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A NEW NON-CUBIC EQUATION OF STATE

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ABSTRACT

A new non-cubic equation of state (EOS) has been developed for pure substances. The density dependence of the equation was devised by fitting critical isotherms of test substances while reproducing the critical point, and enforcing van der Waals' conditions of criticality. Temperature dependence was determined for three of the parameters by forcing reproduction of saturation pressures and saturated liquid and vapour specific volumes at subcritical temperatures. The EOS was completed by developing functions to fit the calculated temperature dependence. A van der Waals-type covolume parameter was included to provide a non-zero density limit, and to avoid generating spurious volume roots.

The new equation was compared to the BWRS equation of state (Starling, 1973) and the Soave-BWR equation (Soave, 1995). The new equation generally showed improvement over the BWRS equation for fitting pure-substance critical isotherms, and for calculating saturation- and other thermodynamic properties, but performed better than the Soave-BWR EOS in only a few areas.

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Dedicated to my wife, Carolynne.

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LIST OF SYMBOLS

A	EOS constant
a_1, a_2, a_3, \ldots	EOS constants
a, b, c	EOS constants
B, C, D, E, F, G, H	Virial coefficients; EOS constants
$B_0, C_0, D_0, E_0, F_0, G_0, H_0$	EOS Constants
Ъ	Covolume parameter
b_0, b_1, b_2, \dots	EOS constants; EOS temperature function constants
C ₁ , C ₂ , C ₃	EOS temperature function constants
d_1, d_2, d_3	EOS temperature function constants
e1, e7, e3	EOS temperature function constants
f	Fugacity
H	Enthalpy
KR	Reduced EOS constant
k_1, k_2, k_3	Adjustable constants in Eqs. (24), (31)
n	Exponent in Eq. (34)
P	Pressure
R	Universal gas constant
S	Regression objective function
с Т	Temperature
V	Specific volume
Y V	adjustable constants in Eq. (24)
v	Hard-sphere reduced density
5 7	Compressibility factor
L	
Greek Symbols	
α	EOS constant
β, γ, δ, ε, φ	Reduced EOS constants in Eqs. (4), (5)
β, γ, δ	Parameters in new EOS enthalpy expression Eqs. (38), (39)
ΔHy	Vaporization enthalpy
φ	Fugacity coefficient
T 0	Molar density
9 9	Acentric factor
w w	Reduced density
Ψ	Reduced demany
Subscripts/Superscripts	
с	Critical
calc	Calculated value
EOS	Equation of state
ERR	Error
exp	Experimental
liq	Liquid
R	Reduced
REP	Repulsive

res	Residual
sat	Saturation
vap	Vapour

1.0 INTRODUCTION

Equations of state are one of the most powerful tools available for calculating fluid thermodynamic properties. In its simplest form, an equation of state (EOS) is a functional relationship between a fluid's pressure, temperature, and density. However, by applying fundamental thermodynamic relations to the basic EOS form, the departures from ideality of all thermodynamic properties can be derived as functions of temperature and density. Equations of state can be applied to both vapour and liquid phases, and when written in pressure-explicit form, a single EOS can represent coexisting vapour and liquid phases simultaneously through multiple density roots.

In order to predict fluid thermodynamic and phase-equilibrium properties accurately, an equation of state (EOS) must first be able to properly represent the pressure-volume-temperature (PVT) behavior of pure substances. Pure-substance PVT behavior in the vicinity of the critical point is particularly difficult to reproduce, and an EOS's ability to fit data in this region depends largely upon its functional form.

Traditionally, cubic equations of state based on the van der Waals equation have been most popular for chemical process design work. However, these equations have limitations that justify consideration of more complex forms. In particular, they are unable to properly represent thermodynamic behavior near the pure-component critical point, especially along the critical isotherm.

Two-parameter cubic equations like the Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK) EOS have too few parameters to simultaneously match all the required conditions at the critical point. Consequently, they normally match van der Waals' derivative

conditions $(\partial P/\partial V = \partial^2 P/\partial V^2 = 0)$ by forcing the parameters *a* and *b* to match critical pressure and temperature, at the expense of the predicted critical volume. Saturated liquid density predictions are poor, and compressed liquid densities are often unsatisfactory as well.

By contrast, non-cubic equations of state have higher-order density terms or exponential terms that potentially provide greater flexibility for expressing near-critical behavior. Non-cubic equations also have many more adjustable parameters than cubic equations, allowing them to match critical point PVT and derivative conditions, as well as saturation properties simultaneously. For these reasons, carefully developed non-cubic EOS have the potential to make better predictions of saturated liquid densities, compressed liquid densities, and fluid thermodynamic properties.

Historically, non-cubic EOS have developed alongside cubics for over 100 years. During that time, their greatest drawback has perhaps been that they typically have many more adjustable constants than cubic EOS, requiring extensive use of data regression to determine best-fit values for the constants. As a rule, the more constants in the equation, the more difficult it becomes to not only determine values for pure-component parameters, but to develop generalized correlations, assign temperature dependence functions, and establish mixing rules. And aside from quartic polynomial equations, analytical solutions are not available for determining density from non-cubic EOS at a given pressure and temperature, thus robust numerical root-solving procedures are required. In the past, these difficulties meant that more computer time was needed to develop and use non-cubic EOS than was required for simpler equations, and their use has consequently been limited.

Although development, generalization, and implementation of non-cubic EOS all pose serious challenges, technological advances over the last decade have significantly improved the speed and storage capacity of desktop computers, making viable the commercial application of non-cubic equations of state.

2.0 NON-CUBIC EQUATIONS OF STATE

2.1 The Virial Equation of State

Although cubic equations of state have traditionally been more popular for chemical process design applications, non-cubic EOS date back just as far. One of the earliest and perhaps best-known equations of state is the Virial EOS, first developed by Thiesen as early as 1885, and modified further by Kammerlingh-Onnes in 1901 (Mason and Spurling, 1969). While the original basis for the equation was empirical, it was later shown that the equation could be derived theoretically by considering the effects of intermolecular forces (Mason and Spurling, 1969).

The Virial EOS is essentially an infinite series in either volume (pressure-explicit form) or pressure (volume-explicit form). The pressure-explicit form of the equation is written

$$P = \frac{RT}{V} + \frac{RTB}{V^2} + \frac{RTC}{V^3} + \dots$$
(1)

where V is specific volume, and B and C are called *virial coefficients*. The virial coefficients take on different values for different gases, but depend only on temperature, and not on pressure or density (Mason and Spurling, 1969). While the Virial EOS does have a theoretical basis, it is valid only for the vapour phase at densities below the critical density (Mason and Spurling, 1969), and therefore cannot be used to represent vapour-liquid equilibrium. And although virial coefficients can be determined experimentally, only the second virial coefficient B can be calculated from experimental measurements with reasonable accuracy (Mason and Spurling, 1969).

2.2 BWR-Type Equations of State

Of the many non-cubic EOS developed after the Virial equation of state, the original Benedict-Webb-Rubin (BWR) EOS and its many variations have perhaps been the best known and most widely used. The BWR equation can be written as:

$$P = \frac{RT}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{E}{V^3} \left(1 + \frac{F}{V^2}\right) \exp\left(\frac{-F}{V^2}\right)$$
(2)

where B, C, D, E, and F are parameters (not to be confused with the virial coefficients in Eq. (1)) whose values, with the exception of F, are temperature dependent. These five constants are used to express the equation's density dependence at constant temperature. The temperature dependence of these parameters is as follows:

$$B = B_0 RT - A_0 - \frac{C_0}{T^2}$$
(3a)

$$C = bRT - a \tag{3b}$$

$$D = a\alpha \tag{3c}$$

$$E = \frac{c}{T^2}$$
(3d)

The BWR EOS was proposed as an improvement to the Beattie-Bridgeman EOS, enabling it to represent high-density fluid properties more accurately (Benedict et al, 1940). While the Beattie-Bridgeman equation was essentially a quartic polynomial in volume with temperature-dependent coefficients, the BWR EOS was unique in that it introduced an exponential term to better represent liquid-phase fugacities at high densities and low temperatures (Benedict et al, 1940). In a sense, the exponential term accounts for the contributions of higher-order virial coefficients, resulting in a compact yet flexible non-cubic form capable of accurately fitting pure-substance critical isotherms, and thus improving PVT predictions—in particular, liquid densities—over those of cubic equations.

Many modifications of the BWR EOS have been developed since the original equation was proposed. One of the best-known was that of Starling (1973), who used the same volume dependence expressed in Eq. (2), but modified Eqs. (3a-d) to arrive at different expressions for the temperature dependence of the parameters in Eq. 2. Starling also introduced a generalization of the pure component parameters in terms of critical properties and acentric factor (Han, 1972; Starling and Han, 1973).

Other modifications have added terms in powers of density not represented in the original equation, or have added additional constants in the temperature dependence expressions. A recent BWR modification was developed by Soave (1995), who proposed the form:

$$Z = 1 + \beta \psi + \gamma \psi^2 + \delta \psi^4 + \varepsilon \psi^2 (1 + \phi \psi^2) \exp(-\phi \psi^2)$$
(4)

where

$$\psi = \frac{\left(RT_{c}/P_{c}\right)}{V}$$
(5a)

Aside from being written in terms of non-dimensional parameters, the essential difference between Eqs. (2) and (4) is that the fourth term in Eq. (4)— $\delta \psi^4$ —is equivalent to having a fifth-power term in reciprocal volume in the pressure-explicit form of the equation, instead of the sixth power shown in Eq. (2).

Soave proposed new generalized functions to express the temperature dependence of the parameters β , γ , δ , and ε as follows:

$$\beta = \beta_{c} + b_{1} \left(1 - \frac{1}{T_{r}^{1.6}} \right) + b_{2} \left(1 - \frac{1}{T_{r}^{3.2}} \right) \omega$$
(5b)

$$\gamma = \gamma_{c} + c_{1} \left(\frac{1}{T_{r}} - 1 \right) + c_{2} \left(\frac{1}{T_{r}} - 1 \right)^{2} + c_{3} \left(\frac{1}{T_{r}} - 1 \right)^{3}$$
 (5c)

$$\delta = \frac{\delta_c}{T_r}$$
(5d)

$$\varepsilon = \varepsilon_{c} + e_{1} \left(\frac{1}{T_{r}} - 1 \right) + e_{2} \left(\frac{1}{T_{r}} - 1 \right)^{2} + e_{3} \left(\frac{1}{T_{r}} - 1 \right)^{3}$$
(5e)

where β_c , γ_c , δ_c , and ε_c are values calculated at the substance critical temperature, and b_1 , b_2 , c_1 , c_2 , c_3 , e_1 , e_2 , and e_3 can be expressed as functions of acentric factor. Parameter ϕ in Eq. (4) takes on a constant value that is the same for all substances.

In developing this BWR modification, Soave paid particular attention to fitting PVT data along critical isotherms of the substances of interest, to promote accuracy in the nearcritical region.

Other BWR modifications have included the equation of Nishiumi (1975), a fifteenconstant equation that extended the range of applicability of the BWRS equation to lower reduced temperatures. This equation was later extended to polar pure substances using three new polar parameters (Nishiumi, 1980).

Platzer and Maurer (1989) also developed a generalization for the Bender EOS (Bender, 1971), a 20-constant modification of the BWR equation. The generalized equation was applied to polar substances as well, through a polar factor. Their generalization generally performed better than Pitzer-type interpolation procedures, such as the Lee-Kesler method as applied to the Bender equation.

2.3 Repulsive Terms

Considerable work has been done recently to better represent the contributions of repulsive intermolecular forces in EOS predictions. It has long been recognized that the repulsive term in the van der Waals-type cubic EOSs

$$P_{REP} = \frac{RT}{v-b}$$
(6)

does not properly represent the high-density behavior of hard-sphere fluids (Carnahan and Starling, 1972). One approach to developing a better repulsive term has been through computer simulation, using simplified intermolecular potential functions to model molecular interactions. The results are then fit using a semi-empirical expression. Carnahan and Starling (1969) developed an empirical equation that accurately fit results of computer simulations of molecules that interact via a hard-sphere potential function. The equation is written as

$$P_{REP} = \frac{RT}{V} \left(\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right)$$
(7)

where

$$y = \frac{b}{4V}$$
(8)

and b is a covolume parameter related to the volume occupied by the molecules. Carnahan and Starling (1972) showed that a complete equation of state can be constructed by adding a suitable term to the hard-sphere expression to represent attractive forces. They found that when Eq. (7) was used instead of Eq. (6) in the van der Waals and Redlich-Kwong equations, calculated enthalpy departures and densities were generally improved for light hydrocarbons and a few non-hydrocarbons commonly found

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in natural gas. They also noted some improvement in fugacities for five light hydrocarbons.

Scott (1971) proposed a simpler hard-sphere repulsive EOS:

$$P_{REP} = \frac{RT}{V} \left(\frac{1+2y}{1-2y} \right)$$
(9)

which approximates Eq. (7), but facilitates the possibility of a cubic EOS.

2.4 Recent Developments

Most BWR-type equations of state are empirical in nature—emphasis is placed on fitting experimental data, rather than on attaching theoretical significance to the various terms. Recently, however, a trend has emerged where new equations of state are developed based on theoretical considerations. Generally, the dependent quantity—usually pressure or Helmholtz energy—is assumed to comprise a series of terms, each accounting for a particular thermodynamic phenomenon or behavior. Often, the equations include a repulsive reference term that is based on the results of molecular simulations using some type of simplified potential function—hard sphere, hard chains, or Lennard-Jones, for example. Other terms then account for phenomena such as polarity and association. Once terms have been included for all desired phenomena, the form of each term is established. The SAFT EOS (Chapman et al., 1989) is an example of this type of equation. Recently, there has been a resurgence of interest in fluids obeying the Lennard-Jones intermolecular potential function. Johnson et al. (1993) carried out molecular-dynamics computer simulations on Lennard-Jones molecules, and used a 32-constant modified BWR EOS to fit the simulated results. Kolafa and Nezbeda (1994) regressed an equation combining a hard-sphere repulsive term (slightly different in form to Eq. (7)) with a complex multi-constant attractive term.

3.0 DEVELOPMENT OF THE NEW EQUATION OF STATE

A new non-cubic equation of state has been developed to correlate PVT data for pure substances. Emphasis has been placed on accurate reproduction of PVT data in the vicinity of pure component critical points.

3.1 Objectives and General Approach

The main objective of the current project was to effort to develop a new non-cubic equation of state suitable for use in engineering applications, having the following characteristics:

- Accurate reproduction of PVT data in the vicinity of pure-component critical points, more accurately than other commonly used non-cubic EOS of similar complexity. In particular, superior reproduction of pure-component critical isotherms using as few adjustable constants as possible.
- ii. Accurate reproduction of pure component saturation PVT data, using as few adjustable constants as possible to represent the temperature dependence of the critical-isotherm adjustable constants described in (i) above.

A further objective was to assess how modifying the basic equation to include a hardsphere repulsive term, either of the van der Waals type [Eq. (6)] or the perturbed hard sphere type [Eqs. (7), (8), (9)], would affect the accuracy with which the equation could reproduce pure-component critical isotherm data. There are many ways to develop a new equation of state. The approach adopted for the new equation was to treat the influences of volume and temperature on predicted pressures separately. The first part of this work focused on establishing a functional form to express the pressure as a function of volume (or density) at constant temperature. Once the density-dependent form of the EOS had been established, the effect of temperature was incorporated by examining how the EOS constants in that form would have to vary in order to match pure-substance saturation- and supercritical PVT data. The overall procedure was recursive, because results from the temperature dependence study uncovered weaknesses in the original density-dependent form that had to be rectified before temperature dependence could be finalized.

3.2 Density Dependence: Fitting the Critical Isotherm

For a pure substance, the critical isotherm is probably the most difficult to fit using an equation of state. The critical isotherm for methane is shown on logarithmic coordinates in Figure 3-1. The figure clearly shows the three distinct regions that a successful EOS must reproduce: a liquid-like (high density) region to the left of the critical point where small changes in density result in large changes in pressure, a near-critical region, and a vapour-like (low density) region to the right of the critical point, where the slope is much more gentle. Perhaps the most severe restriction imposed on an EOS when fitting the critical isotherm arises from what are commonly called *van der Waals conditions*: the first and second derivatives of pressure with respect to volume at constant temperature both take on zero values at the critical point. This can be expressed mathematically as:

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$$\left(\frac{\partial P}{\partial V}\right)_{T} = 0$$
 at $T=T_{c}, V=V_{c}$ (10a)

$$\left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{V}^2}\right)_{\mathrm{T}} = 0 \quad \text{at } \mathbf{T} = \mathbf{T}_{\mathrm{c}}, \, \mathbf{V} = \mathbf{V}_{\mathrm{c}}$$
(10b)

Eqs. (10a,b) indicate that the critical isotherm has an inflection point, located at the critical point. As a result of these two conditions, the critical isotherm is extremely "flat" in the vicinity of the critical point, and a very flexible equation of state is required to fit the isotherm within acceptable accuracy while strictly observing the conditions expressed in Eqs. (10a,b). The EOS must also match ideal gas behavior at low densities. The ideal gas limit may be expressed mathematically as

$$\lim_{V \to \infty} \frac{PV}{RT} = 1$$
(11)

The accuracy with which the EOS is able to predict the second virial coefficient serves as a measure of how well the equation is able to fit the vapour-like region of the PVT space, not only for the critical isotherm, but over a wide range of temperature.

In theory, the EOS's required flexibility can be attained by expressing pressure as a polynomial function of volume. In practice, however, attempts to fit critical isotherms in this way require a large number of polynomial terms which in turn result in a large number of adjustable constants. In order to represent saturation PVT data accurately, it is necessary to allow the values of some of these constants to vary with temperature, introducing still more constants. As well, the greater the number of polynomial terms

that are included in the form used to fit the critical isotherm, the higher the degree of the polynomial, potentially resulting in undesirable and unpredictable behavior when the equation is solved implicitly for volume, as well as possible cross-correlation problems. The net result is that a polynomial equation of state would quickly become unwieldy and impractical for engineering use. Developing an EOS with only low-degree polynomial terms and with as few adjustable constants as possible therefore requires consideration of other types of mathematical functions, such as exponential or rational functions.



Figure 3-1 Critical isotherm of methane

3.2.1 Initial Approach

At the outset of this work, the approach to fitting the critical isotherm had three components:

• Identify constraints that the EOS must observe.

- Fit a reference function to the critical isotherm for a particular test substance, observing the identified constraints.
- Develop a function to fit the error between the critical isotherm PVT data and the pressure predicted by the fitted reference function. The resultant EOS form would consist of the sum of the reference function and the error function.

In addition to the van der Waals conditions expressed in Eqs. (10), and the ideal gas limit of Eq. (11), two additional constraints were identified:

$$\left(\frac{\partial^3 P}{\partial V^3}\right)_{T} = 0 \quad \text{at } T=T_c, V=V_c \tag{12}$$

$$P^{EOS} = P_c \qquad \text{at } T=T_c, V=V_c \qquad (13)$$

Eq. (12) is essentially a third van der Waals condition, which is suggested by experimental data (Martin and Hou, 1955). It was thought that inclusion of this condition would improve EOS predictions near the critical point, helping the EOS to reproduce the "flatness" of the critical isotherm in this region. It was also known that additional specifications or constraints will reduce the number of adjustable constants whose values must be determined from empirical data regression. From this perspective, it is desirable to identify as many different physical constraints as possible. One additional specification—the second virial coefficient at the critical temperature—was identified as a possible constraint, but was not investigated until *after* the EOS form had been developed. This aspect of the work is discussed later.

Eq. (13) states that the pressure predicted by the EOS must equal the experimental value of critical pressure exactly, when experimental values of critical temperature and volume are used as inputs.

Eqs. (10)-(13) pose five constraints that the new EOS must observe when reproducing the critical isotherm of a given substance. To meet these constraints, the EOS would have to have at least five parameters (i.e. four adjustable constants plus the ideal gas term). Even then, the values of these parameters would be completely determined by the imposed constraints, leaving no adjustable parameters for data fitting. Regressing the equation to critical isotherm data would therefore require more than four adjustable parameters.

3.2.2 <u>Regression Procedure</u>

In order to determine substance-specific values for the adjustable constants in various equations of state, and to re-fit existing equations of state to the same data to allow fair comparisons, it was necessary to develop an appropriate data-fitting method. While polynomial functions are linear with respect to their adjustable constants, an EOS containing exponential terms (such as in Eqs. (2) and (4)) or rational functions (such as Eqs. (7) or (9)) becomes non-linear in at least some of the parameters. For this reason, a non-linear least-squares method was chosen as the basis for data regression. Initially, an algorithm based on the Gauss-Newton method (Draper and Smith, 1981) was used, but was eventually abandoned in favour of a more reliable method based on the Levenberg-Marquart algorithm (Press et al., 1986).

It was necessary to modify the non-linear least-squares algorithm to enforce the constraints posed by Eqs. (10)-(13). The ideal-gas limit of Eq. (11) was enforced by including a term of first degree in inverse specific volume such as the first term in the right-hand side of Eq. (1), with the constant being numerically equal to *RT*. Initially, the van der Waals conditions of Eqs. (10) and (12) were enforced by including a penalty function in the least-squares objective function that was to be minimized. The penalty function was computed by determining the associated derivatives numerically at each iteration, and multiplying them by a large number; minimization of the objective function thereby had the effect of forcing the three derivatives to take on very small values. Also, the condition of matching the critical point expressed in Eq. (13) was enforced by applying a large weighting factor in the objective function to the pressure error computed at the critical volume.

Using penalty functions and weighting factors to force compliance with the constraints introduced a tedious trial-and-error procedure that had to be followed to determine appropriate values of these factors. In addition, these methods did not force *exact* compliance with the constraints—the critical-point derivatives and the difference between the predicted and actual critical pressure still retained small non-zero residual values. It was decided that a more effective method would be to enforce these constraints algebraically by setting the equations for the residual pressure (i.e. the difference between the actual critical pressure and that predicted by the EOS) and its derivatives to zero at the critical point, and solving the resulting system of equations simultaneously. By using this method to determine values only for constants in the reference polynomial term, the

resulting system of equations is linear, and their solution, carried out repeatedly after a given number of iterations in the non-linear least-squares algorithm, is straightforward.

Although the EOS is written in pressure-explicit form, it is common when calculating thermodynamic properties or phase equilibrium to specify pressure and solve the EOS implicitly for the corresponding density. Since the critical isotherm is very flat in the vicinity of the critical point, small differences in the specified pressure will cause a large variation in the corresponding density predicted by the EOS. For this reason, accurate prediction of density in the vicinity of the critical point requires that the EOS's adjustable constants be determined using a regression procedure that minimizes errors in density as well as pressure. This procedure is referred to herein as simultaneous regression. One drawback of the simultaneous regression procedure is that it requires implicit solution of the EOS for density at a given pressure. It was found, however, that since the number of near-critical data points along the critical isotherms of the substances of interest was small compared to the total number of data points, simultaneous regression had a relatively small effect on the final values of the adjustable constants. For this reason, the regression procedure used to develop the new EOS form was based on pressure errors Simultaneous regression was used only once the form of the new EOS was only. finalized, to determine final values for the adjustable constants. Constants obtained from the pressure-regression were used as initial guesses.

3.2.3 EOS Development

For the first attempt at fitting the critical isotherm, a sixth degree polynomial in volume was chosen as a reference term

$$P^{REF} = RT\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^4 + a_5\rho^5 + a_6\rho^6$$
(14)

It had been observed in this work that a sixth degree polynomial was able to fit the critical isotherm of test substances with high accuracy from low densities all the way up to the critical point. Also, the error between the predicted and experimental pressures appeared very regular at densities greater than critical, indicating that this error could possibly be fit by adding a relatively simple error term to the reference EOS. By contrast, when the BWR EOS [Eq. (2)] was fit to the critical isotherm of methane while observing the constraints of Eqs. (10)-(13), the error was irregular and difficult to fit, making it difficult to develop a suitable error term. With five adjustable constants plus an ideal gas term, the sixth degree polynomial was capable of meeting the five constraints of Eqs. (10)-(13) while still leaving one adjustable constant for regression of the test-substance PVT data. Methane was chosen as the test substance, largely because it is the major component of natural gas, and because it has a reasonable critical compressibility and its acentric factor is nearly zero.

Smoothed critical isotherm data for methane, obtained from an accurate 33-constant EOS (Angus et al., 1976a), was used for the regression. During the development of the tables of smoothed properties in that reference, the authors fit the 33-constant EOS to a large number of independent sets of experimental data. Although the experimental errors for

the individual data sets were not reported in detail, the authors did compare the errors between their equation and the data for several different properties. For single-phase pressure and density measurements, the majority of the smoothed data was within 1 percent of the experimental values, and much of it was within 0.5 percent. With the exception of a few points, the smoothed vapour pressures were within approximately 0.4 percent of the data. Smoothed saturated liquid densities were largely within 0.5 percent, and saturated vapour densities were mainly within 1 percent of the data except near the critical point. For enthalpy of vaporization, the maximum difference was 102.8 J/mol at 180 K, which corresponded to 2.54 percent of the experimental value, with the majority of the points being within 1 percent.

For this work, the values of pressure and volume along the critical isotherm were interpolated between smoothed values at tabulated temperatures of 190 K and 195 K. Since the lower isotherm was less than 0.6°C away from the critical temperature of 190.55 K, it was expected that errors introduced by the interpolation would be negligible.

Once the reference term had been fitted to the PVT data for methane, the error between the pressure predicted by the reference term and the pressure from the PVT data was plotted on a logarithmic scale as a function of volume. At densities greater than the critical density, the pressure error appeared as a straight line on the plot, so an errorfitting term expressing the logarithm of the error as a linear function of volume was added to the reference term, written equivalently as

$$P^{ERR}\Big|_{\rho>\rho_c} = C\exp(D - EV)$$
(15)

The combination of reference term and error term was then able to fit the critical isotherm well, except in the immediate vicinity of the critical point.

To fit the error in critical region, a second error term was developed. It was desired that this term fit the error near the critical point, but not affect the data fit at sub-critical densities, which was already very good using only the reference term. For this purpose, a fourth degree polynomial in density was used. The density in this term was shifted by an amount equal to the critical density, in order to take on a value of zero at the critical point, since exact prediction of the critical pressure—as expressed in Eq. (13)—was a constraint already imposed on the reference term. In order to force this term to vanish at densities lower than the critical density where its contribution was not required, it was multiplied by a "switching function"—essentially an S-shaped curve that switches between a value of 0 and a value of 1 over a very short range of density in the vicinity of the critical point.

The resulting overall EOS was obtained by summing the reference term [Eq. (14)], the first error term [Eq. (15)], and the second error term, and was written as

$$P = RT\rho + a_{2}\rho^{2} + a_{3}\rho^{3} + a_{4}\rho^{4} + a_{5}\rho^{5} + a_{6}\rho^{6}$$

$$+ \left[\frac{\rho^{B}}{A + \rho^{B}}\right] \left[b_{0} + b_{1}(\rho - \rho_{C}) + b_{2}(\rho - \rho_{C})^{2} + b_{3}(\rho - \rho_{C})^{3} + b_{4}(\rho - \rho_{C})^{4}\right] \quad (16)$$

$$+ C \exp(D - \frac{E}{\rho})$$

Percent error in pressure along the critical isotherm of methane is shown for Eq. (16) as a function of reduced volume in Figure 3-2. The figure shows that while the error is fairly low at high densities (low reduced volumes), it becomes unacceptably large in the vicinity of the critical point, and at low-to-intermediate volumes to the right of the critical point. It was also decided that the resulting EOS had too many adjustable parameters, and that inclusion of the second error term (i.e. the density-shifted polynomial multiplied by the switching function) made the equation too complex. Subsequently, ways in which Eq. (16) could be simplified were considered.

Closer examination showed that the second term in Eq. (16)—plotted on a logarithmic scale as a function of specific volume—appeared approximately as a straight line. This indicated that the term could be equivalently represented by an exponential function of density of the same form as Eq. (15), but having different values for the adjustable constants. The modified equation retained the sixth-degree polynomial as the reference term, and was written

$$P = RT\rho + a_{2}\rho^{2} + a_{3}\rho^{3} + a_{4}\rho^{4} + a_{5}\rho^{5} + a_{6}\rho^{6} + C\exp(D - \frac{E}{\rho}) + F\exp(G - \frac{H}{\rho})$$
(17)

Percent error in pressure along the critical isotherm of methane is shown for Eq. (17) in Figure 3-3 as a function of reduced volume. While the form of Eq. (17) is less complex than that of Eq. (16), Figure 3-3 shows that its use provides only a slight improvement in the fit to the data for volumes less than the critical volume, but worsens the fit at volumes greater than the critical volume.


Figure 3-2 Error in pressure along C₁ critical isotherm for Eq. (16)

At this point, a different approach was taken. First, the degree of the reference polynomial term was reduced to five by dropping the last term in Eq. (14). As the reference term now contained only four adjustable constants in addition to the ideal gas term, values of these constants would be completely specified by enforcing the conditions in Eqs. (10)–(13). Now, the only adjustable constants available for fitting the data would be those found in the error terms.

The second step was to re-examine the error terms in Eq. (17). Before doing so, however, values for the four adjustable constants in the reference term were determined for methane by enforcing the conditions, and the pressure error of the reference term relative to the critical isotherm data was examined, again on logarithmic coordinates. It was found that for this simplified reference term, the pressure error away from the critical

point was a smooth curve---not quite a straight line, but close enough that a low degree polynomial in volume, placed inside the exponential, would likely provide a good fit.



Figure 3-3 Error in pressure along C₁ critical isotherm for Eq. (17)

This effectively allowed the two exponential terms in Eq. (17) to be combined into a single term. Near the critical point, the pressure error curved more sharply, tending to zero error at the critical point itself. To account for this, extra higher-degree terms were added to the volume polynomial inside the new exponential error function. Initially, a fifth-degree polynomial in volume was chosen, leading to another EOS form as follows:

$$P = RT\rho + a_{2}\rho^{2} + a_{3}\rho^{3} + a_{4}\rho^{4} + a_{5}\rho^{5}$$

$$+ a_{6} \exp(a_{7}V + a_{8}V^{2} + a_{9}V^{3} + a_{10}V^{4} + a_{11}V^{5})$$
(18)

Eq. (18) was fit to data for methane, and the pressure error—shown in Figure 3-4 as a function of volume—was again examined. It began to appear that enforcing the thirdderivative condition of Eq. (12) was overly restrictive, and was probably degrading the quality of the fit in the vicinity of the critical point, rather than improving it. For all subsequent trials, it was dropped from use as a specification.

At this point, it was decided as a next step to examine variations on the basic form expressed in Eq. (18), but with fewer adjustable parameters. For both the reference term and the polynomial term inside the exponential, two approaches were taken: drop the terms with the highest degree in volume, and drop terms with even powers of volume.

Comparison of these and other variations on Eq. (18) led to new forms as follows:

$$P = RT\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^4 + a_5 \exp(a_6V + a_7V^3)$$
(19a)

$$P = RT\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^4 + a_5 \exp(a_6V + a_7V^2)$$
(19b)

$$P = RT\rho + a_2\rho^3 + a_3\rho^5 + a_4\rho^7 + a_5 \exp(a_6V + a_7V^3)$$
(19c)

$$P = RT\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^5 + a_5 \exp(a_6V + a_7V^3)$$
(19d)

$$P = RT\rho + a_2\rho^2 + a_3\rho^3 + a_4\rho^5 + a_5 \exp(a_6V + a_7V^2)$$
(19e)

$$P = RT\rho + a_2\rho^2 + a_3\rho^4 + a_4\rho^6 + a_5 \exp(a_6V + a_7V^3)$$
(19f)

Average absolute errors in pressure along the critical isotherm of methane were as follows: Eq. (19a)—0.78%, Eq. (19b)—0.62%, Eq. (19c)—21.8%, Eq. (19d)—0.49%, Eq. (19f)—1.13%. The AAD% for Eq. (19e) was lower than that of Eq. (19c), but higher than the AAD% of the other equations.



Figure 3-4 Error in pressure along C_1 critical isotherm for Eq. (18)

Of the six equations, Eq. (19d) resulted in the best fit for methane, and was selected for further development.

The pressure error exhibited by Eq. (19d) showed considerable improvement over earlier forms—Eqs. (16) and (17)—being essentially the first of the many forms examined that could fit the critical isotherm of a test substance within acceptable error limits. At this point, a sensitivity analysis was carried out in an attempt to further reduce the number of adjustable parameters in the equation. Each of the six parameters in Eq. (19d) was perturbed by 2% of its best-fit value, and the effect on the equation's pressure error was examined. It was found that the pressure error was sensitive to perturbations in parameters a_2 to a_6 in the equation, but showed very little sensitivity to perturbations in a_7 —the equation was modified thereafter to exclude parameter a_7 , resulting in the following equation:

$$P = \frac{RT}{V} + \frac{a_2}{V^2} + \frac{a_3}{V^3} + \frac{a_4}{V^5} + a_5 \exp(a_6 V)$$
(20)

Figure 3-5 shows the error in pressure for Eq. (20) along the critical isotherm of methane. In this figure—and in others presented later in the text for other equations—the error takes on a definite negative bias, especially at reduced volumes greater than unity. This is mainly because the best-fit value of the second virial coefficient, which is directly proportional to parameter a_2 , differs from the experimental value, as discussed in Section 5.1. Shortly after Eq. (20) was devised, a flaw was identified in its form. The equation was regressed to critical isotherms for additional substances, and in all cases, it was observed that the adjustable constants alternated in sign— a_2 took on a negative value, a_3 was positive, and a_4 was negative. This meant that in the limit, as specific volume approached a value of zero, the reference polynomial would tend to $-\infty$, since the coefficient of the highest power in specific volume took on a negative value. The exponential term's zero-volume limit, however, takes on a finite value, equal to the constant a_5 . The result was that the pressure predicted by the overall EOS tended to $-\infty$ as specific volume approached zero.



Figure 3-5 Error in pressure along C₁ critical isotherm for Eq. (20)

In practical terms, the equation was able to fit the critical isotherm for test substances, but at some low specific volume—and correspondingly high pressure—the predicted isotherm would "turn-around", as shown in Figure 3-6. Correcting the problem would have to rely on one of two solutions:

- Modifying the reference term to take on a zero-volume limit of +∞.
- Modifying the error term to take on zero-volume limit of +∞, which it would have to approach more rapidly than the reference term approached -∞.

Attempts to modify the error term tended to degrade the equation's ability to fit critical isotherms, and so were abandoned. It was found that the simplest and most effective solution was to add another volumetric term to the polynomial portion of the equation. The new term would then have the highest power in reciprocal volume, and as long as it

had a positive-valued coefficient, the reference term—and therefore the overall EOS would approach the correct limit as volume tended to zero. After trying different powers of V, a seventh-degree term was chosen. Fortunately, this added only one extra parameter to the equation.



Figure 3-6 Critical isotherm of C_1 predicted by Eq. (20)

With the new seventh-degree term being added to the equation, the power of the secondhighest-degree term was re-examined. It was found that changing the degree of this term from *five* to *six* reduced the overall average deviation in *pressure* along the critical isotherm of the test substance, methane, and so the change was adopted. At that point, the basic volume-dependent form of the equation could then be written as

$$P = \frac{RT}{V} + \frac{B_0}{V^2} + \frac{C_0}{V^3} + \frac{D_0}{V^6} + \frac{E_0}{V^7} + F_0 \exp(G_0 V)$$
(21)

This version of the EOS was reported by Kedge and Trebble (1999).

3.2.4 Alternate Repulsive Terms

For an empirical EOS, greater emphasis is normally placed on the equation's ability to fit thermodynamic property data, than on the theoretical significance of its terms. This does not mean, however, that empirical equations cannot represent the contributions of attractive and repulsive intermolecular forces, at least in an approximate and qualitative way. Indeed, van der Waals' original cubic EOS was based on the concept that macroscopic deviations from the ideal gas law could be attributed to the separate contributions of attractive and repulsive forces. Here, attractive forces were incorporated into the equation through a term representing a negative deviation from the ideal gas pressure, while repulsive forces were thought to arise from the volume occupied by the molecules themselves—or *excluded volume*—as represented by the "covolume" parameter, b. Substituting V-b in an EOS instead of V—and thereby creating a vertical asymptote at V=b—is perhaps the simplest way of representing the effect of excluded volume on PVT behavior.

Unlike common cubic EOS, little attention has been paid to representing repulsive forces directly in non-cubic equations of state. Most BWR-type EOS simply use the ideal gas equation as the leading term, without incorporating a co-volume parameter. To determine whether there would be any advantage to including some representation of repulsive forces in the new EOS—either through a covolume parameter, or a hard-sphere type term—three alternate versions of Eq. (21) were derived and were fit to the critical

isotherm of methane for comparison. The three alternate equations were written as follows:

$$P = \frac{RT}{(V-b)} + \frac{B_0}{V^2} + \frac{C_0}{V^3} + \frac{D_0}{V^6} + \frac{E_0}{V^7} + F_0 \exp(G_0 V)$$
(22a)

$$P = \frac{RT}{(V-b)} + \frac{B_0}{(V-b)^2} + \frac{C_0}{(V-b)^3} + \frac{D_0}{(V-b)^6} + \frac{E_0}{(V-b)^7} + F_0 \exp(G_0 V)$$
(22b)

$$P = \frac{RT}{V} \left(\frac{1+2y}{1-2y} \right) + \frac{B_0}{V^2} + \frac{C_0}{V^3} + \frac{D_0}{V^6} + \frac{E_0}{V^7} + F_0 \exp(G_0 V)$$
(22c)

where, again, y = b/4V, and b is a covolume parameter. In Eq. (22a,b), repulsive forces are represented by a van der Waals-type covolume, whereas in Eq. (22c), the repulsive forces are incorporated by using the Scott Hard-Sphere expression as the leading term in the equation.

Figure 3-7 shows the error in predicted pressure along the critical isotherm of methane for Eq. (21), as well as the three alternate versions (Eqs. (22)). Eq. (21) gave the lowest Average Absolute Deviation (%AAD: 0.379%), mainly because it gave the best fit in the liquid-like region. All three alternate equations gave better fits, however, in the vapourlike region (greater-than-critical volumes).

Figure 3-8 shows the error in the predicted specific volume, again for the critical isotherm of methane. In this case, Eq. (21) gives the highest %AAD. The pattern is the same as for pressure—Eq. (21) performs best in the liquid-like region, while all three alternatives perform better in the vapour-like region. The difference, however, is that

here, the deviations in the vapour-like region are much greater than in the liquid-like region, and make a larger contribution to the %AAD. For the pressure errors, low errors in the liquid-like region tended to offset the deviations in the vapour-like region.

Comparing the two alternatives where only the leading term was modified to incorporate hard-sphere repulsions (Eq. (22a, c)), both figures show that using the Scott HS term results in a better critical isotherm fit than simply using the van der Waals covolume. When a covolume parameter is used, however, a comparision of the curves for Eq. (22a, b) shows that better fits are obtained by including the covolume in *each* term, rather than in the first term only.



Figure 3-7 Error in pressure along C₁ critical isotherm for alternate versions of the new EOS



Figure 3-8 Error in specific volume along C₁ critical isotherm for alternate versions of the new EOS

It is interesting to note how the regressed values of parameter b vary between the alternate equations. First, the way the Scott equation [Eq. (9)] is written results in a vertical asymptote at $V = \frac{1}{2} b^{\text{SCOTT}}$. As a consequence, we would expect the value of b^{SCOTT} to be approximately twice the value of that used in the van der Waals co-volume term, in order for the two terms to have approximately the same asymptote.

Table 3-1 shows the best fit values for parameter 'b' in each of the three alternate equations, obtained by simultaneous regression along the critical isotherm of methane.

As expected, the value of b in Eq. (22c) is approximately twice that in Eq. (22a), indicating that each of these versions of the EOS would have a vertical asymptote at approximately the same value of V. The best-fit value of b for Eq. (22b) was lower than

that of Eq. (22a) by approximately a factor of 10. At the same time, this equation yielded the lowest overall value for the regression objective function.

Table 3-1 Values of 'b'		
parameter for alternate		
versions of the new EOS		
Equation	́b'	
-	(cm ³ /mol)	
22a	22.14	
22b	1.94	
22c	43.00	

3.2.5 Additional Specifications: Second Virial Coefficients and Third Derivatives

Equations (10), (11), and (13) express three constraints that were enforced when fitting candidate equations of state to pure-component critical isotherms. Each constraint that is specified reduces by one the number of adjustable constants whose values must be determined from data regression. Additional constraints are possible, but were not included in the EOS development phase of the project. In this section, two additional constraints—enforcing the second virial coefficient at the critical temperature, and forcing the third derivative of pressure with respect to volume to zero at the critical point—are investigated to determine their effects on the quality of critical isotherm fits obtained using the new EOS.

The first additional constraint considered was the second virial coefficient, B, which is the coefficient of the reciprocal-volume-squared term in the Virial EOS [Eq. (1)]. This term represents the first deviations from ideal gas behavior that are observed as pressure is increased. We would therefore expect that forcing the EOS to take on the correct value of B would improve the equation's fit in the vapour-like region along the critical isotherm. Conversely, we would expect that if the correct value of B were *not* forced, but rather left as an adjustable parameter, accurate fitting would require the value obtained from regression to be close to the correct value.

Figure 3-9 shows the deviations in pressure along the critical isotherm of methane, when Eq. (21) is forced to take on the correct value of B. The relationship between B and the second coefficient of Eq. (21) is as follows:

$$B_0 = RTB \tag{22d}$$

An experimental value of B was not available for methane at its critical temperature. Instead, the EOS was forced to match a value calculated from the correlation of Tsonopolous (1974). The figures show that forcing the correct value of B greatly improves the fit along the vapour-like portion of the critical isotherm, but drastically degrades the fit in the liquid-like region. This result is not surprising, considering that Eq. (21) was not specifically developed to fit the error that results when the correct B is enforced. Another difficulty encountered when B is forced is that the alternating sequence of signs for successive polynomial terms is not preserved—as a result, the highest-degree polynomial term in Eq. (21) takes on a negative value, which reintroduces the critical isotherm 'turn-around' problem described in Section 3.2.3. While these results indicate that forcing a correct value of B is not a successful strategy for Eq. (21), this does not necessarily mean that a suitable error term could not be developed to replace the existing exponential term.



Figure 3-9 Error in pressure along C₁ critical isotherm for new EOS with forced second virial coefficient

The second additional constraint examined was to force the third derivative of pressure with respect to volume to take on a value of zero at the critical point, described by Eq. (12). As discussed in Section 3.2.1, this constraint was originally included as one of the conditions to be enforced during development of the new EOS, but was dropped after it proved too detrimental to fitting pure-component critical isotherms. At this point, the third-derivative constraint was re-examined to observe its effects on the finished EOS.

Figure 3-10 shows the deviations in pressure along the critical isotherm of methane, when—in addition to the three constraints described by Eq. (10) and (13)—the third

derivative of Eq. (21) is forced to take on a value of zero at the critical point. It is worth noting that the deviations in both pressure and volume exhibited under these conditions are similar to those shown in Figure 9, for enforcement of the critical second virial coefficient. The fit in the vapour-like region to the right of the critical point is very good, whereas large deviations occur in the liquid-like region left of the critical point.



Figure 3-10 Error in pressure along C₁ critical isotherm for new EOS with third derivative forced to zero at critical point

The similarities between the critical isotherm fits obtained with the two constraints separately occur because forcing the EOS to take on the correct B value results in a third derivative that is nearly zero. At the same time, forcing the third derivative to zero at the critical point results in a best-fit B value that is very near the correct value. It is not known whether this is a general result, applicable to all non-cubic EOS, or whether it is unique to Eq. (21).

3.2.6 Sensitivity Analysis

To understand the behavior of the new EOS along pure-component critical isotherms, it is useful to determine which parameters contribute most to the calculated pressure over various ranges of specific volume. A parameter sensitivity analysis can help in this regard.

In the analysis, each EOS parameter is increased one at a time by 1% of its value. The incremental percent deviation in pressure, or *differential error*—that is, the difference between the pressure error calculated with best-fit parameters and that calculated with the perturbed parameter—is then plotted as a function of reduced volume. The resulting plot shows the ranges of specific volume where the contribution of the term in the EOS associated with the selected parameter is significant to the calculated pressure.

Figures 3-11 (a-f) show results of the sensitivity analysis carried out for Eq. (21). Figure 3-11 (a) shows that a 1% forward perturbation in parameter B₀ has its greatest impact in the liquid-like region near the critical point, at a reduced volume of approximately 0.66. It also shows that the second-degree term in Eq. (21) makes a significant contribution to the calculated pressure between $V_R = 1$ and $V_R = 10$, which is as expected, since this term essentially represents the second virial coefficient.



Figure 3-11(a) Sensitivity of fit along C_1 critical isotherm to 1% perturbation in B_0 [Eq. (21)]



Figure 3-11(b) Sensitivity of fit along C_1 critical isotherm to 1% perturbation in C_0 [Eq. (21)]



Figure 3-11(c) Sensitivity of fit along C₁ critical isotherm to 1% perturbation in D₀ [Eq. (21)]



Figure 3-11(d) Sensitivity of fit along C_1 critical isotherm to 1% perturbation in F_0 [Eq. (21)]



Figure 3-11(e) Sensitivity of fit along C_1 critical isotherm to 1% perturbation in G_0 [Eq. (21)]



Figure 3-11(f) Sensitivity of fit along C_1 critical isotherm to 1% perturbation in E_0 [Eq. (21)]

Figure 3-11 (b) shows the results of a 1% forward perturbation in parameter C_0 . The EOS term associated with this parameter makes almost no contribution to the calculated pressure in the vapour-like region, starting only to contribute significantly immediately near the critical point itself. This term's contribution to the calculated pressure is greatest in the same vicinity as the second-degree term, near $V_R = 0.61$.

Figure 3-11 (c) shows results of the analysis for parameter D_0 . Here, we see that the EOS term associated with this parameter again makes virtually no contribution to the calculated pressure in the vapour-like region. The strength of this term's contribution increases with decreasing volume, starting at the critical point.

The differential error at the critical point resulting from a 1% forward perturbation in D_0 is less, however, than from the same perturbation in parameter C_0 . We can also see that the peak of the curve has shifted left, indicating that successive polynomial terms make their maximum contributions to pressure at lower and lower volumes.

Figures 3-11 (d) and (e) show results of forward perturbations to parameters F_0 and G_0 , the two parameters associated with the exponential term. Perturbations to either term has no effect on calculated pressures in the vapour-like region, or at the critical point. The maximum sensitivity to perturbations in both parameters occurs at approximately the same value of V_R —approximately 0.44. The figure also shows that of these two parameters, the calculated pressure is more sensitive to perturbations in parameter G_0 , the parameter *inside* the exponential. Finally, Figure 3-11 (f) shows results of perturbations in parameter E_0 , the coefficient of the highest-degree polynomial term in Eq (21). The figure shows that this term makes no contribution to the calculated pressure in the vapour-like region, and very little at the critical point. The differential error reaches a plateau between $V_R = 0.39$ -0.46, and begins to increase again with decreasing V_R , as this EOS term begins to dominate the pressure calculation.

3.3 Temperature Dependence of EOS Parameters

The first step in the EOS development process, which was the subject of Section 3.2, led to Eq. (21)—a functional form expressing the variation of pressure with specific volume at constant temperature. For the equation to be complete, however, it must incorporate the effects of temperature as well as volume. Eq. (21) was developed by fitting data at only one temperature—the critical temperature—but, since this isotherm is the most difficult to fit, we should expect the resulting form to be able to fit data at any other temperature as well.

Eq. (21) contains six adjustable parameters, whose values can be selected optimally to fit P-V data along a given isotherm. In developing Eq. (21), best-fit values were determined for these parameters along the critical isotherm of methane. These values represent the optimum fit to P-V data at the critical temperature, but *only* at this temperature. In Eq. (21), the only term expressing the effect of temperature on pressure is the ideal gas term, which is clearly not sufficient to represent temperature effects in real fluids. This is particularly true at sub-critical temperatures, where calculated isotherms must exhibit multiple volume roots in order to represent both vapour and liquid phases simultaneously. By allowing some of the coefficients in the equation of state to vary with temperature, the EOS can represent both sub- and super-critical isotherms, and can reproduce puresubstance vapour pressure behavior as well. To complete the development of the new equation of state, it was necessary to express some of these parameters as analytical functions of temperature. This was the second stage in the development of the new EOS.

3.3.1 General Approach

The objective of the second part of the EOS development process was to express the coefficients in the new equation as functions of temperature. Before analytical functions could be developed, it was first necessary to determine how the values of the EOS parameters would have to vary with temperature. This was accomplished by reproducing saturation data—vapour pressures, and saturated liquid and vapour specific volumes—for one test substance at sub-critical temperatures, and by fitting PVT data at supercritical temperatures. At each temperature where data was available, new values were obtained for those parameters that were allowed to vary with temperature. Once the variation of these parameters with temperature had been established, a trial-and-error procedure was carried out to find analytical functions that could fit the parameters as functions of temperature.

At the beginning of this stage of development, the basic form of the new EOS [Eq. (21)] was used. However, as the work proceeded, it became necessary to adopt the modified form of Eq. (22a), incorporating a van der Waals-type covolume to overcome problems

with spurious roots at sub-critical temperatures. This decision is discussed further in Section 3.3.5

3.3.2 Determining Temperature Dependence

The first step toward incorporating temperature dependence into the new EOS was to determine the variation of the EOS parameters with temperature. To determine how the parameters would have to vary, it was decided to focus on reproducing pure-component saturation envelopes for sub-critical temperatures, and on fitting single-phase PVT data at supercritical temperatures.

At each sub-critical temperature, three conditions must be reproduced—the vapour pressure, and the saturated vapour and liquid specific volumes. Since the density-dependent form of the new EOS contains six adjustable parameters, it was only necessary for three of these parameters to be made temperature dependent in order to match these three conditions *exactly* at each temperature. On this basis, a procedure was devised to determine the values for three selected parameters at each temperature that would allow Eq. (21) to match vapour pressure and saturated specific volumes exactly. Values for the remaining three parameters, which were *not* made temperature dependent, were held constant at their critical-isotherm values.

Before proceeding, it had to be decided which three parameters would be temperature dependent. Since virial coefficients are known to vary with temperature, and some understanding of how second and third virial coefficients has been established (Dymond & Smith, 1969), the EOS parameters corresponding to these coefficients— B_0 and C_0 —

were chosen first. It was decided initially that the third temperature-dependent parameter should be one of the two associated with the exponential term—either F_0 or G_0 . Since the exponential term makes a large contribution to the calculated pressure at liquid-like densities, and since the slope of the linear expression inside the exponential could be loosely related to the fluid's isothermal bulk modulus—a quantity known to vary with temperature— G_0 was selected as the third parameter. It was decided that a second combination of temperature-dependent parameters— B_0 , C_0 , and D_0 —would be considered for comparison as well, to ensure the best choice of the third parameter.

To determine values of the three temperature-dependent parameters at each temperature, the EOS was written twice—once expressing the saturation pressure in terms of the known saturated liquid specific volume, and once in terms of the saturated vapour specific volume. After rearranging these equations, and substituting one into the other, we have equations for two EOS parameters in Eq. 22a (B_0 and C_0) in terms of the remaining parameters.

$$C_{0} = \left[\frac{1}{V_{\text{sat,L}}} - \frac{1}{V_{\text{sat,V}}}\right] \left(V_{\text{sat,V}}^{2} K_{V} - V_{\text{sat,L}}^{2} K_{L}\right)$$
(23a)

$$B_0 = V_{sat,L}^2 K_L - \frac{C_0}{V_{sat,L}}$$
(23b)

where

$$K_{x} = \frac{B_{0}}{V_{sat,x}^{2}} + \frac{C_{0}}{V_{sat,x}^{3}} = P^{sat} - \frac{RT^{sat}}{V_{sat,x} - b} - \frac{D_{0}}{V_{sat,x}^{6}} - \frac{E_{0}}{V_{sat,x}^{7}} - F_{0} \exp(G_{0}V_{sat,x})$$
(23c)

and x designates either liquid (L) or vapour (V).

We can then iterate to find the value of a third parameter at which the fugacities at the saturated liquid and vapour specific volumes are equal. The final result is a set of parameters B_0 , C_0 , and a third parameter, that exactly matches the experimental vapour pressure, and saturated vapour and liquid specific volumes.

Following this procedure, the temperature dependence of the two sets of parameters was calculated for methane. Using these parameter sets, the ability of the EOS to reproduce subcritical single-phase PVT data was examined. It was found that using D_0 as the third term resulted in better reproduction of subcritical isotherms then when G_0 was used. It was thereafter decided that D_0 would be the third temperature-dependent parameter. When these calculations were carried out originally, the form of the EOS had not yet been modified to use the sixth power of inverse specific volume instead of the fifth power, so the temperature calculations were carried out using the fifth-power version, which is equivalent to Eq. (20) with a V⁻⁷ term added to it.

At supercritical temperatures (220K, 300K, 450K, and 600K), the EOS was fit to singlephase PVT data by linear least-squares fits, with B_0 , C_0 , and D_0 as adjustable parameters.

Figure 3-12 (a-c) show the results of the temperature dependence calculations for B_0 , C_0 , and D_0 respectively, carried out with the form of Eq. (20) with a V⁻⁷ term added to it. The plots are shown on reduced coordinates. In all of the figures, we see that the values take a sharp upward turn near the critical point, with the effect being most pronounced for parameter C_0 . It is likely that the turn is related to each term's contribution toward meeting the critical constraints of Eqs. (10) and (13), and if these constraints had not been enforced, we would expect a smoother variation through the critical region.

This forewarns of a difficulty associated with developing analytical functions to express the temperature dependence of the three EOS parameters: the unusual behavior near the critical point would clearly be difficult to fit with any reasonable function.

To preserve the critical conditions that were enforced at the critical point when the critical isotherm was fit—which means exactly reproducing critical values for the three parameters—we do so at the expense of accuracy near the critical point. At this point, the challenge was to develop simple functions that could still accurately reproduce saturation data when forced to match critical values of the three temperature-dependent parameters.



Figure 3-12(a) Temperature dependence of parameter B_0 in Eq. (20) modified to include V⁻⁷ term



Figure 3-12(b) Temperature dependence of parameter C_0 in Eq. (20) modified to include V^{-7} term



Figure 3-12(c) Temperature dependence of parameter D_0 in Eq. (20) modified to include V^{-7} term

3.3.3 <u>Temperature Function Development</u>

Section 3.3.2 described the procedure by which the required temperature dependence of the parameters in Eq. (21) was determined. For each parameter, the procedure resulted in a set of calculated data expressing the value of the parameter at discrete temperatures. To complete the equation of state, it was necessary to develop mathematical functions that would be capable of fitting the temperature dependence data, referred to herein as *temperature functions*.

As mentioned briefly in Section 3.3.2, the behavior of the EOS parameters in the vicinity of the critical point would be difficult to fit with an analytical function---there would necessarily be a tradeoff between achieving accuracy *near* the critical point, and predicting the critical point itself. It was decided that the temperature functions must reproduce the critical values of the parameters exactly, in order to reproduce the critical point and preserve the enforcement of the van der Waals critical conditions---both of which had been emphasized during initial EOS development.

The first types of temperature functions considered were based on *a priori* expressions for second and third virial coefficients. Since parameters B_0 and C_0 essentially correspond to second and third virial coefficients, it was thought that perhaps known empirical relations expressing these coefficients as functions of temperature could be adopted.

One well-known empirical expression for the second virial coefficient of polar and nonpolar gases is the corresponding-states correlation of Tsonopolous (1974). This correlation expresses the reduced second virial coefficient as a polynomial function of inverse reduced temperature. Tsonopolous gives numerical values for the coefficients, but in this work, the coefficients were taken as adjustable parameters.

A similar empirical corresponding-states correlation for third virial coefficients was proposed by Orbey and Vera (1983), and was written as a polynomial function of inverse reduced temperature. Again, it was assumed that the expression's coefficients could be considered adjustable.

Preliminary examination of these two forms revealed that each would contribute five adjustable constants to the EOS. This number was considered too high, and the idea of using *a priori* virial coefficient forms was abandoned in favor of finding simpler expressions.

One characteristic of the two virial coefficient expressions was retained for further study: the expansion of the virial coefficients in powers of *reciprocal* temperature, instead of the temperature directly. An initial screening quickly revealed that the curves expressing temperature dependence of the EOS parameters [Figs. 3-12 (a-c)] were fit better using polynomials in reciprocal temperature. This approach was therefore adopted in the search for temperature functions.

It was also realized that dividing the temperature-dependent EOS parameter values by various powers of temperature might be able to smooth the curves shown in Figs. 3-12 (a-c), making them easier to fit with simple expressions. Based on these considerations, the first temperature functions investigated were of the form:

$$\frac{K_{R}}{T_{R}^{x}} = k_{1} + \frac{k_{2}}{T_{R}^{y}} + \frac{k_{3}}{T_{R}^{2y}} + \frac{k_{4}}{T_{R}^{3y}} + \frac{k_{5}}{T_{R}^{4y}} + \dots$$
(24)

where K_R is the reduced EOS parameter at reduced temperature T_R , x and y are adjustable constants, and k_i is the *i*th polynomial coefficient of the temperature function. Candidate functions were screened by plotting (K_R/T_R^x) vs. T_R^y , and fitting various truncations of Eq. (24) to the plots using linear regression. Parameters x and y were varied manually to identify optimum values.

Initial screening led to selection of x = 0.8 and y = 1.5 for B₀, x = 6 and y = 6.5 for C₀, and x = 0 and y = 1 for D₀. For B₀ and D₀, Eq. (24) was truncated after the fourth term, whereas for C₀, it was truncated after the third term. The leading constant— k_1 —in Eq. (24) was expressed as $1-k_2-k_3-k_4-...$ to ensure that the critical values of the parameters were preserved at T_R = 1. These considerations led to initial expressions as follows:

$$B_{0}(T) = B_{0}^{crit} \left[(1 - b_{2} - b_{3} - b_{4}) T_{R}^{0.8} + \frac{b_{2}}{T_{R}^{0.7}} + \frac{b_{3}}{T_{R}^{2.2}} + \frac{b_{4}}{T_{R}^{3.7}} \right]$$
(25)

$$C_{0}(T) = C_{0}^{crit} \left[(1 - c_{2} - c_{3})T_{R}^{6} + \frac{c_{2}}{T_{R}^{0.5}} + \frac{c_{3}}{T_{R}^{7}} \right]$$
(26)

$$D_{0}(T) = D_{0}^{crit} \left[(1 - d_{2} - d_{3} - d_{4}) + \frac{d_{2}}{T_{R}} + \frac{d_{3}}{T_{R}^{2}} + \frac{d_{4}}{T_{R}^{3}} \right]$$
(27)

Initially, the values of the adjustable constants b_i , c_i , and d_i were determined by fitting Eq. (25)-(27) directly to the known values of B_0 , C_0 , and D_0 at discrete temperatures, as calculated by the method described later in Section 3.3.2.

Although Eq. (25)-(27) gave good fits, it was thought that the non-integer exponents in Eq. (25) & (26) might not apply well to other substances besides methane. For comparison, a second set of functions was devised for the three EOS parameters, setting parameter y = 1 in Eq. (24), and restricting parameter x to integer values only. It was found that truncating Eq. (24) after the fourth term on the right-hand side was sufficient for all three EOS parameters.

After several trials, a second set of expressions was devised, as follows:

$$B_{0}(T) = B_{0}^{crit} \left[(1 - b_{1} - b_{2} - b_{3})T_{R} + b_{1} + \frac{b_{2}}{T_{R}} + \frac{b_{3}}{T_{R}^{2}} \right]$$
(28)

$$C_{0}(T) = C_{0}^{crit} \left[(1 - c_{1} - c_{2} - c_{3} - c_{4})T_{R}^{2} + c_{1}T_{R} + c_{2} + \frac{c_{3}}{T_{R}} + \frac{c_{4}}{T_{R}^{2}} \right]$$
(29)

$$D_{0}(T) = D_{0}^{crit} \left[(1 - d_{1} - d_{2} - d_{3})T_{R} + d_{1} + \frac{d_{2}}{T_{R}} + \frac{d_{3}}{T_{R}^{2}} \right]$$
(30)

The same expression was used for parameters B_0 and D_0 , corresponding to setting x = 1 in Eq. (24). The expression for C_0 , Eq. (29), is similar to the other two, except that it has an additional term (the T_R^2 term) which results from setting x = 2 in Eq. (24).

Figures 3-13 to 3-15 show fits of both sets of expressions, represented by Eq. (25)-(27) and Eq. (28)-(30), to the calculated values of each of the three EOS parameters as functions of temperature. These fits were carried out by minimizing the sum of squares of errors directly, as opposed to the sum of squares of *percent* errors, because the program used for these regressions (Microsoft Excel 97) was not able to regress percent errors. Table 3-2 shows for each temperature-dependent parameter the error between the known (calculated) reduced parameter value and the value predicted using the fitted temperature functions. As the table and figures show, the second set of temperature functions produced a better fit to the temperature-dependent EOS parameters, particularly at subcritical temperatures. For this reason, and because of their greater simplicity and lower order, the second set of temperature functions represented by Eq. (28)-(30) was selected over the original set.

Parameter	Absolute Average Deviation	
	Set 1	Set 2
	[Eqs. (25)-(27)]	[Eqs. (28)-(30)]
B ₀	0.016	0.012
C ₀	0.037	0.023
D_0	0.055	0.026

 Table 3-2 Comparison of errors for two sets of temperature functions

To complete the comparison, a set of logarithmic expressions was briefly considered, having the general form

$$\ln\left(\frac{K_{R}}{T_{R}}\right) = k_{1} + \frac{k_{2}}{T_{R}} + \frac{k_{3}}{T_{R}^{2}} + \frac{k_{4}}{T_{R}^{3}} + \frac{k_{5}}{T_{R}^{4}} + \dots$$
(31)



Figure 3-13 Comparison of temperature functions for fitting $B_0(T)$ for methane



Figure 3-14 Comparison of temperature functions for fitting $C_0(T)$ for methane



Figure 3-15 Comparison of temperature functions for fitting $D_0(T)$ for methane

A version of this expression was applied to parameter C_0 , but it was found necessary to include terms up to and including the fourth power in inverse reduced temperature in order to fit as well as Eq. (29), and so Eq. (31) was dropped from further consideration. As well, a temperature function of the form

$$D_{0}(T) = D_{0}^{ent}[(1 - d_{1} - d_{2} - d_{3}) + d_{1}T_{R} + d_{2}T_{R}^{2} + d_{2}T_{R}^{3}]$$
(32)

was tried for parameter D_0 . It was found, however, that when this equation—along with best-fit values for d_1 , d_2 , and d_3 —was used in conjunction with Eq. (28) & (29) to predict saturation properties of methane, the resulting saturation specific volumes were less accurate than when Eq. (30) was used for D_0 . It was then decided that expressions such as Eq. (32), written in terms of reduced temperature directly rather than inverse reduced temperature, would not be considered further.

3.3.4 <u>Temperature Function Regression</u>

While the temperature functions were being developed, values of the temperaturefunction constants b_i , c_i , and d_i were determined by fitting the temperature functions to the calculated EOS parameters at several discrete temperatures. This was necessary in order to determine the forms of the temperature functions, but it is not the best way to obtain values for the temperature-function constants. Ultimately, we are more concerned with matching saturation pressures and specific volumes than with reproducing exact values of the EOS constants at individual temperatures—calculating the temperaturedependent values of EOS constants merely represents an intermediate step on the way to calculating fluid properties. As a result, true best-fit values of temperature-function constants are obtained only when errors between predicted and experimental saturation properties are minimized directly.

A regression program was developed to carry out this minimization. The objective function was defined as

$$S^{2} = \sum \left(\frac{P_{exp}^{sat} - P_{calc}^{sat}}{P_{exp}^{sat}}\right)_{i}^{2} + \sum \left(\frac{V_{exp}^{sat,vap} - V_{calc}^{sat,vap}}{V_{exp}^{sat,vap}}\right)_{i}^{2} + \sum \left(\frac{V_{exp}^{sat,liq} - V_{calc}^{sat,liq}}{V_{exp}^{sat,liq}}\right)_{i}^{2} + \sum \left(\frac{P_{exp}^{supercritical} - P_{calc}^{supercritical}}{P_{exp}^{supercritical}}\right)_{i}^{2}$$
(33)

where summations are carried out over all experimental (or smoothed) data points. Minimization of S^2 in Eq. (33) represents a non-linear least-squares regression problem, for which the Marquart-Levenberg algorithm was again employed. Evaluation of S^2 entails calculating saturation pressure, saturation specific volumes, and supercritical pressures at each data point. Other key parameters that must be calculated in the minimization routine are the derivatives of S^2 with respect to the regression variables—in this case, the temperature-function constants. These derivatives were calculated numerically using a forward difference approximation. Values of the constants obtained from regressing the temperature functions to the EOS parameters calculated at discrete temperatures were used as initial guesses for the direct regression to the fluid properties database. This procedure was carried out for methane, and allowed re-regression of the constants in previously published equations of state, to ensure a fair comparison with the new EOS.

3.3.5 Spurious Roots

Once the temperature functions describing the temperature dependence of the new equation's parameters were developed, the new EOS was fit to two other substances sulfur dioxide and n-pentane. While the EOS was being fit to n-pentane, it was found that the equation produced very large errors in calculated saturation properties for a few low-pressure points, but performed well otherwise. Further investigation revealed the cause: the EOS was generating spurious roots at low reduced temperatures. Instead of exhibiting three volume roots at sub-critical temperatures, the equation had five roots.

In itself, this does not present a problem, as long as the smallest volume root occurs within the specified tolerance of the experimental saturated liquid specific volume. The problem lies with the abrupt transition between the three-root and five-root conditions.
The additional roots do not just suddenly appear within the calculated saturation envelope, but rather begin as an inflection in the isotherm at pressures somewhat above the saturation pressure. The inflection represents a non-physical condition, but since the magnitude of the inflection is small at first, it does not actually contribute extra roots at the saturation pressure of interest. As the temperature is decreased, the magnitude of the inflection becomes larger and larger until finally, the bottom of the inflection intersects the saturation pressure, giving rise to two extra roots. Isotherms exhibiting these inflections are shown in Figure 3-16 (a,b) for Eq. (21). In Figure 3-16 (a), the inflections do not give rise to spurious volume roots at the vapour pressure until the temperature falls below approximately 433K. Figure 3-16 (b) provides a magnified view of the 433K isotherm, and clearly shows the spurious roots in relation to the actual physical roots.

This behavior presents two problems. First, within the range of temperatures between where the inflection in the isotherm first appears, and where the inflection actually intersects the saturation pressure, the calculated isotherm does not properly represent the true thermodynamic behavior of the fluid—multiple volume roots are not actually found along real fluid isotherms outside the two-phase region at pressures above the saturation pressure.

The second problem is that if the temperature functions are smooth and continuous across the temperature at which the sudden transition occurs between the three- and five-root conditions, the root representing the saturated liquid specific volume will not correspond to the lowest volume root, but rather to the third-lowest root. As such, the new roots are spurious and not physically possible.



Figure 3-16 (a) Spurious inflections in sub-critical isotherms of n-pentane with Eq. (21)



Figure 3-16 (b) Spurious roots along 433 K isotherm of n-pentane with Eq. (21)

It is conceivable that a set of values could be chosen for the temperature-dependent EOS parameters so that the lowest volume root *does* correspond to the experimental saturated liquid volume, but this would likely result in discontinuities in the temperature functions. And even if such discontinuities were acceptable, this would not eliminate the problem of inflections in the isotherm above the saturation pressure.

At this point, it was decided that the new EOS should be modified to prevent spurious root formation. These roots form because the large negative contributions to pressure from some polynomial terms in the EOS briefly dominate the calculated pressure, until the specific volume becomes low enough for the V^{-7} term—which has a positive-valued coefficient—to cancel this negative contribution and again introduce the proper slope.

The first approach to eliminating the spurious roots was therefore to increase the value of the coefficient of the V⁻⁷ term at the temperatures where the inflections would normally occur. This would compensate for the increasing negative contributions of the V⁻⁶ term with decreasing temperature, thus avoiding the formation of isotherm inflections and spurious roots altogether. Since adding new parameters to the EOS was undesirable, it was decided that the temperature dependence of the V⁻⁷ term would be represented simply by dividing the term by the reduced temperature raised to an unspecified power *n*:

$$E_0(T) = \frac{E_0^{cm}}{T_R^a}$$
(34)

The value of the exponent would then be determined by trial and error as the minimum value required to eliminate inflections in the isotherm. This type of temperature

dependence is similar to that found for the V^{-5} term in the Soave-BWR equation, and for the exponential term in the BWRS equation. For n-pentane, it was found that a value of n=2 was sufficient in Eq. (34) to eliminate spurious roots. This created a new problem, however: for both methane and n-pentane, the average absolute deviations in the calculated saturation properties were now higher than both the BWRS and Soave-BWR equations. Since this would eliminate the new EOS as a candidate for further development, other solutions were sought.

The next solution that was investigated was to incorporate a van der Waals-type covolume into the equation. It was thought that if the EOS had a vertical asymptote at a volume somewhat greater than zero, the spurious roots would not be as likely to form. Versions of the new EOS with covolumes and hard-sphere terms were already investigated and described in Section 3.2.4. It was decided that the version having a covolume in only the first term would be considered. Of the three equations examined in Section 3.2.4, Eq. (22a) did not produce the best fit to the critical isotherm of the test substance, methane. However, the other equations were ruled out for two reasons:

- Eq. (22a) is mathematically simpler than the hard-sphere version [Eq. 22c].
- The best-fit value of the covolume parameter in Eq. (22b)—which incorporates the covolume into the denominator of each polynomial term—is an order of magnitude lower than that of Eq. (22a). With the vertical asymptote occurring at such a small specific volume, it is unlikely that using Eq. (22b) would overcome the spurious root problem at all.

In any case, it was shown in Section 3.2.4 that incorporating a covolume even in the first term improved the fit of the critical isotherm for methane. And using a covolume instead of allowing the V^{-7} term to vary with temperature has the benefit of adding only one extra parameter to the EOS—one that is temperature independent, physically sensible, and easily generalizable.

For the investigation, values of the EOS parameters were determined by fitting the EOS to saturation data and supercritical PVT data by the same procedure used originally for Eq. (21), described in Section 3.3.4. The temperature functions were not modified—the forms remained as written in Eqs. (28)-(30).

Subcritical isotherms of n-pentane, calculated using the temperature-dependent form of Eq. (22a), were examined. It was found that with the covolume parameter, spurious roots and other isotherm inflections do not occur within the range of the data used in this work. At this point, the form of the new EOS was finalized, using Eq. (22a) to express the equation's volume dependence, and Eqs. (28)-(30) to express its temperature dependence.

It is important to note that although incorporating a covolume into the first term of the EOS prevented spurious roots from forming in the three substances investigated here, this solution may not work for all substances. In particular, during regression of the EOS to pure-substance critical isotherms, the best-fit covolumes for some substances—water and CO_2 —tended toward negative values. Since negative covolumes have no physical meaning, the regressions were repeated, this time limiting the covolume to positive

values. In both cases, the best-fit value tended toward zero, and this may expose these substances to spurious root problems.

It is also worth mentioning that a second unrelated cause of spurious roots was discovered as well. In the regression procedure for determining values for the EOS parameters, the equation is fit not only to saturation data, but to PVT data at supercritical temperatures as well. The supercritical PVT data was included to ensure that the EOS would perform well as supercritical temperatures. It was found, however, that when the regression was carried out *without* the supercritical PVT data, the EOS performed poorly at supercritical temperatures—so poorly that spurious inflections appeared along the liquid-like portions of the isotherms. These inflections were severe enough to give rise to multiple volume roots, which in reality do not exist at supercritical temperatures. When the supercritical PVT data was included in the regression, no such inflections appeared.

3.4 Thermodynamic Properties from the New EOS

The most important use of an equation of state is to calculate fluid thermodynamic properties. Expressions for these properties as functions of temperature and specific volume can be derived using fundamental thermodynamic relations between properties—fugacity, enthalpy, or entropy, for example—and state variables: pressure, temperature, and specific volume. The problem with these fundamental relations, however, is that they are normally expressed in terms of integrals and derivatives of state variables. The EOS provides an analytical relationship between pressure, temperature, and specific

volume, which allows us to derive direct functional expressions for thermodynamic properties from the fundamental relations.

Like any equation of state, the new EOS [Eq. (22a) and Eqs. (28)-(30)] can be used to derive expressions for thermodynamic properties. And because these expressions are derived using a unique PVT relationship (the EOS), the expressions for the properties are unique to that EOS. In the present work, expressions were derived for two thermodynamic properties: *fugacity*, required to calculate vapour pressures to determine the temperature dependence of EOS parameters, and *enthalpy*, used to assess the adequacy of the temperature dependence of the new EOS's parameters.

3.4.1 Fugacity

Pure-component fugacity is obtained using the following fundamental thermodyamic relation:

$$\ln \phi = Z - 1 - \ln Z - \frac{1}{RT} \int_{\pi}^{V} (P - \frac{RT}{V}) dV$$
 (35)

from which the pure-component fugacity expression for the new EOS can be written:

$$\ln\phi = \frac{b}{V-b} + \frac{2B_{o}}{RTV} + \frac{3C_{o}}{2RTV^{2}} + \frac{6D_{o}}{5RTV^{5}} + \frac{7E_{o}}{6RTV^{6}} + \left(\frac{G_{o}V-1}{G_{o}RT}\right)F_{o}\exp(G_{o}V) - \ln(\frac{V-b}{V}) - \ln Z$$
(36)

where ϕ is the fugacity coefficient, defined as f/P, and Z is the compressibility factor.

3.4.2 Enthalpy Residual

Enthalpy residual—the deviation of a real fluid's enthalpy from the corresponding ideal gas value—can be derived from the following fundamental relation:

$$H^{res} = H^{ideal} - H = RT - PV + \int_{\infty}^{V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_{V} \right] dV$$
(37)

leading to the enthalpy departure expression for the new EOS, which, after algebraic rearrangement, is written as

$$H^{res} = -\frac{R T b}{V - b} - \frac{(B_0 + \beta)}{V} - \frac{(C_0 + \gamma)}{2V^2} - \frac{(D_0 + \delta)}{5V^5} - \frac{7E_0}{6V^6} + \frac{(1 - G_0 V)}{G_0} F_0 \exp(G_0 V)$$
(38)

$$\beta = B_0^{crit} \left[b_1 + \frac{2b_2}{T_R} + \frac{3b_3}{T_R^2} \right]$$
(39a)

$$\gamma = C_0^{crit} \left[c_1 T_R + 2c_2 + \frac{3c_3}{T_R} + \frac{4c_4}{T_R^2} \right]$$
(39b)

$$\delta = D_0^{\text{crit}} \left[4 \left(1 - d_1 - d_2 - d_3 \right) T_R + 5 d_1 + \frac{6 d_2}{T_R} + \frac{7 d_3}{T_R^2} \right]$$
(39c)

In these equations, H^{res} is the enthalpy residual, H^{ideal} is the ideal gas enthalpy at the temperature of interest, and H is the actual enthalpy of the fluid at the temperature and pressure of interest.

The enthalpy of vaporization at a given saturation temperature can then be calculated as the difference between the saturated-liquid and saturated-vapour enthalpy residuals at that temperature:

$$\Delta H_{v} = (H_{sat}^{res})_{vapour} - (H_{sat}^{res})_{liquid}$$
(40)

To compare the new EOS with previously published equations, several different thermodynamic quantities were calculated for a number of substances. The new equation was compared to both Starling's version of the BWR equation (BWRS: Starling, 1973), and Soave's modification (SBWR: Soave, 1995).

The BWRS equation used here was modified slightly: in Starling's original version, two of the parameters used to express the temperature dependence of the parameter C in Eq. (2) are also used to express the temperature dependence of the coefficient D, as follows:

$$C = bRT - a - \frac{d}{T}$$
(41a)

$$D = \alpha \left(a + \frac{d}{T}\right) \tag{41b}$$

The effect of this constraint is that these two parameters are not independent of one another. In the Soave BWR equation, however, these parameters *are* independent. Since one of the goals of this work was to identify the best functional form for fitting purecomponent critical isotherms and saturation properties, it was decided that the comparison would be more reliable if parameters C and D were independent of one another in the BWRS equation, rather than being constrained to vary together in a seemingly arbitrary way. This move makes the BWRS equation slightly more flexible, and ensures that any deficiencies in its performance compared to the other two EOS cannot be attributed to an explicit dependence between C and D.

Starling's expressions for the temperature functions were also rearranged to force reproduction of the critical values obtained from regression of the critical isotherm. This ensures that the critical point is reproduced exactly, and that the van der Waals conditions [Eq. (10a,b)] are preserved at the critical point. The temperature functions used for the modified BWRS equation were as follows:

$$B(T) = B^{crit} \left[(1 - b_1 - b_2 - b_3 - b_4) T_R + b_1 + \frac{b_2}{T_R^2} + \frac{b_3}{T_R^3} + \frac{b_4}{T_R^4} \right]$$
(42a)

$$C(T) = C^{crit} \left[(1 - c_1 - c_2)T_R + c_1 + \frac{c_2}{T_R} \right]$$
(42b)

$$D(T) = D^{crit} \left[1 - d_1 + \frac{d_1}{T_R} \right]$$
(42c)

$$E(T) = \frac{E^{cnt}}{T_{R}^{2}}$$
(42d)

4.1 Pure-Component Critical Isotherms

The new EOS [Eq. (22a), Eqs. (28)-(30)], and the two BWR modifications were fit to the critical isotherms of seven substances—methane (Angus et al., 1976a), propane

(Goodwin and Haynes, 1982), n-pentane (Canjar and Manning, 1967), hydrogen (McCarty et al., 1981), carbon dioxide (Angus et al., 1976b), sulfur dioxide (Kang et al., 1961), and water (Keenan et al., 1978)—in order to compare average and maximum absolute deviations in both pressure and volume from smoothed data or experimental data. The three critical conditions, represented by Eq. (10) and (13), were enforced in the fitting procedure. Figures 4-1(a,b) through 4-7(a,b) show errors in pressure and specific volume along the critical isotherms of the seven substances of interest. Table 4-1 shows the results of the comparisons in terms of average and maximum deviations.

Comparing Average Absolute Percent Deviations (%AAD) in Table 4-1, we see that for pressure, the new EOS has the lowest values overall, while for specific volume, the SBWR equation has the lowest overall values. For specific volume, the SBWR equation is followed very closely by the new EOS. For BWRS, the overall %AADs—averaged over all seven substances—were higher than those of both SBWR and the new EOS. For all three equations, average values of %AAD were less than 1 percent in both pressure and specific volume.

The new EOS had the lowest overall Maximum Absolute Percent Deviation (%MAD) for pressure, while SBWR had the highest. For specific volume, the new EOS's value was also lowest, followed by SBWR. For both pressure and specific volume, the new EOS had lower %MAD values than the BWRS equation. Maximum deviations tended to occur in the immediate vicinity of the critical point.



Figure 4-1 (a) Comparison of errors in pressure along C₁ critical isotherm for new EOS and modified BWR equations



Figure 4-1 (b) Comparison of errors in specific volume along C₁ critical isotherm for new EOS and modified BWR equations



Figure 4-2 (a) Comparison of errors in pressure along C₃ critical isotherm for new EOS and modified BWR equations



Figure 4-2 (b) Comparison of errors in specific volume along C₃ critical isotherm for new EOS and modified BWR equations



Figure 4-3 (a) Comparison of errors in pressure along n-C₅ critical isotherm for new EOS and modified BWR equations



Figure 4-3 (b) Comparison of errors in specific volume along n-C₅ critical isotherm for new EOS and modified BWR equations



Figure 4-4 (a) Comparison of errors in pressure along H₂ critical isotherm for new EOS and modified BWR equations



Figure 4-4 (b) Comparison of errors in specific volume along H₂ critical isotherm for new EOS and modified BWR equations



Figure 4-5 (a) Comparison of errors in pressure along CO₂ critical isotherm for new EOS and modified BWR equations



Figure 4-5 (b) Comparison of errors in specific volume along CO₂ critical isotherm for new EOS and modified BWR equations



Figure 4-6 (a) Comparison of errors in pressure along SO₂ critical isotherm for new EOS and modified BWR equations



Figure 4-6 (b) Comparison of errors in specific volume along SO₂ critical isotherm for new EOS and modified BWR equations



Figure 4-7 (a) Comparison of errors in pressure along H₂O critical isotherm for new EOS and modified BWR equations



Figure 4-7 (b) Comparison of errors in specific volume along H₂O critical isotherm for new EOS and modified BWR equations

Substance	EOS	Pressure		Volume		
		%AAD	%MAD	%AAD	%MAD	
Methane	New EOS	0.384	1.494	0.357	2.775	
	BWRS	0.441	1.306	0.386	3.116	
	Soave-BWR	0.948	3.813	0.314	1.359	
Propane	New EOS	0.345	0.972	0.276	1.326	
	BWRS	0.427	1.373	0.513	3.767	
	Soave-BWR	0.302	0.843	0.248	1.679	
n-Pentane	New EOS	0.651	4.527	0.330	1.088	
	BWRS	0.786	5.061	0.637	3.365	
	Soave-BWR	0.652	4.858	0.393	1.567	
H2	New EOS	0.499	1.475	0.478	2.655	
	BWRS	1.357	4.411	0.836	3.769	
	Soave-BWR	0.708	2.022	0.516	2.653	
CO2	New EOS	0.870	6.830	0.442	4.775	
	BWRS	0.665	7.093	0.498	6.028	
	Soave-BWR	0.582	7.574	0.376	6.417	
SO2	New EOS	1.054	7.525	0.344	1.800	
	BWRS	1.135	7.515	0.576	2.511	
	Soave-BWR	1.057	7.773	0.408	1.898	
Water	New EOS	0.711	2.400	0.630	7.014	
	BWRS	0.409	2.933	0.519	7.127	
	Soave-BWR	0.415	2.923	0.519	7.018	
Average	New EOS	0.645	3.603	0.408	3.062	
	BWRS	0.746	4.242	0.566	4.241	
	Soave-BWR	0.666	4.258	0.396	3.227	

 Table 4-1
 Comparison of errors between predicted and experimental pressures and specific volumes along pure substance critical isotherms

For all three equations, the largest maximum deviations (%MAD) in pressure occurred for CO_2 and SO_2 , while the largest %MAD in specific volume occurred for water.

4.2 Saturation Properties

Using the new EOS and the two BWR modifications, saturation properties were calculated for three substances: methane (Angus et al., 1976a), n-pentane (Canjar and Manning, 1967), and sulfur dioxide (Kang et al., 1961), chosen respectively to represent

light hydrocarbons, intermediate-weight hydrocarbons, and polar substances. Selected saturation properties were saturation pressure, saturated vapour specific volume, and saturated liquid specific volume. The adjustable parameters of each EOS were determined using the least-squares procedure described in Section 3.3.4. Table 4-2 shows average and maximum deviations from data for the three equations.

Table 4-2Comparison of errors between predicted and smoothed
experimental saturation properties of methane, n-pentane,
and sulfur dioxide

Substance	EOS	Saturation		Specific Volume			
		Pressure		Saturated Liquid		Saturated Vapour	
		AAD%	MAD%	AAD%	MAD%	AAD%	MAD%
Methane	New EOS (Eq. 22a)	0.13	0.27	0.17	2.67	0.32	4.03
	BWRS	0.17	0.38	0.34	3.76	0.39	5.20
	Soave-BWR	0.02	0.08	0.36	3.31	0.24	3.22
n-Pentane	New EOS (Eq. 22a)	1.14	3.09	1.08	2.66	1.70	10.83
	BWRS	1.13	3.70	0.70	1.47	1.79	6.63
	Soave-BWR	0.33	0.56	0.19	0.81	0.56	4.90
Sulfur	New EOS (Eq. 22a)	0.27	0.68	0.89	2.29	1.89	8.14
Dioxide	BWRS	4.57	8.47	1.97	3.50	6.36	11.85
	Soave-BWR	0.43	1.33	0.31	1.02	0.62	1.23

For all three substances, the Soave BWR equation gave the best overall fits. In terms of average deviations, the new EOS generally performed better than the BWRS equation, with the exception of the saturation pressure and saturated liquid volume for n-Pentane. For maximum deviations, the new EOS performed better than BWRS as well, except for the saturated liquid and vapour specific volumes for n-Pentane. The only two cases where the new EOS performed better than the Soave BWR equation were for the saturated liquid volume of methane and the saturation pressure of sulfur dioxide—both average and maximum deviations.

Figures 4-8 to 4-16 show percent error as functions of temperature for saturation pressure, and saturated liquid and vapour specific volumes, for the three substances of interest.

Generally, the deviations in saturation pressure for all equations and substances (Figures 4-8 to 4-10) tend to oscillate smoothly between positive (overprediction) and negative (underprediction) errors, the difference between equations being the magnitude of the oscillation peaks.



Figure 4-8 Error in saturation pressure for methane



Figure 4-9 Error in saturation pressure for n-pentane



Figure 4-10 Error in saturation pressure for SO₂



Figure 4-11 Error in liquid specific volume for methane



Figure 4-12 Error in saturated liquid specific volume for n-pentane



Figure 4-13 Error in saturated liquid specific volume for SO₂



Figure 4-14 Error in saturated vapour specific volume for methane



Figure 4-15 Error in saturated vapour specific volume for n-pentane



Figure 4-16 Error in saturated vapour specific volume for SO₂

Deviations for saturation specific volumes are generally not as regular. As shown in Figures 4-11 to 4-15, the error curves for both saturated liquid and vapour specific volumes exhibit sharp peaks at subcritical temperatures immediately below the critical point. For most equations and substances, the maximum deviations over the range of reduced temperatures considered occurred at these peaks, with the exception of the BWRS equation for SO₂. At subcritical temperatures away from the near-critical peaks, the deviations tended to oscillate between positive and negative values.

4.3 Single-Phase PVT

Pressures along supercritical isotherms were calculated for three substances—methane, sulfur dioxide, and n-pentane—using the new EOS and the two BWR modifications, and were compared to smoothed and experimental data for those substances. Table 4-3 shows the results of the comparisons.

Table 4-3 Comparison of errors between predicted and experimental
pressures along supercritical isotherms of methane, pentane,
and sulfur dioxide

Substance	Max Tr	Max Pr	New EOS (Eq. 22a)		BWRS		Soave-BWR	
			AAD%	MAD%	AAD%	MAD%	AAD%	MAD%
Methane	2.36	152	4.26	26.11	1.29	5.28	0.57	5.13
n-Pentane	1.73	7.15	2.00	14.98	1.12	8.81	4.31	15.60
Sulfur Dioxide	1.21	4.05	0.56	3.21	4.10	28.43	4.96	18.37

The table shows that in terms of both average and maximum absolute deviations, the new EOS performs better than the Soave BWR equation for two of the three substances (sulfur dioxide and n-pentane), but performs better than the BWRS equation for only one

of the three substances (sulfur dioxide). The maximum errors tended to occur on the steep liquid-like portions of the isotherms, and at high pressures.

4.4 Enthalpy of Vaporization

The enthalpy of vaporization was calculated for methane using the new equation as well as the two modified BWR equations. Table 4-4 shows the average and maximum absolute errors between calculated values and smoothed data for the three EOS. While the Soave BWR equation had the lowest average deviation, the AAD for new EOS was very close behind. The AAD for the BWRS equation was somewhat higher than for the other two equations, but the AAD for all three equations was small compared with the average magnitude of the vaporization enthalpy. The new EOS had the lowest maximum deviation, with the Soave BWR equation close behind. The MAD for the BWRS equation was considerably higher than for the other two equations.

EOS	Vaporization Enthalpy			
	AAD (J/mol)	MAD (J/mol		
New	20.0	176.5		
BWRS	24.8	242.6		
Soave BWR	15.2	1 82.8		

 Table 4-4
 Error in vaporization enthalpy for methane

Figure 4-17 shows the error between calculated vaporization enthalpy and smoothed data as a function of reduced temperature for methane. For all three EOS, the error oscillates between positive and negative values for the full range of temperatures, except near the critical point. The maximum errors occurred in the immediate vicinity of the critical point, where all three EOS tended to underpredict the vaporization enthalpy.



Figure 4-17 Error in vaporization enthalpy of methane

4.6 Comparing Exponential Terms

Upon first inspection, the new EOS may appear similar to the BWR equation—both are essentially polynomial expansions in specific volume added to an exponential term. This similarity is superficial, however, because the exponential term in the new equation serves a different purpose than the one in the BWR equation and its modifications.

Figure 4-18 shows the contributions to calculated pressure of the exponential terms for three equations—the new EOS [Eq. (22a)], the BWRS equation, and the Soave BWR equation—as functions of reduced volume along the critical isotherm of methane. The critical isotherm is superimposed on the figure to show the relative magnitude of each exponential term compared to the actual pressure that the EOS must predict.



Figure 4-18 Comparison of EOS exponential terms along methane critical isotherm

The figure shows that in the two BWR modifications, the exponential term makes its most significant contribution near the critical point, and in the liquid-like part of the nearcritical region. For the BWRS equation, the exponential term contributes 95.3 percent of the calculated critical pressure, meaning that the remaining terms make only a minor positive contribution equal to 4.7 percent of the computed value. For the Soave-BWR equation, the exponential term makes an even larger contribution at the critical point, equal to 154.2 percent of the calculated pressure. This means that the sum of the remaining terms in the equation make a *negative* contribution equal to -54.2 percent of the calculated value.

As specific volume is decreased below the critical value, the exponential terms in these two equations rise to reach a maximum, and then fall off again as the critical isotherm becomes steeper. This maximum occurs at a reduced volume of approximately 0.58 for methane.

By contrast, the exponential term in the new EOS makes almost no contribution at specific volumes equal to or greater than the critical volume, and does not start making a significant contribution to the pressure calculated by the EOS until the reduced volume falls below approximately 0.75. Below this value, the exponential term increases rapidly, reaching a value equal to 100 percent of the calculated pressure at a reduced volume of 0.47. In this way, the purpose of the exponential term is to improve the equation's fit along the steep liquid-like branch of the isotherm. This is quite unlike the role played by the exponential term in the modified BWR equations, where it contributes little to the calculated pressure along this portion of the isotherm.

5.0 DISCUSSION

For a new EOS to be useful, it must have some redeeming feature that makes it preferable to use over other established equations. No comparison of equations of state would be complete without considering how they perform for fluid mixtures—by far the most common EOS application. But if a new EOS does not clearly show some improvement over established equations for predicting the properties of pure components, then there is no point developing it further to apply to mixtures. It would instead be better to focus on improving the generalizations or the mixing rules for existing equations. For this reason, the first stage in developing a new empirical EOS should center exclusively on fitting pure component properties. This was the focus of the present work.

Developing a new EOS that performs better than existing equations is more difficult than it may seem. The difficulty is that while the EOS itself is written in terms of pressure, volume, and temperature, it must also make accurate predictions of thermodynamic properties when fundamental thermodynamic relations are applied to it. And considering the number of different properties that the EOS must be able to predict over a wide range of pressure and temperature—including the region near the critical point—it is not hard to understand why this is difficult even for a non-cubic EOS with 10 or more parameters. But the greater the number of parameters in the EOS, the more difficult it will be to develop generalized correlations and mixing rules for the equation. The result is that a new non-cubic EOS must strike a balance between accuracy—which generally tends to increase the number of parameters—and ease of application to mixtures, for which fewer parameters is better. In the present work, an attempt has been made to identify the non-cubic EOS form that best strikes this balance, with the intention of selecting one form—either the new EOS or an existing BWR modification—for further development for application to fluid mixtures. And while the new EOS clearly showed improvements in some areas over two modified BWR equations that were selected for comparison, the results of the comparisons did not point unambiguously toward any one of the three equations. A discussion of the relative merits and drawbacks of the new EOS follows herein, in terms of the major stages of its development.

5.1 Fitting the Critical Isotherm

Establishing density dependence by fitting the critical isotherm of a pure component is perhaps the greatest challenge in developing a non-cubic equation of state. And by far the most difficult aspect of this challenge is obtaining good fits in the near-critical region while observing critical constraints—matching the critical pressure and setting first and second volume derivatives to zero at $T=T_c$ and $V=V_c$. The degree of success here affects not only the calculation of density at $T=T_c$, but also affects the equation's fit to saturation and thermodynamic property data at subcritical temperatures near the critical point.

This work has shown that for a good fit to the critical isotherm, it is first necessary that the regressed value of the coefficient of the V^{-2} term provide a good prediction of the second virial coefficient at the critical temperature. A sensitivity analysis showed (Figures 3-11(a-f)) that in the vapour-like region along the critical isotherm of methane, only the V^{-2} makes a significant contribution to the predicted pressure. It follows, then, that errors in pressure and specific volume along the vapour-like region of the critical isotherm—especially in the region leading up to the critical point—are largely due to discrepancies between the best-fit value of the V^{-2} term's coefficient (B₀) and the fluid's *actual* second virial coefficient. Conversely, we would expect that the closer the best-fit value is to the actual second virial coefficient, the lower would be the error along the vapour-like portion of the isotherm. This was verified for methane in Section 3.2.5, as shown in Figure 3-9. In this case, where the value of B₀ in Eq. (21) was set equal to BRT (where B is the second virial coefficient of methane, calculated using the Tsonopolous (1974) correlation), the maximum error in pressure along this part of the critical isotherm was 0.25%. This value is lower than the maximum errors in the same region for the new EOS (1.2%) and the two BWR modifications (BWRS: 1.3%; SBWR: 0.5%), all of whose best-fit values of B₀ deviated from the "correct" value. And for these three equations, the larger the deviation from BRT, the higher was the error in the calculated pressure.

By contrast to the vapour-like region, *four* of the seven parameters in the new EOS contribute significantly to the calculated critical pressure: b, B_0 , C_0 , and to a lesser extent D_0 . And all parameters make significant contributions in the liquid-like region. As a consequence, the terms that do not contribute at critical and vapour-like volumes—the exponential term, and the V⁻⁷ term—have to be flexible in the liquid-like region. Otherwise, the coefficients of the remaining terms will be forced to take on values that compromise accuracy in the vapour-like and near-critical regions, where only they contribute. For example, if the accuracy of the equation's fit in the liquid-like region requires the coefficient B_0 to take on a value different from BRT, then accuracy in the

vapour-like region will suffer. If, however, the exponential and higher-order terms are flexible and can accommodate a wide range of B_0 values while still maintaining the same accuracy in the liquid-like region, the B_0 term will be less important here, and B_0 will tend toward the value that improves accuracy in the vapour-like region—a region where accuracy depends solely on the value of B_0 , since it's the only term that contributes there.

With these considerations in mind, it can be seen from Figures 4-1(a,b) to 4-7(a,b) that the new EOS achieves a good balance between accuracy in the vapour-like, near-critical, and liquid-like regions of pure-component critical isotherms. It gave lower average errors in pressure than the BWRS equation for five of the seven substances, and lower average errors in specific volume for six of the substances. It also gave lower average errors in both pressure and specific volume than the Soave-BWR equation for three of the seven substances. The figures show in most cases that improving the fits in the vapourlike regions of the isotherms, especially near the critical point, would likely make the largest reductions in the overall average errors. And as described above, such improvements would only come from improving the EOS's prediction of the second virial coefficient at $T=T_c$.

One way to achieve this might be to reconsider forcing the coefficient B_0 to take on the correct value corresponding to the substance's second virial coefficient at $T=T_c$. Although this approach was tried briefly for the new EOS, and gave poor results in the liquid-like region of methane (Figure 3-9), this was likely because the exponential term—which was essentially an attempt to fit the error between the smoothed experimental data and the sum of the low-degree polynomial terms in the EOS—was not specifically

designed for this case. It is quite possible that this problem could be overcome, and overall errors in pressure and volume could be reduced along the critical isotherm, by modifying the form of the exponential term slightly—perhaps by re-including some higher-order volume terms that were dropped after performing a sensitivity analysis.

The regression procedure used to fit the critical isotherms yielded the variancecovariance matrix for the parameters being regressed. Normalizing this matrix gives the *correlation matrix*, which indicates the strength of the cross correlation between the regressed parameters. In some cases, examination of these cross correlations can be useful—even preferable to the sensitivity analysis performed here—for determining whether an equation has more parameters than it needs to fit the data. However, in this work, even though the correlation matrix was examined, the sensitivity analysis was preferred for three reasons:

- The sensitivity analysis showed the range of reduced volume where each parameter makes its most significant contribution to the calculated pressure. This cannot be ascertained from the correlation matrix.
- The sensitivity analysis can yield information about all parameters in the equation, including those whose values are fixed by the critical constraints. The correlation matrix only shows cross correlation between the regressed parameters.
- Examination of the correlation matrix showed strong cross correlations (greater than 0.9) between the regressed parameters in Eq. (22a)—b, E₀, F₀, and G₀. But this is not unexpected, since these parameters all make their most significant
contributions over a similar range of volumes—the liquid-like portion of the critical isotherm. And each of these parameters was included in the EOS for a specific reason: b to avoid spurious volume roots, E_0 to avoid the "turn-around" problem at high densities, and F_0 and G_0 as the minimum number of terms required inside the exponential to fit the observed behavior. For this reason, even strong cross correlation does not indicate overparameterization of the EOS in this case.

5.2 The Covolume Parameter

As detailed in Section 3.3.5, a van der Waals-type covolume was adopted in the first term of the new EOS to solve the problem of spurious root formation, at least for the three substances examined. Prior to being included in the equation on these grounds, the covolume had been examined as one of three alternatives for representing repulsive intermolecular forces within the equation. It was shown that incorporating a covolume into the first term not only solved the spurious root problem, but also improved the equation's fit to the critical isotherm of methane.

Part of the appeal of adding a covolume to the equation is that without some representation of repulsive forces, the EOS has a zero volume at infinite pressure. Although the new EOS is empirical, and it could perhaps be argued that its behavior at extremely high pressures is unimportant, it seems that some kind of non-zero density limit, however approximate, improves the equation's credibility as a model of fluid behavior.

It can also be seen from Figures 3-7 and 3-8 that incorporating a hard-sphere term [Eq. (9)] instead of a simple van der Waals term, would make very little difference to the quality of the fit to the critical isotherm. In fact, while the %AAD in specific volume for the hard-sphere version of the new EOS [Eq. (22c)] was slightly less than for the first-term covolume version [Eq. (22a)], the %AAD in pressure was slightly higher. Unless a simple repulsive term was developed that had a strong theoretical basis, and showed significant improvements toward fitting pure-component critical isotherms, there is no reason at the moment to adopt a more complicated expression than the simple van der Waals term.

5.3 Temperature Dependence

The procedure used here for developing functions to represent the temperature dependence of the EOS parameters is relatively straightforward: calculate values of three EOS parameters at several sub-critical temperatures by forcing the EOS to match saturation pressure and saturated liquid and vapour specific volumes; at supercritical temperatures, fit the EOS to PV data along individual isotherms making only the chosen three EOS parameters adjustable; then, by trial and error, develop algebraic functions that fit the calculated values of the EOS parameters as functions of temperature.

While the process itself may seem simple, the problem is actually trying to fit the calculated curves of the EOS parameters as functions of temperature. The difficulty arises because of the unusual shape these curves take on near the critical point, as shown in Figures 3-12(a-c). The figures show that the EOS parameters turn upward suddenly as

temperature is increased from subcritical values. This behavior is apparently limited to the near-critical region only, since the parameter values shown in the figures at supercritical temperatures appear to line up smoothly with the values at subcritical temperatures away from the critical point. The difficulty this behavior creates is that in order to preserve the exact prediction of the critical point and enforcement of van der Waals conditions, any temperature function used to fit the curves in Figures 3-12(a-c) must pass through the value at the critical temperature. And as shown in Figure 5-1, a magnification of Figure 3-12(b) near the critical temperature, passing through this point comes at the expense of accuracy in the near-critical region.



Figure 5-1 Expanded view of the fit of Eq. (29) to calculated values of $C_0(T)$ near the critical temperature for methane

Regardless of the form of the temperature functions used to fit these curves, the same problem will arise, unless the basic EOS is altered in some way to reduce or eliminate the anomalous near-critical behavior of the EOS parameters. One way may be to let more than three EOS parameters vary with temperature. Another way may be to incorporate an extra term into Eq. (22a) that becomes active only at the critical point and in its immediate vicinity. In theory, such a term could relieve some of the burden on parameters B_0 , C_0 , and D_0 that now arises from forcing the EOS to match the critical point and meet critical conditions. If in doing so, a near-critical term could smooth out the curves shown in Figures 3-12(a-c) and 5-1, it would be much easier to fit the temperature dependence of the EOS parameters, perhaps with simpler functions requiring fewer parameters. We would consequently expect an improvement in prediction of properties such as saturated liquid and vapour specific volumes, and enthalpy, near the critical point.

5.4 Further Development

In absolute terms, the new EOS fits pure-component properties very well. Its performance is comparable to and often better than established non-cubic EOS such as the BWRS equation and the Soave-BWR equation. However, on average, the Soave-BWR equation fits pure-component properties better than the new equation. As well, the new EOS has 17 parameters in total, including the covolume—five more than the modified BWRS equation used here, and four more than the Soave-BWR equation.

Despite these concerns, the new EOS shows enough promise to warrant further development. This development should focus on three areas:

- Improving the prediction of the second virial coefficient at the critical temperature, perhaps by forcing the EOS to take on the correct value.
- Improving the equation's fit near the critical point, possibly by adding a term that becomes active only in the vicinity of the critical point.
- Reducing the number of parameters used to express temperature dependence of the EOS parameters.

Improvements in these areas would make the new EOS an excellent candidate for generalization and extension to fluid mixtures. It must be considered, however, that with a non-cubic equation of state, the adjustable parameters may be strongly correlated. Such cross correlation can lead to non-unique regressed values for the parameters, making it difficult to develop generalizations and mixing rules. In this regard, the recommendations described above—improving prediction of critical second virial coefficients, and reducing the number of adjustable parameters—may help to make generalization easier.

6.0 CONCLUSIONS

From this work, the following conclusions can be drawn:

- 1. The method used to develop the new non-cubic EOS—adding a low-degree polynomial reference term to an exponential term to fit the error between the reference term and experimental (or smoothed) PV data along a pure-component critical isotherm—works well for fitting critical isotherms accurately.
- 2. When a low-degree polynomial reference term is fit to the vapour-like portion of a pure-component critical isotherm including the critical point, the error along the isotherm between the data and the reference term is confined to the liquid-like region of the isotherm. If the error is then plotted on semilogarithmic coordinates (Y-axis on log scale) as a function of specific volume, the resulting curve is closely approximated by a straight line, meaning that a linear function of volume can be placed inside the exponential error term.
- 3. The Levenberg-Marquart method of non-linear regression provides an efficient means of fitting a non-cubic EOS containing non-linear terms to a pure-component critical isotherm. This applies not only to the new EOS, but to the two modifications of the BWR EOS that were investigated.
- 4. Using an algebraic method within the non-linear regression to enforce critical pressure and van der Waals conditions at the critical point, and solving the resulting equations simultaneously for values of some of the EOS parameters, is

simpler and more reliable than using penalty functions combined with large weighting factors.

- 5. Simultaneously minimizing errors in both pressure and specific volume along the critical isotherm during EOS regression improves the equation's specific volume predictions near the critical point. Using simultaneous regression instead of regression based on pressure alone makes only a small difference in the actual numerical values of the regressed EOS parameters.
- 6. Considering that the exponential term in the new EOS has a finite value when specific volume is zero, it is necessary for the reference term to tend to *positive* infinity as specific volume tends to zero (or to a value of b when the EOS includes a covolume parameter). Otherwise, the new EOS will not exhibit the proper high-density limit, tending instead toward negative infinity as specific volume reaches its minimum value. This can be achieved in two ways: by incorporating a covolume parameter into the first term of the equation, or by ensuring that the coefficient of the highest-degree term in the reference polynomial has a positive value. This observation also applies to BWR-type equations, whose exponential term tends to zero at low specific volumes.
- 7. Modifying the EOS's representation of repulsive intermolecular forces—either through a van der Waals-type covolume, or a hard-sphere term—improves the equation's fit to specific volumes along the critical isotherm of methane.

A greater improvement was observed when a covolume was placed in each polynomial term than when it was placed in only the first term, or when a hardsphere term was used. However, the resulting best-fit covolume was an order of magnitude lower than the values that resulted for the other two methods, which had the expected order of magnitude.

- 8. Including a Scott hard-sphere term in the EOS made almost no difference to the fit along the critical isotherm of methane, when compared to the version of the EOS with a covolume in the first term.
- 9. For the current form of the new EOS, having a linear function of specific volume inside the exponential term, forcing the EOS to take on the correct value of the second virial coefficient improved the fit along the vapour-like portion of the critical isotherm, but degraded the fit severely along the liquid-like portion. Forcing the EOS to take on a zero value for the third derivative of pressure with respect to volume at the critical point produced similar results.
- 10. Along the vapour-like portion of the critical isotherm, only the term with coefficient B₀ contributes significantly to the calculated pressure. At the critical point, three polynomial terms—B₀, C₀, and D₀—as well as the covolume b, make significant contributions to the pressure. All terms in the EOS contribute significantly along the liquid-like portion of the isotherm.
- 11. When three parameters are selected to vary with temperature, plots of the parameters as functions of temperature behave anomalously near the critical

point, turning upward sharply over a small range of temperature. It is difficult to match the required values at the critical temperature using analytical temperature functions, and still achieve a good fit at near-critical temperatures.

- 12. Analytical temperature functions expressing the temperature dependence of EOS parameters in terms of reciprocal temperature generally give better fits than functions written in terms of temperature directly.
- 13. Spurious inflections and volume roots can form along subcritical and supercritical isotherms predicted by non-cubic equations of state. Incorporating a covolume parameter into the first term of the EOS eliminated the problem of spurious volume roots at subcritical temperatures for the three substances examined in this work. Spurious volume roots at supercritical temperatures were encountered when EOS parameters were regressed using saturation data only. These roots were prevented from forming when supercritical PVT data was included in the EOS parameter fitting procedure along with the saturation data.
- 15. The Levenberg-Marquart method for non-linear regression was also robust and reliable for the overall fitting of EOS parameters directly to the database of saturation data and supercritical PVT data.
- 16. The new EOS generally performs better for fitting pure component properties than the 12-constant version of the BWRS equation investigated here, but only performed better than the Soave-BWR equation in select instances. Further work should focus on improving the new EOS's prediction of critical second virial

coefficients, and on minimizing the anomalous behavior of the values of the EOS constants at the critical point, perhaps by developing a special term that becomes active only in the near-critical region.

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APPENDIX: EOS Constants for Selected Pure Components

The EOS constants shown in the tables are for pressure in atmospheres, temperature in degrees Kelvin, and specific volume in cm³/mol:

Constant	Value						
	Methane	Propane	n-Pentane	Hydrogen	Carbon	Sulfur	Water
					Dioxide	Dioxide	
T _C (K)	190.56	369.85	469.77	32.98	304.21	430.65	647.29
Ъ	22.139	66.186	107.132	16.473	0	43.312	0
Bo	-2244319	-9558518	-19389593	-242914	-2863029	-7098559	-4562148
Co	75179745	492796259	1548256033	4294569	94521554	229082860	142413078
D ₀	-8.589E+12	-3.755E+14	-4.184E+15	-9.828E+10	-8.552E+12	-6.495E+13	-3.738E+12
Eo	2.329E+14	-2.227E+16	-6.322E+17	7.214E+11	4.116E+14	-4.813E+14	5.596E+13
Fo	590868	1208320	1014273	206186	480	876597	1067131
G ₀	-0.16542	-0.08185	-0.05200	-0.25811	-0.03206	-0.11993	-0.23383

Table A-1 Pure-component critical constants for new EOS [Eq. (22a)]

Table A-2	Pure-component criti	cal constants fo	or Soave-BWR	equation [Eq. ((4)]	l
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Constant	Value						
	Methane	Propane	n-Pentane	Hydrogen	Carbon	Sulfur	Water
					Dioxide	Dioxide	
β _c	-0.339332	-0.340859	-0.34142	-0.34313	-0.34335	-0.34933	-0.35155
γ _c	-0.007075	-0.006435	-0.004757	0.009481	0.001386	0.01509	0.03025
δ _c	0.000767	0.000695	0.000612	0.000657	0.000558	0.000328	-8.14E-06
ε _c	0.043596	0.043741	0.042549	0.029472	0.037488	0.027114	0.014198
¢с	0.059686	0.056725	0.053933	0.077742	0.057632	0.061422	0.057147

Constant	Value						
	Methane	Propane	n-Pentane	Hydrogen	Carbon	Sulfur	Water
					Dioxide	Dioxide	
B	-1902789	-7760526	-15729256	-202908	-3022143	-5699602	-4545263
С	33050581	204575267	542265045	3413955	50678667	172435218	94269269
D	4.088E+12	3.246E+14	3.987E+15	5.671E+10	5.029E+12	1.816E+13	-2.297E+10
E	50493012	509324892	1757912940	2146833	81177960	161007423	45398522
F	7283	28362	66671	3901	6568	12415	3377

 Table A-3
 Pure-component critical constants for BWRS equation [Eq. (2)]

Table A-4Pure-component temperature constants
for new EOS [Eqs. (28)-(30)]

Constant	Value					
	Methane	n-Pentane	Sulfur			
			Dioxide			
b ₁	0.3976	2.7734	8.1781			
b ₂	0.1418	-2.2292	-7.8077			
b ₃	0.2283	1.1243	3.1431			
ci	1.489	-60.200	-105.598			
c ₂	-1.170	94.346	173.134			
C3	0.277	-64.763	-125.933			
C4	0.558	17.368	35.493			
dı	2.524	22.025	34.993			
d_2	-0.711	-18.286	-31.825			
d ₃	0.224	5.638	10.269			

Constant	Value				
	Methane	n-Pentane	Sulfu r Dioxide		
b ₁	0.4224	1.4398	1.1074		
b ₂ <i>Ф</i>	0.00349	-0.34304	-0.22252		
cl	-0.0273768	5.54E-02	-4.25E-03		
c ₂	3.534E-03	-5.348E-02	-1.792E-02		
c3	1.399E-03	-1.772E-01	-1.057E-01		
el	0.11456	0.19084	0.19618		
e ₂	0.07523	-0.16832	-0.08385		
e ₃	0.00190	0.18027	0.01893		

Table A-5Pure-component temperature constants for
Soave-BWR equation [Eqs. (5b, c, e)]

Table A-6	Pure-component temperature constants for
	BWRS equation [Eqs. (42a, b, c)]

Constant	Value					
	Methane	n-Pentane	Sulfur			
			Dioxide			
bı	1.096	-1.159	27.075			
b ₂	0.3415	4.896	-42.001			
b ₃	-0.1003	-4.102	37.462			
b4	0.0128	1.083	-9.719			
ci	0.4240	-1.223	-16.096			
c ₂	-0.5082	1.525	9.300			
di	0.1647	-0.6183	-2.856			