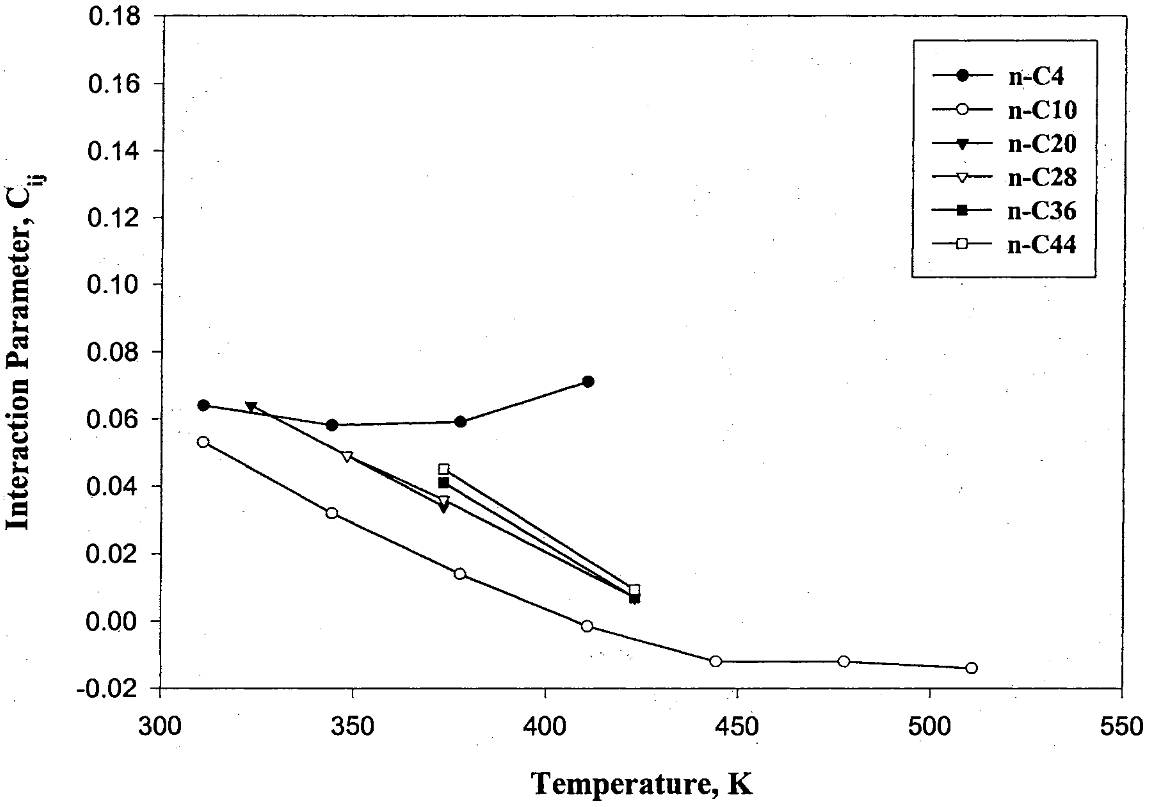

Figure 20. PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

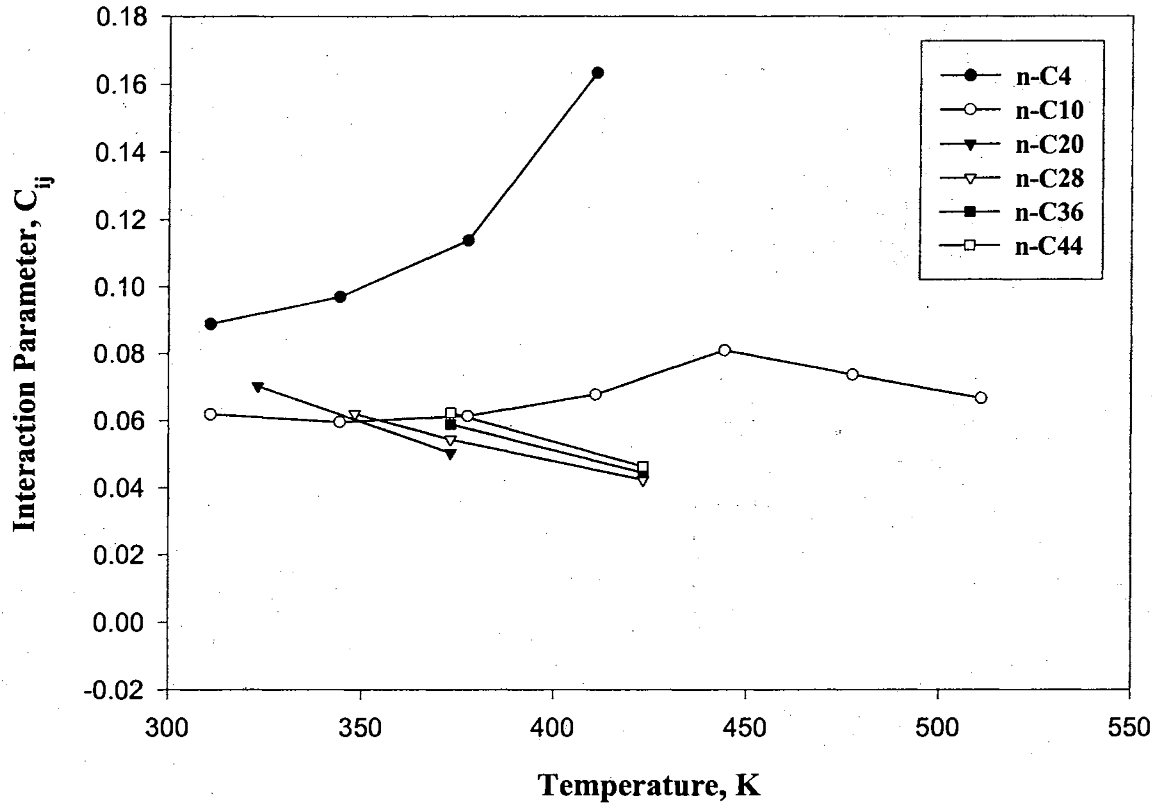

Figure 21. SPHCT Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

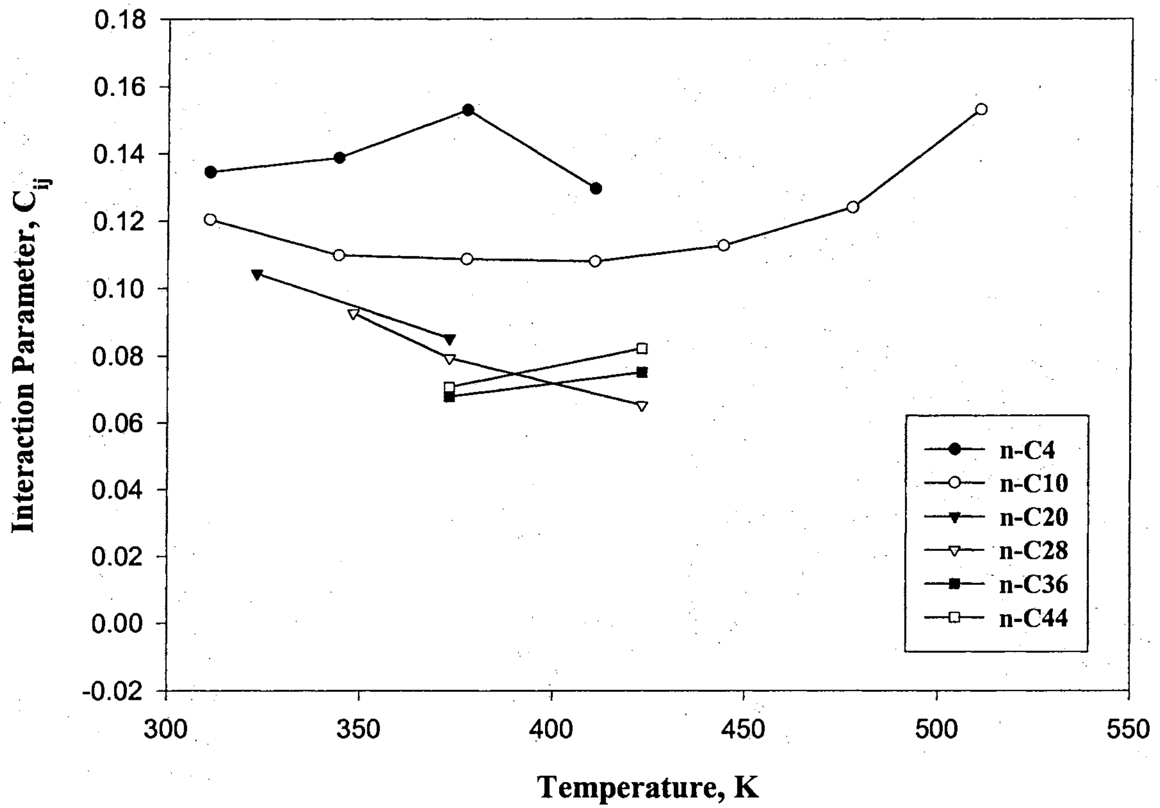

Figure 22. PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

TABLE XVIII

SUMMARY OF RESULTS FOR CALCULATION OF BUBBLE POINT PRESSURES FOR HYDROGEN + N-PARAFFIN SYSTEMS

Case Number	Peng-Robinson		Original PGR		This Work	
	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
2	5.23	4.5	30.29	33.2	4.06	5.8
3	3.22	2.0	3.35	2.7	1.09	1.7

modified PGR equation is the most accurate among the equations considered in predicting bubble point pressures.

Figure 23 shows the effect of carbon number on the optimum interaction parameter of Case 2 for the equations considered. Unlike the ethane and carbon dioxide systems, the modified PGR equation does not contain smaller interaction parameters than the PR and original PGR equations. Apparently, except for the n-C_4 system, the interaction parameters of the original and modified PGR equation are almost equivalent in magnitude with opposite signs. The interaction parameter of the hydrogen + n-C_4 system is almost unthinkable. However, no error was detected during repeat runs. Overall, the interaction parameter values for the selected equations are less sensitive to the carbon number and may be treated as constants. This makes extrapolations to heavier molecular weight compounds for the H_2 systems more reliable.

The effects of temperature on the optimum interaction parameter are shown in Figures 24 to 26. Both the modified and original PGR equations have interaction parameters that are less sensitive to molecular weight of the solute than the PR equation. The interaction parameters for the modified PGR equation showed less variation with temperature than that of the original PGR equation, which may imply that the simple one-fluid mixing rules were sufficient to describe the characteristics of binary mixture systems. Also, the behaviors of the C_{ij} values were opposite to those of the original PGR equation. This observation was similar to that obtained from Figure 23. The C_{ij}'s from the PR equation show a great deal of scatter in comparison with the other equations of state.

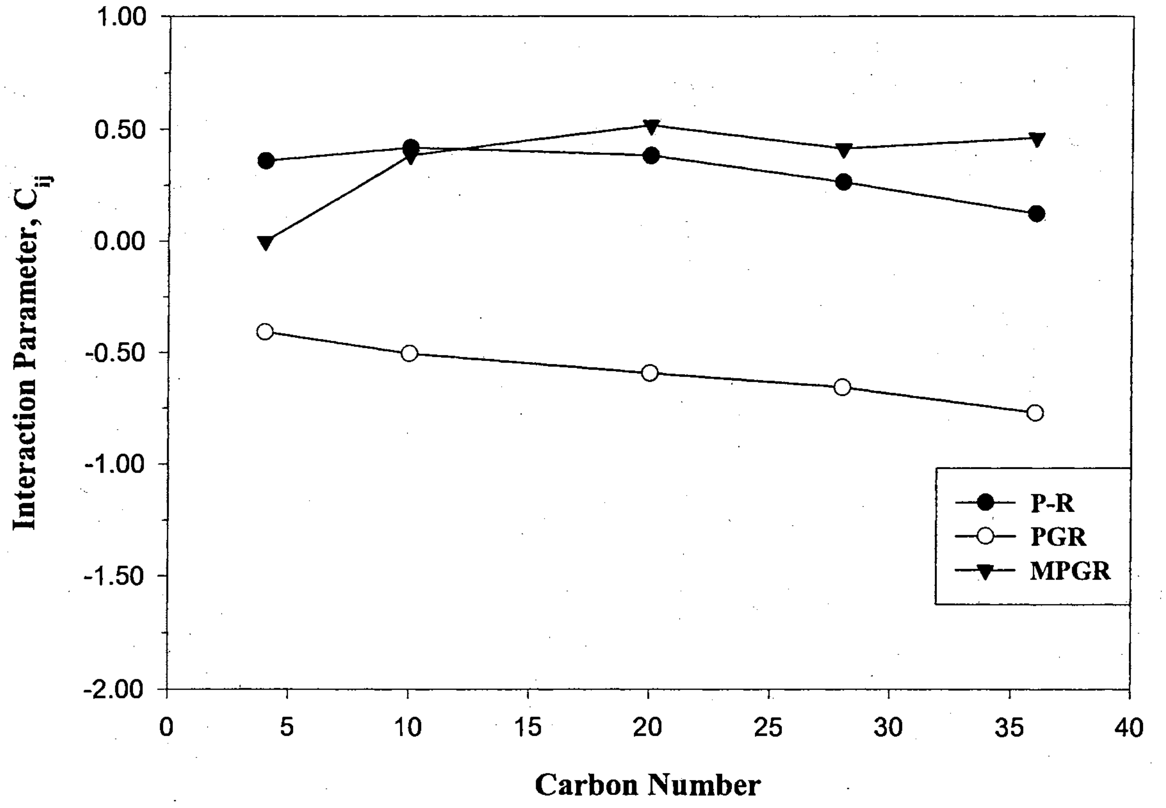

Figure 23. Equation of State Interaction Parameters, C_{ij}, for the Hydrogen + n-Paraffin Systems.

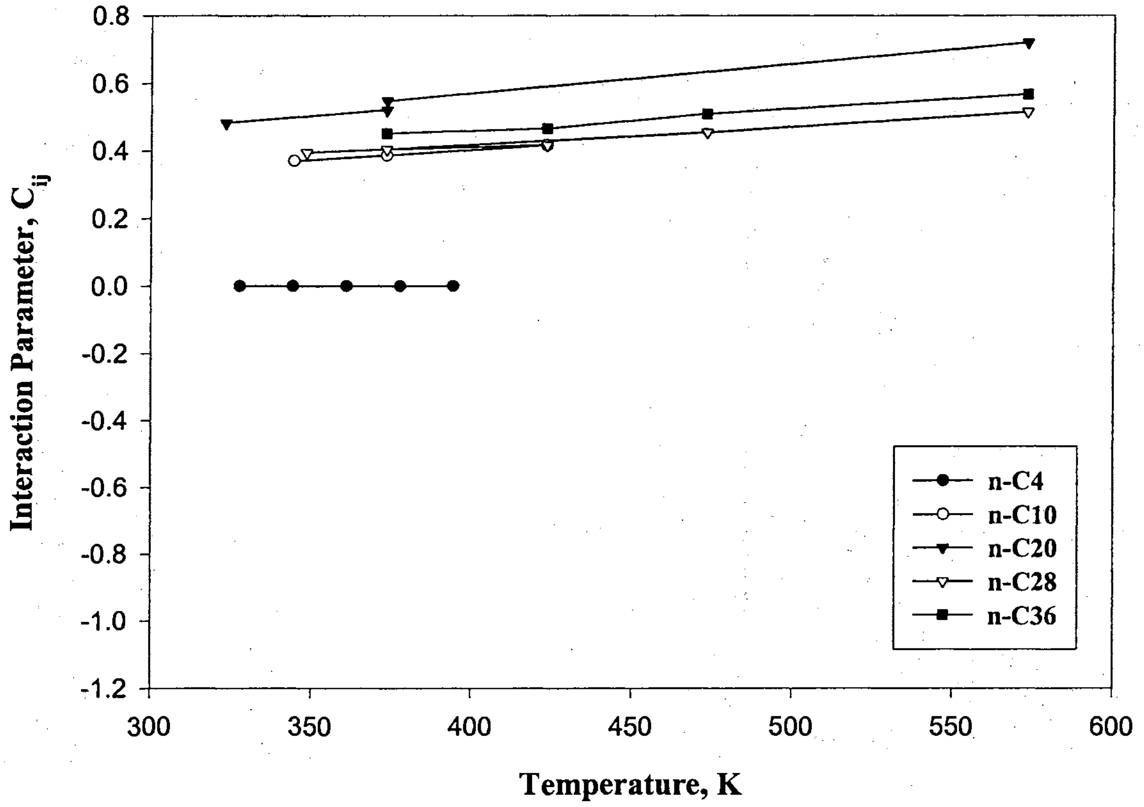

Figure 24. Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.

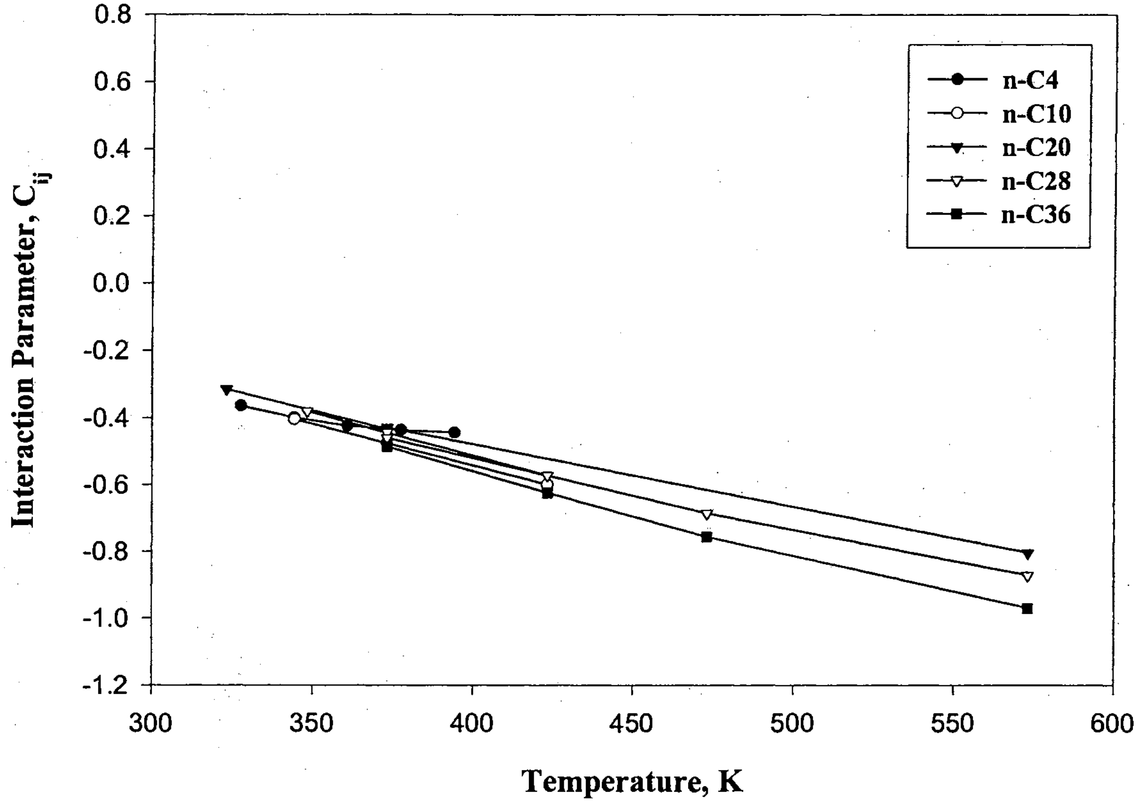

Figure 25. PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.

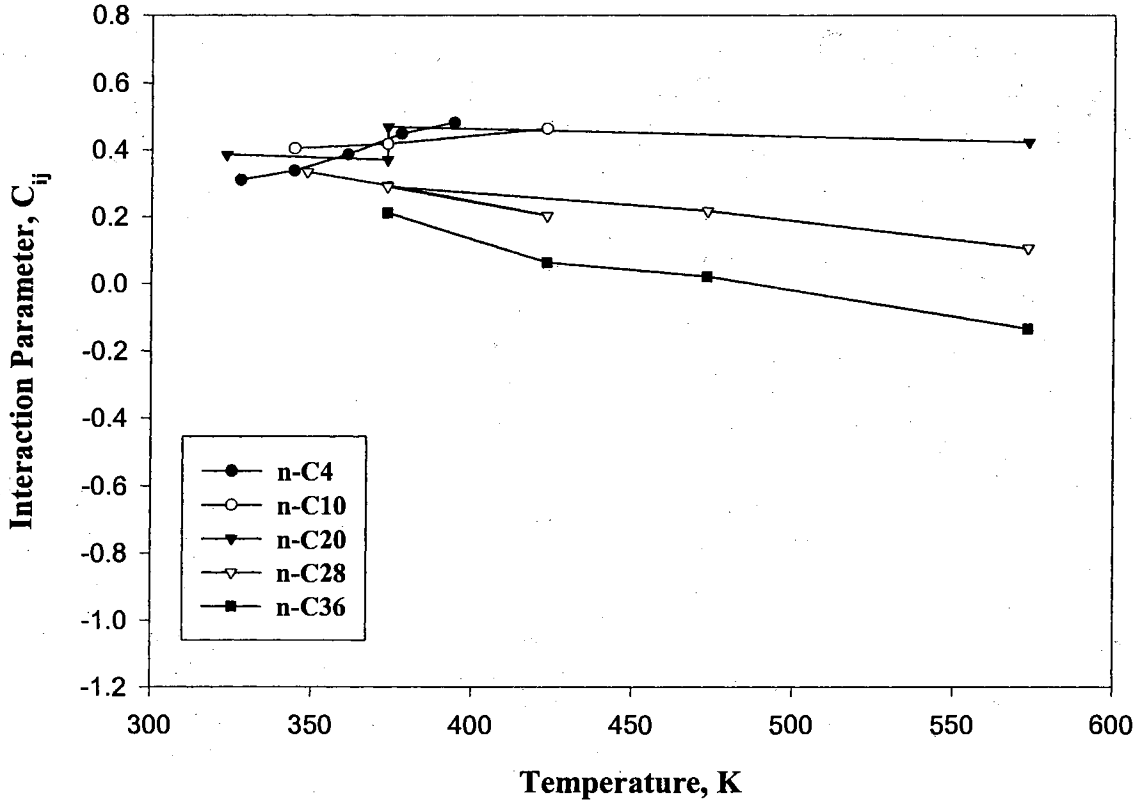

Figure 26. PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.

Since hydrogen is a quantum gas, its molecular potential energy is expected to be significantly different from that of other compounds. Thus, the phase behavior of systems involving hydrogen is different from other binary mixtures such as methane, ethane, carbon dioxide with n-paraffins, and the characteristics of the interaction parameters showed noticeable differences. Nevertheless, the predictive capability of the modified equation was more accurate than the other equations, for systems containing hydrogen.

Conclusions and Recommendations

The modified Park-Gasem-Robinson (PGR) equation of state was evaluated using binary mixture systems of ethane, carbon dioxide, and hydrogen with n-paraffins. The systems contain simple mixtures such as ethane + n-butane and asymmetric mixtures such as ethane + n-tetratetracontane systems. Simple van der Waals one-fluid mixing rules with one interaction parameter, C_{ij}, were used in the evaluation. Throughout the evaluations, the modified PGR equation predicted bubble point pressures within 2 %AAD with one temperature dependent interaction parameter (Case 3).

For ethane + and carbon dioxide + n-paraffin systems, the bubble point pressure prediction results of the modified PGR equation were compared to those of the PR, SPHCT and original PGR equations. With no interaction parameter, the new equation showed the best results among the equations tested. For ethane binaries, the segment-segment interaction models such as the SPHCT, original PGR and modified PGR equations showed better performance than the PR equation in Case 3. The modified PGR equation showed better results than the SPHCT equation in Case 2. For carbon dioxide binaries, the modified equation showed worse performance than the PR and SPHCT equations in Case 2. In Case 3, the modified PGR equation showed comparable results to the SPHCT equation.

For hydrogen + n-paraffin systems, the bubble point pressure predictions of the modified PGR equation were compared to those of the PR and original SPHCT equations. In Case 2, the modified PGR equation gave worse predictions than the PR equation. However, in Case 3, the modified equation performed better than the PR and original PGR equations.

The effects of the carbon number and system temperature on the interaction parameters were studied. The interaction parameters of the modified equation showed less sensitivity to the carbon number for each binary system. The modified equation also showed a weak temperature dependence, resulting in more flexibility. The modified PGR equation has less scattered interaction parameters with the carbon number and, thus, more suitable for extrapolation.

Fundamental changes in the partition function are still necessary for systems containing polar components like carbon dioxide. Also, the assumptions regarding the hard core radius and potential well depth for various compounds should be further studied to improve mixture predictions. Further study on the mixing rules is needed to eliminate the interaction parameter temperature dependence. The mixture database should be expanded to include more types of chemical compounds for use in future equation of state evaluations. The database should include other types of solute compounds (such as CH_4, H_2S and N_2) as well as a wider variety of solvent compounds.

CHAPTER 5

PREDICTING CALORIMETRIC PROPERTIES USING SELECTED EQUATIONS OF STATE

Abstract

Previous evaluations of the modified Park-Gasem-Robinson (PGR) equation of state have documented its ability to predict the equilibrium properties of many pure fluids and mixtures. Shaver (25) has offered modifications to the SPHCT model, which have resulted in improved pure-fluid vapor pressure and phase density predictions. Park (26) introduced a new form of an equation of state, the PGR equation of state, which is based on segment-segment interactions. The predictive capability of the PGR equation was evaluated for vapor pressure and phase densities of pure compounds and for bubble point pressures of selected binary mixture systems. The results were shown to be better or comparable to those of the Peng-Robinson (PR), original SPHCT and modified SPHCT equations of state. In the previous chapters, the modified version of the PGR equation of state was introduced and shown to yield better performance than the original PGR equation of state. In this work, the predictive abilities of the original SPHCT, modified SPHCT and modified PGR equations of state for representing calorimetric properties are evaluated. Specifically, the accuracy of enthalpy and entropy predictions using those selected equations of state are compared to those of the widely used PR equation of state.

The evaluations were conducted for six pure fluids of varying chemical structure and covering the two-phase and single-phase regions. The results indicate that the abilities of the PR, the original SPHCT, the modified SPHCT and the modified PGR equations of state to predict calorimetric properties are similar to their comparative abilities to predict volumetric properties. The absolute average percentage deviations obtained for liquid density, enthalpy, and entropy, respectively, are: 14.4%, 6.6% and 4.4% for PR; 7.1%, 9.0% and 5.6% for the original SPHCT; 12.8%, 11.6% and 8.7% for the modified SPHCT; and 4.0%, 3.3% and 3.6% for the modified PGR equation of state. Thus, the modified PGR equation appears to be more accurate in predicting calorimetric properties than the other equations of state considered.

Introduction

Analytic equations of state have long been recognized as the most convenient way of representing equilibrium phase behavior for process design and optimization calculations. The most commonly used analytic equations are the cubic van der Waals type equations such as the PR and the Soave-Redlich-Kwong (SRK) equations. The cubic equations are largely empirical and have been found to be inherently deficient in their ability to describe mixtures of small and large molecules, mixtures containing polar and associative molecules and mixtures of polymeric compounds. In order to overcome some of these deficiencies and to develop a more theoretically based equation of state capable of describing both vapor and liquid phases, Beret and Prausnitz (5) and Donohue and Prausnitz (6) developed the perturbed-hard-chain theory (PHCT). The PHCT model serves to bridge the gap between conventional equations of state and those used for representation of polymeric liquids. It is applicable to both liquid and vapor phases for compounds ranging in structural complexity from methane to heavy hydrocarbons and polymers. However, the drawback of the PHCT model is its complexity in implementation. In 1986, Kim et al. (9) proposed a simplification to the PHCT equation making it more convenient for engineering calculations. Since its introduction, the simplified perturbed-hard-chain theory (SPHCT) model of Kim et al. (9) has been studied by several investigators. Peters et al. (109, 110) assessed the quality of the phase behavior predictions of the SPHCT for normal alkanes of various sizes and their mixtures. Ponce-Ramirez et al. (46) applied the SPHCT equation to the prediction of phase equilibria of CO_2 + hydrocarbon systems and showed that bubble point pressures can be predicted for these systems with average errors of less than 5%. Gasem and Robinson (24) evaluated the SPHCT equation of state for the prediction of phase behavior of normal paraffins and mixtures of normal paraffins with ethane. They showed that vapor pressures and saturated liquid densities of normal paraffins extending from methane to n-C_{64} can be predicted reasonably well by the SPHCT equation of state; comparable predictions of phase compositions were obtained from the SPHCT and the SRK equation of state for ethane + n-paraffin systems. Other studies on the SPHCT model include those of Georgeton and Teja (111), van Pelt et al. (44) and Garcia-Sanchez et al. (47). In this work, the above studies are complemented by evaluating the SPHCT equation of state for prediction of calorimetric properties, for which there are no studies available.

The SPHCT equation of state has a sound theoretical base in statistical thermodynamics, and its underlying assumptions offer good opportunities for improving its ability to predict thermodynamic properties. Shaver and coworkers (25) offered modifications to the SPHCT model, which yielded improved pure-fluid vapor pressure and phase density predictions for a wide variety of pure fluids. For mixtures, the modified SPHCT was found to be comparable to the original SPHCT model and the PR cubic equation in predicting bubble point pressures, phase compositions and phase densities. In the present work, the modified version of the SPHCT model is also evaluated for the prediction of calorimetric properties.

Park (26) introduced a new equation of state model (PGR equation of state) which is based on segment-segment molecular interactions. The PGR equation of state contains the attractive term of both the cubic and SPHCT equations. This equation was evaluated for the predictions of vapor pressure and phase densities for pure compounds and of bubble point pressures for selected binary mixture systems. The result showed that this equation was comparable to the PR equation and better than both the original and modified SPHCT equations of state. In the present work, the modified version of the PGR model is also evaluated for the prediction of calorimetric properties.

The evaluations were conducted using six pure fluids, covering the two-phase and the single-phase regions. The fluids considered included methane, ethane, propane, benzene, carbon dioxide, and water. The predictive capabilities of the modified PGR, original SPHCT and modified SPHCT models are compared to those of the PR cubic equation of state. This assessment of the accuracy of enthalpy and entropy predictions using the SPHCT and its modifications serves as a valuable complement to the ongoing efforts to evaluate and develop segment-segment interaction models.

The Equations of State

The Original and Modified SPHCT Equations of State

An approximation for the canonical ensemble partition function for chain-like molecules may be presented as a combination of contributions from the ideal gas, the molecular attractions, the molecular repulsions, the molecular translational contribution, and the external and internal rotational/vibrational contributions (6). Kim et al. (9) proposed a simple expression for the attractive term of the partition function by using the model of Lee et al. (23). Further, by adopting Carnahan and Starling's (18) expression for hard-sphere molecular repulsion, Kim et al. (9) developed the following SPHCT equation of state

$$Z = 1 + cZ_{rep} + cZ_{att} \tag{5-1}$$

where

$$Z = \frac{Pv}{RT} \tag{5-2}$$

$$Z_{rep} = \frac{4(\tau\tilde{\rho}) - 2(\tau\tilde{\rho})^2}{(1 - \tau\tilde{\rho})^3} \tag{5-3}$$

$$Z_{att} = -\frac{Z_M a}{cv + a} \tag{5-4}$$

$$a = cv^{*}\left[\exp\left(\frac{1}{2\tilde{T}}\right)-1\right] \tag{5-5}$$

and $\tilde{T} = T/T^{*}$, $\tilde{\rho} = v^{*}/v$, $\tau = 0.7402$, T* and v* are the characteristic temperature and volume, respectively, and Z_M is the maximum coordination number.

Shaver and coworkers (25) carried out an extensive study of the parameters of the above SPHCT model using four selected fluids (methane, water, carbon dioxide and benzene). They found that all property calculations were extremely sensitive to the parameters T* and Z_M, and the parameters were strongly dependent on temperature. The reason for the above behavior was attributed to the inadequacy in the temperature dependence of the attractive term of the SPHCT equation of state. The effect of applying critical point constraints to the SPHCT equation was also investigated. Constraining the SPHCT equation was observed to result in simple correlations to relate T* and v* to c .

Shaver et al. (25) investigated several modifications to the attractive term of the constrained equation using vapor pressure data for four pure paraffins (methane, propane, n-decane and n-tetradecane). They found significant improvement in the predictive capability by including a polynomial correction to the temperature dependence within the exponential part of the attractive term. The proposed modifications to the original SPHCT equation of state included application of critical point constraints and modification in the attractive term of the original equation as follows

$$Z_{att} = -\frac{Z_M a}{cv + a} \tag{5-6}$$

where

$$a = cv^{*}\left[\exp(F_t) - 1\right] \tag{5-7}$$

and

$$F_t = \sum_{i=1}^{k} b_i \left(\frac{1}{2\tilde{T}}\right)^{i/2} \tag{5-8}$$

where b's are constants obtained by regression (25).

The Modified PGR Equation of State

The equation of state proposed by Park (26) was based on the generalized van der Waals partition function for chain-like molecules. The PGR equation of state utilized an expression for the free volume of hard spheres in the repulsive term and augmented generalized cubic equation of state attractive terms. A square-well potential was used to describe the attractive energy between segments of molecules. In this work, this PGR equation of state was modified to provide simplicity and flexibility as well as more accurate prediction capability. The proposed modified PGR equation of state is

$$Z = 1 + c\left(\frac{\beta_1 \tau}{v_r - \beta_2 \tau} - \frac{\alpha Y v_r}{v_r^2 + u v_r + w} - \frac{Q_1 \alpha Y}{v_r + Q_2}\right) \tag{2-45}$$

where

$$\alpha Y = Z_M \left[\exp(F_t) - 1\right] \tag{2-46}$$

$$F_t = \omega_1 \left(\frac{1}{2\tilde{T}}\right)^{1/2} + \omega_2 \left(\frac{1}{2\tilde{T}}\right) + \omega_3 \left(\frac{1}{2\tilde{T}}\right)^{3/2} + \omega_4 \left(\frac{1}{2\tilde{T}}\right)^{2} \tag{2-44}$$

and Z_M, ω_1, ω_2, ω_3, and ω_4 are universal equation of state constants.

Calorimetric Property Calculations

Any calorimetric property (enthalpy, internal energy, Helmholtz energy, Gibbs free energy or entropy) at a given state (T, p) can be expressed as a summation of three quantities

$$X(T, p) = [X(T, p) - X(T, p^o)] + [X(T, p^o) - X(T^o, p^o)] + X(T^o, p^o) \qquad (5\text{-}9)$$

The first quantity, $[X(T, p) - X(T, p^o)]$, is called the departure function, and it represents the isothermal effect of pressure on the property. It is the difference in the value of the property at the temperature-pressure condition of interest and its value in the ideal gas state at the same temperature and reference pressure, p^o.

The second quantity, $[X(T, p^o) - X(T^o, p^o)]$, represents the isobaric effect of temperature on the property in the ideal gas state. It is the difference in the value of the property in the ideal gas state at the temperature of interest and the reference state of T^o, both at the pressure p^o. The last quantity $X(T^o, p^o)$ is the value of the property at the reference state, chosen as (T^o, p^o).

One of the binary sets (U, S) or (H, S) can be used to completely represent the set of calorimetric properties (U, H, A, G and S). For this work, the binary set of (H, S) has been chosen. The reference state chosen for the calculations is

$$
\begin{aligned}
&T^\circ = 0\ \text{K} \\
&p^\circ = 1.01325\ \text{bar} \\
&H(T^\circ, p^\circ) = 0 \qquad (5\text{-}10) \\
&S(T^\circ, p^\circ) = 0
\end{aligned}
$$

This reference state must be kept in mind when comparing the calculated enthalpy and entropy values of this work with experimental data.

Ideal Gas Enthalpy and Entropy

The ideal gas enthalpy and entropy differences can be determined from available standard correlations which have been developed by fitting experimental ideal gas data closely. These correlations produce accurate experimental ideal gas data. Examples of such correlations are those suggested in the API Technical Data Book - Petroleum Refining (112), the correlations of Thinh et al. (113), Passut and Danner (114) and the more recent correlations of Aly and Lee (115). The correlations of Passut and Danner (114) are thermodynamically consistent and predict the absolute values of ideal gas enthalpy, entropy and heat capacity with good accuracy. They have been shown to be better than the correlations of the API Technical Data Book (112) and those of Thinh et al. (113) for both enthalpy and entropy. The correlations of Aly and Lee (115) have been found to be better than those of Passut and Danner (114), but they are more complicated to use. Thus, for this work, the correlations of Passut and Danner (114) have been chosen to predict ideal gas enthalpy and entropy values. The forms of the equations are as follows. For enthalpy,

$$H^\circ = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \tag{5-11}$$

where A, B, C, D, E, and F are derived coefficients with the enthalpy in Btu/lb and the temperature in °R.

The heat capacity and entropy equations are obtained from Equation (5-11) by using the appropriate thermodynamic formulae ($C_p^o = \frac{dH}{dT}$ and $S^o = \int \frac{C_p^o}{T} dT$) to ensure thermodynamic consistency

$$C_p^o = B + 2CT + 3DT^2 + 4ET^3 + 5FT^4 \tag{5-12}$$

$$S^o = B \ln T + 2CT + \frac{3}{2}DT^2 + \frac{4}{3}ET^3 + \frac{5}{4}FT^4 + G \tag{5-13}$$

where G is the constant of integration.

Passut and Danner (114) obtained the constants by fitting the above three equations to experimental ideal gas data of 89 compounds taken from API - Research Project 44 for the entire temperature range. The bases used were 0 Btu/lb at 0°R for enthalpy, and 0 Btu/lb$^\circ$R at 0°R and 1 atm for entropy; the same basis was used for the API-RP 44 tables.

Departure Functions

The enthalpy and entropy departure functions are obtained from the pvT properties of a fluid, as described by an equation of state. For a pressure-explicit equation of state, the departure functions are expressed as follows

$$A - A^{\circ} = -\int_{\infty}^{V} \left(P - \frac{RT}{V} \right) dV - RT \ln \frac{V}{V^{\circ}} \tag{5-14}$$

$$S - S^{\circ} = \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T} \right)_{V} - \frac{R}{V} \right] dV + R \ln \frac{V}{V^{\circ}} \tag{5-15}$$

$$H - H^{\circ} = \left(A - A^{\circ} \right) + T\left(S - S^{\circ} \right) + RT(Z - 1) \tag{5-16}$$

For the modified PGR, the original and the modified SPHCT equations of state, the derived departure function expressions are given in Tables XIX to XXI. Reid et al. (116) have reported the expressions of the departure functions for the generalized cubic equation of state, which we have used in this study.

The departure function (H - H°) does not depend on the value of the ideal gas reference state p° (or V°) while (A - A°) and (S - S°) are dependent on p° (or V°). The most commonly used ideal gas pressure reference states are unit pressure or zero pressure.

Model Evaluation

The abilities of the modified PGR, the original SPHCT and the modified SPHCT equations of state to predict calorimetric properties were evaluated by comparison with experimental data and with predictions generated by the widely used PR cubic equation of state. Following are brief descriptions for the database used, the cases studied, and evaluation results.

TABLE XIX

DEPARTURE FUNCTION EXPRESSIONS FOR THE ORIGINAL SPHCT EQUATION OF STATE.

$$H - H^{\circ} = RT\left[Z - 1 + Z_M cT\left(\frac{da}{dT}\right)\frac{1}{vc + a}\right]$$

$$S - S^{\circ} = -cR\left[\frac{4\tau v^*}{v - \tau v^*} + \frac{(\tau v^*)^2}{(v - \tau v^*)^2} + Z_M \ln\left(\frac{vc}{vc + a}\right)\right]$$

$$+ R\ln\left(\frac{v}{v^{\circ}}\right) + cRTZ_M\left(\frac{1}{vc + a}\right)\left(\frac{da}{dT}\right)$$

For the original SPHCT equation of state

$$\left(\frac{da}{dT}\right) = cv^*\left(-\frac{T^*}{2T^2}\right)\exp\left(\frac{T^*}{2T}\right)$$

---

o ideal gas

TABLE XX

DEPARTURE FUNCTION EXPRESSIONS
FOR THE MODIFIED SPHCT EQUATION OF STATE.

$$H - H^{o} = RT\left[Z - 1 + Z_{M} cT\left(\frac{da}{dT}\right)\frac{1}{vc + a}\right]$$

$$S - S^{o} = -cR\left[\frac{4\tau v^{*}}{v - \tau v^{*}} + \frac{\left(\tau v^{*}\right)^{2}}{\left(v - \tau v^{*}\right)^{2}} + Z_{M}\ln\left(\frac{vc}{vc + a}\right)\right]$$

$$+ R\ln\left(\frac{v}{v^{o}}\right) + cRTZ_{M}\left(\frac{1}{vc + a}\right)\left(\frac{da}{dT}\right)$$

For the modified SPHCT equation of state

$$\left(\frac{da}{dT}\right) = cv^{*}\left(\frac{dF_{t}}{dT}\right)_{v}\exp\left(F_{t}\right)$$

where

$$F_{t} = \sum_{i=1}^{4} b_{i}\left(\frac{T^{*}}{2T}\right)^{i/2}$$

and

$$\left(\frac{\partial F_{t}}{\partial T}\right)_{v} = -\frac{b_{1}}{2}\left(\frac{T^{*}}{2}\right)^{1/2} T^{-3/2} - b_{2}\left(\frac{T^{*}}{2}\right)\frac{1}{T^{2}} - \frac{3}{2}b_{3}\left(\frac{T^{*}}{2}\right)^{3/2} T^{-5/2} - 2b_{4}\left(\frac{T^{*}}{2}\right)^{2}\frac{1}{T^{3}}$$

---

o ideal gas

TABLE XXI

DEPARTURE FUNCTION EXPRESSIONS FOR THE MODIFIED PGR EQUATION OF STATE.

$$H - H^\circ = RT\left[Z - 1 - Z_M cT\left(\frac{da}{dT}\right)_v \Omega\right]$$

$$S - S^\circ = cR\frac{\beta_1}{\beta_2}\ln\left|\frac{v_r - \beta_2\tau}{v_r}\right| - cZ_M R\left[Y + T\left(\frac{\partial Y}{\partial T}\right)_v \Omega\right] + R\ln\left(\frac{v}{v^\circ}\right)$$

where

$$\Omega = \frac{2}{\sqrt{4w - u^2}}\left(\tan^{-1}\frac{2v_r + u}{\sqrt{4w - u^2}} - \frac{\pi}{2}\right) - \frac{Q_1}{Q_2}\ln\left|\frac{v_r - \beta_2\tau}{v_r}\right|$$

and

$$\left(\frac{da}{dT}\right)_v = -\frac{1}{T}\left[\frac{\omega_1}{2}\left(\frac{T^*}{2T}\right)^{1/2} + \omega_2\left(\frac{T^*}{2T}\right) + \frac{3\omega_3}{2}\left(\frac{T^*}{2T}\right)^{3/2} + 2\omega_4\left(\frac{T^*}{2T}\right)^2\right](Y + 1)$$

Database Used

A limited database of six pure fluids including three n-alkanes (methane, ethane and propane) and three polar fluids (carbon dioxide, water and benzene) was used. The sources and ranges of the data used are shown in Table XXII. Where available, saturated data for the six compounds were included from the triple point to the critical point. Unlike the database used in Chapter 3, data points with pressure lower than 0.007 bar and the critical points were included. For four compounds (methane, ethane, propane and benzene), only saturated liquid enthalpy and entropy data were utilized, in addition to the National Institute of Standards and Technology (NIST) saturated liquid and vapor densities. For water and carbon dioxide, data in the single-phase region were also included. No departure data was used in this study.

Reference States

Different sources employ different reference states for reporting calorimetric property data. For example, the reference states employed by NIST to report the calorimetric properties of propane over a range of temperatures and pressures are: The internal energy of propane at the liquid triple point (E_t) = 0 Btu/lb and S(0°R, 1atm)=0 Btu/lb °R. All the reported data in this source are the result of a non-analytic equation of state, developed specifically for propane to derive its thermophysical properties accurately. Data for most pure fluids published by NIST are reported in the above manner, i.e., as results of a substance- specific equation of state. In the above case, to

TABLE XXII

SOURCES AND RANGES OF DATA USED

Compound	Temperature Range (K)	Pressure Range (bar)	Source	No. of Points
Saturated data				
Methane	90.68 - 190.56	0.1174 - 45.988	118	11
Ethane	90.348 - 305.33	0.1131E-04 - 48.71	63	14
Propane	180.0 - 369.9	0.0505 - 42.475	64	27
Carbon dioxide	216.55 - 304.2	5.179 - 73.834	119	18
Water	283.15 - 647.13	0.0123 - 220.55	73	37
Benzene	278.68 - 561.75	0.0478 - 48.7575	70	29
Single-phase data				
Carbon dioxide	273.15 - 313.15	10.0 - 55.0	119	29
Water	373.15 - 673.15	0.5 - 260.0	73	49

achieve $E_t = 0$ Btu/lb, E(0°R, 0 atm) was set to a certain arbitrary value.

The reference states used by the Thermodynamic Research Center at Texas A&M University (67) to report calorimetric property data of hydrocarbons and certain related compounds for API RP-44 tables are: H(0°R, 1atm) = 0, S(0°R, 1atm) = 0. NIST/NRC Steam Tables have used the following reference states for reporting calorimetric property data of water: $E_t = 0$ Btu/lb and $S_t = 0$ Btu/lb°R. Gas Processors Association (GPA) have reported enthalpy data based on two different reference states: (a) H = 0 in the ideal gas state at 0°R, and (b) H = 0 for the elements at 25°C. Presently, GPA reports enthalpy data merely as departure functions, a more favorable method.

As evident, the experimental data and the predictions of an equation of state based on a certain reference state must be brought to a common basis before comparing them. For this, the H(T°, p°) and S(T°, p°) values must be known for the data source. More specifically, as the (T°, p°) values used in this work are (0 K, 1.01325 bar), the values of H(0 K, 1.01325 bar) and S(0 K, 1.01325 bar) based on the source's reference states need to be determined. The H(0 K, 1.01325 bar) and S(0 K, 1.01325 bar) values used in this work, as stated earlier are: H(0 K, 1.01325 bar) = 0 kJ/mol and S(0 K, 1.01325 bar) = 0 kJ/mol K. Determining these quantities for a given source of data is difficult, as they are not explicitly stated in the above manner. To avoid the above problem, a strategy was developed for estimating the H (0 K, 1.01325 bar) and S (0 K, 1.01325 bar) values of a given data-set from easily available information, which could then be used to bring the experimental data and the predictions to a common basis before comparison. Following is a description of the strategy employed.

Strategy to Estimate H (0 K, 1.01325 bar) and S (0 K, 1.01325 bar)

Five of the literature sources of the database used employ the same reference state for entropy as this work, i.e., S(0 K, 1.01325 bar) = 0 kJ/mol K. Thus, for those five compounds, the entropy predictions could be compared directly with experimental data. However, for the entropy data of water and the enthalpy data of all compounds, the above could not be done. The values of H(0 K, 1.01325 bar) and S(0 K, 1.01325 bar) had to be determined or at least estimated.

The underlying assumption of the estimation method used is that the error in the liquid/vapor enthalpy and entropy predictions would be least for that data point (T, p) for which the error in the phase density prediction is least. This assumption has been made by noting the dependence of enthalpy and entropy values on the corresponding phase densities. Thus, the estimation method is as follows:

(1) Phase densities, enthalpy and entropy for each data point are calculated using the selected equation of state.

(2) The data points of minimum absolute percent deviation (APD) for liquid and vapor density predictions are noted.

(3) At the data point of minimum APD for liquid density predictions, the difference between the experimental and the calculated liquid enthalpy (and/or entropy) values is determined. This difference is the estimated value of H(0 K, 1.01325 bar) or S(0 K, 1.01325 bar) for the liquid phase. This value is added to all the calculated liquid enthalpy (or entropy) values to bring them to the same basis as

the experimental values. The resulting calculated values are then compared with experimental values.

(4) The same procedure given in Step 3 is also followed for the vapor phase. The check for the method is that the estimated values of H(0 K, 1.01325 bar) or S(0 K, 1.01325 bar) from the liquid phase and the vapor phase should be very close to experimental data.

Cases Studied

In evaluating the modifications to the original SPHCT equation of state, as suggested by Shaver et al. (25), two cases were studied. Case 1 is the original SPHCT equation with $Z_M = 18$, subjected to the critical point constraints and without the modified attractive term (or any volume translation). Case 2 is the modified SPHCT equation of state with $Z_M = 18$ including the application of the critical point constraints and the modified attractive term. Volume translation was not studied in the present work.

For the original SPHCT equation of state, Case 1 and Case 2, the equation of state parameters used were those obtained by Shaver et al. (25) using the following objective function, SS, involving vapor pressures and phase densities

$$SS = \sum_{i=1}^{n}\left[\left(\frac{P_{calc} - P_{exp}}{P_{exp}}\right)_i^2 + \left(\frac{\rho_{l,calc} - \rho_{l,exp}}{\rho_{l,exp}}\right)_i^2 + \left(\frac{\rho_{v,calc} - \rho_{v,exp}}{\rho_{v,exp}}\right)_i^2\right] \qquad (5\text{-}17)$$

For Case 1 and Case 2, only the SPHCT parameter c was optimized to minimize percentage errors in calculated vapor pressures. The other two parameters (T* and v*) were obtained from the correlation generated by Shaver and coworkers (25). Table XXIII gives a listing of the equation of state parameters used for the six compounds studied, for the original SPHCT equation of state, Case 1 and Case 2. For the modified PGR equation of state, the equation of state parameters presented in Chapter 3 were used. The same objective function of Equation (5-17) was used to optimize the modified PGR equation of state parameters.

Results and Discussion

Tables XXIV and XXV show the results of the liquid density and vapor density predictions of the modified PGR, Case 1, Case 2, the PR and the original SPHCT equations. The constrained SPHCT equation of state (Case 1) showed worse performance than the original SPHCT equation of state for phase density predictions. The constrained SPHCT equation of state showed improved prediction capabilities near critical points but much worse predictions in the low pressure regions. However, the constrained SPHCT equation of state with a modified temperature-dependence term (Case 2) showed preferable performances for vapor density predictions. Since the critical point of each compound was included in the data base used in this study, large %AAD values were obtained. All equations of state except the modified PGR equation of state showed poor performance in predicting vapor pressures for data at low pressures (less than 0.007 bar). The overall results showed that the modified PGR equation handles saturated properties better than the other equations considered in this study.

TABLE XXIII

PURE FLUID EOS PARAMETERS

Compound	Original SPHCT**			Case 1**			Case 2**			Modified PGR		
	c	T* (K)	v* (cc/mol)	c	T* (K)	v* (cc/mol)	c	T* (K)	v* (cc/mol)	c	T* (K)	v* (cc/mol)
Methane	1.0298	80.05	18.889	1.0409	149.78	18.614	1.0003	95.23	18.858	1.0000	81.217	20.413
Ethane	1.2485	120.73	26.988	1.3096	221.34	26.31	1.2423	142.28	26.795	1.3459	116.67	27.809
Propane	1.5015	136.94	35.876	1.5779	252.01	33.886	1.4273	165.27	35.123	1.4821	137.74	37.752
Carbon dioxide	1.9258	104.32	14.486	2.2271	186.79	14.104	1.6258	131.05	15.858	1.9378	104.12	15.593
Water	2.0233	225.08	9.071	2.3534	391.2	9.824	1.9416	266.06	10.568	1.9452	228.95	9.488
Benzene	1.8866	192.59	41.457	1.9049	361.08	41.794	1.6142	242.48	44.417	1.8007	196.03	44.800

** from Shaver (25).

TABLE XXIV

EVALUATION OF PURE FLUID LIQUID DENSITY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD
<u>Saturated data</u>										
Methane	0.041	10.1	0.033	7.2	0.042	12.7	0.039	11.8	0.016	5.4
Ethane	0.033*	7.0*	0.056*	10.2*	0.059*	13.3*	0.056	11.6*	0.019	4.0
Propane	0.033	5.3	0.034	6.2	0.043	8.4	0.044	7.5	0.017	3.1
Carbon dioxide	0.067	6.5	0.062	5.7	0.114	11.0	0.123	12.7	0.052	5.2
Water	0.153	18.5	0.079	8.6	0.183	21.7	0.182	22.4	0.044	4.0
Benzene	0.034	4.8	0.056	8.0	0.065	10.7	0.055	8.2	0.035	5.3
<u>Single-Phase data</u>										
Water	0.563	48.6	0.044	3.6	0.142	12.7	0.138	12.8	0.017	1.3
Overall	0.132	14.4	0.052	7.1	0.094	12.8	0.092	12.4	0.027	4.0

* divergence occurred at low pressure region

TABLE XXV

EVALUATION OF PURE FLUID VAPOR DENSITY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD	RSME g/cc	%AAD
<u>Saturated data</u>										
Methane	0.033	11.2	0.024	9.9	0.020	9.1	0.022	5.3	0.015	9.2
Ethane	0.018*	5.1*	0.033*	8.7*	0.033*	9.6*	0.034*	5.0*	0.021	3.8
Propane	0.014	2.9	0.016	4.9	0.018	8.3	0.021	4.5	0.014	3.7
Carbon dioxide	0.002	1.4	0.015	4.4	0.006	2.3	0.008	2.8	0.005	2.3
Water	0.004	6.1	0.044	11.4	0.033	12.8	0.029	4.2	0.027	8.4
Benzene	0.034	3.7	0.030	5.7	0.027	6.0	0.003	3.5	0.017	2.7
<u>Single-Phase data</u>										
Carbon dioxide	0.002	1.3	0.003	2.8	0.004	1.7	0.003	1.6	0.002	1.8
Water	0.033	133.3	0.004	2.0	0.003	1.3	0.004	1.3	0.002	2.1
Overall	0.022	20.6	0.024	6.2	0.023	6.4	0.013	3.5	0.012	4.3

* divergence occurred at low pressure region

Tables XXVI through XXIX present the prediction results for the PR equation of state, the original SPHCT equation of state, Case 1, Case 2 and the modified PGR equation of state for the liquid phase and vapor phase enthalpy and entropy. Considering these results, the following observations are made:

- The abilities of the PR equation of state, the original SPHCT equation of state, the constrained SPHCT (Case 1), the modified SPHCT equation of state (Case 2) and the modified PGR equation of state to predict calorimetric properties are very similar to their comparative abilities to predict volumetric properties. This was expected, since the calorimetric property calculations depend significantly on the volumetric property values predicted by the equation of state.
- The vapor phase predictions are significantly better than those for the liquid phase, as is often seen using an analytic equation of state. Also typical of these equations is their poor predictions near the triple and the critical points.
- The predictions of the modified PGR equation of state for all liquid phase properties are consistently better than the predictions of the constrained SPHCT equation of state and the constrained modified SPHCT equation of state. Further, for both liquid and vapor phase properties, the predictions of the modified PGR equation of state are better than those of the PR equation of state and the original SPHCT equation of state.
- Regarding the ability to deal with normal fluids (n-alkanes), the PR and modified PGR models are able to predict both volumetric and calorimetric properties of

TABLE XXVI

EVALUATION OF PURE FLUID LIQUID ENTHALPY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD
<u>Saturated data</u>										
Methane	0.303	2.5	0.354	5.3	0.822	8.0	0.530	3.5	0.310	2.9
Ethane	0.454	2.1	0.850	7.8	1.434	8.5	1.333	9.3	0.863	7.1
Propane	0.305	1.3	0.572	3.2	1.229	4.6	0.872	1.8	0.333	1.3
Carbon dioxide	0.667	1.4	0.456	1.8	1.478	4.9	0.880	1.8	0.485	2.1
Water	1.518	26.4	2.028	32.0	7.222	38.5	2.624	8.0	0.856	4.5
Benzene	1.260	10.3	0.832	8.4	1.920	7.3	0.698	5.8	0.593	3.4
<u>Single-Phase data</u>										
Water	0.634	2.0	1.330	4.4	3.334	9.4	1.98	2.2	0.720	2.0
Overall	0.733	6.6	0.919	9.0	2.493	11.6	1.163	4.6	0.585	3.3

TABLE XXVII

EVALUATION OF PURE FLUID VAPOR ENTHALPY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD	RSME kJ/mol	%AAD
<u>Saturated data</u>										
Carbon dioxide	0.618	0.7	0.940	1.7	0.604	0.9	0.665	0.9	0.545	1.4
Water	0.889	1.7	3.321	4.1	2.485	4.4	2.178	2.7	2.741	4.0
<u>Single-Phase data</u>										
Carbon dioxide	0.051	0.1	0.344	0.8	0.198	0.5	0.154	0.4	0.264	0.6
Water	8.133	8.6	1.252	1.2	0.870	0.8	0.697	0.7	1.350	1.2
Overall	2.424	2.8	1.463	2.0	1.042	1.7	0.924	1.2	1.227	1.8

TABLE XXVIII

EVALUATION OF PURE FLUID LIQUID ENTROPY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD
<u>Saturated data</u>										
Methane	0.003	1.1	0.003	2.5	0.012	4.2	0.004	1.7	0.004	2.2
Ethane	0.002	1.2	0.010	3.8	0.009	4.5	0.005	5.7	0.008	4.5
Propane	0.004	0.4	0.002	1.0	0.002	1.6	0.002	0.6	0.001	0.4
Carbon dioxide	0.002	0.8	0.002	1.1	0.007	3.2	0.003	1.2	0.002	1.3
Water	0.003	18.1	0.003	26.2	0.016	38.2	0.006	7.4	0.002	3.7
Benzene	0.003	0.9	0.002	0.8	0.004	1.3	0.004	0.7	0.001	0.5
<u>Single-Phase data</u>										
Water	0.004	8.5	0.004	3.7	0.010	8.2	0.004	1.7	0.002	1.6
Overall	0.004	4.4	0.004	5.6	0.011	8.7	0.004	2.7	0.003	2.0

* kJ/mol/K

TABLE XXIX

EVALUATION OF PURE FLUID VAPOR ENTROPY PREDICTIONS

Component	PR		Original SPHCT		Case 1		Case 2		Modified PGR	
	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD	RSME*	%AAD
<u>Saturated data</u>										
Carbon dioxide	0.004	0.4	0.003	1.1	0.004	0.5	0.003	0.5	0.003	0.9
Water	0.004	0.9	0.005	3.0	0.004	2.9	0.003	1.9	0.004	2.8
<u>Single-Phase data</u>										
Carbon dioxide	0.002	0.1	0.003	0.7	0.004	0.4	0.002	0.3	0.002	0.3
Water	0.006	5.9	0.003	0.9	0.003	0.7	0.002	0.5	0.003	0.9
Overall	0.004	1.8	0.004	1.4	0.004	1.1	0.003	0.8	0.003	1.2

* kJ/mol/K

normal fluids with accuracy close to or better than the PR equation of state predictions.

- For three polar fluids (water, carbon dioxide and benzene), the constrained modified SPHCT equation of state is poor in its volumetric property predictions. However, it is noteworthy that its calorimetric property predictions for polar fluids still compare very favorably with the PR equation of state predictions. Among polar fluids, the constrained, modified SPHCT equation of state shows a distinct improvement over the original and the constrained (Case 1) SPHCT equation of state in the liquid enthalpy and liquid entropy predictions for water.
- For polar fluids, the modified PGR equation of state is much better than the PR, original SPHCT and constrained SPHCT equations in its volumetric and calorimetric liquid property predictions. For calorimetric properties of saturated vapor fluid (Tables XXVII and XXIX), the PR equation of state is better than the modified PGR equation of state. However, the modified PGR equation of state is still much better in its volumetric and calorimetric properties of vapor isotherms.
- Constraining the original SPHCT equation of state has been found to shift the predictions in one direction, i.e., it improves the vapor phase predictions and worsens the liquid phase predictions consistently for all properties.
- The results of the predictions in the single phase data of water and carbon dioxide demonstrate to some extent the ability of the constrained modified SPHCT equation of state and the modified PGR equation of state to describe the single-phase region better than the other equations.

The comparisons presented for the equation of state enthalpy and entropy predictions, and the resultant deviations from experimental values, involve errors originating from both the equation of state departure functions and possible errors from the ideal gas enthalpy expressions (e.g., Equation 5-11). Since the user of calorimetric properties is typically interested in enthalpy and entropy values, evaluations and comparisons are made on such basis instead of comparing departure functions.

Conclusions and Recommendations

Predictions of calorimetric properties of selected pure fluids using several different equations of state were evaluated. The abilities of the PR, the original SPHCT, the modified SPHCT and the modified PGR equations of state to predict calorimetric properties are similar to their comparative abilities to predict volumetric properties.

The predictions of the modified PGR equation of state and the constrained modified SPHCT equation of state (Case 2) for calorimetric properties are consistently better than the predictions of the original SPHCT equation of state and the constrained SPHCT equation of state (Case 1). In addition, the modified PGR equation of state and the constrained modified SPHCT equation of state predictions compare favorably with those obtained by the PR equation of state. Furthermore, the modified PGR equation of state has less difficulty in the triple and critical property calculation.

Based on the present work, the following tasks are recommended:

1. Extensive evaluations for a large variety of systems

2. Evaluations of the equation for binary and ternary mixtures
3. Evaluation and implementation of the volume translation strategy to the modified PGR equation of state
4. Evaluations of departure values for enthalpy and entropy of pure and mixture systems

LITERATURE CITED

1. Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," Chemical Engineering Science, 27, 1197, 1972.

2. Peng, Y. D. and D. B. Robinson, "A New Two-Constant Equation of State," Ind. Eng. Chem. Fundam., 15, 59, 1976.

3. Adachi, Y., H. Sugie and C.Y.L. Benjamin, "Taking Advantage of Available Cubic Equations of State," The Canadian J. of Chemical Engineering, 68, 639, 1990.

4. van Pelt, A., U. K. Deiters, C. J. Peters and J. de Swaan Arons, "The Limiting Behavior of the Simplified-Perturbed-Hard-Chain Theory at High Temperatures," Fluid Phase Equilibria, 90, 45, 1993.

5. Beret, S. and J. M. Prausnitz, "Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules," AIChE Journal, 21, 1123, 1975.

6. Donohue, M. D. and J. M. Prausnitz, "Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," AIChE Journal, 24, 849, 1978.

7. Sandler, I., H. Orbey and B. I. Lee, Models for Thermodynamic and Phase Equilibria Calculation, Marcel Dekker, New York, 1994.

8. Plackov, D., D. E. Mainwaring and R. J. Sadus, "Prediction of One-Component Vapor-Liquid Equilibria from the Triple Point to the Critical Point Using a Simplified Perturbed-Hard-Chain Theory Equation of State," Fluid Phase Equilibria, 109, 171, 1995.

9. Kim, C. H., P. Vimalchand, M. D. Donohue and S. I. Sandler, "Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed Hard Chain Theory," AIChE Journal, 32, 1726, 1986.

10. Prausnitz, J. M. and M. D. Donohue, "Thermodynamic Properties of Fluid Mixtures from Perturbed-Hard-Chain Theory," Gas Processors Association, Proceedings of Fifty-Fifth Annual Convention, 10, 1976.

11. Donohue, M. D., B. K. Kaul and J. M. Prausnitz, "Perturbed-Hard-Chain Theory for Correlation of Thermodynamic Properties," Gas Processors Association, Proceedings of Fifty-Sixth Annual Convention, 36, 1977.

12. Donohue, M. D. and P. Vimalchand, "Recent Improvements in the Perturbed-Hard-Chain Equation," Gas Processors Association, Proceedings of Sixty-Sixth Annual Convention, 165, 1987.

13. Chien, C. H., R. A. Greenkorn and K. C. Chao, "Chain-of-Rotators Equation of State," AIChE Journal, 29, 560, 1983.

14. Donohue, M. D. and P. Vimalchand, "The Perturbed-Hard-Chain Theory. Extensions and Applications," Fluid Phase Equilibria, 40, 185, 1988.

15. Walsh, J. M., G. Jin and M. D. Donohue, "Thermodynamics of Short Chain Polar Compounds," Fluid Phase Equilibria, 65, 209, 1991.

16. Vimalchand, P., Thermodynamics of Multi-Polar Molecules: The Perturbed-Anisotropic-Chain Theory, Ph.D. Dissertation, The Johns Hopkins University, 1986.

17. Vimalchand, P. and M. D. Donohue, "Comparison of Equations of State for Chain Molecules," J. Physical Chemistry, 93, 4355, 1989.

18. Carnahan, N. F. and K. E. Starling, "Equation of State for Nonattracting Rigid Spheres," J. Chemical Physics, 51, 635, 1969.

19. Alder, B. J., D. A. Young and M. A. Mark, "Studies in Molecular Dynamics. I. Corrections to the Augmented van der Waals Theory for Square-Well Fluids," J. Chemical Physics, 56, 3013, 1972.

20. Martin, J. J., "Cubic Equations of State - Which?," Ind. Eng. Chem. Fundam., 18, 81, 1979.

21. Sandler, S. I., "From Molecular Theory to Thermodynamic Models," Chemical Engineering Education, 12, 1990.

22. Lee, L. L., Molecular Thermodynamics of Nonideal Fluids, Butterworth Publishers, Boston, 1988.

23. Lee, K. H., M. Lombardo and S. I. Sandler, "The Generalized van der Waals Partition Function. II. Application to the Square-Well Fluid," Fluid Phase Equilibria, 21, 177, 1985.

24. Gasem, K. A. M. and R. L. Robinson, Jr., "Evaluation of the Simplified Perturbed Hard Chain Theory (SPHCT) for Prediction of Phase Behavior of n-Paraffins and Mixtures of n-Paraffins with Ethane," Fluid Phase Equilibria, 58, 13, 1990.

25. Shaver, R. D., R. L. Robinson, Jr. and K. A. M. Gasem, "Modified SPHCT EOS for Improved Predictions of Equilibrium and Volumetric Properties of Pure Fluids," Fluid Phase Equilibria, 112, 223, 1995.

26. Park, J. K., Ph.D. Dissertation, Binary Vapor-Liquid Equilibrium Measurements for Selected Asymmetric Mixtures and Equation of State Development, Oklahoma State University, Stillwater, Oklahoma, 1994.

27. Elliott, Jr., J. R., S. J. Sresh and M. D. Donohue, "A Simple Equation of State for Nonspherical and Associating Molecules," Ind. Eng. Chem. Res., 29, 1476, 1990.

28. Wilson, G. M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing," J. ACS, 86, 127, 1964.

29. Renon, H. and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," AIChE Journal, 14, 135, 1968.

30. Fredenslund, A., J. Gmehling and P. Rasmussen, Vapor-Liquid Equilibria Using UNIFAC: A Group Contribution Method, Elsevier Scientific Publishing Company, Amsterdam, 1977.

31. Anderko, A., "Equation-of-State Methods for the Modeling of Phase Equilibria," Fluid Phase Equilibria, 61, 145, 1990.

32. Walas, S. M., Phase Equilibrium in Chemical Engineering, Butterworth Publishers, Stoneham, Massachusetts, 1985.

33. Redlich, O. and J. N. S. Kwong, "On Thermodynamics of Solutions V: An Equation of State. Fugacities of Gaseous Solutions," Chemical Reviews, 44, 233, 1949.

34. Horvath, A. L., "Redlich Kwong Equation of State: Review for Chemical Engineering Calculations," Chemical Engineering Science, 29, 1334, 1974.

35. Whichterle, I., "High Pressure Vapor-Liquid Equilibrium. IV. Quantitative Description. Part 2," Fluid Phase Equilibria, 2, 59, 1978.

36. Abbott, M. M., "Cubic Equations of State: An Interpretative Review," Advances in Chemical Series, ACS, 182, 47, 1979.

37. Fuller, G. G., "A Modified Redlich-Kwong-Soave Equation of State Capable of Representing the Liquid State," Ind. Eng. Chem. Fundam., 15, 254, 1976.

38. Heyen, G., "Liquid and Vapor Properties from a Cubic Equation of State," Second. Int. Conf. Phase Eq. Fluid Prop. Chem. Ind., West Berlin, 1980.

39. Schmidt, G. and H. Wenzel, "A Modified van der Waals Equation of State," Chemical Engineering Science, 35, 1503,1980.

40. Harmens, A. and H. Knapp, "Three Parameter Cubic Equation of State for Normal Substances," Ind. Eng. Chem. Fundam., 19, 291, 1980.

41. Lin, H. M., H. Kim, T. M. Guo and K. C. Chao, "Cubic Chain-of-Rotators Equation of State and VLE Calculations," Fluid Phase Equilibria, 13, 143, 1983.

42. Kim, H, H.- M. Lin and K.- C. Chao, "Cubic Chain-of-Rotators Equation of State," Ind. Eng. Chem. Fundam., 25, 75, 1986.

43. Boublik, T. and I. Nezbeda, "Equation of State for Hard Dumbbells," Chemical Physics Letters, 46, 315, 1977.

44. van Pelt, A., C. J. Peters and J. de Swaan Arons, "Application of the Simplified-Perturbed-Hard-Chain Theory for Pure Components Near the Critical Point," Fluid Phase Equilibria, 74, 67, 1992.

45. van Pelt, A., C. J. Peters and J. de Swaan Arons, "Calculation of Critical Lines in Binary Mixtures with the Simplified Perturbed Hard Chain Theory," Fluid Phase Equilibria, 84, 23, 1993.

46. Ponce-Ramirez, L., C. Lira-Galeana and C. Tapia-Medina, "Application of the SPHCT Model to the Prediction of Phase Equilibria in CO_2-hydrocarbon Systems," Fluid Phase Equilibria, 70, 1, 1991.

47. Garcia-Sanchez, F., J. L. Ruiz-Cortina, C. Lira-Galeana and L. Ponce-Ramirez, "Critical Point Calculations for Oil Reservoir Fluid Systems Using the SPHCT Equation of State," Fluid Phase Equilibria, 81, 39, 1992.

48. Wang, L. S. and T. M. Guo, "A Cubic Simplified Perturbed Hard-Chain Equation of State for Fluids with Chainlike Molecules," Canadian J. of Chemical Engineering, 71, 591, 1993.

49. Reed, T. M. and K. E. Gubbins, Applied Statistical Mechanics, McGraw-Hill, New York, 1973.

50. Vera, J. H. and J. M. Prausnitz, "Generalized van der Waals Theory for Dense Fluids," Chem. Eng. J., 3, 1, 1972.

51. Hill, T. L., An Introduction to Statistical Thermodynamics, Addition-Wesley Publishing Company, Inc., Reading, Mass., 1960.

52. Erpenbeck, J. J. and W. W. Wood, "Molecular Dynamics Calculations of the Hard-Sphere Equation of State," J. Statistical Physics, 35 (3/4), 320, 1984.

53. Dickman, R. and C. K. Hall, "High Density Monte Carlo Simulations of Chain Molecules: Bulk Equation of State and Density Profile Near Walls," J. Chemical Physics, 89, 3168, 1988.

54. Ree, F. H. and W. G. Hoover, "Fifth and Sixth Coefficients for Hard Spheres and Hard Disks," J. Chemical Physics, 40, 939, 1964.

55. De Santis, R., F. Gironi and L. Marrelli, "Vapor-Liquid Equilibrium from a Hard-Sphere Equation of State," Ind. Eng. Chem. Fundam., 15, 183, 1976.

56. Nakamura, R., G. J. F. Breedveld and J. M. Prausnitz, "Thermodynamic Properties of Gas Mixtures Containing Common Polar and Nonpolar Components," Ind. Eng. Chem. Proc. Des. Dev., 15, 557, 1976.

57. Nagata, I. and S. Yasuda, "On the Carnahan-Starling Equation of State," J. Chem. Eng. of Japan, 10 (1), 64, 1977.

58. Bokis, C. P., M. D. Donohue and C. K. Hall, "A Local Composition Model for Square-Well Chains Using the Generalized Flory Dimer Theory," J. Physical Chemistry, 96, 11004, 1992.

59. Vimalchand, P., A. Thomas, I. G. Economou and M. D. Donohue, "Effect of Hard-Sphere Structure on Pure-Component Equation of State Calculations," Fluid Phase Equilibria, 73, 39, 1992.

60. Ciocca, G. and I. Nagata, "Density Dependence of the External Degrees of Freedom: Application to a Simplified Version of the Perturbed Hard Chain Theory," Fluid Phase Equilibria, 41, 59, 1988.

61. Gasem, K. A. M., Ph.D. Dissertation, Binary Vapor-Liquid Phase Equilibrium for Carbon Dioxide + Heavy Normal Paraffins, Oklahoma State University, Stillwater, Oklahoma, 1986.

62. Angus, S., B. Armstrong and K. M. de Reuck, International Thermodynamic Tables of the Fluid State - 5. Methane, International Union of Pure and Applied Chemistry, Pergamon Press, New York, 1976.

63. Goodwin, R. D., H. M. Roder and G. C. Straty, Thermophysical Properties of Ethane from 90 to 600 K at Pressures to 700 Bars, NBS, Boulder, Colorado, 1976.

64. Goodwin, R. D. and W. M. Haynes, Thermophysical Properties of Propane from 85 to 700 K at Pressures to 70 MPa, NBS Monogram 170, Boulder, Colorado, 1981.

65. Haynes, W. M. and R. D. Goodwin, Thermophysical Properties of Normal Butane from 135 to 700 K at Pressures to 70 MPa, NBS Monogram 169, Boulder, Colorado, 1982.

66. Vargaftik, N. B., Tables on the Thermophysical Properties of Liquids and Gases, John Wiley and sons, New York, 1975.

67. API Research Project 44, Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamic Research Center, Texas A&M College, College Station, Texas, 1972.

68. Younglove, B. A., "Thermophysical Properties of Fluids. I. Argon, Ethylene, Parahydrogen, Nitrogen, Nitrogen Trifluoride, and Oxygen," J. Physical and Chemical Reference Data, Vol. 11, Supplement No. 1, 1982.

69. Angus, S., B. Armstrong and K. M. de Reuck, International Thermodynamic Tables of the Fluid State - 7. Propylene (Propene), International Union of Pure and Applied Chemistry, Pergamon Press, New York, 1980.

70. Goodwin, R. D., "Benzene Thermophysical Properties from 279 to 900 K at Pressures to 1000 Bar," J. Physical and Chemical Reference Data, 17, 1541, 1988.

71. Perry, R. H., D. W. Green and J. O. Maloney, eds., Perry's Chemical Engineers Handbook, Sixth Edition, McGraw-Hill, New York, 1984.

72. Ely, J. F., J. W. Magee and W. M. Haynes, Thermophysical Properties for Special High CO_2 Content Mixtures, Gas Processors Association, RR-110, 1987.

73. Haar, L., J. S. Gallager and G. S. Kell, NBS/NRC Steam Tables, McGraw-Hill, New York, 1984.

74. Leland, Jr., T. W., P. S. Chappelear and B. W. Gamson, "Prediction of Vapor-Liquid Equilibria from the Corresponding States Principle," AIChE Journal, 8, 482, 1962.

75. Georgeton, G. K., R. L. Smith Jr. and A. S. Teja, "Application of Cubic Equation of State to Polar Fluid and Fluid Mixtures," ACS Symp. Ser., 300, 434, 1986.

76. Lee, T. J., L. L. Lee and K. E. Starling, "Three Parameter, Corresponding States Conformal Solution Mixing Rules for Mixtures of Heavy and Light Hydrocarbons," ACS Symp. Ser., 182, 125, 1979.

77. Johnson, J. K. and R. L. Rowley, "Prediction of Vapor-Liquid Equilibria in Binary Mixtures Containing Polar Components from the Extended Lee-Kesler Corresponding States Technique," Fluid Phase Equilibria, 44, 255, 1989.

78. Wong, D. S. H., S. I. Sandler and A. S. Teja, "Vapor-Liquid Equilibrium Calculations by Use of Generalized Corresponding States Principle. 1. New Mixing Rules. 2. Comparison with Other Methods," Ind. Eng. Chem. Fundam., 23, 38, 1984.

79. Huron, M. J. and J. Vidal, "New Mixing Rules in Simple Equations of State for Representing Vapor-Liquid Equilibria of Strongly Non-Ideal Mixtures," Fluid Phase Equilibria, 3, 255, 1979.

80. Vidal, J., "Mixing Rules and Excess Properties in Cubic Equations of State," Chemical Engineering Science, 33, 787, 1978.

81. Wong, D. S. H. and S. I. Sandler, "A Theoretically Correct Mixing Rule for Cubic Equations of State," AIChE Journal, 38, 671, 1992.

82. Mansoori, G. A. and T. W. Lerand, "Statistical Thermodynamics of Mixtures," J. Chem. Soc., Faraday Trans. 2, 68, 320, 1972.

83. Voros, N. G. and D. P. Tassios, "Vapor-Liquid Equilibria in Nonpolar/Weakly Polar Systems with Different Types of Mixing Rules," Fluid Phase Equilibria, 91, 1, 1993.

84. Marrucho, I. M., A. M. F. Palavra and J. F. Ely, "An Improved Extended-Corresponding-State Theory for Natural Gas Mixtures," International J. of Thermophysics, 15(6), 1261, 1994

85. Clarke, W. P., R. T. Jacobsen, E. W. Lemmon, S. G. Penoncello and S. W. Beyerlein, "An Extended Corresponding-States Model for Predicting Thermodynamic Properties of N_2-Ar-O_2 Mixtures Including Vapor-Liquid Equilibrium," International J. of Thermophysics, 15(6), 1289, 1994.

86. Li, M. H. and F. N. Huang, "Application of Generalized van der Waals Theory and Approximations of Radial Distribution Functions to the Development of Mixing Rules," Fluid Phase Equilibria, 96, 155, 1994.

87. Alvarado, J. J. F. and P. T. Eubank, "Re-examination of Collinearity Tests for Density-Dependent Mixing Rules," Fluid Phase Equilibria, 122, 255, 1996.

88. Orbey, H. and S. I. Sandler, "On the Combination of Equation of State and Excess Free Energy," Fluid Phase Equilibria, 111, 53, 1995.

89. Kalospiros, N. S. and D. Tassios, "Prediction of Vapor-Liquid Equilibria in Polymer Solutions Using an Equation of State/Excess Gibbs Free Energy Model," Ind. Eng. Chem. Res., 34, 2117, 1995.

90. Kalospiros, N. S., N. Tzouvaras, P. Coutsikos and D. P. Tassios, "Analysis of Zero-Reference-Pressure EoS/G^E Models," AIChE Journal, 41, 928, 1995.

91. Brandani, S. and V. Brandani, "On the Inapplicability of Mixing Rules Based on the Infinite Pressure Reference State for Equations of State Which Use the Hard-Sphere Repulsive Term," Fluid Phase Equilibria, 121, 179, 1996.

92. Fischer, K. and J. Gmehling, "Further Development, Status and Results of the PSRK Method for the Prediction of Vapor-Liquid Equilibria and Gas Solubilities," Fluid Phase Equilibria, 121, 185, 1996.

93. Peng, C. L., F. P. Stein and A. S. Gow, "An Enthalpy-Based Cubic Equation of State Mixing Rule for Cross-Prediction of Excess Thermodynamic Properties of Hydrocarbon and Halogenated Refrigerant Mixtures," Fluid Phase Equilibria, 108, 79, 1995.

94. Orbey, H. and S. I. Sandler, "A Comparison of Various Cubic Equation of State Mixing Rules for the Simultaneous Description of Excess Enthalpies and Vapor-Liquid Equilibria," Fluid Phase Equilibria, 121, 67, 1996.

95. Filho, C. V. and G. M. N. Costa, "Influence of the Mixing Rule on the Liquid-Liquid Equilibrium Calculation," Fluid Phase Equilibria, 116, 503, 1996.

96. Huang, H., S. I. Sandler and H. Orbey, "Vapor-Liquid Equilibria of Some Hydrogen + Hydrocarbon Systems with the Wong-Sandler Mixing Rule," Fluid Phase Equilibria, 96, 143, 1994.

97. Voutsas, E. C., C. J. Boukouvalas, N. S. Kalospiros and D. P. Tassios, "The Performance of EoS/G^E Models in the Prediction of Vapor-Liquid Equilibria in Asymmetric Systems," Fluid Phase Equilibria, 116, 480, 1996.

98. Abdel-Ghani, R. M. and R. A. Heidemann, "Comparison of ΔG Excess Mixing Rules for Multi-Phase Equilibria in Some Ternary Systems," Fluid Phase Equilibria, 116, 495, 1996.

99. Mehra, V. S. and G. Thodos, "Vapor-Liquid Equilibrium in the Ethane-n-Butane System," J. Chemical and Engineering Data, 10, 307, 1965.

100. Rodrigues, R. B. J., D. S. McCaffrey, Jr. and J. P. Kohn, "Heterogeneous Phase and Volumetric Equilibrium in the Ethane-n-Octane System," J. Chemical and Engineering Data, 13, 164, 1968.

101. Bufkin, B. A., R. L. Robinson, Jr., S. S. Estera and K. D. Luks, "Solubility of Ethane in n-Decane at Pressures to 8.2 MPa and Temperatures from 278 to 411 K," J. Chemical and Engineering Data, 31, 421, 1986.

102. Raff, A. M., Experimental Determination of the Solubilities of Ethane in Selected n-Paraffin Solvents, M. S. Thesis, Oklahoma State University, Stillwater, Oklahoma, 1989.

103. Robinson, R. L., Jr., J. M. Anderson, M. W. Barrick, B. A. Bufkin and C. H. Ross, "Phase Behavior of Coal Fluids: Data for Correlation Development," DE-FG22-86PC90523, Final Report, United States Department of Energy, January, 1987.

104. Olds, R. H., H. H. Reamer, B. H. Sage and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems. The n-Butane-Carbon Dioxide System," Ind. Eng. Chem., 41, 475, 1949.

105. Reamer, H. H. and B. H. Sage, "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of the n-Decane-CO_2 System", J. Chemical and Engineering Data, 8, 508, 1963.

106. Gasem, K. A. M. and R. L. Robinson, Jr., "Solubilities of Carbon Dioxide in Heavy Normal Paraffins (C_{20}-C_{44}) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K," J. Chemical and Engineering Data, 30, 53, 1985.

107. Klink, A. E., H. Y. Cheh and E. H. Amick, Jr., "The Vapor-Liquid Equilibrium of the Hydrogen - n-Butane System at Elevated Pressures," AIChE Journal, 21, 1142, 1975.

108. Huang, S. H., H. M. Lin, F. N. Tsai and K. C. Chao, "Solubility of Synthesis Gases in Heavy n-Paraffins and Fischer-Tropsch Wax," Ind. Eng. Chem. Res., 27, 162, 1988.

109. Peters, C. J., J. D. Arons, L. Sengers and J. S. Gallagher, "Global Phase Behavior of Short and Long n-Alkanes," AIChE Journal, 34, 834, 1988.

110. Peters, C. J., J. L. de Roo and J. D. Arons, "Measurements and Calculations of Phase-Equilibrium in Binary Mixtures of Propane + Tetratriacontane," Fluid Phase Equilibria, 72, 251, 1992.

111. Georgeton, G. K. and A. S. Teja, "A Group Contribution Equation-of-State Based on the Simplified-Perturbed-Hard-Chain Theory," Ind. Eng. Chem. Res., 27, 657, 1988.

112. American Petroleum Institute, Technical Data Book -- Petroleum Refining, Second Edition, Washington D. C., 1971.

113. Thinh, T. P., J. L. Duran, R. S. Ramalho and S. Kaliaguine, "Equations Improve C_p^* Predictions," Hydrocarbon Processing, 50 (1), 98, 1971.

114. Passut, C. A. and R. P. Danner, "Correlation of Ideal Gas Enthalpy, Heat Capacity, and Entropy," Ind. Eng. Chem. Proc. Des. Dev., 11, 543, 1972.

115. Aly, F. A. and L. L. Lee, "Self-Consistent Equations for Calculating the Ideal Gas Heat Capacity, Enthalpy and Entropy," Fluid Phase Equilibria, 6, 169, 1981.

116. Reid, R. C., J. M. Prausnitz and T. K. Sherwood, The Properties of Gases and Liquids, Second Edition, McGraw Hill Book Company, New York, 1977.

117. Goodwin, R. D., Thermophysical Properties of Methane from 90 to 500K at Pressures to 700 bar, NBS Technical Note 653, NBS, Boulder, Colorado, 1974.

118. Vukalovich, M. P. and V. V. Altunin, Thermophysical Properties of Carbon Dioxide, Collet's Publishers Ltd., London, 1968.

APPENDIX A

EXPANDED FORM OF THE EQUATION OF STATE

To obtain solutions of the equation of state, the fifth order expanded form of t equation was obtained by rearranging the equation of state given in Chapter 2 in the following manner.

$$Z^5 + AZ^4 + BZ^3 + CZ^2 + DZ + E = 0 \qquad \text{(A-1)}$$

where

$$A = \delta(u - \beta_2\tau + Q_2) - 1$$

$$B = \delta^2(w - \beta_2\tau u + Q_2 u - \beta_2\tau Q_2) + \delta(\beta_2\tau - u - 1 - c\beta_1\tau + cZ_M Y - cZ_M YQ_1)$$

$$C = \delta^3[Q_2 w - \beta_2\tau(w + uQ_2)]$$

$$+ \delta^2[\beta_2\tau(u + Q_2) - w - uQ_2 - c\beta_1\tau(u - Q_2) + cZ_M Y(Q_2 - \beta_2\tau + Q_1 u - Q_1\beta_2)]$$

$$D = \delta^3[\beta_2\tau(w - uQ_2) + Q_2 w - c\beta_1\tau w - c\beta_1\tau Q_2 u + (Q_1 w - Q_2\beta_2\tau - Q_1\beta_2\tau u)cZ_M Y]$$

$$- \delta^4(\beta_2\tau w Q_2)$$

$$E = \delta^4(\beta_2\tau w Q_2 - cw\beta_1\tau Q_2 - cZ_M YQ_1\beta_2\tau)$$

and

$$\delta = \frac{pv^*}{RT}$$

When these equations were applied for mixtures, proper mixing rules described in Chapter 4 were used.

APPENDIX B

FUGACITY COEFFICIENT FOR PURE FLUIDS

The fugacity coefficient, ϕ, of a pure component were derived from the expression given below.

$$\ln\phi = Z - 1 - \ln Z - \frac{1}{RT}\int_{\infty}^{v}\left(p - \frac{RT}{v}\right)dv - \cancel{\ln Z} \tag{B-1}$$

The equation of state considered in this work is given as follows.

$$\frac{pv}{RT} = Z^{rep} + Z^{att1} + Z^{att2} \tag{B-2}$$

$$Z^{rep} = 1 + c\frac{\beta_1\tau}{v_r - \beta_2\tau}, \tag{B-3}$$

$$Z^{att1} = -c\frac{Z_M Y v_r}{v_r^2 + uv_r + w} \tag{B-4}$$

$$Z^{att2} = -c\frac{Q_1 Z_M Y}{v_r + Q_2} \tag{B-5}$$

where

$$Y = \exp(F_t) - 1$$

$$F_t = \omega_1\left(\frac{1}{2\tilde{T}}\right)^{1/2} + \omega_2\left(\frac{1}{2\tilde{T}}\right) + \omega_3\left(\frac{1}{2\tilde{T}}\right)^{3/2} + \omega_4\left(\frac{1}{2\tilde{T}}\right)^2$$

$$\tilde{T} = \frac{T}{T^*}$$

and

$$v_r = \frac{v}{v^*}$$

From these equations, the following expression was obtained for integrand:

$$p-\frac{RT}{v}=RT\left(\frac{c\beta_1\tau v^*}{v(v-\beta_2\tau v^*)}-\frac{cZ_MYv^*}{v^2+uv^*v+wv^{*2}}-\frac{Q_1}{Q_2}\frac{cZ_MYv^*}{v(v+v^*)}\right) \tag{B-6}$$

Substituting Equation (B-6) into Equation (B-1) and integrating, the following pure fluid fugacity coefficient expression was derived:

$$\begin{aligned}\ln\phi = {} & -c\frac{\beta_1}{\beta_2}\ln\frac{v_r-\beta_2\tau}{v_r}+cZ_MY\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right)\\ & -cZ_MY\frac{Q_1}{Q_2}\ln\frac{v_r+Q_2}{v_r}+\frac{c\beta_1\tau}{v_r-\beta_2\tau}-\frac{cZ_MYv_r}{v_r^2+uv_r+w}-\frac{Q_1}{Q_2}\frac{cZ_MY}{v_r+Q_2}\end{aligned} \tag{B-7}$$

Values for the EOS constants and substance-specific parameters are described in Chapters 2 and 3.

APPENDIX C

FUGACITY COEFFICIENT EXPRESSION FOR COMPONENTS IN A MIXTURE

The fugacity coefficient, ϕ_i, of a certain component *i* in the mixture were derived from the expression given below.

$$\ln\hat{\phi}_i = -\int_{\infty}^{V}\left[\frac{1}{RT}\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{1}{V}\right]dV - \ln Z \tag{C-1}$$

where V is total volume of a system. As shown in Chapter 4, linear mixing rules for c and v*, and quadratic mixing rules for T* and Y were applied:

$$\langle c\rangle = \frac{1}{n}\sum_{i=1}^{N} n_i c_i$$

$$\langle v^*\rangle = \frac{1}{n^2}\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j v_{ij}^*$$

$$\langle Y\rangle = \frac{1}{n^2}\sum_{i=1}^{N}\sum_{j=1}^{N} n_i n_j\left(\exp(\langle F_t\rangle) - 1\right)$$

where

$$F_t = \sum_{k=1}^{4}\left[\omega_k\left(\frac{\langle T^*\rangle}{2T}\right)^{\frac{k}{2}}\right]$$

$$\langle T^*\rangle = \frac{1}{n^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\varepsilon_{ij}q_i}{c_i kT}$$

and

$$v_{ij}^* = \frac{1}{2}\left(v_i^* + v_j^*\right) \text{ and } \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\left(1 - C_{ij}\right)$$

where N, n, n_i and n_j are the total number of compounds, the total number of moles and number of moles of ith and jth components, respectively. To perform the integration of

Equation (C-1), it was necessary to calculate $\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}}$. All the following partial derivatives have T, V and $n_{j\neq i}$ as constants for convenience unless otherwise mentioned.

$$\begin{aligned}
\frac{1}{RT}\left(\frac{\partial p}{\partial n_i}\right)-\frac{1}{V}=&\frac{\beta_1\tau\frac{\partial n\langle cv^*\rangle}{\partial n_i}}{V\left(V-\beta_2\tau n\langle v^*\rangle\right)}-\frac{Z_M\frac{\partial\langle cYv^*\rangle}{\partial n_i}}{V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2}\\
&-\frac{Q_1Z_M\frac{\partial n\langle cYv^*\rangle}{\partial n_i}}{V\left(V+Q_2n\langle v^*\rangle\right)}+\frac{\beta_1\tau n^2\langle cv^*\rangle\beta_2\tau\frac{\partial n\langle v^*\rangle}{\partial n_i}}{V\left(V-\beta_2\tau n\langle v^*\rangle\right)^2}\\
&+\frac{uZ_Mn^2\langle cYv^*\rangle\frac{\partial n\langle v^*\rangle}{\partial n_i}V}{\left(V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2\right)^2}+\frac{2wZ_Mn^3\langle cYv^*\rangle\langle v^*\rangle\frac{\partial n\langle v^*\rangle}{\partial n_i}}{\left(V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2\right)^2}\\
&+\frac{Q_1Z_Mn^2\langle cYv^*\rangle\frac{\partial n\langle v^*\rangle}{\partial n_i}}{V\left(V+Q_2n\langle v^*\rangle\right)^2}
\end{aligned}\tag{C-2}$$

Substituting Equation (C-2) into Equation (C-1) followed by integration of Equation (C-1) yields the final form of the fugacity coefficient of component i in a mixture.

$$\begin{aligned}
\ln\hat{\phi}_i = {} & \frac{\beta_1}{\beta_2}\left(\frac{1}{\langle v^*\rangle}\frac{1}{n}\frac{\partial n^2\langle cv^*\rangle}{\partial n_i}-\frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\ln\frac{v_r-\beta_2\tau}{v_r} \\
& +\left(\beta_1\tau\frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{1}{v_r-\beta_2\tau} \\
& -\left(\frac{Z_M\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{v_r}{v_r^2+uv_r+w} \\
& +\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right) \\
& -\left(\frac{Z_M\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right) \\
& -\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_i}-\frac{Z_M\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{Q_2}\ln\frac{v_r+Q_2}{v_r} \\
& -\left(\frac{Z_M\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{v_r+Q_2} \\
& -\ln Z
\end{aligned} \qquad \text{(C-3)}$$

where

$$\frac{\partial n\langle cYv^*\rangle}{\partial n_i}=\sum_{j=1}^{N}z_j\left(c_iY_{ij}v_{ji}^*+c_jY_{ji}v_{ij}^*\right)-\langle cYv^*\rangle \qquad \text{(C-4)}$$

$$\frac{\partial n\langle v^*\rangle}{\partial n_i}=\sum_{j=1}^{N}z_j\left(v_{ij}^*+v_{ji}^*\right)-\langle v^*\rangle \qquad \text{(C-5)}$$

and

$$Y_{ij} = \exp\left[\omega_1\left(\frac{T_{ij}^*}{2T}\right)^{1/2} + \omega_2\left(\frac{T_{ij}^*}{2T}\right) + \omega_3\left(\frac{T_{ij}^*}{2T}\right)^{3/2} + \omega_4\left(\frac{T_{ij}^*}{2T}\right)^{2}\right] - 1 \qquad \text{(C-6)}$$

APPENDIX D

MIXTURE EQUATION OF STATE EVALUATIONS

TABLE D.I

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	6.93	-5.84	5.84	24.2	18
2	4	344.3	.0000	.0000	4.72	-3.22	3.22	12.4	17
3	4	377.6	.0000	.0000	2.44	-1.54	1.54	5.2	12
4	4	410.9	.0000	.0000	0.64	-0.35	0.35	1.0	5
5	10	310.9	.0000	.0000	14.61	-13.21	13.21	37.0	11
6	10	344.3	.0000	.0000	16.06	-13.05	13.05	26.9	8
7	10	377.6	.0000	.0000	16.06	-12.95	12.95	21.7	10
8	10	410.9	.0000	.0000	14.96	-12.26	12.26	18.6	10
9	10	444.3	.0000	.0000	17.91	-15.90	15.90	19.3	11
10	10	477.6	.0000	.0000	29.98	-23.13	23.13	23.1	11
11	10	510.9	.0000	.0000	15.86	-13.75	13.75	18.3	9
12	20	323.1	.0000	.0000	11.36	-9.91	9.91	34.7	13
13	20	373.1	.0000	.0000	11.52	-10.17	10.17	23.7	9
14	28	348.1	.0000	.0000	18.25	-13.90	13.90	26.4	8
15	28	373.1	.0000	.0000	13.09	-9.49	9.49	20.0	9
16	28	423.1	.0000	.0000	10.46	-7.31	7.31	13.2	6
17	36	373.1	.0000	.0000	6.73	-5.09	5.09	15.1	10
18	36	423.1	.0000	.0000	9.85	-7.11	7.11	13.6	8
19	44	373.1	.0000	.0000	7.43	-5.09	5.09	13.9	7
20	44	423.1	.0000	.0000	7.99	-5.60	5.60	12.9	7

MODEL OVERALL STATISTICS

RMSE = 13.45 BAR
AAD = 9.44 BAR
MIN DEV = -62.84 BAR
MAX DEV = 0.00 BAR
BIAS = -9.44 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 19.9
MIN %DEV = -46.2
MAX %DEV = .0

TABLE D.II

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.1363	.0000	0.73	-0.30	0.49	1.2	52
2	10	310.9	.1149	.0000	3.26	0.19	2.11	2.9	70
3	20	323.1	.0984	.0000	1.40	0.08	1.16	3.4	22
4	28	348.1	.0833	.0000	4.01	-1.51	2.47	5.9	23
5	36	373.1	.0702	.0000	3.16	-1.19	1.85	4.9	18
6	44	373.1	.0750	.0000	3.29	-1.36	2.03	6.1	14

MODEL OVERALL STATISTICS

RMSE = 2.76 BAR
AAD = 1.59 BAR
MIN DEV = -12.75 BAR
MAX DEV = 11.87 BAR
BIAS = -0.38 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 3.3
MIN %DEV = -13.3
MAX %DEV = 11.6

* minimum temperature, see Table D.I for the full temperature range

TABLE D.III

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.1346	.0000	0.51	0.05	0.36	1.1	18
2	4	344.3	.1388	.0000	0.36	-0.05	0.23	0.6	17
3	4	377.6	.1530	.0000	0.21	-0.04	0.17	0.4	12
4	4	410.9	.1297	.0000	0.80	-0.61	0.61	1.4	5
5	10	310.9	.1205	.0000	2.29	0.88	1.74	4.5	11
6	10	344.3	.1099	.0000	3.72	0.92	2.73	4.1	8
7	10	377.6	.1087	.0000	2.43	0.57	1.73	1.8	10
8	10	410.9	.1081	.0000	1.44	0.11	1.14	1.3	10
9	10	444.3	.1128	.0000	1.06	-0.07	0.80	0.9	11
10	10	477.6	.1240	.0000	1.23	0.03	0.80	0.8	11
11	10	510.9	.1532	.0000	0.97	0.08	0.64	0.9	9
12	20	323.1	.1045	.0000	0.53	-0.16	0.31	1.0	13
13	20	373.1	.0852	.0000	0.97	-0.36	0.71	1.8	9
14	28	348.1	.0926	.0000	3.80	-1.62	2.63	6.0	8
15	28	373.1	.0793	.0000	3.72	-1.51	2.21	5.2	9
16	28	423.1	.0652	.0000	3.76	-1.73	2.46	5.5	6
17	36	373.1	.0678	.0000	2.06	-0.88	1.28	4.2	10
18	36	423.1	.0750	.0000	3.85	-1.47	2.38	5.4	8
19	44	373.1	.0706	.0000	3.12	-1.30	1.95	6.5	7
20	44	423.1	.0822	.0000	3.27	-1.27	2.01	5.5	7

MODEL OVERALL STATISTICS

RMSE	=	2.17	BAR	NO PT	=	199
AAD	=	1.18	BAR	%AAD	=	2.5
MIN DEV	=	-10.01	BAR	MIN %DEV	=	-12.5
MAX DEV	=	8.53	BAR	MAX %DEV	=	11.1
BIAS	=	-0.30	BAR			
RESTRICTIONS	:	NONE				

TABLE D.IV

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	8.07	-7.17	7.17	26.7	18
2	4	344.3	.0000	.0000	6.27	-4.60	4.60	15.7	17
3	4	377.6	.0000	.0000	4.24	-3.16	3.16	9.9	12
4	4	410.9	.0000	.0000	1.53	-0.89	0.89	2.7	5
5	10	310.9	.0000	.0000	16.08	-14.94	14.94	40.2	11
6	10	344.3	.0000	.0000	19.91	-17.09	17.09	31.1	8
7	10	377.6	.0000	.0000	19.91	-16.61	16.61	24.7	10
8	10	410.9	.0000	.0000	16.17	-13.86	13.86	19.9	10
9	10	444.3	.0000	.0000	7.63	-15.89	15.89	19.9	11
10	10	477.6	.0000	.0000	20.34	-17.89	17.89	20.5	11
11	10	510.9	.0000	.0000	22.72	-18.54	18.54	23.6	9
12	20	323.1	.0000	.0000	14.42	-12.95	12.95	46.9	13
13	20	373.1	.0000	.0000	14.04	-12.76	12.76	31.2	9
14	28	348.1	.0000	.0000	22.62	-18.74	18.74	41.6	8
15	28	373.1	.0000	.0000	16.47	-13.36	13.36	34.1	9
16	28	423.1	.0000	.0000	12.10	-9.66	9.66	23.2	6
17	36	373.1	.0000	.0000	11.60	-9.94	9.94	35.8	10
18	36	423.1	.0000	.0000	11.95	-10.11	10.11	24.4	8
19	44	373.1	.0000	.0000	12.32	-10.10	10.10	37.6	7
20	44	423.1	.0000	.0000	9.89	-8.30	8.30	25.0	7

MODEL OVERALL STATISTICS

RMSE = 14.77 BAR
AAD = 11.63 BAR
MIN DEV = -44.28 BAR
MAX DEV = 0.00 BAR
BIAS = -11.63 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 26.8
MIN %DEV = -48.6
MAX %DEV = 0.0

TABLE D.V

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	344.3	.0937	.0000	2.02	-1.19	1.46	3.6	52
2	10	410.9	.0667	.0000	2.89	-0.78	2.16	3.7	70
3	20	323.1	.0626	.0000	3.52	0.76	2.83	8.3	22
4	28	348.1	.0553	.0000	3.41	0.40	2.25	5.1	23
5	36	373.1	.0531	.0000	2.17	0.55	1.68	5.1	18
6	44	373.1	.0551	.0000	2.11	0.37	1.70	5.7	14

MODEL OVERALL STATISTICS

RMSE	=	2.73	BAR	NO PT	=	199
AAD	=	1.99	BAR	%AAD	=	4.6
MIN DEV	=	-10.42	BAR	MIN %DEV	=	-10.2
MAX DEV	=	11.07	BAR	MAX %DEV	=	12.0
BIAS	=	-0.38	BAR			
RESTRICTIONS	:	NONE				

TABLE D.VI

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0885	.0000	1.35	-0.72	0.86	2.1	18
2	4	344.3	.0970	.0000	1.90	-0.79	1.19	2.4	17
3	4	377.6	.1138	.0000	0.56	-0.18	0.49	1.4	12
4	4	410.9	.1634	.0000	2.18	-0.81	1.94	5.1	5
5	10	377.6	.0619	.0000	4.77	-2.21	3.00	3.4	10
6	10	410.9	.0596	.0000	4.63	-2.31	3.20	3.4	10
7	10	444.3	.0614	.0000	2.82	-1.36	2.11	2.3	11
8	10	477.6	.0678	.0000	1.28	-0.59	1.06	1.2	11
9	10	510.9	.0809	.0000	0.89	0.15	0.57	1.0	9
10	10	310.9	.0736	.0000	1.87	-0.40	1.05	2.0	11
11	10	344.3	.0666	.0000	3.94	-1.59	2.10	2.6	8
12	20	323.1	.0703	.0000	0.81	0.26	0.57	2.0	13
13	20	373.1	.0504	.0000	0.36	0.15	0.32	0.9	9
14	28	348.1	.0621	.0000	1.51	0.42	0.91	1.9	8
15	28	373.1	.0544	.0000	0.87	0.29	0.49	1.1	9
16	28	423.1	.0422	.0000	0.56	0.20	0.32	0.7	6
17	36	373.1	.0589	.0000	0.55	0.24	0.41	1.5	10
18	36	423.1	.0444	.0000	0.26	0.05	0.17	0.5	8
19	44	373.1	.0624	.0000	0.59	0.21	0.38	1.2	7
20	44	423.1	.0462	.0000	0.18	0.07	0.15	0.4	7

MODEL OVERALL STATISTICS

RMSE	=	2.10	BAR	NO PT	=	199
AAD	=	1.08	BAR	%AAD	=	1.9
MIN DEV	=	-12.36	BAR	MIN %DEV	=	-9.2
MAX DEV	=	3.92	BAR	MAX %DEV	=	6.4
BIAS	=	-0.49	BAR			
RESTRICTIONS	:	NONE				

TABLE D.VII

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	6.28	-5.59	5.59	21.8	18
2	4	344.3	.0000	.0000	6.23	-5.06	5.07	13.7	17
3	4	377.6	.0000	.0000	4.22	-3.36	3.42	8.0	12
4	4	410.9	.0000	.0000	1.69	-1.36	1.43	3.3	5
5	10	310.9	.0000	.0000	12.24	-11.43	11.43	32.2	11
6	10	344.3	.0000	.0000	11.74	-11.07	11.07	19.7	8
7	10	377.6	.0000	.0000	7.67	-6.83	6.83	8.6	10
8	10	410.9	.0000	.0000	3.65	-1.41	2.35	2.7	10
9	10	444.3	.0000	.0000	4.07	2.69	3.74	6.3	11
10	10	477.6	.0000	.0000	4.85	3.17	4.48	7.5	11
11	10	510.9	.0000	.0000	3.15	2.42	2.70	5.4	9
12	20	323.2	.0000	.0000	14.25	-12.86	12.86	46.9	13
13	20	373.2	.0000	.0000	10.86	-10.01	10.01	25.0	9
14	28	348.2	.0000	.0000	19.90	-16.67	16.67	37.6	8
15	28	373.2	.0000	.0000	12.24	-10.13	10.13	26.5	9
16	28	423.2	.0000	.0000	2.11	-1.86	1.86	5.4	6
17	36	373.2	.0000	.0000	9.17	-7.86	7.86	28.4	10
18	36	423.2	.0000	.0000	2.60	-2.12	2.12	5.0	8
19	44	373.2	.0000	.0000	10.21	-8.34	8.34	30.8	7
20	44	423.2	.0000	.0000	2.69	-2.21	2.21	6.5	7

MODEL OVERALL STATISTICS

RMSE = 8.83 BAR
AAD = 6.62 BAR
MIN DEV = -35.86 BAR
MAX DEV = 6.59 BAR
BIAS = -5.56 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 17.9
MIN %DEV = -48.7
MAX %DEV = 13.6

TABLE D.VIII

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0620	.0000	1.44	-.47	.99	2.4	52
2	10	310.9	.0107	.0000	7.41	1.02	6.47	12.2	70
3	20	323.2	.0507	.0000	5.93	.84	4.89	14.3	22
4	28	348.2	.0328	.0000	7.99	.00	5.16	12.2	23
5	36	373.2	.0242	.0000	5.32	.58	4.43	13.1	18
6	44	373.2	.0258	.0000	4.95	.08	4.11	13.7	14

MODEL OVERALL STATISTICS

RMSE	=	5.95 BAR	NO PT	=	199
AAD	=	4.36 BAR	%AAD	=	10.0
MIN DEV	=	-13.42 BAR	MIN %DEV	=	-35.6
MAX DEV	=	25.18 BAR	MAX %DEV	=	27.2
BIAS	=	.39 BAR			
RESTRICTIONS	:	NONE			

TABLE D.IX

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0643	.0000	.83	-.44	.51	1.2	18
2	4	344.3	.0582	.0000	2.10	-.92	1.33	2.8	17
3	4	377.6	.0594	.0000	1.68	-.49	1.30	2.9	12
4	4	410.9	.0708	.0000	.27	.09	.25	.7	5
5	10	310.9	.0528	.0000	1.25	.44	1.00	2.4	11
6	10	344.3	.0320	.0000	1.37	.47	.90	1.3	8
7	10	377.6	.0139	.0000	1.65	-.62	.79	.9	10
8	10	410.9	-.0015	.0000	4.11	-2.06	2.63	2.6	10
9	10	444.3	-.0121	.0000	5.02	-2.47	3.40	3.4	11
10	10	477.6	-.0121	.0000	4.95	-1.40	3.58	4.4	11
11	10	510.9	-.0142	.0000	3.59	-1.48	2.57	3.1	9
12	20	323.2	.0644	.0000	1.11	.33	.72	2.4	13
13	20	373.2	.0342	.0000	.92	.35	.74	1.9	9
14	28	348.2	.0493	.0000	2.26	.63	1.36	2.8	8
15	28	373.2	.0356	.0000	1.56	.51	.86	1.9	9
16	28	423.2	.0074	.0000	1.06	.41	.62	1.3	6
17	36	373.2	.0405	.0000	.41	.18	.31	1.1	10
18	36	423.2	.0071	.0000	.36	-.03	.23	.5	8
19	44	373.2	.0452	.0000	.24	.08	.18	.7	7
20	44	423.2	.0094	.0000	.17	-.04	.12	.3	7

MODEL OVERALL STATISTICS

RMSE	=	2.36	BAR	NO PT	=	199
AAD	=	1.24	BAR	%AAD	=	2.1
MIN DEV	=	-12.30	BAR	MIN %DEV	=	-7.1
MAX DEV	=	5.92	BAR	MAX %DEV	=	7.2
BIAS	=	-.41	BAR			
RESTRICTIONS	:	NONE				

TABLE D.X

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	5.95	-5.26	5.26	19.7	18
2	4	344.3	.0000	.0000	4.93	-2.34	3.95	11.0	17
3	4	377.6	.0000	.0000	3.90	-0.83	3.24	7.0	12
4	4	410.9	.0000	.0000	1.14	-0.78	0.99	2.4	5
5	10	310.9	.0000	.0000	10.16	-9.50	9.50	26.9	11
6	10	344.3	.0000	.0000	9.08	-8.57	8.57	15.5	8
7	10	377.6	.0000	.0000	5.96	-5.43	5.43	7.0	10
8	10	410.9	.0000	.0000	3.46	-2.43	2.53	2.3	10
9	10	444.3	.0000	.0000	2.91	-1.29	2.12	2.4	11
10	10	477.6	.0000	.0000	13.88	2.43	6.25	4.7	11
11	10	510.9	.0000	.0000	5.01	-3.63	3.63	3.7	9
12	20	323.2	.0000	.0000	9.55	-8.54	8.54	35.6	13
13	20	373.2	.0000	.0000	6.23	-5.63	5.63	13.6	9
14	28	348.2	.0000	.0000	15.83	-13.02	13.02	28.5	8
15	28	373.2	.0000	.0000	8.82	-7.13	7.13	18.0	9
16	28	423.2	.0000	.0000	0.95	-0.25	0.77	2.5	6
17	36	373.2	.0000	.0000	23.24	-6.33	6.33	23.2	10
18	36	423.2	.0000	.0000	3.57	-3.05	3.05	7.6	8
19	44	373.2	.0000	.0000	5.18	-4.31	4.31	16.3	7
20	44	423.2	.0000	.0000	1.20	0.96	0.96	2.7	7

MODEL OVERALL STATISTICS

RMSE	=	7.87	BAR	NO PT	=	199
AAD	=	5.87	BAR	%AAD	=	14.3
MIN DEV	=	-29.42	BAR	MIN %DEV	=	-38.8
MAX DEV	=	41.32	BAR	MAX %DEV	=	24.0
BIAS	=	-4.23	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XI

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0589	.0000	1.35	0.18	1.07	3.3	52
2	10	310.9	.0189	.0000	3.99	-0.51	3.17	6.5	70
3	20	323.2	.0271	.0000	4.14	-1.15	3.67	13.0	22
4	28	348.2	.0266	.0000	4.69	0.57	3.34	8.9	23
5	36	373.2	.0181	.0000	2.95	-0.58	2.53	8.2	18
6	44	373.2	.0060	.0000	3.38	-0.31	2.79	9.6	14

MODEL OVERALL STATISTICS

RMSE	=	3.26	BAR	NO PT	=	199
AAD	=	2.66	BAR	%AAD	=	7.0
MIN DEV	=	-8.66	BAR	MIN %DEV	=	-26.4
MAX DEV	=	12.60	BAR	MAX %DEV	=	26.1
BIAS	=	-0.27	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XII

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0626	.0000	0.92	0.01	0.75	3.1	18
2	4	344.3	.0597	.0000	1.60	0.15	1.32	4.5	17
3	4	377.6	.0523	.0000	1.06	0.36	1.01	3.0	12
4	4	410.9	.0255	.0000	0.56	0.06	0.51	1.3	5
5	10	310.9	.0454	.0000	0.81	-0.25	0.71	2.3	11
6	10	344.3	.0292	.0000	1.17	-0.26	1.05	2.3	8
7	10	377.6	.0189	.0000	0.53	-0.04	0.45	0.7	10
8	10	410.9	.0131	.0000	1.14	0.30	0.86	1.7	10
9	10	444.3	.0114	.0000	1.61	0.47	1.39	2.5	11
10	10	477.6	.0167	.0000	2.07	0.72	1.86	3.1	11
11	10	510.9	.0256	.0000	1.48	0.48	1.35	2.5	9
12	20	323.2	.0464	.0000	0.19	0.02	0.01	0.5	13
13	20	373.2	.0185	.0000	0.15	0.02	0.13	0.3	9
14	28	348.2	.0352	.0000	0.51	-0.20	0.42	1.0	8
15	28	373.2	.0233	.0000	0.26	-0.10	0.20	0.6	9
16	28	423.2	.0175	.0000	0.84	0.11	0.53	1.7	6
17	36	373.2	.0298	.0000	0.33	-0.16	0.31	1.8	10
18	36	423.2	.0108	.0000	0.22	0.04	0.17	0.6	8
19	44	373.2	.0193	.0000	0.33	-0.15	0.28	1.4	7
20	44	423.2	-.0041	.0000	0.10	-0.04	0.09	0.4	7

MODEL OVERALL STATISTICS

RMSE	=	0.86	BAR	NO PT	=	199
AAD	=	0.73	BAR	%AAD	=	2.0
MIN DEV	=	-3.52	BAR	MIN %DEV	=	-4.2
MAX DEV	=	2.76	BAR	MAX %DEV	=	6.6
BIAS	=	0.09	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XIII

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	1.71	-1.50	1.50	3.4	6
2	4	366.5	.0000	.0000	2.08	-1.80	1.80	4.2	8
3	4	394.3	.0000	.0000	0.77	-0.60	0.60	1.6	5
4	8	323.1	.0000	.0000	1.44	-1.35	1.35	4.4	11
5	8	348.1	.0000	.0000	1.92	-1.78	1.78	7.2	13
6	8	373.1	.0000	.0000	1.37	-1.28	1.28	6.7	9
7	10	310.9	.0000	.0000	0.58	-0.47	0.47	3.1	10
8	10	344.3	.0000	.0000	0.66	-0.44	0.50	1.5	7
9	10	377.6	.0000	.0000	0.56	-0.10	0.47	1.7	6
10	10	410.9	.0000	.0000	1.22	-0.32	1.02	2.6	7
11	20	323.1	.0000	.0000	1.40	0.78	1.30	11.4	6
12	20	373.1	.0000	.0000	1.94	0.61	1.79	7.1	6
13	20	423.1	.0000	.0000	2.80	2.27	2.60	9.7	7
14	28	348.1	.0000	.0000	2.54	2.51	2.51	17.2	10
15	28	373.1	.0000	.0000	2.46	2.39	2.39	15.8	7
16	28	423.1	.0000	.0000	3.38	3.28	3.28	15.9	7
17	36	373.1	.0000	.0000	2.67	2.58	2.58	20.3	7
18	36	423.1	.0000	.0000	2.35	2.07	2.07	11.6	6
19	44	373.1	.0000	.0000	3.30	3.23	3.23	26.2	9
20	44	423.1	.0000	.0000	2.33	2.25	2.25	15.7	7

MODEL OVERALL STATISTICS

RMSE	=	2.06 BAR		NO PT	=	154
AAD	=	1.76 BAR		%AAD	=	9.5
MIN DEV	=	-3.42 BAR		MIN %DEV	=	-13.1
MAX DEV	=	4.21 BAR		MAX %DEV	=	48.7
BIAS	=	0.50 BAR				
RESTRICTIONS	:	NONE				

TABLE D.XIV

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0251	.0000	1.14	-0.85	0.95	2.0	19
2	8	323.1	.0185	.0000	0.34	-0.02	0.30	1.7	33
3	10	310.9	.0049	.0000	0.64	-0.10	0.49	2.0	30
4	20	323.1	-.0042	.0000	3.21	-1.44	2.34	7.0	19
5	28	348.1	-.0281	.0000	1.88	-0.76	1.42	6.5	24
6	36	373.1	-.0251	.0000	2.75	-1.29	1.86	7.6	13
7	44	373.1	-.0485	.0000	2.16	-1.07	1.55	8.5	16

MODEL OVERALL STATISTICS

RMSE = 1.79 BAR
AAD = 1.10 BAR
MIN DEV = -7.85 BAR
MAX DEV = 1.82 BAR
BIAS = -0.64 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 4.4
MIN %DEV = -14.7
MAX %DEV = 20.8

* minimum temperature, see Table D.XIII for the full temperature range

TABLE D.XV

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0250	.0000	1.05	-0.75	0.88	1.8	6
2	4	366.5	.0378	.0000	0.90	-0.29	0.71	1.5	8
3	4	394.3	-.0018	.0000	0.70	-0.52	0.52	1.4	5
4	8	323.1	.0137	.0000	0.44	-0.26	0.40	1.3	11
5	8	348.1	.0211	.0000	0.34	0.10	0.29	1.7	13
6	8	373.1	.0199	.0000	0.33	0.06	0.28	1.7	9
7	10	310.9	.0064	.0000	0.20	-0.06	0.15	1.0	10
8	10	344.3	.0020	.0000	0.48	-0.24	0.35	1.3	7
9	10	377.6	-.0025	.0000	0.75	-0.37	0.51	1.5	6
10	10	410.9	-.0043	.0000	1.60	-0.83	1.19	2.5	7
11	20	323.1	-.0224	.0000	2.29	-1.09	1.55	7.4	6
12	20	373.1	-.0144	.0000	3.21	-1.60	2.48	6.4	6
13	20	423.1	-.0305	.0000	3.72	-1.79	2.70	6.3	7
14	28	348.1	-.0424	.0000	1.49	-0.62	1.11	6.1	10
15	28	373.1	-.0439	.0000	2.02	-0.97	1.56	6.9	7
16	28	423.1	-.0552	.0000	2.53	-1.10	1.75	5.9	7
17	36	373.1	-.0634	.0000	2.18	-0.97	1.42	7.5	7
18	36	423.1	-.0458	.0000	2.79	-1.25	2.22	7.7	6
19	44	373.1	-.0923	.0000	2.60	-1.29	1.86	10.5	9
20	44	423.1	-.0706	.0000	1.37	-0.63	0.99	5.4	7

MODEL OVERALL STATISTICS

RMSE = 1.77 BAR
AAD = 1.06 BAR
MIN DEV = -8.08 BAR
MAX DEV = 1.37 BAR
BIAS = -0.65 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 4.1
MIN %DEV = -16.3
MAX %DEV = 18.8

TABLE D.XVI

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	3.54	-2.91	2.91	7.1	6
2	4	366.5	.0000	.0000	4.43	-3.70	3.70	9.0	8
3	4	394.3	.0000	.0000	2.61	-1.83	1.83	5.2	5
4	8	323.1	.0000	.0000	3.39	-3.25	3.25	10.5	11
5	8	348.1	.0000	.0000	4.43	-4.10	4.10	16.1	13
6	8	373.1	.0000	.0000	3.91	-3.59	3.59	18.5	9
7	10	310.9	.0000	.0000	1.54	-1.47	1.47	11.8	10
8	10	344.3	.0000	.0000	2.97	-2.75	2.75	11.3	7
9	10	377.6	.0000	.0000	4.35	-3.94	3.94	12.7	6
10	10	410.9	.0000	.0000	6.85	-6.14	6.14	13.6	7
11	20	323.1	.0000	.0000	2.85	-2.54	2.54	14.6	6
12	20	373.1	.0000	.0000	6.21	-5.75	5.75	15.4	6
13	20	423.1	.0000	.0000	7.93	-7.13	7.13	16.8	7
14	28	348.1	.0000	.0000	3.98	-3.70	3.70	20.9	10
15	28	373.1	.0000	.0000	4.87	-4.31	4.31	21.7	7
16	28	423.1	.0000	.0000	6.07	-5.42	5.42	20.4	7
17	36	373.1	.0000	.0000	4.98	-4.39	4.39	25.9	7
18	36	423.1	.0000	.0000	7.80	-7.02	7.02	25.1	6
19	44	373.1	.0000	.0000	5.10	-4.46	4.46	25.6	9
20	44	423.1	.0000	.0000	5.42	-4.86	4.86	27.6	7

MODEL OVERALL STATISTICS

RMSE	=	4.83 BAR	NO PT	=	154
AAD	=	4.09 BAR	%AAD	=	16.6
MIN DEV	=	-12.36 BAR	MIN %DEV	=	-30.5
MAX DEV	=	0.00 BAR	MAX %DEV	=	0.0
BIAS	=	-4.09 BAR			
RESTRICTIONS	:	NONE			

TABLE D.XVII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0600	.0000	1.79	-1.14	1.50	3.3	19
2	8	323.1	.0290	.0000	1.12	-0.31	0.85	3.5	33
3	10	310.9	.0190	.0000	1.67	-0.62	1.01	3.0	30
4	20	323.1	.0216	.0000	1.55	-0.49	1.19	3.6	19
5	28	348.1	.0292	.0000	0.67	0.00	0.55	2.7	24
6	36	373.1	.0391	.0000	0.83	-0.02	0.58	2.3	13
7	44	373.1	.0401	.0000	0.66	-0.08	0.58	4.1	16

MODEL OVERALL STATISTICS

RMSE = 1.29 BAR
AAD = 0.91 BAR
MIN DEV = -5.43 BAR
MAX DEV = 2.40 BAR
BIAS = -0.40 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 3.2
MIN %DEV = -9.2
MAX %DEV = 9.3

TABLE D.XVIII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0546	.0000	1.47	-0.82	1.20	2.6	6
2	4	366.5	.0653	.0000	1.45	-0.43	1.19	2.6	8
3	4	394.3	.0874	.0000	0.41	-0.06	0.34	0.8	5
4	8	323.1	.0209	.0000	1.70	-0.97	1.21	3.1	11
5	8	348.1	.0308	.0000	0.63	-0.10	0.50	2.1	13
6	8	373.1	.0350	.0000	0.29	0.05	0.25	1.6	9
7	10	310.9	.0157	.0000	0.21	0.12	0.17	1.4	10
8	10	344.3	.0184	.0000	0.15	0.03	0.12	0.7	7
9	10	377.6	.0233	.0000	0.32	-0.11	0.22	0.5	6
10	10	410.9	.0302	.0000	1.06	-0.52	0.75	1.4	7
11	20	323.1	.0174	.0000	0.18	0.04	0.12	0.7	6
12	20	373.1	.0223	.0000	0.86	0.37	0.66	1.7	6
13	20	423.1	.0295	.0000	0.15	0.00	0.14	0.4	7
14	28	348.1	.0266	.0000	0.29	0.07	0.22	1.2	10
15	28	373.1	.0304	.0000	0.64	0.31	0.49	2.4	7
16	28	423.1	.0347	.0000	0.51	0.20	0.34	1.2	7
17	36	373.1	.0369	.0000	0.64	0.19	0.34	1.6	7
18	36	423.1	.0432	.0000	0.30	0.14	0.25	1.0	6
19	44	373.1	.0364	.0000	0.26	-0.09	0.23	1.5	9
20	44	423.1	.0482	.0000	0.52	0.23	0.42	2.4	7

MODEL OVERALL STATISTICS

RMSE = 0.78 BAR
AAD = 0.47 BAR
MIN DEV = -3.90 BAR
MAX DEV = 1.80 BAR
BIAS = -0.09 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 1.6
MIN %DEV = -7.4
MAX %DEV = 5.1

TABLE D.XIX

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	.59	-.07	.53	1.2	6
2	4	366.5	.0000	.0000	.97	-.65	.80	1.7	8
3	4	394.3	.0000	.0000	1.18	-.81	1.01	2.2	5
4	8	323.2	.0000	.0000	2.97	2.64	2.64	7.6	11
5	8	348.2	.0000	.0000	3.19	2.40	2.47	7.2	13
6	8	373.2	.0000	.0000	2.14	1.60	1.60	6.4	9
7	10	310.9	.0000	.0000	1.16	.87	.88	4.9	10
8	10	344.3	.0000	.0000	4.92	4.09	4.09	13.6	7
9	10	377.6	.0000	.0000	7.94	6.70	6.70	19.1	6
10	10	410.9	.0000	.0000	12.14	10.66	10.66	22.6	7
11	20	323.2	.0000	.0000	.69	-.61	.61	4.7	6
12	20	373.2	.0000	.0000	4.40	3.11	3.18	6.0	6
13	20	423.2	.0000	.0000	6.06	4.97	4.97	10.4	7
14	28	348.2	.0000	.0000	1.06	-1.02	1.02	6.3	10
15	28	373.2	.0000	.0000	.51	-.13	.45	3.7	7
16	28	423.2	.0000	.0000	3.25	2.51	2.51	7.6	7
17	36	373.2	.0000	.0000	1.51	-1.40	1.40	9.2	7
18	36	423.2	.0000	.0000	.87	.62	.68	2.0	6
19	44	373.2	.0000	.0000	2.02	-1.75	1.75	9.8	9
20	44	423.2	.0000	.0000	.40	-.34	.35	3.3	7

MODEL OVERALL STATISTICS

RMSE	=	3.95	BAR	NO PT	=	154
AAD	=	2.36	BAR	%AAD	=	7.7
MIN DEV	=	-3.26	BAR	MIN %DEV	=	-11.5
MAX DEV	=	19.04	BAR	MAX %DEV	=	23.4
BIAS	=	1.61	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XX

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0031	.0000	.83	-.24	.67	1.5	19
2	8	323.2	-.0092	.0000	1.76	.92	1.27	4.2	33
3	10	310.9	-.0170	.0000	3.97	1.83	2.58	8.2	30
4	20	323.2	-.0044	.0000	3.22	1.37	2.34	6.7	19
5	28	348.2	.0016	.0000	2.08	.57	1.32	5.7	24
6	36	373.2	.0057	.0000	1.60	.52	1.19	5.2	13
7	44	373.2	.0095	.0000	.96	.11	.69	3.1	16

MODEL OVERALL STATISTICS

RMSE	=	2.47	BAR	NO PT	=	154
AAD	=	1.53	BAR	%AAD	=	5.1
MIN DEV	=	-1.91	BAR	MIN %DEV	=	-16.9
MAX DEV	=	12.11	BAR	MAX %DEV	=	14.7
BIAS	=	.84	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XXI

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	-.0028	.0000	.61	-.29	.56	1.2	6
2	4	366.5	.0041	.0000	.77	-.23	.62	1.4	8
3	4	394.3	.0097	.0000	.76	-.13	.67	1.6	5
4	8	323.2	-.0115	.0000	1.99	1.14	1.40	3.6	11
5	8	348.2	-.0079	.0000	2.01	1.10	1.54	5.3	13
6	8	373.2	-.0091	.0000	.97	.36	.73	3.2	9
7	10	310.9	-.0049	.0000	.64	.30	.43	2.8	10
8	10	344.3	-.0171	.0000	1.70	.87	1.25	4.4	7
9	10	377.6	-.0262	.0000	2.05	.96	1.38	3.9	6
10	10	410.9	-.0368	.0000	2.48	1.25	1.71	3.4	7
11	20	323.2	.0050	.0000	.66	.23	.42	1.8	6
12	20	373.2	-.0063	.0000	2.24	.93	1.72	4.5	6
13	20	423.2	-.0140	.0000	1.36	.51	.96	2.1	7
14	28	348.2	.0070	.0000	.43	.12	.31	1.6	10
15	28	373.2	.0031	.0000	.94	.44	.71	3.4	7
16	28	423.2	-.0100	.0000	.95	.37	.63	2.2	7
17	36	373.2	.0116	.0000	.74	.22	.39	1.8	7
18	36	423.2	-.0020	.0000	.45	.21	.36	1.4	6
19	44	373.2	.0127	.0000	.26	-.08	.23	1.4	9
20	44	423.2	.0046	.0000	.56	.25	.45	2.6	7

MODEL OVERALL STATISTICS

RMSE	=	1.34 BAR		NO PT	=	154
AAD	=	.84 BAR		%AAD	=	2.8
MIN DEV	=	-1.23 BAR		MIN %DEV	=	-11.4
MAX DEV	=	5.28 BAR		MAX %DEV	=	8.3
BIAS	=	.46 BAR				
RESTRICTIONS	:	NONE				

TABLE D.XXII

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	1.87	-0.18	1.82	3.9	6
2	4	366.5	.0000	.0000	2.87	-2.79	2.79	6.2	8
3	4	394.3	.0000	.0000	2.52	-0.77	2.38	5.8	5
4	8	323.2	.0000	.0000	0.79	-0.53	0.74	2.6	11
5	8	348.2	.0000	.0000	1.24	-1.16	1.16	6.3	13
6	8	373.2	.0000	.0000	1.55	-1.38	1.38	8.5	9
7	10	310.9	.0000	.0000	0.34	-0.11	0.28	3.0	10
8	10	344.3	.0000	.0000	1.65	1.13	1.19	3.4	7
9	10	377.6	.0000	.0000	2.57	1.91	1.91	4.4	6
10	10	410.9	.0000	.0000	3.93	3.18	3.18	5.9	7
11	20	323.2	.0000	.0000	2.20	-1.96	1.96	11.2	6
12	20	373.2	.0000	.0000	2.40	-2.32	2.32	7.1	6
13	20	423.2	.0000	.0000	1.78	-1.69	1.69	4.4	7
14	28	348.2	.0000	.0000	0.34	-0.26	0.28	2.0	10
15	28	373.2	.0000	.0000	0.68	0.29	0.52	2.7	7
16	28	423.2	.0000	.0000	2.52	1.95	1.95	5.9	7
17	36	373.2	.0000	.0000	0.62	-0.52	0.54	4.1	7
18	36	423.2	.0000	.0000	0.94	0.74	0.76	2.2	6
19	44	373.2	.0000	.0000	1.63	-1.38	1.38	7.4	9
20	44	423.2	.0000	.0000	0.78	-0.76	0.76	5.4	7

MODEL OVERALL STATISTICS

RMSE	=	1.55	BAR	NO PT	=	154
AAD	=	1.35	BAR	%AAD	=	5.0
MIN DEV	=	-3.57	BAR	MIN %DEV	=	-16.3
MAX DEV	=	7.09	BAR	MAX %DEV	=	8.6
BIAS	=	-0.40	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XXIII

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0271	.0000	0.83	-0.08	0.69	1.6	19
2	8	323.2	.0075	.0000	0.68	-0.09	0.51	2.8	33
3	10	310.9	-.0009	.0000	2.22	1.20	1.39	3.9	30
4	20	323.2	.0111	.0000	1.28	0.59	0.89	2.3	19
5	28	348.2	.0001	.0000	1.43	0.56	0.84	3.4	24
6	36	373.2	.0010	.0000	0.89	0.23	0.70	3.1	13
7	44	373.2	.0093	.0000	0.49	0.08	0.36	2.0	16

MODEL OVERALL STATISTICS

RMSE	=	1.19 BAR		NO PT	=	154
AAD	=	0.80 BAR		%AAD	=	2.8
MIN DEV	=	-2.13 BAR		MIN %DEV	=	-12.2
MAX DEV	=	6.80 BAR		MAX %DEV	=	9.6
BIAS	=	0.40 BAR				
RESTRICTIONS	:	NONE				

TABLE D.XXIV

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0206	.0000	0.73	-0.14	0.67	1.5	6
2	4	366.5	.0277	.0000	0.70	-0.01	0.61	1.4	8
3	4	394.3	.0403	.0000	0.42	0.08	0.35	0.9	5
4	8	323.2	.0053	.0000	0.43	0.11	0.34	1.0	11
5	8	348.2	.0072	.0000	0.63	-0.16	0.51	3.2	13
6	8	373.2	.0116	.0000	0.77	-0.18	0.56	3.2	9
7	10	310.9	.0028	.0000	0.47	0.21	0.33	2.3	10
8	10	344.3	-.0011	.0000	1.47	0.94	1.04	3.1	7
9	10	377.6	-.0055	.0000	1.53	0.82	1.01	2.6	6
10	10	410.9	-.0091	.0000	1.95	1.12	1.30	2.3	7
11	20	323.2	.0137	.0000	0.11	0.03	0.08	0.6	6
12	20	373.2	.0092	.0000	0.94	0.25	0.77	2.3	6
13	20	423.2	.0077	.0000	0.65	0.29	0.43	0.8	7
14	28	348.2	.0016	.0000	0.28	0.00	0.21	1.2	10
15	28	373.2	-.0002	.0000	0.65	0.26	0.50	2.7	7
16	28	423.2	-.0081	.0000	0.74	0.29	0.49	1.7	7
17	36	373.2	.0054	.0000	0.68	0.27	0.32	1.2	7
18	36	423.2	-.0037	.0000	0.21	-0.02	0.16	1.0	6
19	44	373.2	.0099	.0000	0.27	-0.07	0.22	1.6	9
20	44	423.2	.0070	.0000	0.39	0.09	0.32	2.2	7

MODEL OVERALL STATISTICS

RMSE	=	0.68	BAR	NO PT	=	154
AAD	=	0.50	BAR	%AAD	=	1.9
MIN DEV	=	-1.73	BAR	MIN %DEV	=	-11.6
MAX DEV	=	4.14	BAR	MAX %DEV	=	6.2
BIAS	=	0.18	BAR			
RESTRICTIONS	:	NONE				

TABLE D.XXV

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR HYDROGEN + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.3598	.0000	8.12	-1.15	6.14	5.9	60
2	10	344.3	.4177	.0000	2.53	0.14	1.79	1.8	21
3	20	323.1	.3836	.0000	1.35	0.35	1.09	2.5	37
4	28	348.1	.2649	.0000	3.05	-0.02	2.40	4.1	35
5	36	373.1	.1232	.0000	4.04	0.16	3.38	7.0	27

MODEL OVERALL STATISTICS

RMSE	=	5.23	BAR	NO PT	=	180
AAD	=	3.45	BAR	%AAD	=	4.5
MIN DEV	=	-14.93	BAR	MIN %DEV	=	-16.7
MAX DEV	=	25.09	BAR	MAX %DEV	=	4.9
BIAS	=	-0.28	BAR			
RESTRICTIONS	:	NONE				

* minimum temperature, see Table D.XXVI for the full temperature range

TABLE D.XXVI

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR HYDROGEN + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.3091	.0000	4.91	1.04	3.89	4.1	13
2	4	344.2	.3369	.0000	4.18	0.74	2.88	3.1	12
3	4	360.9	.3868	.0000	4.04	0.43	2.77	2.7	11
4	4	377.5	.4490	.0000	5.47	0.21	3.93	3.8	12
5	4	394.2	.4815	.0000	7.72	-0.56	5.56	4.9	12
6	10	344.3	.4043	.0000	1.64	0.40	1.11	1.0	9
7	10	373.1	.4174	.0000	0.77	0.20	0.55	0.6	6
8	10	423.1	.4636	.0000	0.36	0.09	0.33	0.5	6
9	20	323.1	.3856	.0000	1.00	0.37	0.83	1.1	7
10	20	373.1	.3703	.0000	0.52	0.16	0.40	0.7	9
11	20	373.3	.4690	.0000	0.53	0.24	0.47	1.9	5
14	20	573.2	.4234	.0000	0.25	0.03	0.23	1.0	5
15	28	348.1	.3330	.0000	0.41	0.15	0.33	0.4	6
16	28	373.1	.2934	.0000	0.22	0.07	0.17	0.2	5
17	28	423.1	.2026	.0000	0.44	-0.05	0.30	0.4	9
18	28	373.2	.2889	.0000	0.65	0.04	0.49	1.5	5
19	28	473.2	.2170	.0000	0.54	0.21	0.43	1.5	5
20	28	573.1	.1048	.0000	0.32	0.12	0.25	1.1	5
21	36	373.1	.2114	.0000	1.86	0.95	1.59	3.3	11
22	36	423.1	.0625	.0000	0.62	-0.22	0.54	0.8	6
23	36	473.0	.0210	.0000	1.04	0.43	0.75	2.9	5
24	36	573.1	-.1357	.0000	0.53	0.25	0.48	1.9	5

MODEL OVERALL STATISTICS

RMSE = 3.22 BAR
AAD = 1.66 BAR
MIN DEV = -6.91 BAR
MAX DEV = 21.89 BAR
BIAS = 0.28 BAR
RESTRICTIONS : NONE

NO PT = 180
%AAD = 2.0
MIN %DEV = -11.2
MAX %DEV = 13.0

TABLE D.XXVII

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 3)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	-.4080	.0000	9.68	-.12	7.63	7.8	60
2	10	344.3	-.5060	.0000	32.16	-11.61	27.48	29.4	21
3	20	323.2	-.5951	.0000	36.07	-19.12	27.28	50.3	37
4	28	348.2	-.6579	.0000	36.48	-20.30	27.91	48.8	35
5	36	373.2	-.7714	.0000	39.94	-21.55	28.99	48.9	27

MODEL OVERALL STATISTICS

RMSE	=	30.29	BAR	NO PT	=	180
AAD	=	21.13	BAR	%AAD	=	33.2
MIN DEV	=	**	BAR	MIN %DEV	=	-76.5
MAX DEV	=	39.41	BAR	MAX %DEV	=	81.4
BIAS	=	-12.51	BAR			
RESTRICTIONS	:	NONE				

** lower than -100.0

TABLE D.XXVIII

BUBBLE POINT CALCULATIONS USING PGR EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	-.3636	.0000	1.62	-.40	1.45	1.7	13
2	4	344.2	-.3991	.0000	1.98	-.58	1.36	1.5	12
3	4	360.9	-.4244	.0000	2.92	-1.00	2.22	2.5	11
4	4	377.6	-.4373	.0000	2.29	-.68	2.02	2.6	12
5	4	394.2	-.4438	.0000	2.55	-.39	2.18	2.5	12
6	10	344.3	-.4037	.0000	6.52	-2.77	4.97	4.7	9
7	10	373.2	-.4770	.0000	5.31	-2.20	4.25	4.4	6
8	10	423.2	-.6002	.0000	3.23	-1.26	2.51	3.1	6
9	20	323.2	-.3148	.0000	4.26	-1.88	3.18	4.0	7
10	20	373.2	-.4337	.0000	3.93	-1.79	2.79	4.2	9
11	20	373.3	-.4290	.0000	.69	-.17	.42	1.1	5
14	20	573.2	-.8041	.0000	.58	-.15	.43	1.2	5
15	28	348.2	-.3796	.0000	4.16	-1.65	3.30	3.9	6
16	28	373.2	-.4452	.0000	4.02	-1.51	2.96	3.8	5
17	28	423.2	-.5725	.0000	3.13	-1.21	2.20	3.2	9
18	28	373.2	-.4612	.0000	.89	-.38	.69	2.5	5
19	28	473.2	-.6855	.0000	.23	-.08	.13	.4	5
20	28	573.1	-.8729	.0000	.24	-.02	.21	.9	5
21	36	373.2	-.4864	.0000	6.27	-2.10	3.53	3.9	11
22	36	423.2	-.6249	.0000	3.58	-1.52	2.88	3.7	6
23	36	473.1	-.7559	.0000	.52	.24	.44	1.9	5
24	36	573.1	-.9712	.0000	.34	.17	.30	1.3	5

MODEL OVERALL STATISTICS

RMSE = 3.35 BAR
AAD = 2.09 BAR
MIN DEV = -16.70 BAR
MAX DEV = 3.61 BAR
BIAS = -.99 BAR
RESTRICTIONS : NONE

NO PT = 180
%AAD = 2.7
MIN %DEV = -10.0
MAX %DEV = 8.3

TABLE D.XXIX

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 2)

ISO	CN	T(K)*	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.0000	.0000	2.03	1.70	1.70	2.0	60
2	10	344.3	.3831	.0000	6.24	-0.36	4.72	5.1	21
3	20	323.2	.5190	.0000	6.95	-0.83	4.99	10.7	37
4	28	348.2	.4135	.0000	3.38	-1.37	2.65	6.4	35
5	36	373.2	.4620	.0000	3.81	-0.92	2.81	7.0	27

MODEL OVERALL STATISTICS

RMSE	=	4.06	BAR	NO PT	=	180
AAD	=	3.08	BAR	%AAD	=	5.8
MIN DEV	=	-12.12	BAR	MIN %DEV	=	-24.7
MAX DEV	=	21.76	BAR	MAX %DEV	=	6.6
BIAS	=	-0.05	BAR			
RESTRICTIONS		:	NONE			

TABLE D.XXX

BUBBLE POINT CALCULATIONS USING MODIFIED PGR EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.0000	.0000	3.46	3.45	3.45	3.8	13
2	4	344.2	.0000	.0000	2.23	2.19	2.19	2.6	12
3	4	360.9	.0000	.0000	1.42	1.35	1.35	1.7	11
4	4	377.6	.0000	.0000	0.79	0.76	0.76	0.8	12
5	4	394.2	.0000	.0000	0.69	0.66	0.66	0.7	12
6	10	344.3	.3694	.0000	1.24	0.16	0.95	1.0	9
7	10	373.2	.3852	.0000	0.32	0.12	0.34	0.3	6
8	10	423.2	.4159	.0000	0.24	-0.16	0.18	0.4	6
9	20	323.2	.4823	.0000	1.24	-0.63	1.07	2.1	7
10	20	373.2	.5208	.0000	0.81	-0.24	0.68	1.5	9
11	20	373.3	.5480	.0000	0.48	-0.34	0.38	2.4	5
14	20	573.2	.7199	.0000	0.18	-0.03	0.15	1.0	5
15	28	348.2	.3941	.0000	0.84	0.01	0.73	1.0	6
16	28	373.2	.4035	.0000	0.83	0.11	0.57	0.8	5
17	28	423.2	.4160	.0000	0.44	-0.34	0.35	0.9	9
18	28	373.2	.4037	.0000	0.69	-0.21	0.49	1.7	5
19	28	473.2	.4541	.0000	0.51	-0.32	0.44	2.3	5
20	28	573.1	.5143	.0000	0.50	0.10	0.31	1.4	5
21	36	373.2	.4514	.0000	2.05	-0.62	1.67	4.8	11
22	36	423.2	.4657	.0000	0.86	-0.32	0.76	1.2	6
23	36	473.1	.5087	.0000	0.96	0.38	0.73	3.3	5
24	36	573.1	.5674	.0000	0.61	-0.3	0.52	3.0	5

MODEL OVERALL STATISTICS

RMSE = 1.09 BAR
AAD = 0.98 BAR
MIN DEV = -2.74 BAR
MAX DEV = 4.36 BAR
BIAS = 0.46 BAR
RESTRICTIONS : NONE

NO PT = 180
%AAD = 1.7
MIN %DEV = -16.7
MAX %DEV = 9.3

VITA

Kyoung Ho Row

Candidate for the Degree of

Doctor of Philosophy

Thesis: EVALUATION OF THE MODIFIED PARK-GASEM-ROBINSON EQUATION OF STATE AND CALCULATION OF CALORIMETRIC PROPERTIES USING EQUATIONS OF STATE

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Seoul, Korea, March 22, 1964, the son of Ikhwan and Hyangae Row

Education: Received Bachelor of Science Degree in Chemical Engineering from Yonsei University, Seoul, Korea, in February 1987; Received Master of Science Degree in Chemical Engineering from Florida Institute of Technology, Melbourne, Florida, in March 1991; completed requirements for the Doctor of Philosophy Degree at Oklahoma State University in May 1998.

Professional Experience: Research and Teaching Assistant, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, 1992 - 1997.

Membership in Professional Society: American Institute of Chemical Engineers; Omega Chi Epsilon; The Korean Scientists and Engineers Association in America, Inc.