Mixing Rules for a NonCubic Equation of State

Kedge, Christopher J.

doctoral thesis

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Mixing Rules for a Non-Cubic Equation of State

By

Christopher J. Kedge

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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SEPTEMBER, 2007

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ABSTRACT

Excess free energy based mixing rules have been developed for multi-constant non-cubic equation of state (EOS). The concept of matching EOS-calculated infinite-pressure excess Helmholtz energy to the excess Gibbs energy calculated from an activity coefficient model (ACM)—traditionally used only with cubic EOS—was extended and applied to two non-cubic EOS: the BWR equation (Benedict et al., 1940), and the EOS of Kedge and Trebble (1999).

For both non-cubic EOS, it was necessary to introduce an additional binary interaction parameter into the mixing rule for parameter B—the coefficient of the density-squared term in both EOS, closely related to the second virial coefficient—in order to fit VLE data for high-pressure binary systems such as carbon dioxide + water, and carbon dioxide + ethanol. The additional interaction parameter could be incorporated through either the $A^E$-based mixing rule, or through a reformulated rule that preserves the quadratic composition dependence of the EOS-calculated mixture second virial coefficient.

Excellent VLE predictions were obtained with both EOS for the test system ethanol + water, using ACM parameters obtained from the literature. For the CO$_2$ + ethanol system, it was found that activity coefficient model parameters could be obtained by first fitting a simpler model (the PRSV cubic EOS of Stryjek and Vera (1986)) with the Wong-Sandler mixing rules (Wong and Sandler, 1992)) to the experimental VLE data, and then fitting an ACM (the NRTL equation of Renon and Prausnitz (1968)) to the excess Gibbs energy (G$^E$) curve calculated from the PRSV equation. NRTL parameters
obtained in this way were successfully used to model the isothermal VLE behavior of the system at 291.15 K using the new mixing rules and both non-cubic EOS.

For the CO₂ + water system, it was necessary to fit the EOS/excess-free-energy mixing rule models directly to experimental VLE data, taking the EOS binary interaction parameters and the NRTL parameters as adjustable constants. Both the new EOS and the BWR equations were able to fit the data reasonably well using the new mixing rules.
ACKNOWLEDGMENTS

I would like to thank Dr. Mark Treble for being a great supervisor all these years. I thank my parents, Robert and Kathleen Kedge, for unwavering support. I thank friends Alex Huddleston and Ivan Dixon for accommodating my erratic working hours. I thank Drs. M.S. Kallos, D.-Y. Peng, M.A. Satyro, and W.J.D. Shaw for helpful comments and suggestions. And I thank my wife, Carolynne, for standing by patiently through another thesis.
To Carolynne
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LIST OF SYMBOLS

A, A0, B0, C0, D0, E0, F0, G0, H0
a, b, c, d, e, f, g
B, C, D, E, F, G
Cp
b
b1, b2, b3
c1, c2, c3, c4
d1, d2, d3
e1, e2, e3
f
G
H
H1, J1, K1, L1, M1, N1
J
kij, l_{ij}
M
n
P
Q_i, S_i, U_i, X_i, Y_i
R
S
T
V
\bar{V}
W
Z

Greek Symbols

\alpha
\alpha_i
\alpha_{12}, \tau_{12}, \tau_{21}, G_{12}, G_{21}
\beta, \gamma, \delta, \epsilon, \phi
\Delta A'
\gamma
\phi
\hat{\phi}
\psi

Molar Helmholtz free energy
EOS Constants
EOS constants
EOS constants; Virial coefficients
Constant-pressure specific heat
Co-volume parameter
EOS temperature function constants
EOS temperature function constants
EOS temperature function constants
EOS temperature function constants
Fugacity
Molar Gibbs free energy
Enthalpy
Molar derivatives of mixture EOS constants (used in partial fugacity coefficient expressions)
Term in expression for excess Helmholtz energy
Binary interaction parameters
EOS parameter of interest in Eq. (15)
Number of moles; Exponent in Eq. (8)
Pressure
Molar derivatives of mixture EOS constants (used in partial fugacity coefficient expressions)
Universal gas constant
Regression objective function
Temperature
Molar specific volume
Total volume
Weighting factor for PVT points in Eq. (11)
Compressibility factor

Molar constant of infinite-pressure excess
Helmholtz energy from activity coefficient model
Constants in NRTL activity coefficient model
Reduced EOS constants in Eqs. (4) and (5)
Helmholtz energy residual
EOS constant; activity coefficient
Fugacity coefficient
Partial fugacity coefficient
Reduced density
### Subscripts/Superscripts

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<tr>
<td>c; crit</td>
<td>Critical</td>
</tr>
<tr>
<td>calc</td>
<td>Calculated value</td>
</tr>
<tr>
<td>E</td>
<td>Excess</td>
</tr>
<tr>
<td>EOS</td>
<td>Equation of state</td>
</tr>
<tr>
<td>ERR</td>
<td>Error</td>
</tr>
<tr>
<td>exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>IG</td>
<td>Ideal gas</td>
</tr>
<tr>
<td>i, j</td>
<td>Indices for components in a mixture</td>
</tr>
<tr>
<td>liq</td>
<td>Liquid</td>
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<td>m; mix</td>
<td>Mixture</td>
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<td>NC</td>
<td>Near critical</td>
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<tr>
<td>R</td>
<td>Reduced</td>
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<td>REP</td>
<td>Repulsion</td>
</tr>
<tr>
<td>sat</td>
<td>Saturation</td>
</tr>
<tr>
<td>sp</td>
<td>Single phase</td>
</tr>
<tr>
<td>vap</td>
<td>Vapour</td>
</tr>
<tr>
<td>x</td>
<td>Liquid mole fraction</td>
</tr>
<tr>
<td>y</td>
<td>Vapour mole fraction</td>
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<tr>
<td>2V</td>
<td>Second virial</td>
</tr>
<tr>
<td>∞</td>
<td>At infinite pressure</td>
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<td>γ</td>
<td>Activity coefficient model</td>
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### Abbreviations

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CHAPTER 1
INTRODUCTION

1.1 Equations of State

Equations of state (EOS) are powerful tools for calculating fluid thermodynamic properties. By applying fundamental thermodynamic relations to an EOS, the departures of all thermodynamic properties from ideal behavior 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 simultaneously represent coexisting vapour and liquid phases by way of multiple density roots.

For chemical process design work, cubic equations based on the van der Waals EOS have traditionally been the most popular EOS form. However, cubic EOS have limitations that make more complex EOS forms worth considering. One of the main drawbacks to using cubic EOS is that they normally do not predict the correct location of the critical point. Often, the critical pressure and temperature are reproduced at the expense of the critical volume, leading to errors in saturated- and compressed-liquid densities.

By contrast, non-cubic equations of state may have higher-order density terms or exponential terms that provide greater flexibility, particularly in the vicinity of the pure-component critical point. Non-cubic EOS typically have many more adjustable parameters, 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 more accurate predictions of essentially all thermodynamic properties, including second virial coefficients, saturation pressure,
saturated and compressed liquid densities, and thermal properties such as internal energy, enthalpy, and specific heats. Non-cubic EOS also have the potential to predict the shape of the liquid-vapour coexistence curve near pure-component critical points more accurately than cubic EOS.

Historically, the greatest drawback to using non-cubic EOS has been the large number of adjustable constants. Determining substance-specific values for these constants requires extensive non-linear data regression. 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 extend the EOS’s applicability to fluid mixtures. And aside from quartic polynomial equations, analytical solutions are not available for determining density from non-cubic EOS, and thus robust numerical root-solving procedures are required. In the past, these difficulties meant that more effort and computer time were required to develop and use non-cubic EOS than were needed for simpler equations, and consequently, use of non-cubic EOS has been somewhat limited.

Although development of non-cubic EOS can be difficult, technological advances in recent years have significantly improved the speed and storage capacity of desktop computers, making viable the commercial application of non-cubic equations of state, not only for pure components, but for fluid mixtures as well.

The traditional way to apply an equation of state to mixtures is to use the van der Waals one-fluid concept. This idea, originally proposed by van der Waals, is that the equation of state for fluid mixtures has the same functional form as for pure components. Then, all
that is needed to apply the equation to mixtures is a way to calculate the equation of state parameters for the mixture. A further assumption is that the mixture EOS parameters can be expressed as functions of the pure-component parameters for the constituents of the mixture. Such functions are known as mixing rules.

Equation of state mixing rules are typically empirical expressions with perhaps some limited basis in theory. These so-called classical mixing rules are typically linear or quadratic in composition, perhaps with some type of interaction parameter that allows an empirical correction to the basic mathematical form. Generally, classical mixing rules work well for mixtures of substances that exhibit nearly-ideal thermodynamic behavior. However, as the mixture constituents become more non-ideal—polar and associating substances, for example, or those with large or asymmetrical molecules—it becomes increasingly difficult to reproduce the mixture’s phase equilibrium behavior using simple EOS and classical mixing rules. For this reason, chemical engineers have turned to more complex kinds of mixing rules, ones that allow more direct control over how the mixture’s non-ideality is expressed.

Ultimately, a mixture’s vapour-liquid equilibrium behavior is governed by Gibbs free energy, and the way in which it varies with pressure, temperature, and mixture composition. For ideal mixtures, the mixture Gibbs energy can be expressed as a simple composition-weighted sum of the pure-component Gibbs energies, plus a term related to the change in entropy that accompanies the formation of an ideal solution. For non-ideal mixtures, this simple rule no longer applies. However, it can be convenient to represent the true mixture Gibbs energy as the sum of an ideal part—the Gibbs energy that the
mixture would have if it behaved ideally—and an *excess* part, which is the difference between the true Gibbs energy and the ideal value. The mixture’s non-ideality is thus captured entirely by the excess Gibbs free energy ($G^E$).

Viewed in this way, it becomes apparent that an equation of state’s ability to reproduce mixture phase equilibria is dictated by how well it can capture the variation of excess Gibbs free energy with pressure, temperature, and composition. Depending on how complex that variation is, it can be difficult for classical mixing rules to properly represent mixture excess Gibbs energies. Even for binary mixtures, it may not be possible to reproduce the shape of the excess Gibbs energy surface using a single constant interaction parameter, as many common mixing rules attempt to do.

### 1.2 Research Objectives

The three main objectives of the current work were as follows:

i. To develop a term for a new non-cubic equation of state (Kedge and Trebble, 1999; Kedge, 2000) that would improve the equation’s performance in the vicinity of pure-component critical points.

ii. To investigate the use of the Carnahan-Starling repulsion term as a way to improve the new EOS’s performance for pure components.

iii. To develop and demonstrate a methodology for applying the concept of excess-free-energy mixing rules to multi-constant non-cubic equations of state, including the new EOS.
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 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 (Mason and Spurling, 1969).

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

\[ P = \frac{RT}{V} + \frac{RTB}{V^2} + \frac{RTC}{V^3} + \ldots \]  

(1)

where \( V \) is specific volume, and \( B \) and \( C \) are called *virial coefficients*. The virial coefficients take on different values for each substance, but are functions of temperature only (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, 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).
Despite these shortcomings, some features of the virial equation ensure that it is still relevant today. In particular, the second virial coefficient captures the first deviations from ideal behavior in low pressure gases. Even for modern EOS that are used to represent both the liquid and vapour phases simultaneously, it is important that their second virial coefficients—as calculated from a virial expansion—are as close as possible to the correct values, in order to properly represent low-pressure vapour phase behavior.

2.2 BWR-Type Equations of State

Of the many non-cubic EOS developed after the virial EOS, the original Benedict-Webb-Rubin (BWR) equation and its many variations have been the 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 substance-specific parameters 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 expressed as follows:

\[ B = B_oRT - A_o - \frac{C_o}{T^2} \]  

(3a)

\[ C = bRT - a \]  

(3b)
\[ D = a\alpha \]  
\[ E = \frac{c}{T^2} \]  

The BWR EOS was proposed as an improvement to the Beattie-Bridgeman EOS, allowing 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 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 improving PVT predictions—especially liquid densities—over those of cubic equations.

The BWR EOS has been modified many times since 1940, when the original equation was proposed. One of the best-known variations was that of Starling (1973), who used the same volume dependence as Eq. (2), but modified Eqs. (3a-d) to arrive at different expressions for the temperature dependence of the parameters in Eq. 2. Han and Starling also introduced a generalization of the pure component parameters in terms of critical properties and acentric factor (Han, 1972; Starling, 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.
Such modifications have included the equations of Bender (1971), Nishiumi (1975, 1980), and Platzer and Maurer (1989).

More recently, the BWR equation was modified by Soave (1995), who proposed the form:

\[ Z = 1 + \beta \psi + \gamma \psi^2 + \delta \psi^4 + \varepsilon \psi^2 (1 + \phi \psi^2) \exp(-\phi \psi^2) \]  \hspace{1cm} (4a)

or equivalently

\[ P = \frac{RT}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^4} + \frac{E}{V^5} \left(1 + \frac{F}{V^2}\right) \exp\left(-\frac{F}{V^2}\right) \]  \hspace{1cm} (4b)

In Eq. (4), the parameter \( \Psi \) represents reduced density as follows:

\[ \psi = \frac{\left(\frac{RT_c}{P_c}\right)}{V} \]  \hspace{1cm} (5a)

The essential difference between the original BWR equation (Eq. (2)) and the SBWR equation (Eqs. (4)) is that Eq. (4b) includes a fifth-power term in reciprocal volume instead of the sixth power shown in Eq. (2).

Soave proposed new generalized functions to express the temperature dependence of the parameters \( \beta, \gamma, \delta, \) and \( \varepsilon \) as follows:

\[ \beta = \beta_c + b_1 \left(1 - \frac{1}{T_{r,1.8}}\right) + b_2 \left(1 - \frac{1}{T_{r,3.2}}\right) \omega \]  \hspace{1cm} (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 \( \beta_c, \gamma_c, \delta_c, \) and \( \varepsilon_c \) 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 \( \phi \) 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 near-critical region.

2.3 The New Equation of State

Prior to the current study, a new non-cubic equation of state had been developed for pure substances (Kedge and Trebble, 1999; Kedge, 2000). The new EOS is written as:

\[
P = \frac{RT}{(V - b)} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{E}{V^7} + F \exp(GV) 
\]

(6)
where \(b, B, C, D, E, F, \) and \(G\) are substance-specific constants. Three of these parameters \((B, C, D)\) were made temperature dependent, as follows:

\[
B(T) = B_{\text{crit}} \left( (1 - b_1 - b_2 - b_3)T_R + b_1 + \frac{b_2}{T_R^2} + \frac{b_3}{T_R^2} \right) \tag{7a}
\]

\[
C(T) = C_{\text{crit}} \left( (1 - c_1 - c_2 - c_3 - c_4)T_R^2 + c_1T_R + c_2 + \frac{c_3}{T_R} + \frac{c_4}{T_R^2} \right) \tag{7b}
\]

\[
D(T) = D_{\text{crit}} \left( (1 - d_1 - d_2 - d_3)T_R + d_1 + \frac{d_2}{T_R} + \frac{d_3}{T_R^2} \right) \tag{7c}
\]

In the original work, the equation was fit to PVT and vapour-liquid coexistence data for three substances: methane, n-pentane, and sulfur dioxide. While the equation was able to reproduce the original PVT data quite accurately, it did not result in a uniform improvement over Starling’s (1973) and Soave’s (1995) modifications of the BWR equation for all properties and for all substances studied.

Martin and Hou (1955) identified several general characteristics of the PVT behavior exhibited by pure substances. Based on this work, Peng (2007) identified five conditions that an equation of state must meet in order to properly represent pure-component PVT behavior over the full range of pressure and temperature. Specifically, an EOS must meet the following criteria:

i. The EOS must revert to ideal gas behavior as pressure approaches zero.
ii. The critical isotherm must exhibit a point of inflection and zero slope. In addition, the third derivative of pressure with respect to volume at the EOS-calculated critical point should be zero, or slightly negative, and the fourth derivative should equal zero.

iii. The slope of PV vs. P (or Z vs. P) at constant temperature may be greater than, equal to, or less than zero, depending on temperature. However, the slope must change smoothly and in the order given above as the temperature proceeds from high to low. The temperature for which $\partial(PV)/\partial P = 0$ as pressure approaches zero is called the Boyle temperature.

iv. The limiting value of V/T along an isobar must approach that of an ideal gas at high temperature. That is, the limit as temperature approaches infinity of $(\partial V/\partial T)_p$ should equal R/P, and of $(\partial^2 V/\partial T^2)_p$ should equal zero.

v. The isometrics—that is, lines of constant volume—should be almost linear, except at low temperatures and high densities. As such, $(\partial^2 P/\partial T^2)_V$ is approximately zero for most conditions, and exactly as temperature approaches infinity.

To meet the first condition, equations of state include a repulsion term—usually either an ideal gas term, a van der Waals-type term, or a hard-sphere term such as that of Carnahan and Starling—which reduces to the ideal gas law at low pressures. In addition, all other terms in the EOS must vanish as pressure approaches zero. Meeting the other four
conditions, however, relies less upon the functional form of the EOS than on the values of the adjustable constants. As such, if an EOS is to meet the remaining conditions, the conditions must be enforced as part of the regression procedure used to determine the values of the constants for a given pure substance. If these conditions are not enforced, then there is no guarantee that the EOS will meet these criteria for that substance, particularly because several of the conditions (points iii, iv, and v) represent limiting behaviors that may lie outside of the pressure and temperature range of the PVT data to which the EOS constants were fit.

The new EOS meets the first criterion as a result of the van der Waals term (the first term on the right hand side of Eq. (6)). The EOS meets the second criterion by virtue of enforcing the first and second derivative conditions at the critical point, as well as mechanical stability along the critical isotherm, during the pure-component regression procedure. The third, fourth, and fifth criteria have not been explicitly enforced in the regression procedure, and so the EOS does not necessarily meet them unconditionally. However, there is nothing about the EOS’s functional form that would prevent these conditions from being enforced by modifying the pure-component regression procedure accordingly.

During development of the new EOS, it was observed that forcing the equation to reproduce the pure-component critical point and the van der Waals derivative conditions seemed to increase the error in saturated liquid and vapour densities in the vicinity of the critical point. It was noted (Kedge, 2000) that the new equation’s accuracy in that region
could potentially be improved by developing a term that would become active only in the vicinity of the critical point. Developing such a term was thus the focus of the first part of the current study, as described in the next chapter.
CHAPTER 3
MODIFICATIONS TO THE NEW EOS

3.1 Improving EOS Performance Near Pure-Component Critical Points

Many equations of state have difficulty fitting pure-component PVT data near the critical point. Even non-cubic EOS with multiple temperature-dependent parameters can exhibit large errors in saturated liquid and vapour specific volumes at near-critical temperatures. In an earlier work (Kedge and Trebble, 1999; Kedge, 2000), during development of the new non-cubic equation of state, it was observed that errors in calculated pressure and specific volume along pure-component critical isotherms are comparatively large near the critical point. Fig. 3-1 shows these errors for methane, which was used as the test substance for much of the EOS development work. Error is shown plotted against reduced volume, which is defined as specific volume divided by Vc, the specific volume at the critical point.

At the same time, near-critical anomalies were observed in the calculated temperature dependence of parameters B, C, and D in Eq. (6). During development of the EOS, three parameters were allowed to vary with temperature. The temperature dependence of these parameters—the way in which they would need to vary in order to accurately fit experimental phase equilibrium data—was then calculated by matching saturation pressure and saturated liquid and vapour specific volumes at subcritical temperatures, and by fitting whole isotherms at supercritical temperatures. Because the equation was intended to match the critical point exactly, the functions used to express temperature
dependence of the EOS parameters—hereafter called temperature functions—had to pass through the calculated value at the critical temperature. This made it difficult for the temperature functions to reproduce the required values near the critical temperature, resulting in relatively large errors in saturated liquid and vapour volumes in that region.

![Figure 3-1](image)

**Figure 3-1** Error in pressure and specific volume for new EOS (Eq. (6)) along critical isotherm of methane

As an example, Fig. 3-2 shows this anomaly for parameter C for methane. In the figure, the circles represent the values that C must take on to exactly match saturation pressure and saturated liquid and vapor densities at each temperature, while the solid line represents the EOS approximation to these values (Eq. (7b)), using best-fit parameters. In the original EOS, critical values of the temperature-dependent parameters were determined by fitting the critical isotherm alone.
Fig. 3-2 shows that forcing Eq. (7b) to pass through the calculated value at the critical point—and thereby forcing the EOS to reproduce the actual critical point—creates a discrepancy between the EOS and the required C values at reduced temperatures between 0.85 and 1.0. Reduced temperature is defined as temperature divided by \( T_c \), the temperature at the critical point.

![Graph showing variation of parameter C with temperature](image)

**Figure 3-2** Variation with temperature of parameter C in Eq. (6) without near-critical term, for methane (parameters determined by three-step regression)

To resolve these problems that existed at the conclusion of the earlier work (Kedge, 2000), a term was developed as part of the current Ph.D. study, which could be added to the EOS to help correct near-critical errors in calculated pressures and volumes along pure-substance critical isotherms, and in saturated liquid and vapour specific volumes at near-critical temperatures.
3.2 The Near-Critical Correction Term

3.2.1 Development

The present work to develop a near-critical correction term began by attempting to correct errors in pressure and volume along the critical isotherm for Eq. (1). Methane was used as a test substance, with data from the IUPAC tables (Angus et al., 1976a).

The first step was to fit the EOS to the critical isotherm without forcing it to reproduce the critical pressure. Removing this constraint would then allow the EOS more freedom to fit the near-critical data points on the critical isotherm. It was decided that the term should be explicit in pressure so it could be added directly to the EOS, should reach its maximum value at the critical volume, and should vanish at volumes away from the critical point. Admittedly, a term of this type is analytic at the critical point and as a result cannot reproduce the theoretical critical exponents. However, it was decided that such a term, while not theoretically rigorous, would still be worth pursuing if it could improve the fit of PVT data in the near-critical region.

At this point, consideration was given to what shape the near-critical term would need to have in order to correct the critical pressure to the proper value.

The first form considered was a bell-shaped exponential term centered around the critical volume, which was essentially the same as the equation for the normal probability distribution. However, this term could not be integrated analytically, resulting in a pure-component fugacity expression containing the Gaussian error function. Other forms were
therefore considered, and a similar symmetrical term centered about the critical volume was finally selected as follows:

\[ P_{NC} = \frac{e}{1 + f(V - V_c)^n} \]  

(8)

where e, f, and n are adjustable parameters, and Vc is the critical volume. The parameter n must be an even number in order to vanish at both sub- and super-critical volumes. After several regression trials using the EOS modified to include Eq. (8), a value of 2 was selected for the parameter n in Eq. (8), since it gave a smoother critical isotherm and a less complicated fugacity expression than when a value of 4 was used.

It was also decided to make the volume at which the term reaches its peak value into an adjustable parameter, rather than forcing it to be centered about the critical volume. Because the NC term is symmetrical, its derivative of pressure with respect to volume is zero at the volume where it reaches its peak value. If the peak coincides with the critical volume, then the derivative of the remaining EOS terms together must also equal zero at \( V = V_c \) in order for the overall EOS to meet the first van der Waals derivative condition (that is, the derivative of pressure with respect to specific volume must equal zero at \( V = V_c \) and \( T = T_c \)). Allowing the NC term’s peak volume to move away from \( V_c \) frees the remaining EOS terms from this restriction, and the increased flexibility improves the NC term’s performance significantly.

The final result was the following three-parameter expression:
leading to the overall equation for pressure:

\[ P = P_{\text{EOS}} + P_{\text{NC}} \]  

where \( P_{\text{EOS}} \) is the pressure calculated from the base equation of state (Eq. (6)).

Fig. 3-3 shows the pressure correction provided by Eq. (9) as a function of reduced volume for methane, using parameters determined by fitting the overall EOS (that is, Eq. (6) + Eq. (9)) to the critical isotherm of methane.

![Figure 3-3](image-url)  
**Figure 3-3** Pressure contribution of near-critical term of Eq. (9) for methane when added to non-cubic EOS (Eq. (6))
As the figure shows, the peak of the curve occurs at $V = g$, and the height of the peak is numerically equal to the value of parameter $e$. The parameter $f$ in Eq. (9) essentially controls the width of the curve.

It should be noted that although parameter $g$ in Eq. (9) is adjustable—it effectively shifts the peak of the correction term away from $V_c$—this does not affect the location of the critical point calculated from the overall EOS. The regression procedure ensures that the calculated critical point matches the experimental $T_c$, $P_c$, and $V_c$, regardless of whether $g$ is made adjustable or fixed at $g = V_c$.

Originally, it was considered to make parameter $e$ in Eq. (9) temperature dependent so that the near-critical term would vanish away from the critical point in both temperature and volume. However, this was later deemed to be unnecessary, because the presence of the NC term at temperatures away from the critical point did not adversely affect calculated thermodynamic properties or the shape of isotherms. The near-critical term is therefore active at all temperatures.

In an earlier work, Monnery et al. (1998) used a bell-shaped Gaussian term to provide a temperature-dependent correction to a Peneloux-type volume shift (Peneloux et al., 1982) for the Peng-Robinson EOS. However, this application is actually quite different than the near-critical term developed in the current work. In particular, the term of Monnery et al. is applied to a volume correction that is calculated independently of the EOS and is added to the EOS-calculated liquid-phase specific volume, in order to improve the accuracy of the calculated liquid volume. The near-critical (NC) term in the current work, however, is
actually part of the EOS, and as such, contributes directly to the pressure calculated from the EOS. In this way, it affects not only near-critical liquid volumes, but vapour volumes, saturation pressures, and other thermodynamic properties as well.

Another key difference is that the term of Monnery et al. is a function of temperature, vanishing at reduced temperatures far from the critical temperature, and is independent of specific volume. By contrast, the new NC term is a function of specific volume only, and is independent of temperature.

3.2.2 Regression Algorithm

Originally, a three step procedure was used to determine best-fit values for the EOS parameters for pure components:

i. Fit the EOS to the critical isotherm to determine critical values for the EOS parameters. The van der Waals conditions of criticality were enforced at this step.

ii. Calculate the temperature dependence for three EOS parameters by forcing the EOS to exactly match vapour pressure and saturated liquid and vapour specific volumes at subcritical temperatures, and by least-squares regression to minimize pressure errors along whole isotherms at supercritical temperatures.

iii. Fit the EOS directly to the database of vapour pressures, saturation volumes, and supercritical PVT data using a non-linear least-squares algorithm, holding the critical values of the EOS parameters constant to ensure exact reproduction of the
critical point. Supercritical pressure data were given a lower weighting in the regression than the saturation data, but were included to ensure that calculated isotherms would not develop spurious roots or inflections at supercritical temperatures.

The regression algorithm used in steps (i) and (iii) was a non-linear least-squares procedure based on the Levenberg-Marquardt method as described by Press et al. (1986).

From the results of the regressions, it was observed that while the near-critical term improved the fit of the EOS along the critical isotherm, it did little to improve the near-critical fit of saturation pressures and volumes. At this point, it was reasoned that high accuracy along the critical isotherm at the expense of accuracy in saturation properties and along other isotherms was not warranted, as long as the critical pressure was reproduced, and the van der Waals derivative conditions were enforced. The regression procedure was therefore modified so that the critical isotherm would be regressed simultaneously with the saturation properties and single-phase isotherms. The modified procedure—referred to hereafter as global regression—ensured reproduction of the critical pressure and enforcement of the van der Waals derivative conditions.

The objective function minimized by the program was as follows:

\[
S^2 = \sum_i \left( \frac{P_{\text{sat exp}} - P_{\text{sat calc}}}{P_{\text{exp}}} \right)_i^2 + \sum_i \left( \frac{V_{\text{sat,vap exp}} - V_{\text{sat,vap calc}}}{V_{\text{exp}}} \right)_i^2 \\
+ \sum_i \left( \frac{V_{\text{sat,liq exp}} - V_{\text{sat,liq calc}}}{V_{\text{exp}}} \right)_i^2 + W \sum_i \left( \frac{P_{\text{sp exp}} - P_{\text{sp calc}}}{P_{\text{exp}}} \right)_i^2 + W \sum_i \left( \frac{V_{\text{sp exp}} - V_{\text{sp calc}}}{V_{\text{exp}}} \right)_i^2
\]  

(11)
3.2.3 **Mechanical Stability Along the Critical Isotherm**

During the least-squares regression work, it was noticed that the near-critical term could lead to a mechanically unstable critical isotherm at the best-fit condition—that is, small sections of the critical isotherm would exhibit a positive slope on a plot of pressure vs. specific volume in the near-critical region.

Non-linear regression is an iterative process where best-fit values of the adjustable parameters are found by making successive corrections to the initial guesses until convergence. It was therefore necessary to modify the regression procedure to check for mechanical stability after each regression iteration, and reject that iteration’s corrections if the slope was found to be positive anywhere along the isotherm. The program would then repeat the iteration with smaller and smaller corrections until mechanical stability was restored, and move on to the next iteration. A requirement of this approach was that the initial guesses for EOS parameters had to produce a mechanically stable critical isotherm at the first iteration; otherwise, there was no guarantee that the critical isotherm would be mechanically stable with the final converged values.

3.3 **Effects of the New Term**

In this work, the near-critical term was applied to both the new non-cubic EOS (Eq. (6)), and to the cubic EOS of Trebble and Bishnoi (1987), and the NC term’s effects on EOS fits to pure-component critical isotherms, vapour-liquid coexistence curves, and constant-pressure specific heat residuals were examined.
The Trebble-Bishnoi (TB) cubic EOS is written as:

\[ P = \frac{RT}{(V - b)} - \frac{a\alpha}{V^2 + (b + c)V - bc - d^2} \]  

(12a)

In this work, the original \( \alpha \) function was replaced with a general three-parameter function of reduced temperature as follows:

\[ \alpha = 1 + m (1 - T_R) + n (1 - T_R)^2 + o (1 - T_R)^3 \]  

(12b)

The function was modified in this way to provide greater flexibility in matching pure-component vapour pressures near the critical point. Development of the near-critical term was carried out using the non-cubic EOS (Eq. (6)), and was applied afterward to the TB equation to assess the merits of using it with cubic EOS.

Pure component parameters for the new EOS with and without the near-critical term are shown in Table A-1 in Appendix A. Parameters for the TB EOS are shown in Table A-2.

3.3.1 Critical Isotherm

Fig. 3-4 demonstrates the effect of the near-critical term on the pure-substance critical isotherm, with methane as the test substance.

The solid line represents the critical isotherm calculated using the overall EOS (Eqs. (6) and (9)), with parameters determined by global regression. Also, for the purpose of illustration, the near-critical term was subtracted from the EOS entirely, with the parameters in the remaining part of the EOS fixed at their regressed values.
The isotherm calculated at $T = T_c$ by the remaining terms in the equation (middle dotted line in the figure) actually shows the three-root characteristics of a subcritical isotherm. By extension, this means that the remaining EOS terms without the NC term would predict a different location for the critical point—at a higher pressure and a slightly different temperature and volume—than actually occurs. In other words, the other EOS terms together behave as though the critical point were located at a higher pressure.

Figs. 3-5 and 3-6 show errors in pressure and specific volume that result when Eq. (6) is fit to the critical isotherm of methane, with and without the near-critical term (Eq. (9)). The figures show that including the near-critical term in the equation significantly improves the EOS’s ability to fit the critical isotherm.

**Figure 3-4** Effect of near-critical term on methane critical isotherm
**Figure 3-5** Error in pressure along critical isotherm of methane for new EOS

**Figure 3-6** Error in specific volume along critical isotherm of methane for new EOS
Table 3-1 shows average absolute deviations (%AAD) and maximum absolute deviations (%MAD) in pressure and volume for both Eq. (6) and the TB EOS (Eq. (12a)), when the EOS is fit to the critical isotherm of methane with and without the near-critical term.

<table>
<thead>
<tr>
<th>EOS</th>
<th>Pressure %AAD</th>
<th>Pressure %MAD</th>
<th>Specific volume %AAD</th>
<th>Specific volume %MAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-cubic (Eqs. (1)-(4))</td>
<td>0.39</td>
<td>1.93</td>
<td>0.31</td>
<td>1.94</td>
</tr>
<tr>
<td>Non-cubic + NC term</td>
<td>0.14</td>
<td>0.67</td>
<td>0.09</td>
<td>0.38</td>
</tr>
<tr>
<td>TB</td>
<td>5.38</td>
<td>24.00</td>
<td>2.05</td>
<td>9.18</td>
</tr>
<tr>
<td>TB + NC term</td>
<td>2.37</td>
<td>8.31</td>
<td>0.82</td>
<td>2.48</td>
</tr>
</tbody>
</table>

3.3.2 Vapour-Liquid Coexistence Curve

Fig. 3-7 shows vapour-liquid coexistence curves for methane calculated using Eq. (1), both with and without the near-critical term, plotted along with the experimental data. The figure shows that including the near-critical term significantly improves the fit of saturated liquid and vapour specific volumes in the near-critical region.

As described earlier, when the NC term is added to the EOS and the overall equation is fit to pure-component PVT and VLE data, the EOS terms other than the NC term together behave as though the critical point were located at a higher pressure. This is demonstrated in Fig. 3-8 which, like Fig. 3-7, shows coexistence curves calculated with and without the NC term.
Pressure (atm)

Data (Angus et al. (1976))

New EOS with NC term

New EOS without NC term

Specific Volume (cm³/mol)

Figure 3-7 Effect of near-critical term on methane vapour-liquid coexistence curve calculated with new EOS (best-fit parameters)

Pressure (atm)

Data (Angus et al. (1976))

New EOS with NC term

New EOS with NC term removed

Predicted critical point with NC term removed

Specific Volume (cm³/mol)

Figure 3-8 Effect of near-critical term on methane vapour-liquid coexistence curve calculated with new EOS
But unlike Fig. 3-7, where the curves were calculated using two different sets of optimized parameters (one set with the NC term, and one set without, as listed in Table A-1), the dashed curve was calculated using the same set of parameters as the solid curve, but with the NC term merely left out.

Figs. 3-7 and 3-8 show that the main effect of the near-critical term is to shoulder some of the burden of reproducing the ‘flatness’ of the top of the coexistence curve and the critical isotherm, allowing the remaining EOS to behave as though the critical point were located in a more convenient, easier-to-fit place.

Table 3-2 shows average absolute deviations (%AAD) and maximum absolute deviations (%MAD) in vapour pressure, saturated liquid specific volume, and saturated vapour specific volume for both the new EOS and the TB EOS (Eq. (12a)) when the parameters are determined using the global regression procedure.

<table>
<thead>
<tr>
<th>EOS</th>
<th>Saturation Pressure</th>
<th>Specific volume</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%AAD</td>
<td>%MAD</td>
<td>%AAD</td>
<td>%MAD</td>
</tr>
<tr>
<td>Non-cubic (Eqs. (1)-(4))</td>
<td>0.21</td>
<td>0.43</td>
<td>0.20</td>
<td>2.45</td>
</tr>
<tr>
<td>Non-cubic + NC term</td>
<td>0.13</td>
<td>0.26</td>
<td>0.17</td>
<td>0.94</td>
</tr>
<tr>
<td>TB</td>
<td>0.71</td>
<td>1.26</td>
<td>2.36</td>
<td>6.49</td>
</tr>
<tr>
<td>TB + NC term</td>
<td>0.94</td>
<td>1.74</td>
<td>2.06</td>
<td>3.43</td>
</tr>
</tbody>
</table>

The results in Tables 3-1 and 3-2 indicate that while the improvements brought by the near critical term are significant for both EOS, Eq. (12a) still does not approach the
accuracy of the non-cubic equation even with the near-critical term. For this reason, the application of the near-critical term to cubic EOS was not investigated further.

3.3.3 Temperature Function Anomalies

Fig. 3-9 shows the revised fit of parameter C from Eq. (6) when the near-critical term has been added to the EOS, and global regression is used instead of the three-step procedure described in Section 3.2.2. The figure shows that the near-critical term, in combination with global regression, reduces the magnitude of the anomaly, allowing Eq. (7b) to better represent the calculated temperature dependence of C. A similar result is obtained for parameters B and D as well.

**Figure 3-9** Variation with temperature of parameter C in Eq. (6) with near-critical term, for methane (parameters determined by global regression)
3.3.4 Thermal Properties

Figure 3-10 shows the effect of the near-critical term on the isobaric specific heat residual (defined as $C_p - C_p^*$) for several temperatures just above and below the critical temperature (190.56 K). The figure also shows the contribution of the near-critical term to the total residual for two temperatures, 192 K and 194 K. Figure 3-10 shows that the $C_p$ residual curves are smooth, and that the near-critical term does not cause any unexpected behavior.

![Figure 3-10: Effect of near-critical term on calculated $C_p$ residual for methane](image)

For isochoric specific heat ($C_V$), the residual depends on the derivatives of pressure with respect to temperature, but not with respect to volume. Since the near-critical term is
independent of temperature, it does not have any effect on isochoric specific heat residuals calculated from the EOS.

$C_V$ diverges near the critical point, though not nearly as rapidly as $C_P$. With $C_P$, an equation of state is able to reproduce this behavior by virtue of enforcing the van der Waals derivative conditions at the critical point, since $(\partial P/\partial V)_T$ appears in the denominator of one of the terms in the expression for the $C_P$ residual. However, with $C_V$—which depends on $(\partial^3 P/\partial T^2)_V$—the EOS will not necessarily reproduce the expected near-critical divergence unless $C_V$ data is included in the data set used in the regression of pure-component EOS parameters.

### 3.4 Repulsion Terms

In most equations of state, the leading term is taken to represent the effects of intermolecular repulsive forces. The contribution of repulsive interactions to the pressure calculated from an EOS is hereafter referred to as repulsion pressure. The simplest EOS representation of repulsion pressure is the van der Waals-type repulsive term, expressed as

$$P_{RE} = \frac{RT}{V - b}$$

(13)

where $b$ is a co-volume parameter that is related to the excluded volume occupied by the fluid’s molecules. The effect of this term is essentially to insert a volume asymptote into the EOS, such that pressure becomes infinite at $V = b$. As such, the specific volume calculated from the equation of state for a given pressure does not fall below the value of
b. The van der Waals term in Eq. (13) is simple, but is not particularly accurate in representing the repulsive part of a fluid’s pressure.

One potentially more realistic approach is to treat the molecules as though they were non-attracting rigid spheres. With this assumption, it is possible to derive an exact infinite-series representation of the repulsion pressure of hard spheres (Ree and Hoover, 1967). To incorporate hard-sphere repulsions into an EOS, however, it is necessary to express the repulsion pressure in closed form. Exact closed-form expressions have not been found, but a number of approximations have been proposed.

Perhaps the best-known closed-form expression for hard-sphere repulsion pressure is that of Carnahan and Starling (1969, 1972). An infinite-series expansion of the Carnahan-Starling expression shows close agreement between its coefficients and those of the exact series for the first several terms. One apparent drawback in using this expression is that any EOS into which it is incorporated will automatically become non-cubic.

A simpler hard-sphere expression was proposed by Scott (1971). The Scott expression is simpler in form, and when used instead of the van der Waals term, still allows a cubic EOS to remain cubic.

During development of Eq. (6), but before developing the near-critical term, the effect of using different leading terms on the equation’s fit along the critical isotherm of methane was examined (Kedge, 2000). Originally, three alternatives were considered: a simple ideal gas term, a van der Waals-type repulsive term, and a hard-sphere expression.
Because of its simpler form, the equation of Scott was selected as the hard sphere term in that work, rather than the potentially more accurate Carnahan-Starling expression. It was observed that the Scott term gave a marginally better fit to the critical isotherm than did the van der Waals term, but at the time it was decided that the improvement was too small to warrant adopting the slightly more complicated Scott term over the van der Waals term.

After the near-critical term was developed, it was thought that it would be prudent to re-examine the effect of a hard-sphere term in the equation in conjunction with the near-critical term, not only in terms of its ability to reproduce the critical isotherm, but the vapour-liquid co-existence curve as well. The CS term can be expressed as

$$P_{REP} = \frac{RT}{V} \left[ \frac{V^3 + bV^2 + b^2V - b^3}{(V - b)^3} \right]$$

(14)

Since \(b\) in Eq. (14) is taken to be an adjustable parameter, it was not divided by the factor of 4 as is traditionally done when writing the CS equation, but rather the factor was absorbed into the best-fit value of \(b\) determined from data regression.

3.5 Application to Pure Components

In the earlier work (Kedge and Trebble, 1999; Kedge, 2000), the new EOS (with the van der Waals repulsion term) was compared to the SBWR equation (Soave, 1995), and it was found that while the new equation showed improvement over SBWR in some areas, the SBWR still showed significantly better fits to pure component data in others areas.
Fig. 3-11 shows the temperature dependence of parameter C in the SBWR equation Eq. (4b) calculated by forcing the EOS to exactly match saturation pressures and densities.

![Graph showing the variation of parameter C with temperature](image)

**Figure 3-11**  Variation of parameter C in Eq. (4b) with temperature for methane

The figure shows a near-critical anomaly in the calculated temperature dependence similar to that shown in Fig. 3-2 for Eq. (6). The magnitudes of anomalies for the other two temperature-dependent parameters were significantly smaller than for this parameter.

Based on experience with Eq. (6) before adding the near-critical term, the presence of such an anomaly would suggest that significant errors should be expected in the near-critical saturated liquid and vapor densities calculated using SBWR. This was found to be the case.
In the previous investigation (Kedge and Trebble, 1999; Kedge, 2000), it was also observed that Eq. (4b) is better able to fit pure-substance critical isotherms near the critical point than the original version of Eq. (6) without the near-critical term.

One possible explanation is that as Fig. 3-12 shows for methane, the exponential term in SBWR is actually the sum of two bell-shaped terms which make their largest contribution to the EOS-calculated pressure in the general vicinity of the critical point, between reduced volumes of approximately 0.5 and 1.2, becoming inactive at both lower and higher volumes.

![Critical isotherm of methane](image)

**Figure 3-12** Contribution of exponential terms in Eq. (4b) to calculated pressure along critical isotherm of methane

It seems likely that because the contributions of the exponential term are confined to the region where the slope of the critical isotherm changes most rapidly, the remaining EOS
terms carry less responsibility for fitting this hard-to-fit region, much in the same way as the also bell-shaped near-critical term does for Eq. (6).

In order to compare Eq. (4b) with versions of Eq. (6) containing the two alternate repulsive terms, the global regression method was used to re-fit the parameters in Eq. (4b) to data for methane. The best-fit parameters are shown in Table A-3 in Appendix A.

In this work, two versions of the new non-cubic EOS—using both the van der Waals expression and the Carnahan-Starling equation as the leading term—as well as the SBWR equation, were fit to the properties of methane using the same global regression technique. Data used in the regression included PVT data along the critical isotherm and three supercritical isotherms, saturation pressures, and saturated liquid and vapour densities. The data for methane was taken from the IUPAC tables (Angus et al., 1976a).

The PVT data included points for pressures up to 986 atmospheres and temperatures up to 450 K. The saturation data included points at temperatures ranging from 90.68 K to the critical temperature of 190.555 K.

Because there were many more supercritical PVT data points than saturation data points, supercritical pressure errors were assigned a weight of 0.01 in the regressions relative to saturation pressures and densities, so that pressure errors along supercritical isotherms would not dominate the regressions. Although this value is somewhat arbitrary, it was applied consistently for all three equations of state.
Table 3-3 shows results of the regressions to property data for methane for the three EOS. The table shows that replacing the van der Waals term in Eq. (6) with the Carnahan-Starling term reduces average absolute deviations (%AAD) considerably, and except for saturation pressures, also reduces the maximum absolute deviations (%MAD) by a significant amount as well.

Table 3-3  Errors in saturation pressure, saturation specific volumes, and supercritical pressures of methane

<table>
<thead>
<tr>
<th>EOS</th>
<th>Saturation Pressure</th>
<th>Specific volume</th>
<th>Pressure along supercritical isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%AAD</td>
<td>%MAD</td>
<td>%AAD</td>
</tr>
<tr>
<td>Eq. (1) with vdW term</td>
<td>0.13</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>Eq. (1) with CS term</td>
<td>0.10</td>
<td>0.33</td>
<td>0.12</td>
</tr>
<tr>
<td>SBWR</td>
<td>0.08</td>
<td>0.24</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The table also shows that the SBWR equation is slightly better at reproducing saturation pressures and pressure along supercritical isotherms, but that the Carnahan-Starling version of Eq. (6) provides significantly better reproduction of saturated liquid and vapor specific volumes.

At this point, it was decided that with these two improvements—adding the near-critical term, and adopting the Carnahan-Starling repulsive term—the new EOS was able to represent pure-components sufficiently accurately that the focus of the study could now turn to applying the EOS to fluid mixtures.
CHAPTER 4
APPLYING EQUATIONS OF STATE TO FLUID MIXTURES

4.1 Equation-of-State Mixing Rules

The most common way to apply an EOS to fluid mixtures is through the *one fluid* concept, where the EOS is assumed to apply to both pure components and mixtures as long as appropriate values are selected for the mixture EOS constants. The assumption is that the mixture’s PVT behavior will have the same temperature- and density dependence as pure components, and that there is no need to add mixture-only terms or modify the functional form of the EOS. To use this approach, however, we must have a way of calculating the EOS parameters for the mixture. For this purpose, we rely on *mixing rules*.

Mixing rules are formulas that express mixture EOS parameters as functions of three elements: mixture composition, properties of the constituent pure components (either critical properties, or EOS constants directly), and mixture-specific constants to characterize interactions between different components.

EOS mixing rules fall broadly into three main categories:

- Classical mixing rules
- Excess-free-energy mixing rules
- Density-dependent mixing rules
Of these three groups, classical mixing rules have been around longest, and are the ones used most often in chemical process engineering. Density-dependent and excess-free-energy mixing rules are more recent innovations, and were developed as attempts to overcome some of the limitations of classical mixing rules.

Classical mixing rules are also more firmly rooted in the one-fluid concept than the other two types. Excess-free-energy mixing rules follow the one-fluid concept in the sense that they do not directly modify the temperature- or density-dependence of the EOS; however, they can introduce temperature-dependent constants that effectively modify the temperature dependence of some parameters for the mixture, as compared to the EOS’s pure-component form. Density-dependent mixing rules, on the other hand, introduce mixture-only terms into the EOS form which can be functions of both density and composition.

Although classical mixing rules are used more often than the others, they do not accurately reproduce the pressure-volume-temperature (PVT) and phase equilibrium behavior of strongly non-ideal mixtures. For such mixtures, both density-dependent and excess-free-energy mixing rules can improve the accuracy of EOS calculations. But as pointed out by Poling et al. (2001), excess-free-energy mixing rules are more often recommended for this purpose. And as discussed by Orbey and Sandler (1998), excess-free-energy mixing rules retain an important feature of the one-fluid concept, which is that the EOS for both pure fluids and mixtures have the same density dependence.
For these reasons, density-dependent mixing rules have not been considered further in the current study. Both classical and excess-free-energy mixing rules are discussed further in the sections that follow.

4.2 Classical Mixing Rules

With classical mixing rules, the mixture EOS parameters are calculated from pure-component properties and the mixture composition. This category can be further divided into two main approaches: the corresponding states approach, and the van der Waals approach. Of the two, the van der Waals approach has become prevalent in present-day industrial use.

In the corresponding states approach, the central idea is that mixtures will exhibit the same PVT behavior as pure components at the same reduced conditions. Applying the corresponding states methodology requires that a corresponding-states-type generalized correlation be available for pure components, whereby the EOS parameters can be calculated from the pure substance’s critical properties. Using appropriate values for the mixture critical properties, the mixture EOS parameters can also be calculated directly from the generalized correlation.

In this approach, mixing rules are used to calculate effective critical properties for the mixture, which are referred to as pseudocritical properties, since in general they do not coincide with the true critical properties of the mixture. Although there are a number of possible ways to express mixing rules for pseudocritical properties, the simplest formulations are Kay’s rules (Kay, 1936), which are simply composition-weighted sums
of the individual pure-component critical properties. According to Poling et al. (2001), Kay’s rules provide acceptable values for pseudocritical temperature, volume, and compressibility, as well as acentric factor. For pseudocritical pressure, however, they recommend using the rule of Prausnitz and Gunn (1958a,b), in which pseudocritical pressure is calculated using pseudocritical compressibility, volume, and temperature from Kay’s rules.

The second and more common form of classical mixing rule is the van der Waals type. Here, mixture EOS parameters are calculated from the pure-component EOS parameters instead of from pure-component critical properties. Again, there are numerous possible ways to formulate mixing rules of this type, but two forms—linear and quadratic—have come to prevail in industrial use.

The linear mixing rule is the simplest van der Waals-type expression. Here, the mixture EOS parameter is expressed as a composition-weighted sum of the individual pure-component parameters. The linear mixing rule is written as

\[ M_{\text{mix}} = \sum x_i M_i \]  

(15)

where \( M \) is the EOS parameter of interest, and \( x_i \) is the mole fraction of the \( i \)th pure component in the mixture. Linear mixing rules do not allow the incorporation of mixture-specific interaction parameters into the calculation.

The quadratic rule is slightly more complex than the linear rule, but is still relatively simple. The quadratic rule essentially expresses the mixture parameter as the sum of
contributions from all possible pairings of pure components in the mixture, with each contribution weighted by the product of the mole fractions of the two components in the pair. The quadratic mixing rule can be written as

$$M_{\text{mix}} = \sum_i \sum_j x_i x_j M_{ij}$$  \hspace{1cm} (16)

where $M_{ij}$ is referred to as the cross term for the pair consisting of the $i^{\text{th}}$ and $j^{\text{th}}$ components. For $i = j$, the $M_{ij}$ term is equal to the corresponding pure-component value.

The quadratic form of this mixing rule has a theoretical basis, as it can be derived from statistical mechanics for the virial equation of state (Mason and Spurling, 1969). However, virial theory does not prescribe a precise form to the cross coefficients in terms of the pure-component EOS parameters, thus creating some empirical flexibility in how those terms are defined. For instance, it can be shown that if the cross term is defined as the arithmetic average of the two pure-component EOS parameters and is not modified with a binary interaction parameter, the quadratic rule of Eq. (16) reduces to the linear rule of Eq. (15).

Numerous forms have been proposed over the years for the cross term in Eq. (16), but the two that have found the widest application, particularly with cubic EOS, are the arithmetic mean, expressed as

$$M_{ij} = \left( \frac{M_i + M_j}{2} \right) \left( 1 - k_{ij} \right)$$  \hspace{1cm} (17)
and the geometric mean, written as

\[ M_{ij} = \sqrt{M_i M_j (1 - k_{ij})} \]  

(18)

In Eqs. (17) and (18), \( k_{ij} \) is a binary interaction parameter, essentially a correction factor specific to the binary pairing between components i and j. It should be noted that these two approaches are mathematically equivalent in the sense that the same value of \( M_{ij} \) can be calculated from either expression with the appropriate value of \( k_{ij} \). Another important observation, however, is that with the geometric mean expression (Eq. (18)), parameter M must have the same sign for both components to avoid a negative value under the square root sign. This restriction does not apply to the arithmetic mean expression in Eq. (17).

4.2.1 Classical Mixing Rules for Specific Equations of State

Classical mixing rules have been adopted for use with a number of specific equations of state. Applications of classical mixing rules to virial, cubic, and BWR-type EOS are discussed in detail in the sections that follow.

4.2.2 The Virial Equation

Mixing rules for the virial equation of state can be derived from statistical mechanics. It has been found that successively higher virial coefficients arise from interactions between successively higher numbers of molecules. As such, the second virial coefficient has been shown to depend on interactions between pairs of molecules, while third virial coefficients depend on interactions between groups of three molecules, and so on. As a
consequence, it has been found that mixture second virial coefficients are quadratic in composition—that is, B is the summation of contributions from all possible pairings of components in the mixture, and each contribution is proportional to the product of the mole fractions of the two substances in the pair. By the same token, third virial coefficients have a cubic composition dependence, and higher-order coefficients have still higher-order composition dependencies.

\[
B = \sum_i \sum_j x_i x_j B_{ij}
\]  

(19)

\[
C = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk}
\]  

(20)

But even with the composition dependence established, there is still the matter of how to define the cross coefficients in Eqs. (19) and (20). Virial theory shows how these coefficients can be calculated from potential energy functions between groups of two or more molecules. However, it is not clear from the theory how the cross terms might be calculated from pure-component EOS parameters.

4.2.3 Cubic Equations

As discussed earlier, most cubic EOS in use today can trace their origins to the van der Waals equation. The mixing rules for that equation were originally proposed by Berthelot and were used extensively by van der Waals and his colleagues (Prausnitz et al., 1986). Berthelot proposed a quadratic rule for the attractive parameter, \(a\), and a linear rule for the co-volume as follows:
\[ a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \]  \hspace{1cm} (21)

\[ b = \sum_i x_i b_i \]  \hspace{1cm} (22)

Eq. (21) is simply the geometric mean expression (Eq. (18)) without the mixture-specific binary interaction parameter. The geometric mean was originally proposed on an empirical basis, but was later shown by London to have some theoretical justification, at least when applied to intermolecular potential energies (Prausnitz et al., 1986). London showed that the potential energy between molecules of two different simple non-polar substances was approximately equal to the geometric mean of the two pure-substance pair potentials at the same intermolecular separation distance.

The mixing rules expressed in Eqs. (21) and (22) have persisted to this day for two-parameter cubic equations. More recent cubic EOS, such as Soave’s modification of the Redlich-Kwong EOS (Soave, 1972) and the Peng-Robinson equation (Peng and Robinson, 1976) have modified Eq. (21) to include a binary interaction parameter

\[ a(T) = \sum_i \sum_j x_i x_j \sqrt{a(T)_i a(T)_j} (1 - k_{ij}) \]  \hspace{1cm} (23)

In this way, the contribution from each binary pair to the mixture \( a(T) \) can be tuned, albeit coarsely, to match experimental binary mixture data. Note that in Eq. (23), the pure-component parameters \( a(T)_i \) are first calculated at the mixture temperature. Most cubic EOS do not apply a binary interaction parameter to the co-volume parameter, \( b \), and thus its mixing rule reverts to the linear form shown in Eq. (22).
4.2.4 **BWR-type Equations**

BWR-type equations have several adjustable parameters, some of which are coefficients of density, and others which are coefficients of the functions that express the temperature dependence of the density coefficients. In the original BWR equation, linear mixing rules were proposed, and as such, did not include any binary interaction parameters.

Bishnoi and Robinson (1972) proposed a different set of mixing rules that incorporated both higher-order composition dependence for the various parameters, as well as a binary interaction parameter for EOS constants associated with the second and third virial coefficients (as determined from a virial expansion of the BWR equation). For constants associated with the second virial coefficient, they proposed quadratic mixing rules, while for parameters associated with third and higher virial coefficients, cubic rules were prescribed. The cubic cross coefficient between a given group of three substances was defined as the products of the binary cross coefficients for the three possible pairings in the group. In this way, only binary interaction parameters are required, as opposed to interaction parameters specifically for ternary mixtures.

For his modification of the BWR equation, Starling (1973) proposed a new set of mixing rules. For parameters associated with the second virial coefficient, he used the mixing rules proposed by Bishnoi and Robinson. For the higher-order terms, however, he used the same mixing rules as the original BWR equation—linear rules in varying powers of the EOS coefficients. Two such rules are shown for example in Eqs. (24) and (25).
Binary interaction parameters are supplied only for parameters associated with the temperature dependence of parameter B. It is important to note that in each of the instances described above, a separate mixing rule is provided for each individual coefficient, even those within the temperature functions. As such, mixture values are first calculated for each individual parameter, and are then inserted into the temperature functions to calculate the value of the mixture density coefficient at the temperature of interest. This is in contrast to the approach described previously for cubic equations, where the mixing rule is applied to the density coefficient directly, rather than to the constants in the temperature function.

### 4.3 Excess Free Energy Mixing Rules

Over time, it became apparent that equations of state with classical mixing rules could not accurately reproduce the thermodynamic properties and phase equilibria of non-ideal mixtures, such as those containing polar or associating compounds. For such mixtures, the traditional approach has been to use activity coefficients to model their phase equilibrium behavior. Activity coefficients ultimately provide liquid-phase fugacities by matching experimental data on excess Gibbs energy of mixtures. Unlike an EOS, however, they cannot be used to calculate other properties such as density or enthalpy.
Nearly thirty years ago, a method was proposed (Huron and Vidal, 1979) by which the accurate excess Gibbs energy predictions of an activity coefficient model could be incorporated into an equation of state. As such, the combined model would retain the advantages of both the EOS and the activity coefficient model, and hopefully compensate for each other’s shortcomings at the same time.

Huron and Vidal’s approach was to derive an expression for excess Gibbs energy from an EOS, and equate it to the $G^E$ calculated from the activity coefficient model. As derived from an EOS, $G^E$ is dependent on both temperature and pressure, whereas $G^E$ calculated from an activity coefficient model depends on temperature but not pressure. Ultimately this means that the $G^E$ match between the EOS and the activity coefficient model can only be made at one pressure. Huron and Vidal chose infinite pressure as the condition at which to force the $G^E$ match.

One problem with this approach is that the EOS-derived $G^E$ expression becomes infinite as pressure approaches infinity, unless the excess volume tends to zero at the same time. For EOS with a van der Waals-type repulsion term, this can only be ensured by specifying a linear mixing rule for the co-volume parameter.

Another difficulty with carrying out the match at infinite pressure is that because $G^E$ varies strongly with pressure—and equations of state capture this pressure dependence—activity coefficient model parameters derived from low-pressure vapour-liquid equilibrium (VLE) data cannot be used directly. This is inconvenient, since the most
readily available $G^E$ data were measured at low pressure (see for example the DECHEMA collection of Gmehling, et al., 1988).

As a way to avoid such problems, Mollerup (1986) suggested carrying out the EOS-ACM match at zero pressure instead of infinite pressure. Models based on this idea were later developed by Heidemann and Kokal (1990), Michelsen (1990a,b), and Dahl and Michelsen (1990). One difficulty associated with this approach is that it requires a liquid density root from the EOS for each pure component at the pressure and temperature of the mixture. However, there is no guarantee that a liquid density root will exist for all components in the mixture. As a result, the zero-pressure methods cited above have had to incorporate approximate extrapolation techniques to overcome this difficulty.

4.4 Mixing Rules Based on Excess Helmholtz Free Energy

In 1992, Wong and Sandler proposed another alternative. Noting the complications described above which arise when the EOS-ACM match is carried out at either zero pressure or infinite pressure, they proposed instead to use excess Helmholtz energy as the basis for matching the EOS to the $G^E$ model. Citing the earlier work of Suen et. al. (1989) and Sheng et. al. (1992), they chose infinite pressure as the condition at which to force the match, with two main justifications:

- Excess Helmholtz energy is far less dependent on pressure than is excess Gibbs energy.

- At low pressure, $G^E$ is approximately equal to $A^E$. 
In combination, these observations suggest that the low-pressure $G^E$ calculated from an activity coefficient model can serve as an approximation to the low-pressure $A^E$, which in turn approximates the $A^E$ at infinite pressure. As such, Wong and Sandler’s approach forces a match between infinite-pressure $A^E$ derived from the EOS and the low-pressure $G^E$ prediction of the activity coefficient model. The main benefits of this method are that low-pressure pure-component liquid density roots—which may not exist at the mixture conditions—are not required, and the existing body of low-pressure activity coefficient model parameters reported in the literature can be used.

To implement this approach, Wong and Sandler used the two-parameter Peng-Robinson EOS (Peng and Robinson, 1976), and wrote mixing rules for the two-parameters as follows:

\[
b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \tag{26}
\]

\[
\frac{G^E_i}{C} = \frac{a}{b} - \sum_i x_i \frac{a_i}{b_i} \tag{27}
\]

where $G^E_i$ is the excess Gibbs energy from the activity coefficient model, and $C$ is a numerical constant. Eq. (26) expresses the quadratic composition dependence of the second virial coefficient, while Eq. (27) expresses the match between the infinite pressure $A^E$ expression from the EOS and the $G^E$ from the activity coefficient model.

It has been shown by Wong et. al. (1992) and by Huang and Sandler (1992) that the Wong-Sandler mixing rule extrapolates well to high pressures and temperatures, using
activity coefficient parameters derived from data measured at low pressures and moderate temperatures. These authors demonstrated that high-pressure-and-temperature VLE behavior of several non-ideal binary and ternary systems could be predicted accurately without the need to introduce temperature-dependent parameters in the underlying activity coefficient model.

However, Michelsen and Heidemann (1996) later showed that the Wong-Sandler model’s extrapolatory abilities may be somewhat fortuitous. They analyzed the contributions of various terms to the excess free energy mixing rules, and found that for the Wong-Sandler rule, the EOS-calculated $G^E$ at low pressure was only partially attributable to the activity coefficient model, with the remainder being due to the second virial coefficient interaction term. There is also a small contribution that arises from the pure-component parameters.

Michelsen and Heidemann also investigated the calculation of excess enthalpy ($H^E$), which is a major component of excess Gibbs energy. They showed that the Wong-Sandler model tends to overpredict $H^E$ of binary mixtures compared to the underlying activity coefficient model, and that this overprediction in part cancels the underlying ACM’s tendency to underpredict $H^E$ as compared to the experimental data. They point out that this cancellation may be responsible for much of the Wong-Sandler model’s ability to extrapolate accurately to conditions beyond those at which the model parameters were originally fit.
Michelsen and Heidemann also demonstrate that because the ACM is only partially responsible for the calculated value of $G^E$, subtle variations in $G^E$ behavior can result in false liquid-liquid phase split predictions from the Wong-Sandler model, even though the ACM itself does not predict such behavior. They further point out that with other excess-free-energy mixing rules—those that do not enforce the quadratic composition dependence of the second virial coefficient—there is no second-virial interaction contribution to the EOS-calculated $G^E$. As a result, the EOS-calculated value of $G^E$ is more directly attributable to the underlying ACM, and the non-physical liquid-liquid splitting is not predicted.

As a final point, Michelsen and Heidemann mention that other mixing rules, such as the original Huron-Vidal rule, or the modified Huron-Vidal (MHV-1) rule (Michelsen, 1990) could also be modified to enforce a quadratic composition dependence on the mixture second virial coefficient, but instead their developers choose to use a linear mixing rule for the co-volume parameter in the two-parameter EOS. Using the binary system n-pentane + methanol as an example, they show that the vapour-phase excess Gibbs energy is an order of magnitude lower than that in the liquid phase, and that the vapour-phase $G^E$ calculated from the Wong-Sandler rule was only marginally different from that calculated using a second modified Huron-Vidal rule, MHV-2 (Dahl and Michelsen, 1990), which does not enforce the quadratic composition dependence. Michelsen and Heidemann conclude that the accuracy of the Wong-Sandler approach in predicting VLE behavior—at least for the n-pentane + methanol mixture—cannot be attributed to the rigorous treatment of the mixture second virial coefficient.
Satyro and Trebble (1996) observed that Eqs. (26) and (27) create an implicit temperature dependence in the mixture b parameter, which results in negative isochoric heat capacities at high pressures. To correct this thermodynamic inconsistency, Satyro and Trebble (1998) proposed to use an explicit classical quadratic expression for mixture b instead of Eq. (26) as follows:

$$b = \sum \sum x_i x_j \left( \frac{b_i + b_j}{2} \right) (1 - l_{ij})$$  \hspace{1cm} (28)

They noted that when Eq. (28) is applied to the Peng-Robinson EOS instead of Eq. (26), the quadratic composition dependence of the mixture second virial coefficient is no longer enforced. However, they pointed out that cubic EOS generally make poor predictions of mixture B, and that using Eq. (28) did not worsen the predictions for the binary systems they studied. This is consistent with Michelsen and Heidemann’s (1996) observation that the rigorous treatment of the mixture second virial coefficient’s composition dependence in the Wong-Sandler mixing rule was probably not responsible for its success in predicting VLE of non-ideal mixtures.
CHAPTER 5
DEVELOPMENT OF THE NEW MIXING RULES

5.1 Preliminary Evaluation of Wong-Sandler Mixing Rules

One main objective of the current research was to develop mixing rules for the new equation of state. It was recognized that for a non-cubic EOS to be viable as an alternative to popular cubic EOS, it would need to apply not only to nearly-ideal mixtures, but to non-ideal mixtures as well. It was therefore decided to investigate the excess-free-energy type mixing rules, as they had already proven successful in this regard for cubic EOS. In particular, based on the experience of Satyro and Trebble (1996, 1998), it was decided that the infinite-pressure Helmholtz energy approach of Wong and Sandler (1992) would be the focus of the work.

Before attempting to develop excess-free-energy mixing rules for non-cubic EOS, it is helpful to understand how they behave when applied to cubic EOS. The purpose of this part of the study was to investigate firsthand the behavior of excess-Helmholtz-energy-based mixing rules as they apply to cubic EOS, and to confirm the assertion that EOS-calculated $A^E$ is nearly invariant with pressure—the central justification for using Helmholtz energy instead of Gibbs energy.

As an example, Wong and Sandler showed a graph of $A^E$ calculated for the methanol + benzene binary system using the PRSV equation of state, plotted against composition. They pointed out that the $A^E$ curves at 1 bar and 1000 bar were virtually identical.
However, a significant binary interaction parameter \( k_{ij} = 0.2808 \) was required to give an optimal match between the EOS-calculated and ACM-calculated \( A^E \).

To investigate the pressure invariance of EOS-calculated \( A^E \), and to allow direct comparison with work on non-cubic EOS carried in the current study, saturation pressures and \( A^E \) were calculated for the ethanol + water system at 393.15 K using the PRSV equation of state with the Wong-Sandler mixing rules. This was the same test system used for the later non-cubic EOS work.

PRSV parameters were obtained from Orbey and Sandler (1998), and are shown in Table A-4 in Appendix A. Mixture \( A^E \) was calculated using the Non-Random Two-Liquid (NRTL) activity coefficient model (Renon and Prausnitz, 1968). NRTL parameters for the ethanol + water system were obtained from the DECHEMA collection (Gmehling et al., 1988), and are shown in Table A-5. The PRSV binary interaction parameter was determined by matching \( A^E \) calculated from the EOS with that calculated from the NRTL equation at equimolar composition and a pressure of one atmosphere. As Fig. 5-1 shows, this resulted in a very good match between the two curves over the entire composition range.

Fig. 5-2 shows the corresponding P-x-y diagram, plotted against the experimental data that Gmehling et al. (1988) had used originally in fitting the NRTL parameters. The figure shows excellent agreement with both the NRTL-calculated \( A^E \), as well as with experimental P-x-y data.
Figure 5-1  Comparison of NRTL- and PRSV-calculated $G^E$ curves for ethanol + water system at 393.15 K ($k_{ij} = 0.24$ and $k_{ij} = 0$)

Figure 5-2  Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: WS-PRSV model ($k_{ij} = 0.24$)
It should be noted, however, that the optimized value of $k_{ij} = 0.24$ is fairly large. As Fig. 5-1 shows, when the EOS calculation is repeated with $k_{ij} = 0$, the agreement between the EOS and the activity coefficient model is not nearly as good. Furthermore, the calculation with $k_{ij} = 0$ reveals two important things:

- First, the EOS-calculated $A^E$ curve does not remain constant, but has a strong tendency to drift from its infinite pressure reference condition as pressure is reduced to low levels.

- Second, although $A^E$ does tend to drift, the overall shape of the curve remains the same. This makes it possible to bring the low-pressure $A^E$ curve back into agreement with the activity coefficient model using only a single binary interaction parameter. It is likely that the EOS-calculated $A^E$ curve is constrained to maintain the same general shape over a wide range of pressure because of its low-degree cubic form.

As mentioned earlier, Fig. 5-1 shows that the EOS and the activity coefficient model can be made to agree very well at low pressures when a binary interaction parameter is applied. But although the EOS- and NRTL-calculated $A^E$ curves agree at both infinite and low pressure, this does not guarantee that the curves maintain the same level of agreement at all pressures in between.

To determine whether this was indeed the case, $A^E$ curves were calculated using the PRSV EOS at various pressures between low-pressure and infinite-pressure endpoints. The calculations were again carried out for the ethanol + water system at 393.15 K, using the optimized value of the binary interaction parameter ($k_{ij} = 0.24$).
The calculation showed that although the EOS- and NRTL-calculated curves matched well at low- and infinite pressure, the agreement between the curves is not maintained over the full range of pressure. Fig. 5-3 shows EOS-calculated $A^E$ curves at several different pressures. In the figure, the EOS-calculated curve can be seen to drift somewhat from its infinite-pressure form as pressure is lowered.

![Graph](image)

**Figure 5-3** PRSV-calculated $A^E$ curves for ethanol + water system at 393.15 K ($k_{ij} = 0.24$) at various pressures

However, the curve comes back into agreement with the activity coefficient model at around 800 atm, and remains almost constant between 800 atm and one atm.

The variation of the EOS-calculated $A^E$ curve with pressure is also shown in Fig. 5-4 in a slightly different way. From Fig. 5-1, it can be seen that the curve of $A^E$ versus pressure reaches a maximum at some intermediate composition between pure ethanol and pure
water. In Fig. 5-1, the maximum value of reduced $A^E$ (i.e., $A^E$ divided by RT) is approximately 0.29 for the curve calculated using the optimized $k_{ij}$. This peak value of the reduced $A^E$ curve can be plotted against pressure to show how the curve drifts over a wide range of pressures. Fig. 5-4a presents such a plot, with curves representing both zero- and optimized interaction parameters.

![Figure 5-4a](image_url)

**Figure 5-4a** Variation of peak value along PRSV-calculated $A^E$ curve with pressure, for ethanol + water system at 393.15 K: Wong-Sandler mixing rules

The figure shows that without an interaction parameter (lower curve), the peak value of the reduced $A^E$ curve drifts downward from its infinite-pressure reference level of approximately 0.29, reaching a minimum value of approximately 0.14 at about 3400 atmospheres, and then leveling off at a value of about 0.16 between pressures of one and 100 atmospheres.
These observations have important corollaries for non-cubic EOS. First, because of their higher-order non-cubic functional forms, we should not necessarily expect the shape of the uncorrected $A^E$ curve to be the same at low pressure as it was at infinite pressure, where it was forced to match the activity coefficient model curve. As a consequence, it may not be possible to bring the EOS-calculated curve back into agreement with the ACM-calculated curve using only a single binary interaction parameter.

It is interesting to note that similar behavior is exhibited by the PRSV EOS when the conventional mixing rules are used (quadratic mixing rule with a binary interaction parameter for ‘a’, and a linear mixing rule for ‘b’).

![Graph showing variation of peak value along PRSV-calculated $A^E$ curve with pressure, for ethanol + water system at 393.15 K: conventional mixing rules.](image)

**Figure 5-4b** Variation of peak value along PRSV-calculated $A^E$ curve with pressure, for ethanol + water system at 393.15 K: conventional mixing rules
As Fig 5-4b shows, the peak value of the EOS-calculated $A^E$ curve still shows a strong tendency to drift from its infinite-pressure value as pressure is reduced, leveling off at pressures below approximately 1000 atmospheres.

The figure also shows that with conventional mixing rules, the binary interaction parameter produces only a coarse shifting of the entire curve, which tends to retain its overall shape when the interaction parameter is applied. By contrast, the interaction parameter in the Wong-Sandler mixing rule affects only the low-to-medium pressure value, with no effect on the high-pressure portion of the curve.

### 5.2 Special Considerations for Non-Cubic EOS

An initial review revealed three main issues must be resolved when applying excess-free-energy mixing rules to non-cubic EOS. These issues do not arise with cubic EOS.

- First, it must be decided whether to apply the mixing rules directly to the density parameters, or instead to the individual temperature function parameters.

- Second, an EOS parameter must be selected into which the excess free energy will be inserted to force the match between the EOS and the ACM.

- Third, mixing rules must be provided for all the remaining parameters in the EOS.
5.2.1 Density Parameters vs. Temperature Function Parameters

The first main consideration when developing mixing rules for a non-cubic EOS is whether to apply the mixing rules directly to the temperature-dependent density parameters, or instead to the individual temperature function parameters. Both approaches have precedents: non-cubic EOS such as the BWR equation have had mixing rules applied to each temperature function parameter (Bishnoi and Robinson, 1972; Starling, 1973), whereas cubic EOS have typically had their mixing rules applied directly to their density parameters, once they have been calculated for the individual pure components at the temperature of the mixture. This latter approach is also normally applied to the virial equation of state, and has made its way into empirical correlations for mixture virial coefficients (Tsonopolous, 1974). Neither approach has any obvious advantage in terms of improving the accuracy of the EOS’s predictions. However, applying the mixing rules to the density parameters offers one practical benefit: non-cubic EOS have many fewer density parameters than temperature function parameters, so fewer mixing rules would be needed. For the BWR equation, this approach would reduce the required number of mixing rules from eight to five. For Starling’s modification of BWR, the number would be reduced from eleven to five.

The density parameter approach brings the added benefit that the mixing rules would be independent of the functional form of the EOS temperature functions. It would therefore be possible to modify the temperature functions without affecting the mixing rules.

For these reasons, the density parameter approach was selected for the current work.
5.2.2 Selecting an EOS Parameter for Excess Free Energy Matching

The second main consideration when applying excess free energy mixing rules to a multi-constant non-cubic equation of state is the selection of a parameter to be used to force the free energy match between the EOS and the activity coefficient model. With cubic EOS, the choice is straightforward, particularly for two-parameter cubics such as Peng-Robinson or Soave-Redlich-Kwong. For a non-cubic EOS, however, there are many parameters to choose from. The choice can be simplified by considering the fundamental purpose of excess free energy mixing rules, which is to improve the EOS’s ability to represent the liquid-phase excess Gibbs energy of fluid mixtures. It could therefore be argued that the selected parameter should be the coefficient of a term that is active mainly in the liquid phase—that is, at liquid-like densities—and to which the excess Gibbs energy is particularly sensitive. This logic further suggests that parameters associated with terms that vanish at high densities—such as the near-critical term in Eq. (2), or the exponential term in Eq. (8)—would not be good choices.

5.2.3 Mixing Rules for Remaining EOS Parameters

The third consideration for applying excess free energy mixing rules to a non-cubic EOS is to select the form of the mixing rules for the remaining EOS parameters that are not being used for the $G^E$ match between the EOS and the ACM. This point is particularly important, because merely asserting that excess free energy calculated from the EOS and ACM should match at a particular condition is only sufficient to specify a mixing rule for one parameter. This principle gives no guidance as to what form the mixing rules for the
remaining EOS parameters should take. In the current work, it was decided that linear mixing rules would provide a reasonable starting point, because they are simple and have been used in the past for some non-cubic EOS parameters, such as in the BWR equation. Also, when a simple arithmetic average is used for the cross term, the widely-used quadratic mixing rule reduces to a linear expression.

5.3 Initial Approach to Mixing Rule Development

Based on the above considerations, a preliminary approach was established for developing the new mixing rules. The main characteristics of this approach were as follows:

- The mixing rules would be applied to both the original BWR equation and the new EOS.

- The mixing rules would be applied directly to the density parameters, not to the individual temperature function parameters.

- The excess-free-energy match would be carried out using the coefficient of one of the high order polynomial terms—C, D, or E in Eq. (6), and C or D in Eq. (2).

- Linear mixing rules would be used for the remaining EOS parameters.

- The excess-free-energy match would be carried out by matching the infinite-pressure excess Helmholtz energy from the EOS to the low-pressure excess Gibbs energy from the activity coefficient model, after Wong and Sandler (1992). This
approach was selected for the initial work because it was deemed to be simpler than the low-pressure approaches, which require ad-hoc extrapolation procedures in the event that low pressure liquid-density roots do not exist for one or more pure components in the mixture.

- The test system for mixing rule development would be ethanol + water, because mixtures of these components exhibit low saturation pressures at moderate temperatures where experimental data is available, and the system is sufficiently non-ideal.

5.4 Repulsion Terms

In order for the infinite-pressure excess free energy approach to be successful, the equation of state must have a finite density in the limit of infinite pressure. In cubic EOS, the so-called repulsion term provides this density limit. Essentially all past applications of excess-free-energy mixing rules have used the Peng-Robinson equation of state, or variations such as PRSV (Stryjek and Vera, 1986a,b). Like many other EOS, the Peng-Robinson equation uses the van der Waals repulsion term, which, at infinite pressure, yields a limiting specific volume that is numerically equal to the co-volume parameter, b.

The two non-cubic EOS being investigated in this work take different approaches for representing intermolecular repulsions. The BWR equation (Eq. (2)) uses an ideal gas term for this purpose, which gives infinite density—and infinite Helmholtz energy—at infinite pressure. On the other hand, it was proposed earlier in the current study (see Chapter 3) to adopt the Carnahan-Starling (CS) term (Carnahan and Starling, 1969) to
represent intermolecular repulsions in the new EOS. In the form shown in Eq. (12), the
CS term yields a limiting specific volume equal to its co-volume parameter.

However, a derivation of excess Helmholtz energy carried out for the new EOS during
the current study seemed to indicate that $A^E$ does not exhibit a finite value in the limit of
infinite pressure when the CS term is used. It was later found that this result had been
documented by Brandani and Brandani (1996). These authors concluded that infinite-
pressure free energy mixing rules cannot be applied to EOS that use the Carnahan-
Starling expression as its repulsion term.

Before proceeding, it was therefore decided to modify both the new EOS and the BWR
equation to use the van der Waals expression as their leading term, to ensure a finite
value of Helmholtz energy at infinite pressure.

### 5.5 Excess Helmholtz Energy at Infinite Pressure

Expressions for excess Helmholtz energy in the limit of infinite pressure ($A^E_{\infty}$) were
derived for both the new EOS and the modified BWR equation. The derivations are
provided in Appendix B. For a given equation of state, $A^E_{\infty}$ can be expressed as

$$A^E_{\infty} = J^\infty_m - \sum_i x_i J^\infty_i$$

(29)

where the subscript $m$ refers to the mixture, and the subscript $i$ refers to the $i^{th}$ pure
component. For the new EOS, $J^\infty$ is written as
For the modified BWR equation, $J^\infty$ is written as

$$J^\infty = \frac{B}{b} + \frac{C}{2b^2} + \frac{D}{5b^5} + \frac{E}{6b^6} - \frac{F}{G} \exp(Gb) + \frac{e}{\sqrt{f}} \left[ \tan^{-1}(\sqrt{f}(b-g)) - \frac{\pi}{2} \right]$$

(30)

5.6 The New Mixing Rules

5.6.1 Preliminary Observations

The effort to develop new excess-free-energy mixing rules centered initially on the new EOS, modified to use the van der Waals repulsion term. For simplicity, the near-critical term was omitted from the equation in the preliminary work.

The first step was to apply the mixing rules to the test mixture (ethanol + water), but without the excess free energy correction. As mentioned earlier, linear mixing rules were used for the initial step. A parameter was then chosen for incorporating the excess Gibbs energy from the ACM into the EOS. At first, parameter B in Eq. (6) was selected for this purpose.

During the initial trial, three difficulties were encountered. First, it was noticed that as the mixture composition was varied from pure water to pure ethanol at the test temperature of 323.15 K, the mixture isotherm—as plotted on a diagram of pressure against specific volume—did not interpolate smoothly between those of the pure components at the same temperature. Fig. 5-5 illustrates this behavior, and shows pure
component isotherms at 323.15 K for water and ethanol, as well as for mixtures of 2.67 mole percent and 50 mole percent ethanol.

![Graph showing calculated isotherms for mixtures of ethanol and water using new EOS with linear mixing rules.](image)

**Figure 5-5** Calculated isotherms at 323.15 K for mixtures of ethanol and water using new EOS with linear mixing rules.

The figure shows that when even a small amount of ethanol was added to water, the resulting EOS-calculated mixture isotherm shifted far to the right, such that it was much closer to the isotherm for pure ethanol than for pure water. As such, the EOS would predict a liquid density that is also much closer to that of ethanol than water, even though the system is mostly water. It is very unlikely that such behavior would be observed in actual experiments. And as the figure shows, at a composition of 50 mole percent ethanol, the mixture isotherm actually crosses over the isotherm of pure ethanol, meaning
that the EOS would predict a higher density for the mixture than for either of the pure components. Again, this behavior is not realistic.

The second difficulty was that the binary saturation-pressure calculations, carried out to allow comparison of phase equilibrium calculation with experimental data, would not converge. This problem was ultimately traced to the use of linear mixing rules for some of the parameters. If we examine Eqs. (29) and (30), the expression for excess Helmholtz energy derived from the new EOS, we can see that each term in the EOS makes its own contribution to the total.

As such, a given set of mixing rules will generally produce a false excess Helmholtz energy, even for ideal mixtures, unless some kind of correction is made. Depending on the exact form of the mixing rules, this false $A^E$ might not be large, in which case it might be easy to correct through traditional means such as binary interaction parameters ($k_{ij}$). But in some cases, the false $A^E$ may be so large that it cannot be easily corrected using $k_{ij}$ parameters or excess-free-energy matching.

As an example, consider applying the Wong-Sandler methodology to the new EOS, with linear mixing rules for all parameters except B. For parameter B, the mixing rule will be based on the infinite-pressure $A^E$ match between the EOS and the ACM. Now, if we apply the linear mixing rules and equate the infinite-pressure $A^E$ from the EOS (Eqs. (29) and (30)) to the $G^E$ from the activity coefficient model, then upon rearranging for parameter B, we have the following expression:
This single mixing rule lumps the entire excess free energy correction into a single EOS parameter, B. It is apparent upon inspecting Eq. (32) that the magnitude of the correction to B depends not only on the value of $A_E^\infty$ from the activity coefficient model, but on the sum of the ‘residual’ contributions from all other EOS parameters. In fact, even for an ideal mixture where $A_E^\infty$ equals zero, the correction can still be large if the forms of the other mixing rules produce large residual contributions to $A_E^\infty$. The net effect, therefore, is that parameter B must not only match the ACM-calculated $A_E^\infty$, but must also cancel out the artificial $A_E^\infty$ created by the mixing rules for the other parameters.

In this initial trial for the new EOS, it was found that the artificial $A_E^\infty / RT$ contribution from the exponential term was extremely large. This occurred because the pure-component values of F for water and ethanol determined by regression to experimental data were different by three orders of magnitude. With a linear mixing rule, adding even the slightest amount of ethanol to pure water had a dramatic effect on the value of F for the mixture. In turn, this created a very large artificial contribution to $A_E^\infty$. And since the actual experimentally-determined value of $A_E^\infty / RT$ for the mixture only peaks at 0.289, the parameter B had to make up the difference. Overall, the total $A_E^\infty$ correction which parameter B is required to absorb is many times larger than the actual value of $A_E^\infty$ itself. This has a large impact on the value of B for the mixture.
The problem this creates is that EOS parameters are not necessarily free to take on arbitrary values. Parameter B, for example, makes a large contribution to the mixture’s second virial coefficient, and as such, can only take on certain values without compromising the EOS’s predictions of low-pressure vapour-phase PVT behavior and fugacities.

In the initial trial with the new EOS, the mixture second virial coefficient had the wrong sign and order of magnitude to the extent that even low-pressure binary saturation point calculations would not converge.

5.6.2 The Zero-\(A^E\_\infty\) Approach

At this point, it was apparent that the new mixing rules should not be allowed to produce an artificial excess Helmholtz energy. That way, the magnitude of the overall \(A^E\) correction to the chosen parameter would be smaller, and would be more closely related to the degree of non-ideality of the mixture. It was realized that this could be accomplished by using the expression for infinite-pressure Helmholtz free energy itself (Eqs. (29)–(31)) to dictate the form of the mixing rules.

In Eqs. (29)-(31), each mixture term has associated with it a corresponding composition-weighted pure-component sum. If each mixture term is set equal to its associated pure-component sum, the result is a set of mixing rules which, by definition, yields a value of zero for \(A^E\_\infty\). But not only will the total mixture \(A^E\_\infty\) equal zero, the individual contribution associated with each EOS term will also equal zero. In this way, the mixing rule for the parameter selected for the EOS-ACM match would no longer need to include
terms canceling the artificial Helmholtz energies arising from arbitrary mixing rules for the other EOS terms. In Eq. (32), for example, most of the terms on the right hand side would no longer be required. This methodology is hereafter referred to as the zero-$A^E_\infty$ approach.

It must be noted that this approach provides a mixing rule for each term in the $A^E_\infty$ expression, and not necessarily for each EOS parameter. In the BWR equation, for example, the exponential term contains two EOS parameters, $E$ and $F$. The zero-$A^E_\infty$ approach only provides one mixing rule for the exponential term, and thus for only one of these two parameters. For the other parameter, an additional mixing rule must still be supplied. For this additional rule, we are free in principle to choose its form, since it will not affect the exponential term’s contribution to $A^E_\infty$. However, we would expect that some forms would work better than others.

For the new EOS, the zero-$A^E_\infty$ mixing rules are expressed as

$$B = b \sum_i x_i \frac{B_i}{b_i}$$  \hspace{1cm} (33)

$$C = b^2 \sum_i x_i \frac{C_i}{b_i^2}$$  \hspace{1cm} (34)

$$D = b^5 \sum_i x_i \frac{D_i}{b_i^5}$$  \hspace{1cm} (35)

$$E = b^6 \sum_i x_i \frac{E_i}{b_i^6}$$  \hspace{1cm} (36)
The co-volume, \( b \), is one of the parameters for which the zero-\( A^E_\infty \) approach does not provide a mixing rule. The traditional quadratic mixing rule (Eq. (28)) was therefore specified for this parameter.

For the EOS’s exponential term, the zero-\( A^E_\infty \) methodology presents a choice between two possible mixing rules:

\[
F = \frac{G \sum x_i \frac{F_i}{G_i} \exp(G_i b_i)}{\exp(G b)}
\]  \( (37a) \)

or

\[
G = \frac{F \exp(G b)}{\sum x_i \frac{F_i}{G_i} \exp(G_i b_i)}
\]  \( (37b) \)

Only one of Eqs. (37a) or (37b) can be chosen, and a supplementary mixing rule must be supplied for the other parameter. Eq. (37a) was initially preferred because it provides an explicit expression for \( F \). Eq. (37b) is implicit in \( G \), and would require an iterative solution. A linear mixing rule was therefore specified for parameter \( G \) as follows:

\[
G = \sum x_i G_i
\]  \( (38) \)

A similar situation arises for the near-critical term because the term contains three EOS parameters. And although explicit expressions can be written for two of them, the most
straightforward mixing rule results from rearranging the zero-A\textsuperscript{E}∞ expression in terms of parameter ‘e’ as follows:

\[
e = \frac{\sqrt{f} \sum_i x_i \frac{e_i}{\sqrt{f_i}} \left[ \tan^{-1} \left( \sqrt{f_i} (b_i - g_i) \right) - \frac{\pi}{2} \right]}{\tan^{-1} \left( \sqrt{f} (b - g) \right) - \frac{\pi}{2}} \tag{39}
\]

Linear mixing rules were selected for the remaining two parameters:

\[
f = \sum_i x_i f_i \tag{40}
\]

\[
g = \sum_i x_i g_i \tag{41}
\]

Although the near-critical term was included in the derivations of the excess Helmholtz energy expressions and partial fugacity coefficients, it was omitted from the EOS during further development and application of the zero-A\textsuperscript{E}∞ mixing rules. It was judged that the near-critical term—while serving an important purpose for modeling pure-component PVT and VLE behavior—was not essential for proving the concept of extending excess-free-energy mixing rules to non-cubic EOS, and that including this term at a preliminary stage might complicate the troubleshooting that would be inevitably be required during mixing rule development. For these reasons, the near-critical term was omitted from the new EOS during this part of the work.
For the BWR equation, the new zero-$A_{\infty}^E$ mixing rules are expressed as

\[
\begin{align*}
    b &= \sum_i \sum_j x_i x_j \left( \frac{b_i + b_j}{2} \right) (1 - 1_{ij}) \tag{42} \\
    B &= b \sum_i x_i \frac{B_i}{b_i} \tag{43} \\
    C &= b^2 \sum_i x_i \frac{C_i}{b_i^2} \tag{44} \\
    D &= b^3 \sum_i x_i \frac{D_i}{b_i^3} \tag{45}
\end{align*}
\]

\[
E = \frac{F \sum_i x_i \frac{E_i}{F_i} \left[ \left( 1 + \frac{F_i}{2b_i^2} \right) \exp \left( -\frac{F_i}{b_i^2} \right) - 1 \right]}{\left[ \left( 1 + \frac{F}{2b^2} \right) \exp \left( -\frac{F}{b^2} \right) - 1 \right]} \tag{46}
\]

\[
F = \left[ \sum_i x_i F_i^{0.5} \right]^2 \tag{47}
\]

The mixing rule selected for parameter $F$ is the one originally proposed by Benedict et al. (1940) and later adopted by Starling (1973). For the co-volume, the classical quadratic mixing rule (Eq. (28)) was again specified.

As discussed earlier, these mixing rules result in an $A_{\infty}^E$ of zero by definition, and must be modified to incorporate $G^E$ predictions from an activity coefficient model. Parameter
D was selected at this stage for both the new EOS and the BWR equation. The modified mixing rule for D is written

\[ D = b^5 \left[ 5A_{\infty}^E + \sum x_i \frac{D_i}{b_i^5} \right] \]  

(48)

for both EOS, because the term containing D is the same in both equations (compare Eqs. (35) and (45)).

In the special case where \( A_{\infty}^E \) is equal to zero, Eq. (48) reduces to the original expression (Eq. (35) or (45)). None of the other EOS parameters appears in Eq. (48), since by definition, their contributions to the mixture \( A_{\infty}^E \) are cancelled exactly by their corresponding pure-component sums.

5.7 Application to the Ethanol + Water Binary System

5.7.1 Results for the BWR Equation

To allow calculation of binary saturation curves, partial fugacity coefficients were first derived, as shown in Appendix C. The NRTL equation (Renon and Prausnitz, 1968) was chosen as the activity coefficient model. Again, the test binary system was ethanol + water at 393.15 K. NRTL Parameters for this system (Gmehling et al., 1988) are shown in Table A-5 in Appendix A, and the corresponding Antoine constants for pure-component vapour pressures are shown in Table A-15.

Pure-component parameters for ethanol and water were determined by least-squares data fitting, using the global regression procedure described in Section 3.2. Pure-component
PVT data for ethanol was taken from the work of Lo and Stiel (1969) and Wilson et al. (1984). Saturation pressures and saturation specific volumes for ethanol were from the work of Raikes and Bowen (1928) and Germann (1928).

Some pure-component data sources—such as the PVT and saturation data for water (Keenan et al., 1978), and the saturation data for ethanol (Raikes and Bowen, 1928)—provide data that has been smoothed over several independent data sets covering a wide range of conditions. As such, these sources often do not comment on the accuracy of the underlying data sets, but instead on the quality of the fit of the smoothing equations to the data. To gain a sense of the accuracy of the underlying data, it is necessary to turn to the original primary data sources cited by the authors of the smoothed data collections.

In some cases, the original primary data sources were available, and could be consulted to assess the accuracy of the data. In general, the data is of high quality. For ethanol, much of the data—including saturation pressure, saturated liquid density, and compressed liquid density—was stated to be accurate to within 0.5% or less. Other data, such as saturated- and single-phase vapour density were accurate to within 4%.

For water, several of the primary data sources cited by Keenan et al. (1978) could not be located easily. However, the sources that were located indicated that the property measurements for which they were used were of high quality. In particular, compressed liquid densities (Kell and Whalley, 1965) were reported to be accurate to within 0.004%, and saturation pressures (Bridgeman and Aldrich, 1964) were within 0.3%.
Two problems were noted during the initial regressions. First, the best-fit value of the co-volume parameter, $b$, for water tended toward a negative value, which is physically meaningless. In addition, the lack of a positive asymptotic volume resulted in spurious inflections in the calculated isotherms. To overcome the problem, the regression was repeated with $b$ held constant for several values between zero and 18 cm$^3$/mol. The latter value was essentially the lowest measured specific volume in the experimental data set, which sets an upper limit for $b$. It was noted that although the global minimum in the objective function occurred at a negative value, there was a local minimum much nearer to the experimental specific volumes. Parameter $b$ was therefore assigned a value of 17 cm$^3$/mol, which is near the local minimum. In a similar manner, the value of $b$ for ethanol was assigned a value of 50 cm$^3$/mol, which is near its own corresponding local minimum.

The second problem that was observed during the regressions was that the BWR equation—using the temperature dependence of Starling and newly-regressed parameters—did a poor job of reproducing the pure-component vapour pressures of both water and ethanol at the temperature of interest (393.15 K). This was the case, even though the regression was based on minimizing percentage errors in vapour pressure, which puts low-pressure data (such as that at 393.15 K) on equal footing with high-pressure data. Although it may seem unusual that a multi-constant non-cubic equation would have difficulty reproducing vapour pressures, it must be considered that the BWR EOS and modifications such as BWRS (Starling, 1973) were originally developed for use mainly with light n-alkane hydrocarbons, and not for polar or other non-ideal substances.
Authors such as Nishiumi (1980) have found it necessary to modify the temperature dependence of the equation’s parameters to include extra terms specifically for modeling polar substances. Even with this modification, Nishiumi (1980) reports that error in vapour pressure for water exceeds 5% at reduced temperatures below 0.42 (T ≈ 324 K) using generalized EOS parameters. It is therefore not surprising that with the original temperature dependence or that of Starling, the BWR equation exhibits vapour pressure errors of similar magnitude.

The inability to reproduce pure-component vapour pressures at the temperature of interest makes it difficult to evaluate mixing rules, because the endpoints of the isothermal binary P-x-y diagram are the pure-component vapour pressures. Even if the mixing rules perform well, the calculated P-x-y curves will be incorrect, thus preventing a fair evaluation of the mixing rules.

To overcome this difficulty, the EOS parameters were re-fit to VLE data over a very narrow range of temperatures that included the temperature of interest. The result was a set of parameters for each component which—although giving relatively poor performance over the full data set—allowed the BWR equation to reproduce the pure-component vapour pressures at 393.15 K with high accuracy. Values of these parameters are shown in Table A-6.

The binary interaction parameter, $l_{ij}$, in the mixing rule for the co-volume (Eq. (28)) was set at the value that gave the best match between the excess Gibbs energy curve calculated from the activity coefficient model directly and the curve calculated from the
EOS after carrying out the excess free energy match. As Fig. 5-6 shows, these two curves match very well, with an average absolute deviation (AAD) in $G^E/RT$ of 0.0024 (as averaged over the number of points at which $G^E/RT$ was computed in order to plot the figure).

![Comparison of NRTL- and EOS-calculated $G^E$ curves for ethanol + water system at 393.15 K: BWR EOS ($l_0=0.0575$)](image)

**Figure 5-6** Comparison of NRTL- and EOS-calculated $G^E$ curves for ethanol + water system at 393.15 K: BWR EOS ($l_0=0.0575$)

At this point, binary saturation point calculations were carried out to produce an isothermal binary P-x-y diagram for comparison with the experimental data. Unlike the earliest attempt using the new EOS, the BWR calculations converged. The calculated dewpoint and bubblepoint curves were compared with the data (Gmehling et al., 1988), and were found to match the data very well, as shown in Fig. 5-7.
Figure 5-7  Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: BWR EOS with $A^E$ correction in parameter ‘D’

In this figure, the average absolute deviation between computed and experimental pressure (AAD-$P$) of 0.032 atm, and an average absolute deviation between computed and experimental ethanol vapour-phase mole fractions (AAD-$y_{C2OH}$) of 0.0072. For both these computations, the liquid-phase mole ethanol fraction, $x_{C2OH}$, was fixed at the experimental value at each data point.

The effect of incorporating the excess-free-energy correction into parameter $C$ was also examined. To do so, the mixing rule for the parameter $C$ first needed to be modified from its original zero-$A^E_{\infty}$ form (Eq. (44)) as follows:

$$C = b^2 \left[ 2A^E_{\infty} + \sum x_i \frac{C_i}{b^2_i} \right]$$  \hspace{1cm} (49)
The associated modified partial fugacity coefficient expression is derived in Appendix C. The saturation-point calculations were repeated, using Eq. (49) as the mixing rule for parameter C, with the mixing rule for D reverting to its original zero-$A^E_\infty$ form (Eq. (45)). The best-fit value of the binary interaction parameter $l_{ij}$ was again determined by trial and error to obtain the best match between the EOS- and NRTL-calculated $G^E$ curves.

Fig. 5-8 shows the resulting isothermal P-x-y curve for $l_{ij} = 0.029$ (AAD-P: 0.038 atm; AAD-$y_{C2OH}$: 0.0051). Comparing Fig. 5-8 to Fig. 5-7 shows that the two calculated curves are virtually indistinguishable, suggesting that the excess-free-energy correction could be implemented into either parameter C or D for this system without detrimental effects.

\[ \text{Figure 5-8} \quad \text{Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: BWR EOS with $A^E$ correction in parameter ‘C’} \]
It was decided at this point to proceed with the $A^E_\infty$ correction incorporated into parameter ‘C’ instead of ‘D’ for this reason, and because this resulted in a smaller value of the binary interaction parameter $l_{ij}$ ($l_{ij} = 0.029$ for the correction in ‘C’, and $l_{ij} = 0.0575$ for the correction in ‘D’).

Figs. 5-9 and 5-10 show the variation with pressure of the peak value of the BWR-calculated $A^E$ curve, with the $A^E_\infty$ correction is incorporated into parameters D and C respectively. The figures show that the infinite-pressure correction from the activity coefficient model attenuates less with falling pressure when the correction is made in parameter C, and thus requires a smaller value of $l_{ij}$ to bring the EOS-calculated curve back into agreement with that from the activity coefficient model.

![Figure 5-9](image.png)

**Figure 5-9** Variation of peak value with pressure along BWR-calculated $A^E$ curve, for ethanol + water system at 393.15 K; $A^E$ correction in parameter ‘D’
Comparing the two figures to Fig. 5-4—essentially the same plot, but prepared with the PRSV equation using Wong-Sandler mixing rules—shows that the $A^E_\infty$ pressure-attenuation behavior of the BWR equation is closer to that of the Wong-Sandler-PRSV model when the $A^E_\infty$ correction is incorporated into parameter C.

Phase equilibrium calculations were carried out for the ethanol + water system at a second temperature, 323.15 K. At this temperature, the saturation pressures are much lower than at 393.15 K. Pure-component EOS parameters were the same as those used in the previous calculation at 393.15 K (Table A-5). NRTL parameters were obtained from the DECHEMA collection (Gmehling et al., 1981) and are shown in Table A-5. Corresponding Antoine parameters from Gmehling et al. (1981) for pure component vapour pressures are shown in Table A-15.
Fig. 5-11 shows the NRTL- and EOS-calculated $G^E$ curves at 323.15 K, with $l_{ij} = 0.009$. As was the case at 393.15 K, the two curves are made to match very well using an optimized binary interaction parameter (AAD: 0.0017).

Fig. 5-12 shows the resulting calculated P-x-y diagram at 323.15 K, along with the experimental data that was originally by Gmehling et al. (1988) to fit the NRTL parameters. Again, the agreement between the calculated and experimental curves is very good (AAD-P: 0.008 atm; AAD-$y_{C2OH}$: 0.0063).

Some of these preliminary results for the BWR equation were documented previously in conference presentations (Kedge and Trebble, 2004b, 2005, 2007).

Figure 5-11 Comparison of NRTL- and EOS-calculated $G^E$ curves for ethanol + water system at 323.15 K: BWR EOS ($l_{ij}=0.009$)
Figure 5-12 Calculated VLE (solid lines) and experimental data for ethanol + water system at 323.15 K: BWR EOS with $A_E$ correction in parameter ‘C’

5.7.2 Results for the New EOS

Having successfully reproduced the P-x-y diagram for ethanol + water at 393.15 K with the BWR equation, the zero-$A_E$ mixing rules were next tested with the new EOS applied to the same system. Pure component parameters were determined by the global regression procedure described in Section 3.2, and are shown in Table A-7. The objective function used by the regression program was as shown in Eq. (11).

The initial fitting was carried out over a wide range of VLE data (vapour pressures, saturated vapour and liquid densities) and PVT data along sub-critical and super-critical isotherms for both substances. The resulting parameters were then used to calculate
values for the temperature-dependent parameters B, C, and D via Eqs. (7a-c) at the temperature of the system.

The pure-component PVT and VLE data was the same as that used for the BWR equation, as described in Section 5.6. NRTL parameters were also the same as those used previously for the BWR EOS (Table A-5). Initial results were poor, as Fig. 5-13 shows.

![Figure 5-13](image)

**Figure 5-13** Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: initial results for new EOS

Fig. 5-14 shows the EOS-calculated $G^E$ curve, along with that calculated from the NRTL equation directly. The figure shows that the two curves are substantially different—so much that they could not be brought into agreement by simply varying the binary interaction parameter $l_{ij}$. Initially, it was suspected that an error had been made in the derivation of the partial fugacity coefficient expression (see Appendix C), since such
errors had been shown in the past to cause similar diverging behavior in phase envelopes calculated with cubic EOS.

![Graph](image)

**Figure 5-14** Excess Gibbs energy predicted by new EOS and by NRTL equation for ethanol + water system at 393.15 K: initial results

However, the derivative term \((\partial P/\partial n_i)\) in the integrand of Eq. (C.1), the molar derivatives \(H_i, K_i, L_i, M_i, N_i, Q_i,\) and \(U_i\), as well as the overall partial fugacity expression itself were carefully checked numerically against their analytical counterparts in Appendix C, and were found to match exactly.

Figs. 5-15 and 5-16 show \(\partial P/\partial n_i\) and \(\hat{\ln \phi_i}\), respectively, calculated both analytically and by numerical differentiation and integration, and plotted as a function of specific volume.
Figure 5-15 $\partial P/\partial n_i$ of water ($x_{C2OH} = 0.1$), calculated analytically and numerically with new EOS for ethanol + water system at 393.15 K.

Figure 5-16 Partial fugacity coefficient of water ($x_{C2OH} = 0.1$), calculated analytically and numerically with new EOS for ethanol + water system at 393.15 K.
The figures show that the numerical and analytical curves are essentially identical, confirming that the derivation of the partial fugacity coefficient expression in Appendix C for the new EOS is correct. At this point, other possible causes of the diverging P-x-y diagram were investigated.

Inspection of the low-pressure EOS-calculated $G^E$ curve (Fig. 5-14) showed that the underlying $A^E$ curve had changed shape considerably as pressure was reduced from the infinite-pressure limit at which the EOS-ACM match had been carried out. This was in contrast to the earlier observation for the PRSV equation with the Wong-Sandler mixing rules, where even though the peak value of the $A^E$ curve was observed to drift with decreasing pressure, the overall shape of the curve had remained the same, as was shown in Fig. 5-1.

At low ethanol mole fractions, the EOS was overestimating both the slope of the $G^E$ curve and $G^E$ itself. Because of this, the EOS-calculated liquid-phase partial fugacities would be much higher than they would be otherwise, if the EOS-calculated $G^E$ curve had more closely matched the “correct” curve represented by the NRTL equation. In turn, such very high liquid-phase fugacities could cause the calculated saturation pressures to be much higher than they would otherwise be. This effect would in turn give rise to the skewed shape of the EOS-calculated $G^E$ curve in Fig. 5-14.

As a first step toward solving the problem, the tendency for the $A^E$ curve to change shape as pressure was reduced from infinity was investigated. This was done by calculating $A^E$ at various pressures with the new EOS (specifically, using Eqs. (B.11) and (B.18) in
Appendix B), with the NRTL coefficients and interaction parameter set to zero. As such, the mixing rules would create a starting condition of $A^E = 0$ at infinite pressure over the entire range of composition, and the variation of $A^E$ as pressure was reduced from infinity could thus be examined.

Fig. 5-17 shows $A^E$ calculated from the new EOS for the ethanol + water system at 393.15 K, at various pressures. The figure shows that although $A^E$ starts out at zero in the limit of infinite pressure, it builds up considerably as pressure is decreased, reaching a peak value at a pressure of approximately 31,700 atm, and still retaining an appreciable non-zero value at a pressure of one atmosphere.

![Variation of excess Helmholtz energy from new EOS with pressure for ethanol + water system at 393.15 K: initial results](image)

**Figure 5-17** Variation of excess Helmholtz energy from new EOS with pressure for ethanol + water system at 393.15 K: initial results
Two possible causes were identified for the changing shape of the $A^E$ curve:

- The unconstrained shape of the isotherms of the constituent pure components (water and ethanol) within the saturation region.

- The three-order-of-magnitude difference between the EOS parameter $F$ for the pure components.

In the first case, it was noticed that although the EOS-calculated isotherms at 393.15 K reproduced the correct pure-component vapour pressures for both ethanol and water, the shape of the isotherms within the saturation region—that is, at specific volumes between those of saturated liquid and saturated vapour—was somewhat irregular. This occurs because, other than being forced to obey Maxwell’s equal area rule, the EOS is essentially unconstrained in this region during the regression.

Fig. 5-18 shows the pure-component isotherms calculated with the new EOS for water and ethanol, using the regressed parameters from Table A-7. Both isotherms are seen to exhibit “bumps” and inflections that are not observed in isotherms calculated with cubic EOS.

It was conjectured that since calculating the partial fugacity coefficient involves integrating the quantity $\partial P/\partial n_i$, the irregularities in the shapes of the isotherms could cause irregularities in the EOS-calculated $A^E$ and $G^E$ curves.
It was reasoned that this effect could be ruled out as a cause of the skewed $G^E$ curve of Fig. 5-14 by forcing the pure-component isotherms to take on a more regular shape within the saturation envelope.

![Graph showing isotherms for ethanol and water](image)

**Figure 5-18**  Isotherms calculated with new EOS for ethanol and water at 393.15 K using preliminary pure-component parameters

It was found that the easiest way to do this was to calculate an artificial path for the isotherm to follow, and include it with the experimental PVT and VLE data during pure-component EOS parameter regression. While this approach is somewhat arbitrary, the artificial path must still meet five conditions at minimum:

- It must reproduce the correct saturated liquid and vapour volumes.
- It must reproduce the correct vapour pressure (via the equal area rule).
• The slope of the artificial portion of the isotherm must match the slope of the experimental isotherm at the saturated liquid and vapour conditions.

A fifth-degree polynomial in reciprocal specific volume was used, since this is the lowest-degree curve without a constant term that could match the five necessary conditions:

\[ P = \frac{A}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^4} + \frac{E}{V^5} \]  

(50)

Equations expressing the five conditions listed above (saturated liquid volume, saturated vapour volume, vapour pressure, saturated liquid isotherm slope, saturated vapour isotherm slope) were then derived from Eq. (50) and solved simultaneously to yield values for parameters A, B, C, D, and E which would then allow Eq. (50) to meet the required five conditions.

The result was an artificial path through the saturation region (sometimes referred to as a van der Waals loop) that matched the experimental data in value and slope at saturated vapour and liquid conditions.

Including this hypothetical path in the regression resulted in pure-component EOS parameters that produced an isotherm shape closer to what would be expected from a cubic EOS, and therefore free of spurious bumps and inflections.

This procedure was carried out initially for water only, since the diverging saturation pressures in the calculated P-x-y diagram occurred at high mole fractions of water.
Fig. 5-19 shows the complete isotherm used in the regression, including both the smoothed experimental data (Lemmon et al., 2005) and the hypothetical van der Waals loop. Fig. 5-20 shows the EOS-calculated pure-component isotherms after the above procedure had been implemented.

It is possible that other techniques could be employed to prevent irregularly-shaped EOS-calculated isotherms, such as ensuring that the fourth derivative of pressure with respect to volume always remains positive within the saturation region.

![Graph](image)

**Figure 5-19** Hypothetical van der Waals loop for water at 393.15 K

This could be accomplished using an algorithm similar to that developed in the current study for maintaining mechanical stability along pure-component critical isotherms (described in Chapter 3). However, the initial guesses for the EOS parameters prior to
data regression would also have to produce isotherms with positive fourth derivatives, which would make the initial guesses onerous to generate.

![Graph showing isotherms with original and revised parameters.](image)

**Figure 5-20** Isotherms calculated with new EOS for water at 393.15 K using original and revised parameters

As was done for the BWR EOS, the revised parameters for water were fit over a limited range of vapour pressures at temperatures near 393.15 K to ensure that the EOS could accurately reproduce the vapour pressure of water at the temperature of interest. This was not strictly necessary for the new EOS, because it was able to reproduce water vapour pressures quite accurately (AAD = 0.399 %) with the original parameters (which had been determined by regression over a wide range of saturation data at reduced temperatures as low as Tr = 0.48). However, since this step had been found necessary for the BWR EOS, it was carried out for the new EOS as well simply for consistency in later comparisons between the two EOS. The revised parameters are shown in Table A-8. The
temperatures are reported only for the temperature of interest (393.15 K) because the temperature function parameters of Eqs. (7a-c) would no longer be valid over a wide range of temperatures.

At this point, the EOS-calculated $G^E$ curve and the ethanol-water P-x-y diagram were recalculated. The revised calculations showed that the diverging saturation pressures seen in Fig. 5-13 had now disappeared. However, the EOS-calculated $G^E$ curve now showed a large negative deviation from ideality, and the resulting EOS-calculated P-x-y diagram exhibited corresponding negative deviations from the experimental data. This is shown in Figs. 5-21 and 5-22 respectively.

![Graph](image)

**Figure 5-21** Excess Gibbs energy predicted by new EOS and by NRTL equation for ethanol + water system at 393.15 K: revised EOS parameters
In addition, it was not possible to bring the negative EOS-calculated $G^E$ curve into agreement with the activity coefficient model by tuning the interaction parameter, $l_{ij}$.

The explanation for this is essentially opposite to the explanation for the diverging saturation pressures observed previously in Fig. 5-13, where large positive $G^E$ deviations resulted in too-high liquid-phase fugacities. Here, vapour-phase fugacities could only match these values at high pressures, which resulted in very high saturation pressures. In Fig. 5-21, the negative $G^E$ curve produces liquid-phase fugacities that are too low. Vapour-phase fugacities can only match these values at very low pressure, resulting in the low saturation pressures shown in Fig. 5-22.
As mentioned earlier, it was suspected that the changing shape of the EOS-calculated $G^E$ curve from high to low pressures might also be caused by the three-order-of-magnitude difference in the value of EOS parameter F, which is the coefficient of the exponential term. To test this possibility, the exponential term was temporarily removed from the EOS, essentially leaving a seventh-degree polynomial, since the near-critical term had already been omitted for the purpose of mixing-rule development. Pure-component parameters were determined by setting parameters F and G equal to zero in the regressions, and are shown in Table A-9.

![Diagram showing the comparison of EOS and NRTL calculated excess Gibbs energy for ethanol + water system at 393.15 K](image)

**Figure 5-23**  Excess Gibbs energy for ethanol + water system at 393.15 K calculated using both NRTL equation and new EOS without exponential term

The resulting EOS-calculated $G^E$ curve and P-x-y diagram (Figs. 5-23 and 5-24, respectively) were found to be qualitatively correct, thus confirming the role of the exponential term in producing the improperly-shaped $G^E$ curve from the EOS.
It had been determined earlier that linear mixing rules did not work well for the exponential term because the rate of change of that term’s contribution to excess Helmholtz energy with respect to composition was too great at low ethanol mole fractions. It was now suspected, however, that this was as much due to the multiple-order-of-magnitude difference between the pure-component values of $F$ for water and ethanol, as it was to the form of the mixing rule itself.

Until this point, the value of $F$ for ethanol had been vastly larger than the value for water. It was decided to revise the pure-component parameters for ethanol by repeating the regression of experimental PVT and VLE data, but this time limiting the value of $F$ to be no more than one order of magnitude larger than that for water. This was accomplished by fixing the value of $F$ while allowing the other EOS parameters to vary in the
regression. The one-order-of-magnitude limit was selected arbitrarily, but would confirm whether or not this was indeed causing the problem.

Again, for consistency with the regression approach used for water, a hypothetical van der Waals loop was calculated for ethanol at 393.15 K, and included in the PVT data set used in the regression. As before—and unlike for water—the regression for ethanol was carried out over a wide range of vapour pressures. It was noted that the EOS was less able to match the hypothetical portion of the isotherm now that restrictions had been placed on the F parameter. However, this did not appear to affect the EOS-calculated $G^E$ or P-x-y curves. Revised EOS parameters for ethanol are shown in Table A-10 (water parameters remained unchanged).

The explicit mixing rule for F (Eq. (37a)) and the corresponding linear rule for G were replaced at this point with the implicit rule for G (Eq. (37b)) and a linear mixing rule for F, as the change resulted in a better match between the EOS- and ACM-calculated $G^E$ curves. Although the mixing rule for G is implicit, it was easily solved using the method of successive substitution.

Fig. 5-25 shows the resulting EOS- and ACM-calculated $G^E$ curves, while Fig. 5-26 shows the resulting EOS-calculated P-x-y diagram, plotted against the experimental data. The figures show considerable improvement over Figs. 5-21 and 5-22, and demonstrate good agreement between the EOS- and ACM-calculated $G^E$ curves (AAD: 0.058), and between the EOS-calculated P-x-y curve and the experimental data (AAD-P: 0.074 atm; AAD-$y_{C2OH}$: 0.0065).
**Figure 5-25** Excess Gibbs energy predicted by new EOS and by NRTL equation for ethanol + water system at 393.15 K: second revision

**Figure 5-26** Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: second revision for new EOS
However, the agreement is not quite as good as for the BWR equation (compare to Figs. 5-6 and 5-7).

As a final modification, the linear mixing rule for parameter F was replaced by a quadratic rule with a binary interaction parameter, $f_{ij}$ (similar to Eq. (5.39)). The values of both $f_{ij}$ and $l_{ij}$ were determined so as to produce the best match between the EOS- and ACM-calculated $G^E$ curves, as shown in Fig. 5-27 (AAD: 0.0022).

**Figure 5-27** Excess Gibbs energy predicted by new EOS and by NRTL equation for ethanol + water system at 393.15 K: third revision

The figure shows that by bringing in an additional interaction parameter, excellent agreement can be obtained between the two curves. And as shown in Fig. 5-28, the resulting EOS-calculated P-x-y diagram is also in excellent agreement with the experimental data (AAD-P: 0.015 atm; AAD-$y_{C2OH}$: 0.014).
Figure 5-28  Calculated VLE (solid lines) and experimental data for ethanol + water system at 393.15 K: third revision for new EOS
CHAPTER 6
APPLICATION TO HIGH-PRESSURE BINARY SYSTEMS

6.1 High-Pressure Binary Systems

Until this point, development of the new mixing rules had been carried out using the ethanol + water binary mixture as the test system. This was a logical first step for excess-free-energy-based mixing rules, since they were first conceived as a way to apply equations of state to non-ideal mixtures that would normally be fit instead with activity-coefficient models. The ethanol + water system is an example of such a mixture.

One characteristic that is common to many non-ideal systems is that they exhibit relatively low saturation pressures. For example, the ethanol + water test system used in this work has a maximum saturation pressure of less than 4.5 atmospheres over the full range of composition at 393.15 K. Under such conditions, it is reasonable to expect that the vapour phase will exhibit nearly-ideal behavior. In fact, activity coefficient data available in collections such as DECHHEMA (Gmehling et al., 1988) are calculated from binary vapour-liquid equilibrium data under the assumption of an ideal vapour phase.

It is therefore reasonable to expect that in order to make accurate phase equilibrium predictions for low pressure systems, it would be sufficient for the mixing rules to focus on producing the correct value for liquid-phase fugacity. Indeed, this is what has been observed for the test system.
Three potential difficulties arise when applying excess-free-energy mixing rules to high-pressure binary systems. First, unlike with low-pressure systems, experimentally determined activity coefficients and corresponding activity coefficient model parameters tend not to be available in the literature. The DEHEMA collection, for example, provides only equation-of-state parameters for such systems, presumably because activity coefficient models are not normally used to calculate phase equilibria in these instances. Even calculating activity coefficients from the experimental data would not be straightforward, because in order to do so, a model would need to be available for calculating vapour-phase partial fugacity coefficients. Normally, this does not present a problem for low pressure systems, because ideal gas behavior is assumed for the vapour phase when calculating activity coefficients from experimental data.

For high-pressure systems, however, an accurate vapour fugacity model would need to take into account substantial deviations from ideality, suggesting that an equation of state of some sort would be required. If saturation pressures were low enough, a virial EOS truncated after the second-virial term might suffice, but a reliable correlation of mixture second virial coefficients would be required for mixtures of the substances of interest, which may fall outside the range of substances normally covered by such correlations. Even so, this approach would only be successful at low-to-moderate pressures. It would be possible to use an equation of state suitable for high pressures to calculate vapour-phase partial fugacity coefficients. However, as mentioned before, common cubic and non-cubic EOS do not typically perform well for non-ideal substances. In any case, pure-component EOS parameters and mixture binary interaction parameters would need to be
optimized for vapour-phase PVT behavior, which is not normally done (although such an approach was proposed by Chueh and Prausnitz (1968)). As such, common EOS would not normally be expected to provide highly-accurate vapour-phase fugacities for non-ideal substances.

The second potential difficulty with applying excess-free-energy mixing rules to high-pressure systems is that at high pressures, the assumption of ideal vapour-phase behavior breaks down, and it is not reasonable to expect that an EOS would be able to reproduce phase equilibrium data or vapour-phase properties without making some kind of vapour-phase correction, as has been done for the liquid phase by incorporating an activity coefficient model into the EOS. It may not be possible to accurately model high-pressure phase behavior without incorporating additional binary interaction parameters to allow for vapour-phase fugacity corrections.

The third potential difficulty is that there is no guarantee that activity coefficients—and thus, excess Gibbs energy—calculated from high pressure phase equilibrium data can be used directly with excess-Helmholtz-energy mixing rules, because the strong dependence of $G^E$ on pressure may mean that $G^E$ is no longer a good approximation to $A^E_{\infty}$—a fundamental tenet of the Wong-Sandler method.

6.2 Application to the CO$_2$ + Ethanol Binary System

As mentioned in Section 6.1, activity coefficient model parameters are typically not available for high-pressure binary systems. Indeed, this was found to be the case for the CO$_2$ + ethanol system. Group contribution methods, such as UNIFAC (Fredenslund, et
al., 1977) represent one option for calculating a $G^E$ curve. This was briefly attempted for the CO$_2$ + ethanol system, but resulted in poor reproduction of the P-x-y diagram when used with the PRSV EOS and the original Wong-Sandler mixing rules. The UNIFAC method was therefore not pursued further with the non-cubic EOS being considered in this study.

It was reasoned that the source of the liquid-phase $G^E$ curve was not particularly important, as long as the curve was sufficiently accurate. It was therefore decided that for the purpose of testing the new mixing rules with this system, it would be reasonable to fit a simpler model to the available experimental P-x-y data, and then extracting the underlying liquid-phase $G^E$ curve from that model for subsequent use with the non-cubic EOS models.

For this purpose, the Wong-Sandler mixing rules applied to the PRSV EOS (the $WS$-$PRSV$ model) were fit to the experimental P-x-y data for the CO$_2$ + ethanol system at 291.15 K (Kodama and Kato, 2005). Pure-component PRSV parameters were obtained from the work of Orbey and Sandler (1998), and are shown in Table A-4. A simple, symmetric activity coefficient model with one adjustable parameter (the two-suffix Margules equation) was used. Two adjustable parameters—the single Margules parameter, plus the binary interaction parameter from the Wong-Sandler mixing rule—were used to fit the data.

Fitting was accomplished using least-squares regression. A computer program based on the Levenberg-Marquardt non-linear least-squares algorithm, as described by Press et al.
(1986), was written for this purpose. The objective function minimized by the program was as follows:

\[ S^2 = \sum_{i=1}^{n} (x_i^{\text{exp}} - x_i^{\text{calc}})^2 + \sum_{i=1}^{n} (y_i^{\text{exp}} - y_i^{\text{calc}})^2 \]  

(51)

where \( n \) is the number of points in the data set. It was found that the WS-PRSV model with two adjustable parameters was able to fit the experimental P-x-y data very well. It was therefore reasoned that the liquid-phase \( G^E \) curve calculated from this model at the composition-varying saturation pressure of the system could act as a good source of \( G^E \) values for the non-cubic EOS. Fig. 6-1 shows the WS-PRSV-calculated \( G^E \) curve at the saturation pressure of the system, plotted against composition.

**Figure 6-1** Excess Gibbs energy calculated with WS-PRSV model, and with NRTL equation for CO\(_2\) + ethanol system at 291.15 K
The NRTL activity coefficient model was then fit to this curve. As Fig. 6-1 shows, the NRTL equation was able to reproduce the WS-PRSV-calculated curve extremely well (AAD: 0.0016). The resulting NRTL parameters were $\tau_{12} = 2.226$, $\tau_{21} = 0.5222$, and $\alpha = 0.43$. These parameters effectively provide a source of $G^E$ values for use with the new mixing rules as applied to both the new EOS and BWR equation.

6.2.1 Results for the BWR Equation

The NRTL parameters reported above were incorporated into the BWR equation using the new mixing rules. For this system, the original regression procedure—fitting the EOS to a large body of pure-component VLE and PVT data over a wide range of pressures and temperatures—was used to determine pure-component parameters for CO$_2$ and ethanol. For this case, it was not necessary to fit the EOS to a limited range of vapour pressures because the wide range of experimental saturation pressures exhibited by this system meant that—unlike for the ethanol + water system—the EOS-calculated P-x-y diagram would not be sensitive to small errors in pure-component vapour pressures. The resulting BWR parameters used for this system are shown in Table A-11.

As discussed in Chapter 5, parameter C was chosen for the match between the EOS and the activity coefficient model (ACM), since it resulted in a smaller value of $l_{ij}$, than when parameter D was used for the match. This also resulted in less variation of $A^E$ as pressure was reduced isothermally from infinity to low pressure. The value of the binary interaction parameter, $l_{ij}$, was determined iteratively to obtain the best match between the EOS- and ACM-calculated $G^E$ curves. For this purpose, the EOS-calculated $G^E$ curve
was calculated at a pressure of 54 atm, which is above the vapour pressure of pure CO$_2$ at the system temperature. This was done to ensure that a pure-CO$_2$ liquid fugacity would be available from the EOS, in order to calculate $G^E$. Although not perfectly rigorous, this approach was considered reasonable because the EOS-calculated $G^E$ curves from the WS-PRSV model were observed to vary little between low pressure and 54 atm.

As shown in Fig. 6-2, the initial attempt with the BWR equation resulted in a poor match between the EOS- and ACM-calculated $G^E$ curves (AAD: 0.104).

![Figure 6-2](image)

**Figure 6-2** Excess Gibbs energy calculated with NRTL equation and BWR EOS, for CO$_2$ + ethanol system at 291.15 K: initial results

As the figure shows, the EOS-calculated $G^E$ curve changed shape considerably between infinite pressure—where the curves match exactly by definition—to 54 atm, where $l_{ij}$ was optimized. In this case, because the shape of the curve had changed so much, the ‘best
fit’ condition was defined as having the same peak value of reduced $G^E$ (approximately 0.434), which resulted in a value of $l_{ij} = -0.315$. Experience with the ethanol + water system had shown that reproduction of the binary P-x-y diagram by the EOS would be very poor if the EOS- and ACM-calculated $G^E$ curves did not match well at the system pressure, so the P-x-y diagram was not calculated.

As discussed in Section 6.1, it was suspected that the poor match between the BWR EOS and the NRTL model was occurring because no correction had been allowed for the effect of pressure on vapour-phase fugacities. It is common practice with equations of state to include a binary interaction parameter that has the effect of correcting the EOS-calculated second virial coefficient—either directly or indirectly—in order to fit binary VLE data. For example, for the BWR equation, the mixing rules of Bishnoi and Robinson (1972), later adopted by Starling (1973) for his version of BWR, include a binary interaction parameter only in coefficients that contribute to the mixture second virial coefficient. As well, the empirical correlation of Tsonopolous (1977) requires a binary interaction parameter to accurately predict mixture second virial coefficients. Together, these observations suggest that it would not be realistic to expect that high-pressure mixture vapour-phase PVT behavior—and thus fugacities—could be calculated accurately without incorporating an additional binary interaction parameter.

One way to make such a vapour-phase correction would be to incorporate a binary interaction parameter into the mixing rule for the EOS parameter $B$. In Eqs. (2) and (6), $B$ is the coefficient of the density-squared term, and as such is closely related to the EOS’s second virial coefficient. The $B$ parameter strongly influences the vapour-phase
properties predicted by the EOS, and is therefore a good candidate for a binary-interaction correction.

The most straightforward way to incorporate a binary interaction parameter into EOS parameter B would be to rewrite the original zero-$A_{E_{\infty}}$ mixing rule of Eq. (31) in its equivalent quadratic form, and then apply the interaction parameter to the cross term.

The resulting mixing rule is as follows:

$$\frac{B}{b} = \sum_i \sum_j x_i x_j \left( \frac{B}{b} \right)_{ij}$$

(52)

with the cross term defined as

$$\left( \frac{B}{b} \right)_{ij} = 0.5 \left( \frac{B_i}{b_i} + \frac{B_j}{b_j} \right) (1 - k_{ij})$$

(53)

and $k_{ij} = 0$ for $i = j$. A second way to incorporate a binary interaction parameter into $B$ would be to reformulate the mixing rule for $B$ as a quadratic mixing rule for the EOS’s mixture second virial coefficient. As discussed in Chapter 4, the quadratic mixing rule for the second virial coefficient has a statistical-mechanical basis, and has been touted as an advantage for equations of state that employ it (Sandler and Wong, 1992; Orbey and Sandler, 1998). However, as reported by Satyro and Trebble (1996, 1998), applying such a mixing rule to a two-parameter cubic EOS in conjunction with an excess-free energy mixing rule leads to a thermodynamic inconsistency caused by the implicit temperature dependence that the quadratic mixing rule introduces into the co-volume parameter, $b$. 
However, because non-cubic equations of state such as BWR or the new EOS have more adjustable parameters, it is possible to implement both a quadratic second-virial mixing rule, as well as an excess-free-energy mixing rule without introducing temperature dependence into the co-volume. For this reason, the use of a quadratic second virial mixing rule was pursued instead of the modified zero-$A_e^{\infty}$ mixing rule of Eqs. (52) and (53). The second virial coefficient $B_{2V}$ can be calculated as

$$B_{2V} = \lim_{V \to \infty} (Z - 1)V$$

(54)

where the subscript ‘2V’ is used to distinguish the second virial coefficient from EOS parameter B. Applied to both the BWR and new EOS, as modified to incorporate the van der Waals repulsion term, the second virial coefficient is written

$$B_{2V} = b + \frac{B}{RT}$$

(55)

The quadratic second virial mixing rule is written as

$$b + \frac{B}{RT} = \sum_i \sum_j \left( b + \frac{B}{RT} \right)_{ij}$$

(56)

Now, if we define the cross terms as follows:

$$\left( b + \frac{B}{RT} \right)_{ij} = b_{ij} + \frac{B_{ij}}{RT}$$

(57)

with $b_{ij}$ defined by Eq. (26), and $B_{ij}$ as defined as
\[ B_{ij} = \left( \frac{B_i + B_j}{2} \right) (1 - k_{ij}) \]  

(58)

then the second virial mixing rule is separable into two parts

\[ \sum_i \sum_j \left( b + \frac{B}{RT} \right)_{ij} = \sum_i \sum_j b_{ij} + \sum_i \sum_j \frac{B_{ij}}{RT} \]  

(59)

Combining Eqs. (57) and (59) with Eq. (26) results in the following mixing rule for parameter B:

\[ B = \sum_i \sum_j x_i x_j B_{ij} \]  

(60)

In both of these cases, the mixing rule for B has been modified from its zero-\( A^E_{\infty} \) version (Eq. (33)). Any deviation from this rule introduces a contribution to \( A^E_{\infty} \) which must be cancelled out in the mixing rule containing the excess-free-energy correction. For parameter C, the mixing rule of Eq. (49) must be modified as follows:

\[ C = b^2 \left[ 2 A^E_c + \sum_i x_i \frac{C_i}{b_i^2} - 2 \left( \frac{B}{b} \sum_i x_i \frac{B_i}{b_i} \right) \right] \]  

(61)

Consequently, the expression for partial fugacity coefficient must be modified as well, as shown in Appendix C.

At this point, it was attempted to match the BWR-calculated \( G^E \) curve to the NRTL curve derived from the fit of the WS-PRSV model to experimental P-x-y data described earlier.
in Section 6.1. As with the first attempt, the infinite-pressure match between the EOS and ACM was incorporated into parameter C.

In the current attempt, the quadratic second virial mixing rule (Eqs. (58) and (60)) was used to allow for a vapour-phase correction. Both interaction parameters, \( l_{ij} \) and \( k_{ij} \), were determined iteratively to give the best match between the EOS- and ACM-calculated \( G^E \) curves.

Fig. 6-3 shows the EOS-calculated \( G^E \) curve using best fit interaction parameters (\( k_{ij} = 0.27 \) and \( l_{ij} = -0.97 \)), along with the ACM-calculated curve.

![Graph](image)

**Figure 6-3** Excess Gibbs energy calculated with NRTL equation and BWR EOS using quadratic second virial mixing rule, for \( \text{CO}_2 + \text{ethanol} \) system at 291.15 K

The figure shows that with the additional binary interaction parameter, the match between the EOS- and ACM-calculated \( G^E \) curves is now quite good (AAD: 0.0041).
Fig. 6-4 shows the resulting EOS-calculated P-x-y diagram along with the experimental data. The figure shows that the BWR equation is now able to reproduce the P-x-y diagram quite well (AAD-P: 2.00 atm; AAD-yCO2: 0.0038).

**Figure 6-4** Calculated VLE (solid lines) and experimental data for CO2 + ethanol system at 291.15 K: BWR EOS with quadratic second mixing virial rule

Results for the BWR equation for the CO2 + ethanol binary system were documented previously in a conference presentation (Kedge and Trebble, 2007).

6.2.2 Results for the New EOS

The CO2 + ethanol system at 291.15 K was modeled using the new EOS with the new mixing rules. Essentially the same procedure was followed as was used for the BWR equation: the activity coefficient model correction was incorporated into parameter C, since for the BWR equation, this was observed to lead to smaller values of the binary
interaction parameter, $l_{ij}$. The quadratic second virial coefficient mixing rule of Eqs. (58) and (60) was specified for parameter B, since—as discussed in Chapter 4—there is some theoretical justification for such a mixing rule. For parameter G, the implicit mixing rule of Eq. (37b) was used, as was discussed in Section 5.7.2 for the ethanol + water system. For parameter F, a quadratic rule was initially used, as had been done with the ethanol + water system. However, it was found that the EOS-calculated $G^E$ curve was insensitive to this parameter, and thus there was no reason to specify a non-zero value for the corresponding binary interaction parameter, $f_{ij}$. As such, the quadratic rule reduces to a linear mixing rule.

Pure-component parameters for CO$_2$ were determined using the regression procedure described in Section 3.2, using VLE and PVT data over a wide range of pressures and temperatures (Angus et al., 1976b). For ethanol, the revised parameters used previously for the ethanol + water system and with the restricted value for parameter F were used for the CO2 + ethanol system. Temperature-dependent parameters B, C, and D were calculated at the temperature of interest (291.15 K) via Eqs. (7a-c). The resulting pure-component parameters are shown in Table A-12.

As was the case for ethanol and water, the data for CO$_2$ used for regression of pure-component EOS constants (Angus et al., 1976b) is a smoothed representation of several individual experimental data sets. The narrative portion of the Angus et al. monograph was not available for review regarding the accuracy of the underlying data sets. However, in a more recent work, Span and Wagner (1996) reviewed a large number of PVT data sets for CO$_2$ that are available in the open literature—including data that had been used
by Angus et al. to develop their smoothed data collection—and report that experimental uncertainties are typically less than 1% in density, 80 mK in temperature, and 1% in pressure.

As with the BWR equation, the binary interaction parameters \( k_{ij} \) and \( l_{ij} \) were optimized iteratively to achieve the best match between the EOS- and ACM-calculated \( G^E \) curves at a pressure of 54 atm, which is above the vapour pressure of CO\(_2\) at 291.15 K.

![Figure 6-5](image)

**Figure 6-5** Excess Gibbs energy calculated with NRTL equation and new EOS using quadratic second virial mixing rule, for CO\(_2\) + ethanol system at 291.15 K

As Fig. 6-5 shows, the two curves were made to agree fairly well with \( k_{ij} = 0.24 \) and \( l_{ij} = 0.05 \) (AAD: 0.0059). The corresponding EOS-calculated P-x-y diagram is shown along with the experimental data in Fig. 6-6. The figure shows reasonable agreement between the EOS-calculated curve and the data (AAD-P: 2.29 atm; AAD-\( y_{CO2} \): 0.0091).
However, the curve does deviate noticeably from the data at CO$_2$ mole fractions between 0.5 and 0.9. This deviation can be explained by looking at the EOS-calculated $G^E$ curve at system pressure, instead of at 54 atmospheres where the excess-free-energy correction was carried out.

Figure 6-6  Calculated VLE (solid lines) and experimental data for CO$_2$ + ethanol system at 291.15 K: new EOS with quadratic second virial mixing rule

Fig. 6-7 shows a portion of the EOS-calculated $G^E$ curve, where the calculation has been carried out at the composition-varying saturation pressure at each point. Only a portion of the curve is shown, because the calculation was only carried out at pressures high enough for the EOS to have a liquid density root for pure CO$_2$. The figure shows that the shape of the EOS-calculated curve is different when calculated at the saturation pressure of the system, than when it is calculated at a constant pressure of 54 atm (Fig. 6-5).
Figure 6-7  Excess Gibbs energy calculated with NRTL equation and new EOS at system saturation pressure, for CO$_2$ + ethanol system at 291.15 K

The figure shows that the EOS- and ACM-calculated curves deviate most at CO$_2$ mole fractions between 0.5 and 0.9—exactly where the discrepancy is observed between the EOS-calculated P-x-y diagram and the experimental data.

6.3  Application to the Water + CO$_2$ Binary System

The new mixing rules were applied to a second high-pressure system, water + CO$_2$ at 523.15 K, using both the new EOS and the BWR equation. This system was chosen for two reasons:

- Saturation pressures at the system temperature are an order of magnitude higher than for the previous system, CO$_2$ + ethanol.
The system temperature is above the critical temperature of one of the components (CO$_2$). As such, both the liquid and vapour phases of water-CO$_2$ mixtures exhibit liquid-like densities over much of the composition range.

Like the CO$_2$ + ethanol system examined earlier, activity coefficient data was not readily available in the literature. And as discussed in Section 6.1, activity coefficients cannot be calculated easily from P-x-y data because of difficulty calculating vapour-phase partial fugacities at high pressures.

The water + CO$_2$ system has been studied by Carroll and Mather (1992). These authors concluded that for accurate vapour-liquid equilibrium calculations, liquid-phase partial fugacities must be corrected to account for non-ideal behavior at temperatures above approximately 373 K. As these authors suggest, we should therefore expect activity coefficients to be close to unity at temperatures below 373 K, but differ from unity at higher temperatures. The former assertion has been confirmed by Kaewsichan et al. (2004), who calculated activity coefficients for this system from experimental P-T-x-y data at temperatures between 283.15 K and 373.15 K, using the Soave-Redlich-Kwong EOS (Soave, 1972) for vapour-phase partial fugacities, and Henry’s law constants for liquid-phase pure-component fugacities. The calculated activity coefficients differed very little from unity over this temperature range.

Another approach reported in the literature for calculating activity coefficients of high-pressure binary systems is to fit experimental P-x-y data using a cubic EOS in combination with an activity coefficient model via excess-free-energy mixing rules. For
example, Apostolou et al. (1995) used the Peng-Robinson EOS with the LCVM mixing rules (Boukouvalas et al., 1994) and the UNIFAC activity coefficient model to correlate gas solubility in a range of solvents, including water. Valderrama and Zavaleta (2005) used the Peng-Robinson EOS with the Wong-Sandler mixing rules and the van Laar activity coefficient model to represent mixtures of CO₂ with n-alkanols. And as described in Section 6.2, this approach was used successfully in the current study to obtain a G^E curve, and ultimately NRTL parameters, for testing the new mixing rules with the CO₂ + ethanol system.

Rather than using literature-reported activity coefficient parameters obtained as described above for models other than the NRTL equation, the approach described in Section 6.2 for the CO₂ + ethanol system was used instead for the water + CO₂ system at 523.15 K. As such, the PRSV EOS with the Wong-Sandler mixing rules and NRTL activity coefficient model was fit to experimental P-x-y data (Gmehling et al., 1988) for this system using the non-linear least-squares computer program described in Section 6.2. For the current case, the program used four adjustable parameters: k_{ij}, plus the three NRTL parameters. A G^E curve was then calculated from the fitted model at 1184 atm, the highest pressure included in the data set. NRTL parameters were then fit to the G^E curve and used in conjunction with the new mixing rules and the two non-cubic EOS.

Fig. 6-8 shows the P-x-y diagram calculated with the WS-PRSV model using best-fit values for k_{ij} and the NRTL parameters (k_{ij} = 0.568, \tau_{12} = 1.7173, \tau_{21} = 0.2741, \alpha = 0.0996). The figure shows that even when all available parameters are taken to be
adjustable for the purpose of data regression, the overall reproduction of the data is not quantitatively correct.

**Figure 6-8** Calculated VLE (solid lines) and experimental data for water + CO₂ system at 523.15 K: best fit WS-PRSV model

The liquid-phase branch of the saturation curve, representing solubility of CO₂ in water, is reproduced fairly well, but the vapour-phase branch of the calculated curve is less accurate. However, for the purpose of testing the new mixing rules, the corresponding \( G^E \) curve from the WS-PRSV model was still used. Fig. 6-9 shows the \( G^E \) curve at 1184 atm calculated with the WS-PRSV model using the best-fit parameters reported above. The NRTL equation was then fit to this curve. As Fig. 6-9 shows, the NRTL equation was able to reproduce the WS-PRSV-calculated curve fairly well (AAD: 0.0066).
Figure 6-9  Excess Gibbs energy calculated with NRTL equation and WS-PRSV model, for water + CO₂ system at 523.15 K and 1184 atm

The resulting NRTL parameters were \( \tau_{12} = -1.1944 \), \( \tau_{21} = 2.5363 \), and \( \alpha = -0.11 \). These parameters were then used to provide a source of \( G^E \) values in the initial test of the new mixing rules, as described in the next section.

It is important to recognize that the activity coefficients or \( G^E \) curve calculated in this way are not independent of the underlying EOS model. The degree to which the \( G^E \) curve determined this way using one EOS/\( G^E \) mixing rule model can be used as the source of \( G^E \) information for a different EOS/\( G^E \) mixing rule model depends on how closely the two EOS models agree in their predictions of vapour-phase partial fugacities, and pure-component liquid-phase fugacities. The less agreement in these quantities, the less likely it is that the calculated \( G^E \) curve from the first model will result in accurate P-x-y calculations using the second model.
6.3.1 Results for the New EOS

The NRTL-calculated $G^E$ curve, as represented by the parameters reported above, was incorporated into the new EOS using the new mixing rules. Again, the quadratic second virial mixing rule (Eqs. (58) and (60)) was used for parameter B. Parameter C was chosen for the match between the EOS and the activity coefficient model. For parameter G, the implicit mixing rule of Eq. (37b) was used, while a linear mixing rule was used for parameter F.

Pure-component EOS parameters for CO$_2$ and water were determined using the non-linear regression procedure described in Chapter 3. For water, the parameters were determined by fitting vapour pressure data over only a limited range of temperatures near 523.15 K, and a hypothetical van der Waals loop was calculated and included in the PVT data set during the regression. Fig. 6-10 shows the smoothed experimental 523.15 K isotherm (Lemmon et al., 2005) and the hypothetical van der Waals loop, along with the EOS-calculated 523.15 K isotherm determined using the best-fit parameters.

Pure-component EOS parameters for CO$_2$ were the same as used previously for the CO$_2$ + ethanol system. Best-fit EOS parameters for both substances at 523.15 K are shown in Table A-13.

Binary interaction parameters $l_{ij}$ and $k_{ij}$ were optimized iteratively to achieve the best match between the EOS- and ACM-calculated $G^E$ curves at 1184 atm, the highest pressure included in the experimental data set for regression purposes. This best match was carried out at high pressure to prevent the EOS-calculated isothermal P-x-y curve
from closing at pressures below 1184 atm, which could occur if the match was carried out at a lower pressure.

![Diagram](image)

**Figure 6-10** Water isotherms at 523.15 K: smoothed data (including hypothetical van der Waals loop) and new-EOS-calculated isotherm

Fig. 6-11 shows the EOS- and ACM-calculated $G^E$ curves at 1184 atm, and indicates that the two curves can be made to agree very well (AAD: 0.0056) with $k_{ij} = 0.05$ and $l_{ij} = 0.12$.

Fig. 6-12 shows the corresponding EOS-calculated P-x-y curve, along with that calculated for the best-fit WS-PRSV model, from which the NRTL parameters used in the new mixing rules were derived. The curve calculated with the new EOS was compared with the WS-PRSV-calculated curve instead of with the experimental data, because the WS-PRSV curve did not match the data particularly well, and by
incorporating NRTL parameters derived from the WS-PRSV model into the new EOS, it is actually the WS-PRSV-calculated curve that we are trying to reproduce with the new EOS.

![Graph](image)

**Figure 6-11** Excess Gibbs energy calculated with NRTL equation and new EOS, for water + CO₂ system at 523.15 K and 1184 atm

The figure shows that the agreement between the two curves is qualitatively reasonable, but quantitatively incorrect. This is true even at 1184 atm, where the \( G^E \) curves from the two models had been brought into close agreement. The disagreement between the P-x-y curves shown in the figure suggests that the predictions of vapour-phase partial fugacities or liquid-phase pure-component fugacities from the two models are too dissimilar for their corresponding \( G^E \) curves to be interchangeable.
Figure 6-12 Calculated VLE (solid lines) and experimental data for water + CO$_2$ system at 523.15 K: new EOS and WS-PRSV model

Since no accurate a priori sources of $G^E$ data could be found for use with the new mixing rules, it was decided at this point to fit the new EOS with the new mixing rules directly to the experimental P-x-y data, in the same manner as had been done for the WS-PRSV model. This would help assess whether the new EOS and the new mixing rules would even be capable of accurately reproducing the experimental P-x-y curve at all. And as mentioned earlier, the use of this approach has been documented in the literature for high-pressure systems where no other source of $G^E$ data is available.

Fitting was accomplished using the non-linear least-squares regression program described in Section 6.2, modified for use with the new EOS and new mixing rules. Five adjustable parameters were used to fit the data: $k_{ij}$, $l_{ij}$, and the three NRTL parameters ($\tau_{12}$, $\tau_{21}$, and
The objective function minimized by the program was shown in Eq. (51). Parameters determined during the earlier attempt using the WS-PRSV-calculated \( G^E \) curve were used as initial guesses in the regression.

Fig. 6-13 shows the resulting fit of the new EOS to the experimental P-x-y data using the new mixing rules. The figure shows that with best-fit values for the five adjustable parameters \( (k_{ij} = -0.055, l_{ij} = -0.33, \tau_{12} = -0.2898, \tau_{21} = 0.3886, \alpha = 2.71) \), the EOS is able to reproduce the data reasonably accurately (AAD-P: 37.97 atm; AAD-\( y_{H2O} \): 0.024).

![Graph showing calculated VLE and experimental data](image)

**Figure 6-13** Calculated VLE (solid lines) and experimental data for water + CO\(_2\) system at 523.15 K: new EOS with best fit \( l_{ij}, k_{ij} \), and NRTL parameters

Fig. 6-14 shows the EOS-calculated \( G^E \) curve at 1184 atm using best-fit parameters, along with the best-fit WS-PRSV-calculated \( G^E \) curve at the same pressure.
Figure 6-14  Excess Gibbs energy calculated with WS-PRSV model and new EOS at 1184 atm using best-fit parameters, for water + CO₂ system at 523.15 K

The figure shows that although the two curves have the same general shape, the curve for the new EOS exhibits a greater peak $G^E$ than the WS-PRSV-calculated curve. Comparing these two curves provides some insight into why the new EOS was earlier unable to reproduce the WS-PRSV-calculated P-x-y curves (Fig. 6-12).

6.3.2  Results for the BWR Equation

As discussed in the previous section, the first attempt at applying the new mixing rules to the water + CO₂ system with the new EOS used NRTL parameters derived from a $G^E$ curve that had been obtained by fitting the WS-PRSV model to experimental P-x-y data. Results were poor, as the P-x-y curve calculated using the new EOS did not match that calculated with the WS-PRSV model with best-fit constants. Because of the poor results
obtained this way with the new EOS, it was decided not to use the WS-PRSV $G^E$ curve with the BWR equation. Instead, it was thought that the $G^E$ curve calculated with the new EOS, after having been fit directly to the experimental P-x-y data, might provide a better source of $G^E$ information for the BWR equation. The NRTL equation was therefore fit to the 1184-atm $G^E$ curve calculated with the new EOS (Fig. 6-14), to provide NRTL parameters for use with the BWR equation. As Fig. 6-15 shows, the NRTL fit was very good (AAD: 0.0019) with parameters $\tau_{12} = 2.5167$, $\tau_{21} = 0.6605$, and $\alpha = 0.34$.

![Figure 6-15](image)

**Figure 6-15** Excess Gibbs energy calculated with NRTL equation, after fit to $G^E$ curve from new EOS at 1184 atm, for water + CO$_2$ system at 523.15 K

Pure-component EOS parameters for water were determined in the same manner as for the new EOS, as described in Section 6.3.1. Accordingly, the data set included smoothed experimental PVT data at 523.15 K (Lemmon et al., 2005) along with the hypothetical van der Waals loop shown in Fig. 6-10. Pure-component CO$_2$ parameters were the same
as used previously for the CO₂ + ethanol system. The resulting best-fit BWR parameters for both substances are shown in Table A-14.

Using the NRTL parameters reported above, the binary interaction parameters \( k_{ij} \) and \( l_{ij} \) were optimized iteratively to achieve the best match between the EOS- and ACM-calculated \( G^E \) curves at 1184 atm. The resulting values were \( k_{ij} = -0.12 \) and \( l_{ij} = -0.5 \). An attempt was then made to calculate the P-x-y curve using the BWR equation with the new mixing rules, and the NRTL/binary parameters reported above. However, the resulting calculated P-x-y curve was poor, exhibiting a maximum saturation pressure and closing the curve at approximately 160 atm. Above this pressure, the EOS predicted that the mixture would exist as a single phase, which is clearly not the case upon inspection of the data. It was therefore decided to fit the BWR equation directly to the experimental P-x-y data, taking the NRTL parameters and binary interaction parameters as adjustable constants, just as was done for the new EOS.

Regression was carried out using the same non-linear least-squares regression program that had been used for the new EOS. Again, the two binary interaction parameters \( k_{ij} \) and \( l_{ij} \), and NRTL parameters \( \tau_{12}, \tau_{21}, \) and \( \alpha \), were taken as adjustable constants. The resulting best-fit parameters were \( k_{ij} = 0.052, l_{ij} = -0.223, \tau_{12} = 2.302, \tau_{21} = -0.7497, \) and \( \alpha = 0.7254 \).

Fig. 6-16 shows the EOS-calculated P-x-y curve determined using the best-fit adjustable parameter values reported above, along with the experimental data. The figure shows
reasonable agreement between the calculated and experimental curves (AAD-P: 82.65 atm; AAD-$y_{H2O}$: 0.045).

**Figure 6-16** Calculated VLE (solid lines) and experimental data for water + CO$_2$ system at 523.15 K: BWR EOS with best-fit $l_{ij}$, $k_{ij}$, and NRTL parameters

The BWR-calculated $G^E$ curve at 1184 atm was compared to the same curve calculated with the new EOS. As indicated in Fig. 6-17, the two curves show reasonable agreement with one another (AAD: 0.011), even though they result from completely independent regressions to the experimental data. This suggests that the two EOS predict similar values for the vapour-phase partial fugacities and liquid-phase pure-component fugacities. It is interesting to note, however, that small differences between these two curves make the difference for the BWR equation between reasonably accurate reproduction of the data (Fig. 6-16) and the poor reproduction that resulted when the BWR-calculated $G^E$ curve was matched to that of the new EOS.
Figure 6-17  Excess Gibbs energy calculated with BWR equation and new EOS at 1184 atm using best-fit parameters, for water + CO₂ system at 523.15 K
CHAPTER 7
DISCUSSION

7.1  EOS Improvements for Pure Components

Before a new equation of state can be applied with confidence to fluid mixtures, it must be able to reproduce thermodynamic data for pure components as accurately as possible. In an earlier study (Kedge, 2000), it was suggested that the performance of the new EOS near pure-component critical points could be improved by adding a special term that becomes active only in the vicinity of the critical point. As such, one of the goals of the current study was to develop a term that could be explicitly added to the EOS, and that would bring about the desired improvement. As described in Section 3.2, a simple three-parameter bell-shaped term was developed for this purpose, and was found to be successful in improving the fit of pure-component VLE and PVT data for a test substance (methane).

The key to the success of the near-critical term is that it vanishes at densities away from the critical density. It had been determined prior to the current study that the criterion of forcing the EOS to exactly match the critical point and associated derivative conditions places a considerable burden on the temperature functions that express the temperature dependence of three of the EOS parameters. In order to meet this condition, the temperature functions are forced to yield sub-optimal values in the vicinity of the critical temperature, since the optimal values of the EOS parameters in this region deviate significantly from the trend observed at subcritical temperatures. This behavior is shown
for EOS parameter C in Fig 3-2, and the resulting errors in the EOS-calculated saturated liquid and vapour specific volumes of methane are shown by the dotted curve in Fig. 3-7.

At the same time, it was observed that the original method for fitting pure-component data—first fitting the critical isotherm, and then fitting the temperature function parameters to VLE and PVT data at sub- and supercritical temperatures, while holding the other parameters constant at their critical values—was logical for determining the functional form of the EOS, but placed unwarranted emphasis on an accurate fit at one temperature (Tc) at the expense of the fits at other temperatures. As a result, the regression procedure was modified to optimize all the EOS parameters over the full range of temperatures. In combination, this revised global regression method, along with the near-critical term, were observed to improve the fit of near-critical saturated liquid and vapour specific volumes considerably.

The second improvement to the pure-component form of the EOS that was undertaken as part of the present work was to replace the leading term in the equation with the Carnahan-Starling repulsion term (Eq. (14)). As part of an earlier study (Kedge, 2000), the effect of different repulsion terms on the EOS’s ability to fit pure component properties was investigated. In that study, however, the Carnahan-Starling term was discounted in favour of the simpler approximation due to Scott (1971). Although the Scott term had shown marginal improvement over the van der Waals (vdW) term, the vDW term was retained instead because of its simplicity.
At the outset of the current study, it was decided that the Carnahan-Starling term should be investigated, on the basis that the Scott term—although touted as a closed-form approximation to the theoretical infinite series for hard spheres—might actually not be a good representation of the Carnahan-Starling term, and that perhaps the earlier conclusions regarding the Scott term might not apply to the Carnahan-Starling term.

In the current study, it was found that replacing the van der Waals term with the CS term resulted in a large enough improvement in the fit of VLE and PVT data for methane to warrant its adoption for pure-component EOS calculations.

Although these two modifications to the EOS have been observed to improve the fit of pure-component data for the test substance (methane), the question still remained whether these modifications could be carried over to fluid mixtures. The near-critical term was found to be integrable with respect to volume, and thus expressions could be derived for both partial fugacity coefficients and excess Helmholtz energy. Furthermore, the term in the $A^E$ expression arising from the near-critical term had a finite value in the limit of infinite pressure. Although the near-critical term complicates the partial fugacity coefficient expression, as shown in Section C.2 of Appendix C, there is no obvious reason that it should not be compatible with the concept of excess-free-energy mixing rules.

The Carnahan-Starling term, on the other hand, has been reported to be incompatible with excess-free-energy mixing rules (Brandani and Brandani, 1996) because the contribution of the CS term to $A^E$ becomes infinite in the limit of infinite pressure. As a result, excess-
free-energy mixing rules based on an infinite-pressure match between $A^E$ from an EOS and $G^E$ from an activity coefficient model cannot be applied to such EOS. For this reason, the van der Waals term was used instead of the CS term for the subsequent work on equation-of-state mixing rules.

### 7.2 Excess-Helmholtz-Energy Mixing Rules

In the current study, the infinite-pressure Helmholtz energy concept—originally applied to cubic EOS by Wong and Sandler (1992)—was extended and applied to both the new EOS and the BWR equation. As in Wong and Sandler’s original work, the expression for excess Helmholtz energy at infinite pressure ($A^E_{\infty}$) was derived from the EOS, and was then set equal to the expression for excess Gibbs energy from an activity coefficient model (the NRTL equation in this work). The resulting overall expression could then be rearranged in terms of one EOS parameter for the mixture. For the co-volume parameter, a classical quadratic mixing rule was specified, following the work of Satyro and Trebble (1998). At this point, the requirements for applying the EOS to mixtures would be fully met for a two-parameter cubic EOS, since this approach provides a mixing rule for two parameters. For non-cubic EOS, however, the approach still leaves several EOS parameters without mixing rules.

The key development in the current study was to use the EOS-derived expression for $A^E_{\infty}$ as the basis for the remaining mixing rules. This was accomplished by setting each mixture term in the $A^E_{\infty}$ expression (Eq. (29)) equal to the corresponding composition-weighted pure-component sum. This not only supplied mixing rules for most of the other
EOS parameters, but also greatly simplified the equation expressing the match between the EOS and the activity coefficient model. It was also shown that the mixing rule for parameter B could be replaced by one that preserves the theoretical quadratic composition dependence of the second virial coefficient without detrimental effects to VLE predictions from the EOS, and while avoiding thermodynamic inconsistencies caused by introducing temperature dependence into the co-volume parameter.

The new zero- $A^E_x$ mixing rules were applied to three non-ideal binary system: ethanol + water, CO$_2$ + ethanol, and CO$_2$ + water (in order of increasing saturation pressure). In general, the mixing rules worked well for both EOS, for all three systems. However, certain limitations became apparent as the work progressed.

First, it was noted that if the EOS is not able to reproduce the pure-component vapour pressure for one or both components of a binary mixture, then the calculated vapour-liquid equilibria will not necessarily be accurate. This was observed during the initial application of the BWR equation to the ethanol + water system. The effect was particularly pronounced because the vapour pressures of both pure components as well as the mixture saturation pressures were all of the same order of magnitude at the temperature of the system. This effect can also be seen in Fig. 5-24, where the new EOS was unable to reproduce the vapour pressure of water accurately because the exponential term had been omitted. The net effect was that the calculated P-x-y curve was shifted upward because the EOS overpredicted the vapour pressure of water.
The second limitation relates to the pure-component parameters for the new EOS. It was observed that both mixture and pure-component isotherms calculated with a non-cubic EOS can develop ‘bumps’ and inflections that cause the shape of the isotherms to deviate from the so-called ‘S’ shape exhibited by cubic EOS. Even though the pure-component isotherms obey the equal-area rule that results in equal saturated-liquid and vapour fugacities, the irregularities in the pure-component isotherms can carry over to mixture isotherms by way of the mixing rules. Liquid-phase partial fugacities for the mixture are sensitive to these isotherm irregularities, leading to abnormalities in EOS-calculated vapour-liquid equilibria, as shown in Fig. 5-13. These abnormalities were found to be so extreme that they could not be corrected using a single binary interaction parameter. Binary interaction parameters are essentially a fine-tuning device, and it is therefore important for a set of mixing rules to produce ‘correctable’ mixture fugacities in the first place.

It was found that the irregularities in the pure-component isotherms calculated from the new EOS could be reduced or eliminated by including a smooth, hypothetical ‘path’ in the PVT data set used in the regression of the pure-component parameters. The actual path is somewhat arbitrary, but must still meet certain minimum conditions: it must reproduce the correct vapour pressure, saturated-liquid and vapour densities, and saturated liquid and vapour isotherm slopes. This technique was shown to be suitable for demonstrating the efficacy of the mixing rules at a single temperature, but may not be practical for regressing pure-component parameters over the full range of vapour pressures and saturation temperatures.
The third limitation also relates to pure-component EOS parameters. After re-fitting the pure-component parameters for water in the new EOS to remove the irregularities discussed above, it was noted that the value of parameter $F$—the coefficient of the exponential term in the new EOS—was still three orders of magnitude larger for ethanol than for water. The result was that when even a small amount of ethanol was added to pure water, the mixture value for $F$ would increase very rapidly, while the other mixture EOS parameters did not. This sudden change in one mixture parameter was out of step with the other EOS parameters, and had a significant effect on mixture liquid-phase excess Helmholtz and Gibbs free energies. Again, this large deviation from the expected free energies was too extreme to be counteracted with a binary interaction parameter.

However, this is not necessarily the fault of the mixing rules. It was found that when pure-component EOS parameters for ethanol were re-fit while limiting the value of $F$ to be within one order of magnitude of the value of $F$ for water, the EOS-calculated low-pressure $G^E$ curve could be brought into agreement with the $G^E$ curve provided by the activity coefficient model—albeit using an additional binary interaction parameter.

This observation supports the earlier assertion that mixing rules must produce mixture fugacities that are within the range of correction by binary interaction parameters. But this would likely be difficult for any set of mixing rules, whether based on the excess-free-energy concept or not, if the pure-component EOS parameters differ by several orders of magnitude, or produce irregularly-shaped mixture isotherms. Taken together, these limitations suggest that some restrictions on pure-component parameters are necessary—restrictions that are not required when the EOS is to be applied only to pure
components and not to mixtures. This is perhaps the reason that most, if not all, EOS for fluid mixtures use some type of generalization scheme for calculating pure-component parameters instead of using parameters determined by unconstrained regression to experimental data. Such generalization methods are often based on the principle of corresponding states, and use acentric factor as a correlating parameter. But such schemes are restrictive, and can reduce the accuracy of the EOS for pure components, which defeats the purpose of using a non-cubic EOS in the first place. As the current work shows, it may be sufficient merely to place generalized restrictions on the order of magnitude of the pure-component parameters, and on the shape of the EOS-calculated mixture isotherms, while still allowing the parameter to be fit to experimental data. However, such generalized restrictions would have to be properly devised by considering a wide range of pure substances of varying molecular sizes, shapes, and degrees of polarity.

The final limitation relates to the source of liquid-phase \( G^E \) information for the mixture, which in essence captures the non-ideal behavior of the system. For many low-pressure binary systems, such as the ethanol + water system studied here, \( G^E \) information is available in the literature in the form of activity coefficient model parameters. These parameters are typically derived from experimental low-pressure vapour-liquid equilibrium data, and can be incorporated directly into an EOS by way of excess-free-energy mixing rules—often quite successfully. The activity coefficients themselves can be easily calculated from experimental P-x-y data assuming that the vapour phase behaves as an ideal gas, which is a valid assumption at low pressures.
However, for systems that exhibit higher saturation pressures, the assumption of an ideal vapour phase no longer applies, and an accurate vapour-phase fugacity model is then required in order to calculate activity coefficients—and thus, liquid-phase $G^E$—from experimental VLE data. The problem this creates is that activity coefficients derived in this way are coupled to a specific vapour fugacity model, such as a particular equation of state. Any inaccuracy in the calculated vapour fugacities will carry over into the activity coefficients. If these activity coefficients are then combined with another equation of state through excess-free-energy mixing rules, the calculated VLE of the system will only match the experimental data if the second equation of state predicts the same vapour-phase partial fugacities as the first EOS. Perhaps for this reason, activity coefficient data and activity coefficient model parameters for high-pressure binary systems are much less readily available in the literature than for low-pressure systems.

In the current study, it was shown that this method could be applied successfully to binary systems that exhibit moderately-high saturation pressures, such as the CO$_2$ + ethanol system. For that system, activity coefficient model parameters were derived by fitting the PRSV equation of state, using the Wong-Sandler mixing rules, to experimental P-x-y data, and then fitting the NRTL equation to the resulting liquid-phase $G^E$ curve at a pressure above the vapour pressure of both components. The NRTL parameters thus derived were incorporated into both the new EOS and the BWR equation through the new mixing rules, and both non-cubic EOS were then shown to reproduce the experimental P-x-y curves reasonably well, as shown in Figs. 6-4 and 6-6 respectively.
For systems with much higher saturation pressures, however, the approach of incorporating activity coefficient model parameters derived from one EOS/ACM model into a second EOS/ACM model was not successful. This was attempted in the current study under two scenarios. First, the WS-PRSV model was fit to experimental P-x-y data for the CO₂ + water system at 523.15 K, and the NRTL equation was the fit to the G^E curve calculated from the fitted model at the highest pressure in the data set (1184 atm). The resulting NRTL parameters were incorporated into the new EOS through the new mixing rules, and binary interaction parameters were adjusted iteratively to achieve the best match between the EOS- and NRTL-calculated G^E curves. In this scenario, it was found that the WS-PRSV model failed to reproduce the experimental P-x-y curve, even at its best-fit condition (Fig. 6-8). Also, the new EOS failed to reproduce the WS-PRSV-calculated P-x-y curve (Fig. 6-12), even though it was using NRTL parameters that were derived from the WS-PRSV model.

In the second scenario, the new EOS with the new mixing rules was fit to the P-x-y data for the same system, and NRTL parameters were then fit to the EOS-calculated G^E curve at 1184 atm. The resulting NRTL parameters were incorporated into the BWR equation using the new mixing rules, and the two binary interaction parameters were again adjusted so that the EOS-calculated G^E curve at 1184 atm best matched that from the NRTL equation. However, the resulting EOS-calculated P-x-y curve did not reproduce the experimental data successfully.

At this point, it was felt that the most reasonable approach for correlating experimental high-pressure P-x-y data using an EOS with excess-free-energy mixing rules would be to
directly fit the model to the data, taking the binary interaction parameters and activity coefficient model parameters as adjustable constants. This approach has precedents in the literature (for example, the work of Apostolou et al. (1995), and that of Valderrama and Zavaleta (2005)), and was advocated in the original paper on excess-free-energy mixing rules by Huron and Vidal (1979). In this regard, both non-cubic EOS models were able to reproduce the experimental P-x-y curves successfully, as shown in Figs. 6-13 and 6-16 for the new EOS and BWR equation respectively. Comparing these figures to each other and to Fig. 6-8 shows that while the best fit was obtained with the new EOS, both non-cubic EOS were better able to reproduce the data than the WS-PRSV model.

Much of the existing literature on excess-free-energy mixing rules has focused on binary mixtures. In the current study, application of the new mixing rules was limited to three binary systems at fixed temperatures. However, there is no reason that the new mixing rules could not be extended for use with multi-component mixtures over a wider range of temperatures. The mixing rules themselves are derived from the expression for $A^E_\infty$ from the EOS of interest, which is not inherently limited to binary systems. And some activity coefficient models—including the NRTL equation—have extended versions for predicting $G^E$ of multi-component mixtures that only require mixture-specific constants for binary pairs of components. Indeed, the main issue that would need to be addressed before the mixing rules could be applied to multi-component systems would be how best to determine binary interaction parameters and activity coefficient model parameters over a wide range of temperatures. Also, in order to calculate thermal properties such as
enthalpy, entropy, and heat capacities, it would be necessary to either specify temperature-independent binary and ACM parameters, or to include temperature functions expressing their temperature dependence into the model.

Ideally, these parameters would be determined for individual pairs of substances by fitting VLE data over a wide range of temperatures. It is also possible that some of these parameters would exhibit an inherent temperature dependence, such that ignoring this dependence (by specifying fixed, temperature-independent values) would degrade the quality of the model’s predictions over a wide range of temperatures. The temperature dependence of these parameters could be incorporated into the EOS/ACM model by expressing the parameters as functions of temperature, and then fitting the constants of the temperature functions to the experimental database. Activity coefficient model parameters are sometimes reported as simple functions of temperature for individual binary mixtures (see, for example, Gmehling et al., 1988), and such temperature dependence could be incorporated into the model as well. In other cases, however, the literature reports only best-fit ACM parameters at individual temperatures, and makes no attempt to correlate them as functions of temperature.

Some parameters would not be amenable to this type of treatment, however. In particular, the parameter \( l_{ij} \)—the binary interaction parameter associated with the co-volume—should remain independent of temperature, to avoid creating a temperature-dependent co-volume. As documented by Salim and Trebble (1991), and Satyro and Trebble (1998), a temperature-dependent co-volume parameter this leads to thermodynamic inconsistencies such as negative isochoric heat capacities.
Finally, it would also be necessary to evaluate the quality of mixture thermal properties calculated with the new mixing rules—with or without temperature-dependent binary and ACM parameters—as compared to experimental data, before they could be used to predict such properties with confidence. But although this was beyond the scope of the current study, the present work has provided a firm foundation for extending the concept of excess-free-energy mixing rules to multi-constant non-cubic equations of state.
CHAPTER 8

CONCLUSIONS

The major original contribution of this work has been to develop a methodology that allows multi-constant non-cubic equations of state to accurately model vapour-liquid equilibria for mixtures of non-ideal substances, which previously had not been possible. From this work, the following conclusions can be drawn:

1. Adding a simple, non-temperature-dependent near-critical term to an equation of state can improve the equation’s fit to pure-component saturation and PVT data.

2. Adding the new near-critical term to a cubic EOS—in this case the Trebble-Bishnoi equation—makes the EOS non-cubic, and although the quality of the EOS fit to PVT and VLE data for a test substance (methane) generally improved, the improvements were not dramatic.

3. Replacing the leading term in the new non-cubic EOS with the Carnahan-Starling expression improves the EOS’s ability to fit pure-component PVT and VLE data, as compared to the simple van der Waals repulsion term. However, the Carnahan-Starling (CS) term cannot be used if the EOS is to be applied to fluid mixtures using mixing rules based on excess Helmholtz energy at infinite pressure. This is because the CS term does not produce a finite value of excess Helmholtz energy at infinite pressure. For this reason, a simpler expression must be used instead, such as the van der Waals term used in this work.
4. The principle of excess-free-energy mixing rules—in particular, the concept of matching the infinite-pressure $A^E$ calculated from an equation of state to the low-pressure $G^E$ predictions of an activity coefficient model—can be successfully extended to multi-constant non-cubic equations of state.

5. The expression for excess Helmholtz energy at infinite pressure ($A^E_{\infty}$) can be used as the basis for a mixing rule for each term in the equation of state, by setting each mixture term in the expression equal to the composition-weighted sum of the corresponding pure-component terms. This results in a value of $A^E_{\infty}$ that is equal to zero by definition, before the $G^E$ prediction from the activity coefficient model is incorporated into the EOS. Using the $A^E_{\infty}$ expression as the basis for the mixing rules also simplifies the equation expressing the $G^E$ match between the EOS and the activity coefficient model.

6. For both the new EOS and the BWR equation, better results were obtained when the infinite-pressure excess Helmholtz energy correction was incorporated into EOS parameter C, than when the correction was made to parameter D.

7. For low-pressure non-ideal systems, such as the ethanol + water system, the new mixing rules can incorporate activity-coefficient-model parameters taken directly from the literature.

8. Fitting of VLE data for moderate- and high-pressure binary systems can be improved by introducing an additional binary interaction parameter for the EOS parameter associated with the second virial coefficient. This binary interaction
parameter can be incorporated into the EOS parameter B for the mixture in two ways: either by modifying the $A^E$ based mixing rule, or by reformulating the mixing rule for B such that it observes the theoretical quadratic composition dependence of the second virial coefficient.

9. For binary systems exhibiting moderately-high saturation pressures, such as the CO$_2$ + ethanol system, activity coefficient model parameters can be derived by first fitting a simpler model (in this case, the PRSV EOS with the Wong-Sandler mixing rules) to experimental isothermal P-x-y data for the system, and fitting the activity coefficient model the resulting curve of $G^E$ expressed as a function of composition. These parameters can then be used directly with either the new EOS or the BWR equation by way of the new mixing rules.

10. Use of excess free energy mixing rules for fitting VLE data of very-high-pressure binary systems, such as CO$_2$ + water, requires that the activity coefficient model parameters and the EOS binary interaction parameters be determined by least-squares data regression. Activity coefficient model parameters derived by fitting the resulting EOS-calculated $G^E$ curve were not found to be transferable to other EOS/excess-free-energy mixing rule models.

11. When fitted to isothermal P-x-y data for a high-pressure binary system (CO$_2$ + water) using the new mixing rules, both the new EOS and the BWR equation were better able to reproduce the experimental data than the cubic PRSV EOS using the Wong-Sandler mixing rules, which had also been fitted to the date using
the same procedure. Of the three models, the new EOS was best able to fit the data.

At this stage, the newly proposed mixing rules have the following main limitations:

1. The EOS to which the mixing rules are being applied must be able to accurately reproduce the properties of the pure components in the mixture, which may not be the case, especially for some highly non-ideal substances.

2. Pure-component EOS constants must produce smooth S-shaped isotherms inside the vapour-liquid coexistence curve. This requires additional constraints to be applied during the regression of pure component parameters, which are not required for the EOS to model the pure components themselves.

3. The new mixing rules have so far only been applied to binary mixtures. Before they can be applied to multi-component mixtures, an activity coefficient model must be available that is capable of calculating GE for multi-component mixtures. Some models, such as the NRTL equation, have this capability. However, this requirement does limit the pool of activity coefficient models that can be used with the mixing rules.

4. The mixing rules require a source of $G^E$ data for the mixture in the form of values for activity coefficient model constants, or alternatively, experimental VLE data from which ACM constants can be determined by regression.
5. The temperature dependence of the activity coefficient model parameters and EOS binary interaction parameters has not been investigated. As such, the applicability of the new mixing rules for calculating mixture thermodynamic properties other than those related to vapour-liquid equilibrium has not yet been demonstrated.
CHAPTER 9
RECOMMENDATIONS

9.1 Recommended Form of the New Mixing Rules

9.1.1 Application to the New EOS

At this stage, the following form of the new EOS is recommended for use with the new mixing rules:

\[ P = \frac{RT}{(V - b)} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{E}{V^7} + F\exp(GV) \]  \hspace{1cm} (62)

\[ B(T) = B^{\text{crit}} \left[ (1 - b_1 - b_2 - b_3)T_R + b_1 + \frac{b_2}{T_R} + \frac{b_3}{T_R^2} \right] \]  \hspace{1cm} (63a)

\[ C(T) = C^{\text{crit}} \left[ (1 - c_1 - c_2 - c_3 - c_4)T_R^2 + c_1T_R + c_2 + \frac{c_3}{T_R} + \frac{c_4}{T_R^2} \right] \]  \hspace{1cm} (63b)

\[ D(T) = D^{\text{crit}} \left[ (1 - d_1 - d_2 - d_3)T_R + d_1 + \frac{d_2}{T_R} + \frac{d_3}{T_R^2} \right] \]  \hspace{1cm} (63c)

This version of the new EOS uses the van der Waals repulsion term because it provides a finite value of excess Helmholtz energy at infinite pressure. It also omits the near-critical term, which has not yet been tested with the new mixing rules.
The following form of the new mixing rules is recommended at this stage for use with the new EOS:

\[
b = \sum_i \sum_j x_i x_j \left( \frac{b_i + b_j}{2} \right) (1 - l_{ij}) \quad (64)
\]

\[
B = \sum_i \sum_j x_i x_j \left( \frac{B_i + B_j}{2} \right) (1 - k_{ij}) \quad (65)
\]

\[
C = b^2 \left[ 2A^E_\infty + \sum_i x_i \frac{C_i}{b_i^2} - 2 \left( \frac{B - \sum_i x_i B_i}{b} \right) \right] \quad (66)
\]

\[
D = b^5 \sum_i x_i \frac{D_i}{b_i^5} \quad (67)
\]

\[
E = b^6 \sum_i x_i \frac{E_i}{b_i^6} \quad (68)
\]

\[
F = \sum_i \sum_j x_i x_j \left( \frac{F_i + F_j}{2} \right) (1 - f_{ij}) \quad (69)
\]

\[
G = \frac{F \exp(Gb)}{\sum_i x_i \frac{F_i \exp(G_i b_i)}{G_i}} \quad (70)
\]

As discussed earlier, this form of the mixing rules maintains the theoretical quadratic composition dependence of the second virial coefficient (Eq. (65)), applies the \(A^E_\infty\) correction from the activity coefficient model to parameter ‘C’ (Eq. (66)), and uses the
implicit form of the zero-$A^E_{\infty}$ mixing rule for parameter ‘G’. This is the form of the mixing rules that was ultimately used for modeling the water + CO$_2$ binary system, the final system investigated in the study.

9.1.2 **Application to the BWR EOS**

At this stage, the original functional form of the BWR equation, modified to include a van der Waals repulsion term, is recommended for use with the new mixing rule as follows:

$$P = \frac{RT}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{E}{V^3} \left(1 + \frac{F}{V^2}\right) \exp\left(\frac{-F}{V^2}\right)$$  \hspace{1cm} (71)

With this form, there are several options for expressing the temperature dependence of parameters B, C, D, and E. Options include the original expressions of Benedict et al. (1940) (described earlier as Eqs. (3a-d)), the modified temperature dependence of Starling (1973), or the version proposed by Nishiumi (1980) for use with polar substances. The Starling and Nishiumi versions of the equation have the same volume dependence as the original (Eq. (71)), and thus the new mixing rules apply to these versions as well.

The following form of the new mixing rules is recommended for use with the BWR equation at this stage:

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2}\right) (1 - l_{ij})$$  \hspace{1cm} (72)
As discussed previously, this form of the mixing rules maintains the theoretical quadratic composition dependence of the second virial coefficient (Eq. (73)), applies the $A^E_\infty$ correction from the activity coefficient model to parameter ‘C’ (Eq. (74)).

9.2 Recommendations for Further Work

The following steps are recommended for future work on excess free energy mixing rules for non-cubic equations of state:

1. Apply the new mixing rules to a ternary mixture, to test their applicability for calculating vapour-liquid equilibria for multicomponent mixtures.
2. Investigate the temperature dependence requirements of the ACM parameters and binary interaction parameters.

3. Investigate the applicability of the new mixing rules for calculating thermal properties such as enthalpy and specific heats for binary mixtures, and for other properties such as mixture densities.

4. Compare the new mixing rules with classical mixing rules for application to mixtures of nearly-ideal substances, such as light hydrocarbons.

5. Investigate the applicability of the new mixing rules with the version of the new EOS that includes the near-critical term.

6. Apply the new mixing rules to a wider range of non-ideal mixtures.

7. Apply the new mixing rules to other non-cubic EOS, such as Soave’s version of the BWR equation (Soave, 1995, 1996).
REFERENCES


Boukouvalas, C., N. Spiliotis, P. Coutsikos, N. Tzouvaras, and D. Tassios, “Prediction of Vapor-Liquid Equilibrium with the LCVM model: A Linear Combination of the Vidal and Michelsen Rules coupled with the Original UNIFAC and the t-mPR EoS”, Fluid Phase Equilibria, 92 (1994) 75.


Kedge, C.J., and M.A. Trebble, presentation to the 54th Canadian Chemical Engineering Conference, Calgary, Alberta, Oct. 3-6, 2004b.


APPENDIX A: EOS CONSTANTS

The EOS constants shown in the tables correspond to pressure in atmospheres, temperature in degrees Kelvin, and molar specific volume in cm³/mol.

Table A-1 Parameters for non-cubic EOS (Eqs. (6) and (7)) for methane

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value Without NC term</th>
<th>Value With NC term</th>
<th>Constant</th>
<th>Value Without NC term</th>
<th>Value With NC term</th>
</tr>
</thead>
<tbody>
<tr>
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<td>22.209</td>
<td>22.272</td>
<td>b₁</td>
<td>2.6796</td>
<td>2.7143</td>
</tr>
<tr>
<td>B₀</td>
<td>-2242283</td>
<td>-2235249</td>
<td>b₂</td>
<td>-1.6264</td>
<td>-1.6203</td>
</tr>
<tr>
<td>C₀</td>
<td>74621708</td>
<td>74081467</td>
<td>b₃</td>
<td>0.6714</td>
<td>0.6743</td>
</tr>
<tr>
<td>D₀</td>
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<td>-8.821E+12</td>
<td>c₁</td>
<td>-1.5686</td>
<td>-1.6522</td>
</tr>
<tr>
<td>E₀</td>
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<td>2.548E+14</td>
<td>c₂</td>
<td>5.6128</td>
<td>5.6665</td>
</tr>
<tr>
<td>F₀</td>
<td>647081</td>
<td>498648</td>
<td>c₃</td>
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<td>-4.8423</td>
</tr>
<tr>
<td>G₀</td>
<td>-0.16724</td>
<td>-0.16429</td>
<td>c₄</td>
<td>1.8400</td>
<td>1.8520</td>
</tr>
<tr>
<td>e</td>
<td>--</td>
<td>-0.15488</td>
<td>d₁</td>
<td>3.5864</td>
<td>3.6318</td>
</tr>
<tr>
<td>f</td>
<td>--</td>
<td>3.1091E-03</td>
<td>d₂</td>
<td>-1.6301</td>
<td>-1.6337</td>
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<tr>
<td>g</td>
<td>--</td>
<td>106.577</td>
<td>d₃</td>
<td>0.4759</td>
<td>0.4714</td>
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Table A-2 Parameters for TB EOS (Eqs. (11) and (12)) for methane

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<th>Value With NC term</th>
<th>Constant</th>
<th>Value Without NC term</th>
<th>Value With NC term</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
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<td>2821508</td>
<td>f</td>
<td>--</td>
<td>5.7805E-03</td>
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<tr>
<td>b</td>
<td>33.933</td>
<td>33.784</td>
<td>g</td>
<td>--</td>
<td>90.587</td>
</tr>
<tr>
<td>c</td>
<td>48.045</td>
<td>43.060</td>
<td>m</td>
<td>0.14768</td>
<td>0.16187</td>
</tr>
<tr>
<td>d</td>
<td>38.820</td>
<td>38.125</td>
<td>n</td>
<td>6.5624E-02</td>
<td>8.1637E-02</td>
</tr>
<tr>
<td>e</td>
<td>--</td>
<td>0.23989</td>
<td>o</td>
<td>0.22661</td>
<td>0.23073</td>
</tr>
</tbody>
</table>
Table A-3  Pure-component critical constants for Soave-BWR equation (Eq. (4)) for methane

<table>
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<th>Value</th>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>$\beta_c$</td>
<td>-0.33933</td>
<td>$c_1$</td>
<td>-0.027377</td>
</tr>
<tr>
<td>$\gamma_c$</td>
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<td>$c_2$</td>
<td>3.5337E-03</td>
</tr>
<tr>
<td>$\delta_c$</td>
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<td>$c_3$</td>
<td>1.3986E-03</td>
</tr>
<tr>
<td>$\epsilon_c$</td>
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<td>$c_1$</td>
<td>0.11456</td>
</tr>
<tr>
<td>$\phi_c$</td>
<td>0.059686</td>
<td>$c_2$</td>
<td>0.075233</td>
</tr>
<tr>
<td>$b_1$</td>
<td>0.422366</td>
<td>$c_3$</td>
<td>1.9016E-03</td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.003491</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A-4  PRSV Parameters for water and ethanol

<table>
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<th>Substance</th>
<th>Water</th>
<th>Ethanol</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_c$ atm</td>
<td>218.011</td>
<td>60.67604</td>
<td>72.855</td>
</tr>
<tr>
<td>$T_c$ K</td>
<td>647.29</td>
<td>513.92</td>
<td>304.21</td>
</tr>
<tr>
<td>$\omega$ --</td>
<td>0.3438</td>
<td>0.6444</td>
<td>0.2250</td>
</tr>
<tr>
<td>$\kappa_1$ --</td>
<td>-0.06635</td>
<td>-0.03374</td>
<td>0.04285</td>
</tr>
</tbody>
</table>

Table A-5  NRTL Parameters for water and ethanol at 393.15 K and 323.15 K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>393.15 K</td>
</tr>
<tr>
<td>$\tau_{12}$</td>
<td>0.3430</td>
</tr>
<tr>
<td>$\tau_{21}$</td>
<td>1.5360</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.6576</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>0.7981</td>
</tr>
<tr>
<td>$G_{21}$</td>
<td>0.3642</td>
</tr>
</tbody>
</table>
Table A-6  BWR Parameters for water and ethanol at 393.15 K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Substance</th>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td></td>
<td>17.0</td>
<td>50.0</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-9031471.4</td>
<td>-1.94 x 10^7</td>
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<tr>
<td>C</td>
<td></td>
<td>-1.22 x 10^8</td>
<td>-2.94 x 10^9</td>
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<tr>
<td>D</td>
<td></td>
<td>-1.06 x 10^{11}</td>
<td>2.84 x 10^{14}</td>
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<tr>
<td>E</td>
<td></td>
<td>339165566</td>
<td>4.32 x 10^9</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>488.8</td>
<td>5778.2</td>
</tr>
</tbody>
</table>

Table A-7  New EOS: Initial pure-component parameters for water and ethanol

<table>
<thead>
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<th>Parameter</th>
<th>Substance</th>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td></td>
<td>17.44</td>
<td>47</td>
</tr>
<tr>
<td>B^{crit}</td>
<td></td>
<td>-5610067</td>
<td>-12093185</td>
</tr>
<tr>
<td>C^{crit}</td>
<td></td>
<td>135572493</td>
<td>778945796</td>
</tr>
<tr>
<td>D^{crit}</td>
<td></td>
<td>-7.0587 x 10^{12}</td>
<td>-8.4463 x 10^{14}</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>1.32012 x 10^{14}</td>
<td>5.5811 x 10^{16}</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>214613</td>
<td>2899120080</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>-0.17808</td>
<td>-0.23288</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>b_1</td>
<td></td>
<td>-4.84608</td>
<td>4.23040</td>
</tr>
<tr>
<td>b_2</td>
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<td>-2.22969</td>
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<td>b_3</td>
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<td>1.15131</td>
</tr>
<tr>
<td>c_1</td>
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<td>-5.91944</td>
<td>-10.31030</td>
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<tr>
<td>c_2</td>
<td></td>
<td>0.68970</td>
<td>15.54927</td>
</tr>
<tr>
<td>c_3</td>
<td></td>
<td>4.86573</td>
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</tr>
<tr>
<td>c_4</td>
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<td>-1.18748</td>
<td>3.38037</td>
</tr>
<tr>
<td>d_1</td>
<td></td>
<td>2.52292</td>
<td>4.24377</td>
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<tr>
<td>d_2</td>
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<td>-0.52292</td>
<td>-1.40388</td>
</tr>
<tr>
<td>d_3</td>
<td></td>
<td>0.13785</td>
<td>0.41754</td>
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</tbody>
</table>
Table A-8  New EOS: Revised pure-component parameters for water and ethanol at 393.15 K

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<th>Parameter</th>
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<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
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<td>15.0</td>
<td>47.0</td>
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<tr>
<td>B</td>
<td></td>
<td>-4155942</td>
<td>-19939964</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>-57284224</td>
<td>1847298580</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>-1.1350E+12</td>
<td>-1.18343E+15</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>3.1320E+12</td>
<td>5.5811E+16</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>2476486</td>
<td>2899120080</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>-0.22822</td>
<td>-0.23288</td>
</tr>
</tbody>
</table>

Table A-9  New EOS: Pure-component parameters for water and ethanol at 393.15 K, omitting exponential term

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Substance</th>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td></td>
<td>15.7</td>
<td>52.3</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-5809195</td>
<td>-18913344</td>
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<td>C</td>
<td></td>
<td>39781234</td>
<td>1315564510</td>
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<tr>
<td>D</td>
<td></td>
<td>8.2250E+11</td>
<td>-3.82883E+14</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>-1.4952E+13</td>
<td>1.1316E+16</td>
</tr>
<tr>
<td>F</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td></td>
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Table A-10  New EOS: Pure-component parameters for water and ethanol at 393.15 K—second revision

<table>
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<th>Water</th>
<th>Ethanol</th>
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<tbody>
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<tr>
<td>B</td>
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<td>-18734052</td>
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<td>C</td>
<td></td>
<td>-57284224</td>
<td>1489356377</td>
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<td>-1.1350E+12</td>
<td>-2.34271E+14</td>
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<tr>
<td>E</td>
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<td>24700000</td>
</tr>
<tr>
<td>G</td>
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<td>-0.14773</td>
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</table>
Table A-11  BWR Parameters for CO$_2$ and ethanol at 291.15 K

<table>
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<th>Substance</th>
<th>CO$_2$</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
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</tr>
<tr>
<td>C</td>
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<td>-1048183156</td>
<td></td>
</tr>
<tr>
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Table A-12  New EOS: Pure-component parameters for CO$_2$ and ethanol at 291.15 K

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<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<tr>
<td>C</td>
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<td>2938004753</td>
<td></td>
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<tr>
<td>D</td>
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<tr>
<td>E</td>
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<td>-2.2249E+15</td>
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<tr>
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<td>24699659</td>
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</table>

Table A-13  New EOS: Pure-component parameters for CO$_2$ and water at 523.15 K

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<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>b</td>
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<td>C</td>
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<td>210802183</td>
<td></td>
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<td>D</td>
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<td>E</td>
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<tr>
<td>F</td>
<td>1300153</td>
<td>256199</td>
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<tr>
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</table>
Table A-14  BWR Parameters for $\text{CO}_2$ and water at 523.15 K

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<th>$\text{CO}_2$</th>
<th>Water</th>
</tr>
</thead>
<tbody>
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<td>25.0</td>
<td>17.0</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-1804437</td>
<td>-6971350</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>24393602</td>
<td>28030064.66</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>6.7116E+12</td>
<td>1.47334E+11</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>3.5757E+07</td>
<td>1.5101E+08</td>
</tr>
<tr>
<td>F</td>
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<td>4853</td>
<td>1534</td>
</tr>
</tbody>
</table>

Table A-15  Antoine equation* parameters for water and ethanol at 393.15 K and 323.15 K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>393.15 K</td>
<td>323.15 K</td>
<td>393.15 K</td>
</tr>
<tr>
<td>A</td>
<td>7.5867</td>
<td>8.1122</td>
<td>8.0177</td>
</tr>
<tr>
<td>B</td>
<td>1281.590</td>
<td>1592.864</td>
<td>1715.700</td>
</tr>
<tr>
<td>C</td>
<td>193.768</td>
<td>226.184</td>
<td>234.268</td>
</tr>
</tbody>
</table>

*form of Antoine equation used by Gmehling et al. (1981, 1988):

$$\log[p_i^0] = A - \frac{B}{T + C}$$

for $p_i^0$ (vapour pressure) in mm Hg, and $T$ (temperature) in °C
APPENDIX B: DERIVATION OF EXCESS HELMHOLTZ FREE ENERGY

B.1 Derivation

For a mixture, an excess property is defined as the difference between the actual value of a property, and the value it would have for an ideal mixture. For excess Helmholtz energy, the basic equation is

\[ A^E = A_m - \sum x_i A_i - RT \sum x_i \ln x_i \]  

(B.1)

where \( A \) is molar Helmholtz energy, subscript \( m \) refers to the mixture, and subscript \( i \) refers to the \( i^{th} \) pure component in the mixture. The last term on the right-hand side of Eq. (B.1) is the change in entropy that accompanies the formation of an ideal solution.

Like any thermodynamic property, Helmholtz energy can be defined in terms of its residual, or departure, from ideal gas behavior as follows:

\[ \Delta A' = A - A^{IG} \]  

(B.2)

where the subscript \( IG \) refers to the ideal gas state, and the term \( \Delta A' \) is the Helmholtz energy residual. Upon rearranging Eq. (B.2) and applying it to both the mixture and to its individual constituent pure components, we can write

\[ A_m = A_m^{IG} + \Delta A'_m \]  

(B.3)

\[ A_i = A_i^{IG} + \Delta A'_i \]  

(B.4)
Here, the subscripts and superscripts are as they were defined earlier.

Substituting Eqs. (B.3) and (B.4) into Eq. (B.1) gives

\[
A^E = A^{IG}_m + \Delta A'_m - \sum_i x_i A^{IG}_i - \sum_i x_i \Delta A'_i - RT \sum_i x_i \ln x_i \quad (B.5)
\]

Now, it can also be shown that the Helmholtz energy of an ideal gas mixture is

\[
A^{IG}_m = \sum_i x_i A^{IG}_i + RT \sum_i x_i \ln x_i \quad (B.6)
\]

After substituting Eq. (B.6) into Eq. (B.5) and rearranging, we have

\[
A^E = \Delta A'_m - \sum_i x_i \Delta A'_i \quad (B.7)
\]

Now, \( \Delta A' \) is defined as \( \Delta A' = A - A^{\text{ideal}} \), which can be expressed as

\[
\Delta A' = \int_{V_m}^{\infty} \left( P - \frac{RT}{V} \right) dV - RT \ln Z \quad (B.8)
\]

Substituting Eq. (B.8) into Eq. (B.7) gives the following expression:

\[
A^E = \int_{V_m}^{\infty} \left( P - \frac{RT}{V} \right) dV - \sum_i x_i \int_{V_i}^{\infty} \left( P - \frac{RT}{V} \right) dV - RT \sum_i x_i \ln \left( \frac{Z_m}{Z_i} \right) \quad (B.9)
\]

Finally, excess Helmholtz energy at infinite pressure can be derived by taking the limit as follows:

\[
A^{E}_{\infty} = \lim_{P \to \infty} A^E \quad (B.10)
\]
This limit is best taken after Eq. (B.9) has been applied to the specific EOS of interest.

### B.2 The BWR Equation of State

Applying Eq. (B.9) to the BWR equation of state (Eq. (2), modified to include the van der Waals repulsion term), we can write the following expression for excess Helmholtz free energy:

\[
A^E = J_m - \sum_i x_i J_i - RT \sum_i x_i \ln \left( \frac{V_m - b_m}{V_i - b_i} \right) \tag{B.11}
\]

where

\[
J = \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{5V^5} - \frac{E}{F} \left[ \left( 1 + \frac{F}{2V^2} \right) \exp \left( - \frac{F}{V^2} \right) - 1 \right] \tag{B.12}
\]

Now, when we take the limit as $P$ approaches infinity, we see that

\[
\lim_{P \to \infty} V_m = b_m \tag{B.13}
\]

\[
\lim_{P \to \infty} V_i = b_i \tag{B.14}
\]

\[
\lim_{P \to \infty} \ln \left( \frac{V_m - b_m}{V_i - b_i} \right) = 0 \tag{B.15}
\]

which leaves us with the following expression for $A^E_{\infty}$:

\[
A^E_{\infty} = J_m^\infty - \sum_i x_i J_i^\infty \tag{B.16}
\]
where

$$J^\infty = \frac{B}{b} + \frac{C}{2b^2} + \frac{D}{5b^5} - \frac{E}{F} \left[ \left( 1 + \frac{F}{2b^2} \right) \exp \left( - \frac{F}{b^2} \right) - 1 \right]$$  \hspace{1cm} (B.17)

### B.3 The New Equation of State

Applying Eq. (B.9) to the new EOS (Eq. (6), modified to include the van der Waals repulsion term), we have the same expression for $A^E$ as derived for the BWR equation in Eq. (B.11). In this case, however, the $J$ term is defined as follows:

$$J = \frac{B}{V} + \frac{C}{2V^2} + \frac{D}{5V^5} + \frac{E}{6V^6} - \frac{F}{G} \exp \left( GV \right) + \frac{e}{\sqrt{f}} \left[ \tan^{-1} \left( \sqrt{f} \left( V - G \right) \right) - \frac{\pi}{2} \right]$$  \hspace{1cm} (B.18)

And taking the limit as $P$ approaches infinity gives the same general expression (Eq. (B.16)) for $A^E_\infty$ that was derived for the BWR equation. For the new EOS, $J^\infty$ is defined as

$$J^\infty = \frac{B}{b} + \frac{C}{2b^2} + \frac{D}{5b^5} + \frac{E}{6b^6} - \frac{F}{G} \exp \left( Gb \right) + \frac{e}{\sqrt{f}} \left[ \tan^{-1} \left( \sqrt{f} \left( b - G \right) \right) - \frac{\pi}{2} \right]$$  \hspace{1cm} (B.19)
APPENDIX C: DERIVATION OF PARTIAL FUGACITY COEFFICIENT

C.1 BWR Equation

For any pressure-explicit equation of state, an expression for the partial fugacity coefficient can be derived from the following thermodynamic relation:

\[
RT \ln \phi_i = \int V \left( \frac{\partial P}{\partial n_i} - \frac{RT}{V} \right) dV - RT \ln Z \tag{C.1}
\]

The equation of state must first be rewritten in terms of total volume \( V \) and total number of moles \( n \). For the BWR equation, this results in the following expression:

\[
P = \frac{nRT}{V - nb} + \frac{n^2B}{V^2} + \frac{n^3C}{V^3} + \frac{n^4D}{V^4} + \frac{n^5E}{V^5} \left( 1 + \frac{n^2F}{V^2} \right) \exp \left( -\frac{n^2F}{V^2} \right) \tag{C.2}
\]

The derivative on the right-hand side of Eq. (C.1) can be written as

\[
\frac{\partial P}{\partial n_i} = \frac{RT}{V - nb} + \frac{nRTH_i}{(V - nb)^2} + \frac{nK_i}{V^2} + \frac{n^2L_i}{V^3} + \frac{n^5M_i}{V^6} \tag{C.3}
\]

where

\[
H_i = \frac{\partial (nb)}{\partial n_i} \tag{C.4a}
\]
Substituting Eqs. (C.3) and (C.4) into Eq. (C.1), integrating, and substituting $V = \overline{V}/n$

gives

$$\text{RT} \ln \hat{\phi}_i = -\text{RT} \ln \left(1 - \frac{b}{V}\right) + \frac{\text{RTH}_i}{V-b} + \frac{K_i}{V} + \frac{L_i}{2V^2} + \frac{M_i}{5V^5}$$

$$- \left(\frac{N_i}{F} + \frac{N_i}{2V^2} - \frac{\text{EQ}_i}{F V^2} - \frac{\text{EQ}_i}{F^2} - \frac{\text{EQ}_i}{2V^4}\right) \exp\left(-\frac{F}{V^2}\right)$$

$$- \frac{\text{EQ}_i}{F^2} + \frac{N_i}{F} - \text{RT} \ln Z$$

For the mixing rules given by Eqs. (42) to Eq. (47), the derivatives in Eqs. (C.4) can be
expressed as

$$H_i = 2 \sum_j x_j b_{ij} - b$$
\[ K_i = B_i \left( \frac{b}{b_i} \right) + \frac{BH}{b} \tag{C.7} \]

\[ L_i = C_i \left( \frac{b}{b_i} \right)^2 + \frac{2CH}{b} \tag{C.8} \]

\[ M_i = D_i \left( \frac{b}{b_i} \right)^5 + \frac{5DH}{b} \tag{C.9} \]

\[ Q_i = 2\sqrt{FF_i} \tag{C.10} \]

\[ N_i = -\frac{E}{2b^2} \left( \frac{FW_i}{2b^2} + \frac{W_i}{2} \right) \exp\left( -\frac{F}{b^2} \right) + \frac{EQ_i}{F} + \frac{F E_i Y_i}{Y} \tag{C.11a} \]

where

\[ W_i = \frac{\partial (-F/b^2)}{\partial n_i} = \frac{2FH_i}{b^3} - \frac{Q_i}{b^2} \tag{C.11b} \]

\[ Y = \left[ \left( 1 + \frac{F}{2b^2} \right) \exp\left( -\frac{F}{b^2} \right) - 1 \right] \tag{C.11c} \]

\[ Y_i = \left[ \left( 1 + \frac{F_i}{2b_i^2} \right) \exp\left( -\frac{F_i}{b_i^2} \right) - 1 \right] \tag{C.11d} \]
C.2 The New EOS

As described above for the BWR equation, the partial fugacity coefficient can be derived from Eq. (C.1). In terms of total volume and total number of moles, \( n \), the new EOS can be rewritten as:

\[
P = \frac{nRT}{V - nb} + \frac{n^2B}{V^2} + \frac{n^3C}{V^3} + \frac{n^6D}{V^6} + \frac{n^7E}{V^7} + F \exp \left( \frac{GV}{n} \right) + \frac{n^2e}{n^2 + f(V - ng)^2} \tag{C.12}
\]

The derivative on the right-hand side of Eq. (C.1) can be written as

\[
\frac{\partial P}{\partial n_i} = \frac{RT}{V - nb} + \frac{nRTH_i}{(V - nb)^2} + \frac{nK_i}{V^2} + \frac{n^2L_i}{V^3} + \frac{n^3M_i}{V^6} + \frac{n^6N_i}{V^7} + \frac{FQ_iV}{n^2} \exp \left( \frac{GV}{n} \right) + \frac{U_i}{n} \exp \left( \frac{GV}{n} \right) + \frac{nS_i}{n^2 + f(V - ng)^2} \left[ \frac{W_iV^2}{n} + XV + nY \right] \tag{C.13}
\]

In Eq. (C.13), the derivatives \( H_i, K_i, L_i, \) and \( M_i \) are defined in the same way as for the BWR equation (Eqs. (C.4a) to (C.4d)). The remaining derivatives are defined as follows:

\[
N_i = \frac{1}{n^6} \frac{\partial (n^7E)}{\partial n_i} \tag{C.14a}
\]

\[
Q_i = n^2 \frac{\partial (G/n)}{\partial n_i} \tag{C.14b}
\]

\[
U_i = n \frac{\partial F}{\partial n_i} \tag{C.14c}
\]

\[
S_i = \frac{1}{n} \frac{\partial (n^2e)}{\partial n_i} \tag{C.14d}
\]
\[ W_i = \frac{\partial f}{\partial n_i} \]  \hspace{1cm} (C.14e)

\[ X_i = -2 \left( f \frac{\partial (ng)}{\partial n_i} + ng \frac{\partial f}{\partial n_i} \right) \]  \hspace{1cm} (C.14f)

\[ Y_i = 2nfg \frac{\partial (ng)}{\partial n_i} + (ng)^2 \frac{\partial f}{\partial n_i} + 2n \]  \hspace{1cm} (C.14g)

Substituting Eqs. (C.13) and (C.14) into Eq. (C.1), integrating, and substituting \( V = \bar{V}/n \) gives

\[
RT \ln \hat{\phi}_i = -RT \ln \left( 1 - \frac{b}{V} \right) + \frac{RTH_i}{V - b} + \frac{K_i}{V} + \frac{L_i}{2V^2} + \frac{M_i}{5V^5} + \frac{N_i}{6V^6} \]

\[
- \frac{Q_i F}{G} \left( V - \frac{1}{G} \right) \exp(GV) - \frac{U_i}{G} \exp(GV) + \frac{\pi}{2\sqrt{f}} \left( S_i - \frac{e\theta_i}{2} \right) \]

\[
+ aV \left( \frac{2W_i}{f} \right) - ag\theta_i - \frac{aX_i}{f} - \frac{2S_i - e\theta_i}{2\sqrt{f}} \tan^{-1} \left[ \sqrt{f(V - g)} \right] \]

\[ - RT \ln Z \]

where

\[ a = \frac{e}{2(1 + f(V - g)^2)} \]  \hspace{1cm} (C.16)

\[ \theta_i = Y_i + \frac{W_i}{f} + W_i g^2 + X_i g \]  \hspace{1cm} (C.17)

For the mixing rules given by Eqs. (33) to (38), the derivatives \( H_i, K_i, L_i, \) and \( M_i \) are described by the same expressions that were derived for the BWR equation (Eqs. (C.6) to (C.9)). Expressions for the remaining derivatives are as follows:
\[ N_i = E \left( \frac{b}{b_i} \right)^6 + \frac{6EHi_i}{b} \] (C.17)

\[ Q_i = G_i - 2G \] (C.18)

\[ S_i = e^{\frac{f + f_i}{2f}} + \sum x_i \beta_i \left[ \frac{2(f_i-f)(b-g)f_i^{-0.5} + \sqrt{f_i} (H_i - b + g - g_i)}{1 + f(b-g)^2} \right] \left[ \tan^{-1} \left( \sqrt{f_i} (b - g) \right) - \frac{\pi}{2} \right] \] (C.19)

\[ U_i = \frac{G}{\exp(Gb)} \left( \frac{F_i}{G_i} \exp(G_i b_i) \right) + F \left( \frac{Q_i}{G} - GH_i - bQ_i \right) \] (C.20)

where

\[ \beta_i = \frac{e_i}{\sqrt{f_i}} \left[ \tan^{-1} \left( \sqrt{f_i} (b_i - g_i) \right) - \frac{\pi}{2} \right] \] (C.21)

\[ W_i = f_i - f \] (C.22)

\[ X_i = 2 (fg - f_i g - g_i f) \] (C.23)

\[ Y_i = 2 fg_i + f_i g^2 - f g^2 + 2 \] (C.24)

**C.3 Modifications to Include the Excess-Free-Energy Correction**

For both the BWR and the new EOS, parameters C and D were considered for incorporating the excess-free-energy correction into the EOS. Since the terms involving C and D are identical in both equations, the mixing rules for these two parameters are
also the same for both equations. As a result, the modifications that must be made to the partial fugacity coefficient expression are also identical.

C.3.1 Excess-Free-Energy Correction in Parameter C

When the excess-free-energy correction is incorporated into parameter C, the modified mixing rule for both the new EOS and the BWR EOS becomes

\[
C = b^2 \left[ 2A^E_{\infty} + \sum_i x_i \frac{C_i}{b_i^2} \right] \tag{C.25}
\]

In the partial fugacity expressions derived in Sections C.1 and C.2, only the derivative \( L_i \) changes as a result of modifying the mixing rule for C. All other derivative terms and the fugacity coefficient expressions themselves remain unchanged.

The definition of \( L_i \) remains the same as originally expressed in Eq. (C.4c). Applying this definition to Eq. (C.25) results in the following modified expression:

\[
L_i = C_i \left( \frac{b}{b_i} \right)^2 + \frac{2CH}{b} + 2b^2 \alpha_i \tag{C.26}
\]

where

\[
\alpha_i = \frac{\partial(nA^E_{\infty})}{\partial n_i} \tag{C.27}
\]
The expression for \(\alpha_i\) depends on the actual activity coefficient model that is chosen to represent \(A^E_\infty\). An expression for \(\alpha_i\) is derived for the NRTL activity coefficient model in Section C.3.3.

C.3.2 Excess-Free-Energy Correction in Parameter D

When the excess-free-energy correction is incorporated into parameter D, the modified mixing rule for both EOS becomes

\[
D = b^s \left[ 5A^E_\infty + \sum_i x_i \frac{D_i}{b_i^s} \right]
\]  

(C.28)

In this case, the only term associated with the partial fugacity coefficient expression that changes is the derivative \(M_i\), which is defined by Eq. (C.4d).

Applying the definition in Eq. (C.4d) to the modified mixing rule of Eq. (C.28) results in the following modified expression:

\[
M_i = D_i \left( \frac{b}{b_i} \right)^5 + \frac{5DH}{b} + 5b^s \alpha_i
\]  

(C.29)

C.3.3 Derivation of \(\alpha_i\) for the NRTL Equation

In this work, the NRTL equation was used to calculate \(A^E_\infty\). For a binary mixture, the equation is written

\[
A^E_\infty \approx G^E = x_i x_j RT \left[ \frac{\tau_{ji}}{x_i + x_j G_{ji}} + \frac{\tau_{ij} G_{ij}}{x_i + x_j G_{ij}} \right]
\]  

(C.30)
where

\[ G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \]  

(C.31)

and

\[ G_{ji} = \exp\left(-\alpha_{ij} \tau_{ji}\right) \]  

(C.32)

In these equations, \( \tau_{ij}, \tau_{ji}, \) and \( \alpha_{ij} \) are mixture-specific constants that may vary with temperature. The parameter \( \alpha_{ij} \) is not to be confused with \( \alpha_i \) defined by Eq. (C.27).

Multiplying Eq. (C.30) by the total number of moles, \( n \), gives

\[ nA_e^\infty \approx n_i n_j RT \left[ \frac{\tau_{ji} G_{ji}}{n_i + n_j G_{ji}} + \frac{\tau_{ij} G_{ij}}{n_j + n_i G_{ij}} \right] \]  

(C.33)

Finally, applying the definition of \( \alpha_i \) from Eq. (C.27) gives

\[ \alpha_i = x_i^2 RT \left[ \frac{\tau_{ji} G_{ji}^2}{(x_i + x_j G_{ji})^2} + \frac{\tau_{ij} G_{ij}^2}{(x_j + x_i G_{ij})^2} \right] \]  

(C.34)
APPENDIX D: USE OF A BINARY INTERACTION PARAMETER TO REPRESENT EXCESS GIBBS ENERGY

For some binary systems, it may be preferable to use a binary interaction parameter to represent the mixture’s $G^E$ behavior instead of an activity coefficient model. This may be particularly true for systems such as light paraffin hydrocarbons, whose phase equilibrium behavior has traditionally been well represented by simple EOS using a single binary interaction parameter, and for which activity coefficient model parameters may not be readily available in the literature.

As shown in the derivation that follows, the new zero-$A^E_\infty$ mixing rule (Eq. (48)) is equivalent to a quadratic mixing rule with a temperature-and-composition-dependent binary interaction parameter. It is also demonstrated below that the reformulated quadratic mixing rule with a constant $k_{ij}$ (that is, independent of temperature and composition) is exactly equivalent to the zero-$A^E_\infty$ mixing rule (Eq. (48)) for the case where $A^E_\infty$ can be represented by the simplest activity coefficient model, the Two-Suffix (symmetric) Margules equation with a temperature-independent coefficient.

If we first consider Eq. (48) as it applies to an ideal mixture, we see that it can be written

$$\frac{D}{5b^5} = \sum_i x_i \frac{D_i}{5b_i^5}$$  \hspace{1cm} (D.1)

The $A^E_\infty$ term does not appear in Eq. (D.1) because it is equal to zero for an ideal mixture. It can be shown that Eq. (D.1) can be rewritten in an equivalent quadratic form
\[
\frac{D}{5b^5} = \sum_i \sum_j x_i x_j \left( \frac{D}{5b^5} \right)_{ij}
\] (D.2)

as long as

\[
\left( \frac{D}{5b^5} \right)_{ij} = \frac{1}{2} \left( \frac{D_i}{5b_i^5} + \frac{D_j}{5b_j^5} \right)
\] (D.3)

Eq. (D.2) applies to an ideal mixture. For non-ideal mixtures, Eq. (D.2) can be modified in the traditional way as follows:

\[
\frac{D}{5b^5} = \sum_i \sum_j x_i x_j \left( \frac{D}{5b^5} \right)_{ij} (1 - k_{ij})
\] (D.4)

where \( k_{ij} \) is a binary interaction coefficient that may or may not vary with temperature or composition. And as is traditionally the case, \( k_{ij} = 0 \) for \( i = j \). Eq. (D.4) can be expanded for a binary mixture as

\[
\frac{D}{5b^5} = x_i^2 \frac{D_i}{5b_i^5} + 2x_i x_j \left( \frac{D}{5b^5} \right)_{ij} (1 - k_{ij}) + x_j^2 \frac{D_j}{5b_j^5}
\] (D.5)

After expanding further and rearranging, we have

\[
\frac{D}{5b^5} = x_i^2 \frac{D_i}{5b_i^5} + 2x_i x_j \left( \frac{D}{5b^5} \right)_{ij} + x_j^2 \frac{D_j}{5b_j^5} - 2k_{ij} x_i x_j \left( \frac{D}{5b^5} \right)_{ij}
\] (D.6)

or equivalently,
\[
\frac{D}{5b^5} = \sum_i \sum_j x_i x_j \left( \frac{D}{5b^5} \right)_j - 2k_{ij} x_i x_j \left( \frac{D}{5b^5} \right)_j
\]  
\hspace{1cm} (D.7)

Now, considering the earlier assertion that the quadratic expression in Eq. (D.2) is equivalent to the linear expression of Eq. (D.1) when the cross term is defined as in Eq. (D.3), we can replace the quadratic expression on the right-hand side of Eq. (D.7) with the equivalent linear expression as follows:

\[
\frac{D}{5b^5} = \sum_i x_i \frac{D_i}{5b_i^5} - 2k_{ij} x_i x_j \left( \frac{D}{5b^5} \right)_j
\]  
\hspace{1cm} (D.8)

Now, comparing Eq. (D.8) with Eq. (48), we can see that

\[
A_x^E = -2k_{ij} x_i x_j \left( \frac{D}{5b^5} \right)_j
\]  
\hspace{1cm} (D.9)

which, after rearranging, can be expressed as

\[
k_{ij} = -\frac{A_x^E}{2x_i x_j \left( \frac{D}{5b^5} \right)_j}
\]  
\hspace{1cm} (D.10)

A number of common activity coefficient models can be written for binary systems as

\[
G^E = x_i x_j f(x_i, x_j, T)
\]  
\hspace{1cm} (D.11)
Models that can be written in this form include the symmetric Margules equation, the two-parameter Margules equation, the Redlich-Kister equation, and the NRTL equation. Replacing $A_{\infty}^E$ in Eq. (D.10) with the expression for $G^E$ in Eq. (D.11) gives

$$k_{ij} = -\frac{f(x_i, x_j, T)}{2\left(\frac{D}{5b^5}\right)_{ij}} \quad (D.12)$$

Eq. (D.12) establishes the mathematical equivalence of the zero-$A_{\infty}^E$ mixing rule of Eq. (48) and the $k_{ij}$-based quadratic mixing rule of Eq. (D.4), for activity coefficient models that can be expressed in the form of Eq. (D.11).

Now, we consider the Two-Suffix Margules $G^E$ model—perhaps the simplest non-trivial expression capable of satisfying the requirement that $G^E = 0$ at $x_i = 0$ and $x_i = 1$—which is written as

$$G^E = x_i x_j A_{ij} \quad (D.13)$$

As pointed out by Prausnitz et al. (1986), this simple model can provide a good representation of $G^E$ for many simple liquid mixtures whose molecules are similar in size, shape, and chemical nature. For such simple systems, Eq. (D.12) can be rewritten as

$$k_{ij} = -\frac{A_{ij}}{2\left(\frac{D}{5b^5}\right)_{ij}} \quad (D.14)$$
These authors further point out that the coefficient $A_{ij}$ generally varies with temperature, but that for simple systems over a limited range of temperature, $A_{ij}$ is nearly constant. Thus for the special case of binary systems where $G^E$ can be accurately represented by Eq. (D.13) with a temperature-independent coefficient, Eq. (D.14) implies that the quadratic mixing rule of Eq. (D.4) with a constant $k_{ij}$ will give exactly the same result as the zero-$A^E_{\infty}$ mixing rule of Eq. (48).

As a corollary, we would expect that a single constant binary interaction parameter would be inadequate to represent binary interactions in systems whose low-pressure $G^E$ curve is asymmetric in composition, or varies strongly with temperature, since such behavior cannot be accurately reproduced by the symmetric Margules model with a constant coefficient.