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Equations of State for Polar Fluids

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of the degree of Doctor of Philosophy

Abstract

The development of a new cubic equation of state suitable for polar and non-polar fluids and mixtures is described. Several mixing rules for mixtures containing polar components are also tested.

An extensive survey of equations of state is made in order to identify important considerations in equation of state design. Equations of state in general, and cubic equations of the van der Waals form in particular, are examined in the survey. Mixing rules are briefly reviewed as well. The theory of corresponding states, crucial for practical application of equations of state, is also examined.

Expressions are developed based on general forms of cubic equations of state of the van der Waals type,

$$P = \frac{RT}{v-b} - \frac{\alpha(T)a_c}{v^2 + ubv + wb^2}$$

Analysis of extensive pure component saturated data for 97 polar and non-polar fluids shows that a relationship close to $u = -w$ is followed. This is supported by theoretical considerations based on the theory of corresponding states: the line $u = -w$ is close to being a locus of constant β_c $(= b_c/v_c)$, which is the expected behavior for real fluids.

A new equation of state is proposed, based on $u = -w$. Three versions are formulated, differing in the methods used to determine the equation of state constants. In one version, conventional generalization procedures are used, but with Z_c as a fourth corresponding states parameter to account for polar effects. In another version, pure substance correlations for P^s and v_l^s are used to directly calculate the constants at each temperature. In a third version, a new functional form for $\alpha(T)$ is proposed. An extended corresponding-states principle is then used to determine the constants, again using a direct calculation procedure.

The new equation of state is extensively evaluated using pure fluid saturated and liquid phase data, and mixture vapor-liquid equilibrium and volumetric data. Polar and nonpolar fluids and fluid mixtures are considered. Comparisons are made to several cubic equations of state, including recent ones, and including some which were designed for improved description of polar fluids. The new equation gives very good results, outperforming the other equations in almost all cases. The performance of the versions which use direct calculation procedures to determine the constants is especially good.

A study is also made of some recent mixing rules intended for mixtures containing polar fluids. It is found that a two-coefficient Redlich-Kister mixing rule is suitable for most mixtures. An extended version of this mixing rule, with three coefficients, is needed to prevent the prediction of false liquid-phase splitting for highly asymmetric mixtures.

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Notation

Various symbols, superscripts, subscripts, accents and abbreviations used frequently in this work are summarized below. Where appropriate, reference is made to the location in the text where the notation is defined. Some notation, corresponding to specific equations of state and correlations, or limited to small portions of the text, is not included here. All notation is fully defined where it first arises in the text.

Symbols

a, b, c, d	Constants for the cubic equations of state given by Equation 2.15. a and b are common to all cubic equations, and are called the attractive constant and the covolume respectively (see Equation 2.3).
A, B, C, D	Dimensionless forms of a, b c and d. Defined in Equations 3.2–3.5.
B	Second virial coefficient.
C_{ij}	Binary interaction coefficient in Huron-Vidal mixing rule, for components i and j (see equation 2.54).
f	Fugacity.
f, g, h	Quantities related to the classical critical point conditions applied to a cubic equation of state. Defined in Equations 3.29–3.31.
k_{ij},l_{ij},m_{ij}	Binary interaction coefficients, for components i and j (see §2.4.1).

l^*	Dimensionless parameter measuring nonsphericity in microscopic corresponding-states, defined in Equation 2.35.
m, n	Constants in α expressions. Definitions vary according to expressions.
n	Number of moles.
N	Number of data points.
N_c	Number of components in a mixture.
p, q, r	Coefficients of the dimensionless general cubic equation of state, Equation 3.6. Defined in Equations 3.7–3.9.
P	Absolute pressure.
P^*	Reduced pressure in microscopic corresponding-states, defined in Equation 2.32.
r_{ij}	Correlation between parameters i and j.
R	Gas constant, taken as $R = 8.31439\,\mathrm{J \cdot gmol^{-1} \cdot K^{-1}}$.
T	Absolute temperature.
T^*	Reduced temperature in microscopic corresponding-states, defined in Equation 2.34.
u, w	Constants in the Schmidt-Wenzel general form for cubic equations of state, Equation 2.12.
v	Molar volume.
v^*	Reduced volume in microscopic corresponding-states, defined in Equation 2.33.
V	Total volume.
x, y	Mole fractions in the liquid and vapor phases respectively. x is also used to represent mole fractions for any phase.
Z	Compressibility factor, $Z = Pv/RT$.

Z_{ij}	Residual of response i for data point j, defined in §3.2.7.
$\mathbf{Z}$	Matrix of residuals, defined in §3.2.7.
α	Temperature dependent portion of a, defined in Equation 2.22.
α_{ij}	Binary interaction coefficient in Huron-Vidal mixing rule, for components i and j (see Equation 2.54.
β_c	Ratio of b_c to v_c, defined in Equation 3.42.
ζ_c	Critical compressibility factor predicted by an equation of state.
λ	Dimensionless difference between the volume and covolume, defined in Equation 3.86.
μ^*	Reduced dipole moment in microscopic corresponding-states, defined in Equation 2.36.
ϕ	Fugacity coefficient.
ρ	Molar density.
χ	Polar parameter (Halm-Stiel parameter), defined in Equation 2.41.
ω	Pitzer's acentric factor, defined in Equation 2.40.
σ	Standard error, defined in Equation 3.105; molecular radius.
Ω_{ac},Ω_{bc},Ω_{cc},Ω_{dc}	The values of A, B, C and D at the critical point, defined in §3.1.2.

Superscripts, Subscripts and Accents

c	Critical point property.
est	Denotes current estimate in iterative procedures.

i, j, k	Property of components i, j and k in mixture calculations.
l, v	Liquid and vapor property respectively.
calc	Calculated value of a property.
r	Reduced property (i.e., a property divided by its critical point value).
s	Saturated property (i.e., a property on the vapor–liquid coexistence curve).
$\hat{}_i$	Derivative in fugacity coefficient expressions for mixtures, defined in Equation 3.62).

Abbreviations

%AAD	Average of absolute percent deviations, defined in Equation A.2.
%bias	Average of percent deviations, defined in Equation A.1.
BWR	Benedict-Webb-Rubin equation of state.
CT,GCT	Campbell-Thodos v_l^s correlation and its generalized version respectively, given in §4.1.1.
FKT	Frost-Kalkwarf-Thodos P^s correlation, given in §4.1.1.
GT,GGT	Gomez-Thodos P^s correlation and its generalized version respectively, given in §4.1.1.
HBT	Hankinson-Brobst-Thomson v_l^s correlation, given in §4.1.1.
HV	Huron-Vidal local composition mixing rule, Equation 2.54 (the version used in this work is Equation 3.74).
PR	Peng-Robinson equation of state, given in §4.2.
PT	Patel-Teja equation of state, given in §4.2.
RK2	Two-coefficient Redlich-Kister mixing rule, Equation 2.52.

RK2+	Augmented Redlich-Kister mixing rule, Equation 2.53.
RMS	Root of mean of squared deviations, defined in Equation 3.106.
%RMS	Root of mean of squared percent deviations, defined in Equation 3.107.
SIL	Sugie-Iwahori-Lu equation of state, given in §4.2.
SRK	Soave-Redlich-Kwong equation of state, given in §4.2.
SW	Schmidt-Wenzel equation of state, given in §4.2.
TB	Trebble-Bishnoi equation of state, given in §4.2.
TV	Toghiani-Viswanath equation of state, given in §4.2.
TPR	Translated Peng-Robinson equation of state, given in §4.2.
VLE	Vapor–liquid equilibrium
W	Wagner P^s correlation, given in §4.1.1.
I	New equation of state, with constants given by generalized correlations, given in §5.2.1.
II	New equation of state, with constants determined from pure fluid property correlations, given in §5.2.2.
III	New equation of state, with constants determined from selected pure fluid properties, given in §5.2.3.

Chapter 1

Introduction

The equations of state considered in this work relate the pressure P, molar volume v and temperature T of pure fluids. A general form for such an equation of state is

$$f(P, v, T) = 0$$

The function f involves several constants, many of which are specific to individual substances. For application to a wide range of fluids, the constants may be determined for each substance; more commonly, the principle of corresponding states is used to obtain expressions for the constants in terms of pure fluid properties. To describe mixtures, the usual approach is to define mixing rules which relate the equation of state constants of the mixture to those of the pure substances. The equation of state then has the form

$$f(P, v, T, x_i) = 0$$

where x_i denotes the mole fraction of each component i in the mixture.

Equations of state are essential for calculations in process design. The most straightforward application is the calculation of the volumetric behavior of fluids. However, equations of state have many other important applications, because the use of simple thermodynamic relationships allows analytical expressions to be derived for various fluid properties. For example, expressions for the fugacities of pure fluids and of components in a mixture are commonly derived, allowing phase-equilibrium calculations to be made (vapor–liquid equilibrium (VLE) calculations are of particular importance).

A practical equation of state should fulfill several criteria: it must be sufficiently accurate; it must be applicable to a wide range of conditions; it must be applicable to a wide variety of substances; it must not be excessively complex. The first three requirements are obvious; the last is also obvious if it is realized that large proportions of the time used in process design computations can be spent calculating properties derived from equations of state.

A large number of equations of state have been developed. These vary tremendously in accuracy, range of applicability and complexity. The most promising in recent years (in terms of the requirements listed above) are equations of state from perturbation theory, and cubic equations of state. The former are derived from molecular models, using statistical mechanical approaches. These equations have been applied with increasing success in recent years (an example is the perturbed hard-chain equations of state). Unfortunately, they are among the most complex equations of state. They have therefore not been accepted for practical use.

Cubic equations of state are simple extensions of the van der Waals equation of state. Most cubic equations of state can be represented by

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + ubv + wb^2}$$

where R is the gas constant, and a, b, u and w are constants. Cubics have long been popular for practical applications. They are generally simple, and are applicable to a wide range of non-polar compounds. They are also useful over a wide range of operating conditions. Their accuracy is reasonable for most design purposes. Altough some other equations can certainly outperform cubics in any one of these areas, few, if any, of them combine these factors as advantageously as cubic equations of state. Cubic equations of state are particularly good for VLE calculations, and with appropriate mixing rules have approached the accuracy of activity coefficient approaches; cubics are also applicable at much higher pressures than activity coefficient approaches.

Most equations of state developed to date have been restricted to nonpolar fluids. There are several reasons for this: nonpolar fluids are more easily described theoretically; the theory of corresponding states, necessary to obtain useful expressions for equation of state constants, is simpler for nonpolar fluids; many of the early applications of equations of state were for nonpolar fluids (e.g. natural gas, petroleum). This is unfortunate, because many of the fluids currently of importance are polar. Therefore, much of the recent effort in equation of state development has been to describe polar fluids. However, no equation of state has been generally accepted for polar compounds.

Therefore, the main objective of the present research is to develop an equation of state suitable for polar fluids (as well as nonpolar fluids). Only cubic equations of state are considered, because of the advantages listed above.

Mixing rules are required for application of equations of state for mixtures. While simple mixing rules are sufficient for nonpolar fluids, more complex ones are necessary for mixtures containing polar components. Therefore, another active area of research is the development of new mixing rules; many have been recently proposed (for examples, see the brief survey in §2.4). A secondary objective of this work is therefore to survey some promising mixing rules for the description of mixtures involving polar fluids.

This study begins with an extensive survey of the literature on equations of state (particularly cubics). Important points in the design of cubic equations of state are identified. Brief reviews of corresponding-states theory and of mixing rules are also done.

Expressions and methods used in this study are then presented and/or developed. These are general expressions, useful for most cubic equations of state, with most mixing rules.

A new cubic equation of state is developed, using an extensive collection of data for polar and nonpolar fluids. Several methods of determining its constants for a wide variety of substances are also developed.

Finally, the various versions of the new equation are evaluated and compared to previous cubic equations of state, using data for pure fluids and for mixtures, for both polar and nonpolar substances. Several mixing rules are also evaluated.

Chapter 2

Literature Review

Enormous amounts of work have been done on fluid-phase equations of state over the last two centuries. Most of this has taken place since van der Waals' pioneering work in 1873, and continues unabated in modern times. For example, 4779 papers including the term "equation of state" in the title or abstract were listed in the *Chemical Abstracts* from 1967 to 1983; 159 referred to the Redlich-Kwong equation alone [101]. Clearly, any realistic attempt to review this field cannot be comprehensive, even if restricted to consideration of cubic equations of state. Instead, important and influential developments, especially those directly relevant to this work, are examined in this review. These are often illustrated with specific examples from the literature.

The development of equations of state has incorporated three essentially separate parts. The most obvious is the development of the equation itself. The application of equations of state to a wide variety of substances requires the use of the principle of corresponding states. Finally, for application to mixtures, mixing rules for the constants in the equation of state must be considered. This work is mainly concerned with the first part, so most of this review will be about the development of equations of state. A brief discussion of equations of state in general is first given, without going into detail on cubic equations, in order to put the present work in historical and technical context. A more extensive review of the literature on cubic equations of state follows. Corresponding-states theory, which is important for the practical application of equations of state, is then examined. A brief overview of mixing rules for cubic equations of state is also given. Finally, important points from the review relevant to this work are summarized.

2.1 Equations of State

Equations of state which have been of particular practical and/or theoretical importance are discussed here. Three fundamentally important equations of state are first described: the perfect gas law, which is the limiting condition for dilute gases; the van der Waals equation, of great importance in subsequent theoretical and practical developments; the virial equation, which is perhaps the only theoretically correct equation of state. If high density fluids are to be described, other approaches must be used. These include models in statistical mechanics, and semi-empirical and empirical equations.

2.1.1 Perfect Gas Law

The first equation of state was the perfect (or ideal) gas law, a combination of the laws of Boyle, Charles and Avogadro, formulated at the turn of the nineteenth century. The perfect gas law is

$$P = \frac{RT}{v} \tag{2.1}$$

or in terms of compressibility factor,

$$Z = \frac{Pv}{RT} = 1 \tag{2.2}$$

R is the gas constant. It was originally based on empirically observed behavior, but it can also be derived from simple molecular-level kinetic arguments or from statistical mechanics (e.g., see [61,100]). In these derivations, it must be assumed that the molecules of a perfect gas do not interact in any way. The properties of a perfect gas are therefore due to simple (noninteracting) translation of its molecules and to internal molecular contributions, such as molecular vibration and rotation, which are well understood (e.g., see [100]). Intermolecular forces, which are relatively poorly understood and are difficult to describe (e.g., see [61,95,100]), are ignored in a perfect gas.

Intermolecular forces are negligible for dilute gases. Real substances therefore approach perfect gas behavior at low enough densities. The perfect gas law is inaccurate for liquids or for gases near saturation, where intermolecular forces are significant. It nevertheless can be a useful reference point for these cases, and as such has been of great importance. One practical example of this is perfect gas heat capacity, which can be calculated from geometric and spectroscopic information alone (e.g., see [100]).

Equation of state development has been aimed at describing fluids under conditions where the perfect gas law does not apply. However, the perfect gas law is still an important limiting condition: at the low-density limit, an equation of state must simplify to the perfect gas law to be theoretically correct.

2.1.2 The van der Waals Equation

In 1873, van der Waals formulated an equation of state based on molecular kinetic arguments [133]. This was a simple equation, cubic in volume (hence the term "cubic equation"), which could describe both liquid and vapor phases. He developed his equation by specifically addressing the assumption of negligible intermolecular forces required for the molecular kinetic derivation of the perfect gas equation. Abbott [4] has shown how the van der Waals equation can also be derived from other empirical and theoretical considerations.

The van der Waals equation is

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2.3}$$

The first term represents repulsive effects due to the volume b occupied by the molecules, and is often called the covolume. The second term accounts for the effect of attractive forces between the molecules; a is usually called the attractive constant. If a and b are zero, the perfect gas equation is recovered.

Although its quantitative performance is poor, the van der Waals equation gives qualitatively good results; for example, van Kronynenburg and Scott [134] have used it to generate phase diagrams for binary fluid mixtures which have contributed greatly to the understanding of phase behavior. The van der Waals equation has been of great importance in subsequent practical and theoretical developments[1]. Among these, it has served as the basis for cubic equations of state, other empirical equations of state, perturbation theory, and generalized van der Waals theory. Some of these are described subsequently.

2.1.3 The Virial Equation

In the virial equation of state, first developed by Kammerlingh Onnes in 1901 [67], deviations from the perfect gas are described by a power series expansion in density (the "Leiden" form, after Kammerlingh Onnes),

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \tag{2.4}$$

or pressure (the "Berlin" form),

$$Z = 1 + B'P + C'P^2 + D'P^3 + \cdots \tag{2.5}$$

where $B, C, D, \ldots$ $(B', C', D', \ldots)$ are the second, third, fourth, etc. virial coefficients, and ρ is molar density. The virial coefficients are functions of temperature, and are equal to zero for a perfect gas.

The virial equation has been shown to have a sound theoretical foundation in statistical mechanics (e.g., see [61,100]). The resulting expressions for $B, C, D, \ldots$ indicate that the second, third, fourth, etc. virial coefficients represent deviations from the perfect gas due to interactions between two, three, four, etc. molecules. The higher order collisions become important at high densities; therefore, the virial equation requires a large number of coefficients at high densities. At high enough densities (approximately liquid density) the virial expansion series diverges (see [100] for a demonstration of this). This represents a fundamental limit on its range of applicability.

The range of applicability of the virial equation is further limited by practical considerations. Obviously, only a finite number of virial coefficient can be used, so that the high-density limit cannot be reached. More importantly, it is very difficult to accurately measure coefficients beyond the second or third. Only the second virial coefficient has been extensively measured; a critical compilation was made by Dymond and Smith [49].

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[1] van der Waals' contribution was officially recognized in 1912 when he was awarded the Nobel prize in Physics

The practical application of the virial equation has been made possible by the formulation of expressions for the coefficients. One approach has been to calculate them directly from intermolecular potential functions. For example, Hirschfelder et al. [61] gave expressions for the second and third virial coefficients based on the Lennard-Jones potential function. This approach generally yields useful expressions only for the second and third virial coefficients when realistic potential functions are used. Polar fluids require more complex potential functions (such as the Stockmayer potential), resulting in more complex expressions.

It is usually more convenient to calculate virial coefficients from empirical correlations. Reid and coworkers [102,103] give brief critical examinations of various correlations for the second virial coefficient, most of which have used corresponding-states approaches (e.g., see [132]). Generally, good results are obtained for non-polar fluids, while limited success has been achieved for polar fluids.

The virial equation has been of use in the development of other equations of state. This is because the virial equation is theoretically correct at low densities and moderate densities, and because the behavior of the second virial coefficient is well known. The value of the second virial coefficient calculated from an equation of state at low to moderate pressure should therefore follow this behavior reasonably well. The virial equation also provides a theoretical limitation on the form of mixing rules (§2.4).

2.1.4 Statistical Mechanical Approaches

As discussed above, the virial equation is a theoretically correct description of the properties of low and moderate density fluids. However, it cannot be used for dense fluids; other approaches must therefore be used to obtain a theoretical description. The procedures for this are available from statistical mechanics. Two distinct approaches have been widely used: lattice theory, useful for solids and dense fluids, and perturbation theory, useful for dilute and dense fluids. Equations of state resulting from the latter are discussed here; good introductions to perturbation theory are given by Prausnitz et al. [95] and Reed and Gubbins [100].

Perturbation theory is inspired by the van der Waals equation, in which pressure is expressed as a sum of repulsive and attractive contributions.

Generalizing this assumption leads to equations of the form

$$P = \sum_i P_i \tag{2.6}$$

where each term P_i represents a contribution from a particular source. The basic or reference term is usually that due to repulsive effects of the core of the molecule (e.g., the first term in the van der Waals equation). Other terms are "perturbations" of the basic term, added to account for other effects, such as dispersion forces, polar forces and quantum effects.

The van der Waals repulsive pressure contribution,

$$\frac{RT}{v-b} \tag{2.7}$$

is a very simple representation of the pressure of a fluid made up of hard spheres of molar volume b. However, this is well known to be an inaccurate expression, especially at high densities. The expression of Carnahan and Starling [39] is a much more accurate representation of the pressure of a fluid of hard spheres,

$$\rho RT \left[\frac{1 + y + y^2 - y^3}{(1-y)^3} \right] \tag{2.8}$$

where $y = b\rho/4$. It has been widely used in the development of equations of state. These include the equations of Carnahan and Starling [38], in which Equation 2.8 is used, along with simple attractive terms from cubic equations of state. The Carnahan-Starling expression is frequently used as a basis in more sophisticated models, such as the perturbed hard-chain equations of state.

Of course, in general the molecules of real fluids are neither hard nor spheres. More sophisticated models have therefore been proposed. One well known example is by Boublik [31], for a hard convex body. It has been used to describe repulsive forces in the equation of Chen and Kreglewski [40]. Other models include that of Lin et al. [76], using a "chain of rotators" model for the repulsive term. The perturbed hard chain model, in which the molecule is represented by a chain of hard spheres, has received much attention recently (e.g., see Cotterman et al. [43,42] and Sheng and Lu [114]). Generally, more sophisticated models result in more complex expressions.

Perturbations of the basic repulsive term are usually separated into different contributions due to effects such as dispersion forces, polar forces, quantum effects, etc. Expressions for these contributions have been evaluated in a variety of ways. One method is to fit an empirical expression to the properties of a reference fluid; for example, Adler et al. [14] fitted an expression to the non-polar contribution of argon, while Lee and Chao [73] used water as a reference fluid for polar contributions. Other fluids can then be described in terms of deviations from the reference fluid; for example, Chen and Kreglewski [40] used the expression of Adler et al. as a basis for the attractive contributions of non-polar fluids, and Lee and Chao used their expression for water in describing polar contributions. Other approaches include empirical fitting of expressions to results from molecular simulations, or direct derivation of expressions from molecular models (e.g., Cotterman et al. [43] used both). Most expressions for attractive contributions are notable for their high complexity, often involving dozens of constants.

Some of these equations are only applicable to a limited range of substances; however, those based on more realistic molecular models are capable of representing a wide range of substances with good accuracy. The major disadvantage of such equations is their tremendous complexity in comparison to the cubic equations; this has been a barrier to their acceptance in practical applications. However, research is ongoing and appears to bear some promise for the future.

2.1.5 Empirical Equations of State

An enormous number of empirical and semi-empirical equations of state have been proposed. Most of these have had the purpose of accurately describing pure fluid properties. In order to achieve this, these equations have had to be complex and to incorporate a large number of constants. They are often based on the virial equation of state, modified so as to describe high density fluids.

These equations are quite distinct in purpose from simpler equations, such as cubics, which give compact, moderate accuracy description of a wide range of fluid and fluid mixtures. Instead, empirical equations are usually intended for high accuracy description of a limited range of fluids. Their complexity makes it difficult to extend them to a wide range of fluids or to mixtures.

Benedict, Webb and Rubin [29] developed an empirical equation of state which was based on the Beattie-Bridgeman equation [28], itself a modification of the virial equation.

$$\begin{aligned} P &= RT\rho + (B_0RT - A_0 - \frac{C_0}{T^2})\rho + (bRT - a)\rho^3 + a\alpha\rho^6 \\ &\quad + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \end{aligned} \tag{2.9}$$

A_0, B_0, C_0, a, b, c, α and γ are constants. Tabulations of the constants for a variety of substances are collected in Reid et al. [103]. Many modified versions of the Benedict-Webb-Rubin (BWR) equation have been proposed; two of the more important are those of Lee and Kessler [71] and Starling and coworkers [35,142], which are generalized to apply to many types of substances. Reid and coworkers [102,103] reviewed several of these.

The BWR equation and its various modifications have been extensively used in the petroleum industry. They are quite accurate for pure compounds, have been extensively tested, and have been used to generate useful tabulations of properties. The BWR equation was the first equation of state to accurately predict mixture vapor-liquid equilibria [74]. This was because it was designed to predict pure component vapor pressures correctly. This concept has been used in most subsequent equations of state intended for vapor-liquid-equilibria, including cubic equations of state.

Unfortunately, the BWR-based equations of state are obviously complex and highly empirical. This makes it difficult to extend them to new classes of compounds; indeed, they have only been tested for hydrocarbons and a few other compounds of importance in the oil and gas industries; they are definitely not applicable to most polar compounds. A similar problem applies to extrapolation outside the range in which their constants were determined. Mixture calculations are also difficult, because mixing rules for so many empirical constants may not be easy to determine. This was illustrated by Leland [74], using comparisons with simple cubic equations.

Another important class of equations of state are the reference fluid equations. These are highly complex empirical equations of state meant to reproduce the volumetric behavior of single fluids to within experimental error over wide ranges of conditions. They are used to generate accurate reference values for fluids, often for the generation of thermodynamic tables. A well-known example is the steam equation of Keenan et al. [68], meant to represent the behavior of water from 220 K to 1600 K, up to a pressure of 2200 bar. It gives the compressibility factor Z as

$$Z = 1 + \rho Q + \rho^2 \frac{\partial Q}{\partial \rho} T \qquad (2.10)$$

where Q is a complex function of ρ and T involving 52 constants. Other examples of reference fluid equations are those used to generate the IUPAC tables of Angus and coworkers [17,18,19,20,21,22,23,24]. These give compressibility factor as power series in reduced density and temperature, and involve over 30 constants each.

Reference fluid equations are of considerable importance for both practical and theoretical purposes. Lee and Chao [73] give an interesting example. They used perturbation techniques to generate a polar correction for the equation of Chen and Kreglewsky [40]. The basis for this term was the steam equation of Keenan et al. (Equation 2.10).

2.2 Cubic Equations of State

Cubic equations of state (or "cubics") are the most popular in process calculations. While they do not have the accuracy of some of the empirical or theoretical equations discussed above, they are certainly far simpler. They can represent a wide range of compounds, and are relatively easily extended to mixtures.

Some general forms of cubic equations of state are presented and discussed first. The remainder of the discussion refers to these useful general forms. Important aspects of the design of cubic equations of state are considered.

Many equations of state are discussed here. Several of these (namely the Soave-Redlich-Kwong, the Peng-Robinson, the Schmidt-Wenzel, the Patel-Teja, the translated Peng-Robinson, the Trebble-Bishnoi, the Toghiani-Viswanath and the Sugie-Iwahori-Lu equations) are given in full in §4.2. The relative merits of the various cubic equations of state presented here are not extensively discussed in this review. However, those listed above are subsequently evaluated (§6) for comparison with the equations of state proposed in this work. Other evaluations of recent cubics are those of Yu [148], which examined performances for nonpolar fluids, particularly alkanes, and Trebble and Bishnoi [129], which looked at performances for polar and nonpolar fluids.

2.2.1 General Expressions

Theoretically, cubic equations of state are a simple example of perturbation theory. The repulsive term is van der Waals original form. The attractive term is an empirical or semi-empirical expression. The general form of the cubic can also be justified on empirical grounds [4,135]. Almost all cubic equations of state can be represented by general expressions. The following equations use the van der Waals repulsive term, and give general empirical expressions for the attractive term. Note that other general forms are possible (e.g., see [137]); however, the forms presented here are the most useful.

The first general form was proposed by Abbott [3].

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + cv + d} \tag{2.11}$$

a and b correspond to the constants[2] in the van der Waals equation. c and d are additional constants. Various cubic equations of state are represented by Equation 2.11 by specifying values of c and d; for example, the VDW equation is given by $c = d = 0$. Equation 2.11 was used by Abbott and Van Ness [3,135] to obtain useful results on the general behavior of cubics.

Schmidt and Wenzel [111] proposed a variation of Equation 2.11.

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + ubv + wb^2} \tag{2.12}$$

Different forms of cubic equations are now obtained by specifying u and w. Comparison to Equation 2.11 shows that the constants of the two forms are simply related.

$$u = c/b \tag{2.13}$$

$$w = d/b^2 \tag{2.14}$$

This equation has the advantage that u and w are dimensionless. In practice, they take on a limited range of values. Effects of the form of the equation of state are therefore easier to perceive.

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[2] The terminology in the literature for these and other quantities in cubics is vague. In this work, they are called constants, although some may vary with temperature and/or from substance to substance. They are sometimes called parameters by other authors.

Different cubic equations of state can be represented graphically in terms of the relationship between u and w. Figure 2.1 shows the u and w values of several equations of state. The "excluded region" in Figure 2.1 represents values of u and w which can cause the denominator of the attractive term to be equal to zero for finite values of v. Schmidt and Wenzel [111] showed that the conditions $w > -u - 1$ and $w > u^2/4$ must be satisfied to avoid this situation.

Another general form for cubics is given by

$$P = \frac{RT}{v-b} - \frac{a}{(v-c)(v-d)} \tag{2.15}$$

Different forms of equations are now obtained by specifying c and d. The advantage of this form is that it is algebraically simple to manipulate. It has the disadvantage that c and d can be complex numbers. However, this situation does not arise for useful values; it also does not limit the validity of expressions derived from this form. Comparison to Equation 2.12 gives the following relationships between the constants.

$$\begin{aligned} c &= b(-u - \sqrt{u^2 - 4w})/2 && (2.16) \\ d &= b(-u + \sqrt{u^2 - 4w})/2 && (2.17) \\ u &= -(c + d)/b && (2.18) \\ w &= cd/b^2 && (2.19) \end{aligned}$$

Other general forms have been proposed; for example, Van Ness and Abbott [135] gave a five-parameter form. However, almost all cubic equations of state can be represented by the forms given above; only equations of these forms are considered in the present work.

Cubic equations of state can be represented in a general manner in statistical mechanics. This makes it easier to relate cubics to molecular considerations. This is usually called generalized van der Waals theory. Vera and Prausnitz [138] gave a canonical partition function for van der Waals fluids, and showed how it could be used to generate various cubic equations of state. This approach is particularly useful in the development of mixing rules, because it relates the attractive constant a to molecular distribution functions [108].

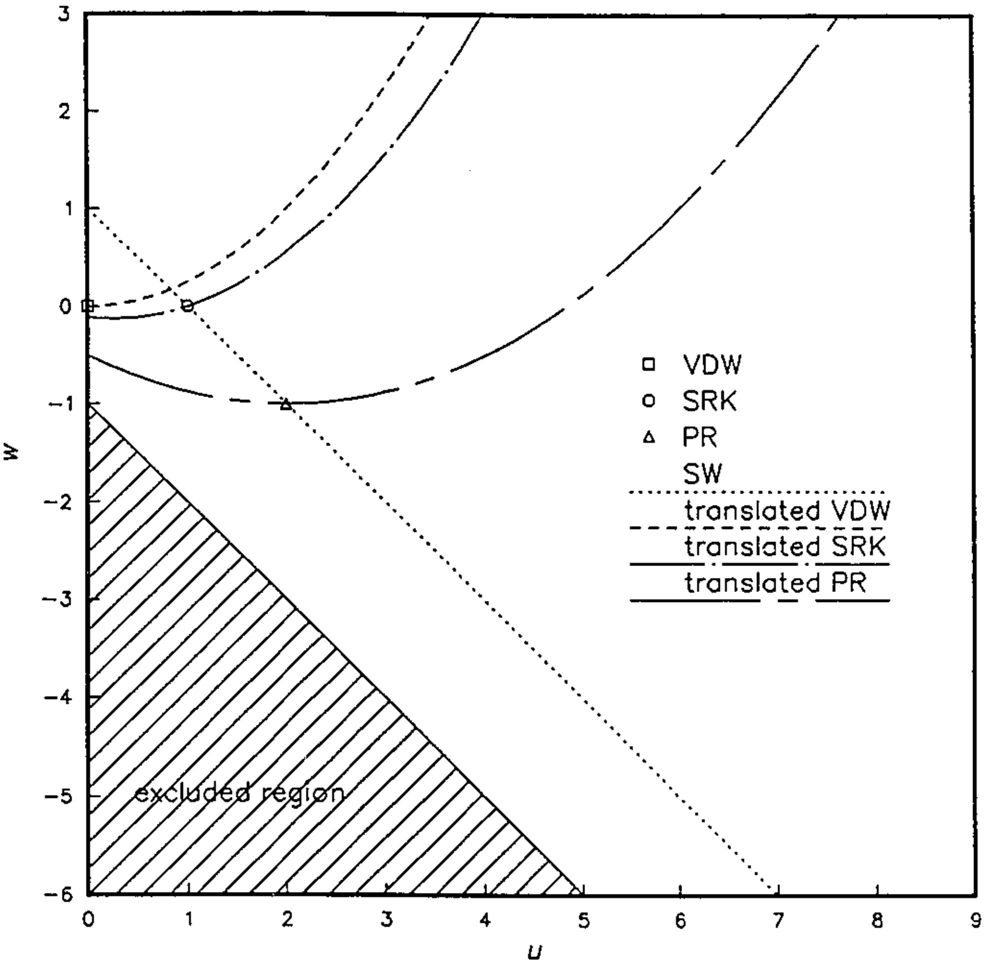

Figure 2.1: u and w values for several equations of state.

2.2.2 Classical Derivative Conditions

The cubic equations of state given in §2.2.1 contain seven unspecified quantities (for Equation 2.12, T, P, v, and four constants). Under a given set of conditions (e.g., T and P), this leaves 5 quantities to be determined. One constraint is obviously the equation of state itself. This leaves four independent quantities to be somehow specified, which is potentially a difficult task to do with accuracy and consistency. Fortunately, additional constraints are available. These were initially suggested by van der Waals, based on the continuity between the vapor and liquid phases at the critical point (denoted by the subscript c).

$$\left(\frac{\partial P}{\partial v}\right)\bigg|_{T_c} = 0 \tag{2.20}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)\bigg|_{T_c} = 0 \tag{2.21}$$

Equations 2.20 and 2.21 are usually called the classical derivative conditions. Critical temperature and pressure are naturally introduced into the equation of state, in the form of reduced temperature T_r $(= T/T_c)$ and reduced pressure P_r $(= P/P_c)$. This forms the basis for the macroscopic principle of corresponding states (§2.3.2). Only two independent quantities at the critical point remain to be determined, greatly simplifying the task of designing equations of state. General expressions that result from the application of Equations 2.20 and 2.21 to Equation 2.15 are developed in §3.1.2.

Imposition of these constraints does result in some limitations on cubic equations of state. Abbott [3] made an important study of this. He demonstrated that cubic equations subjected to the critical point conditions could not describe volumetric behavior near the critical point and away from the critical point simultaneously. For this reason, the critical point volume is not fixed to the experimental value in most cubic equations of state.

Almost all subsequent developments of cubic equations of state have dealt with either specifying the temperature dependency of the constants away from the critical point, or specification of the two remaining quantities at the critical point. These points are discussed in the next two sections.

2.2.3 Temperature Dependence of the Constants

The van der Waals equation of state has constant values of a and b for each substance. It has been repeatedly shown that the constants for any cubic equation of state are in fact functions of temperature (e.g., see Yu [148] and Trebble and Bishnoi [129]). The constant a has an especially strong temperature dependence. This is one reason for the limited accuracy of the van der Waals equation. The temperature dependence of the constant a is usually described by the function $\alpha(T)$, defined as follows.

$$\alpha(T) = \frac{a}{a_c} \tag{2.22}$$

The van der Waals equation has $\alpha = 1$ (i.e., no temperature dependence).

Redlich and Kwong [99] were the first to improve the qualitative performance of cubic equations of state by introducing an empirical modification to the attractive term. They used

$$\alpha = T_r^{-1/2} \tag{2.23}$$

and obtained greatly improved predictions of vapor pressure and vapor-liquid equilibria (VLE) of mixtures.

The next major advance consisted of considering more complex forms for the function α. A highly successful form was that proposed by Soave [118], for the Redlich-Kwong equation.

$$\alpha = [1 + m(1 - T_r^{1/2})]^2 \tag{2.24}$$

This empirical expression was obtained from observation of the behavior of α values calculated from saturated vapor pressure, P^s. The substance-dependent constant m was fixed for several nonpolar fluids by requiring exact prediction of P^s at $T_r = 0.7$. The values of m were then empirically fitted to acentric factor in order to avoid iterative calculations. Improved results for a wide variety of nonpolar fluids were obtained. Soave's expression for α has been incorporated into many subsequent equations of state, with various methods of calculating m. For example, Peng and Robinson [89] determined an empirical function for m in terms of acentric factor, by fitting P^s data. This has been the most common approach. Another common modification has been to incorporate a further (empirical) temperature dependence in m (e.g., see Schmidt and Wenzel [111]). A disadvantage of

Equation 2.24 is that it causes the value of a to go through a minimum at high temperatures, which is not consistent with observed behavior [87].

Many empirical modifications have been made to Soave's expression. The most successful of these was proposed by Styjek and Vera [121,123] in a modified version of the Peng-Robinson equation. This equation of state could reproduce the vapor pressure of pure substances with an accuracy similar to the Antoine equation. However, it requires one or more additional constants which must be determined for each substance.

Another form for α was proposed by Heyen [60].

$$\alpha = \exp[m(1 - T_r^n)] \tag{2.25}$$

n is another substance-dependent constant. As with Soave's expression, Equation 2.25 was obtained from observation of the behavior of α values calculated from saturated vapor pressures. This expression has the advantage that the value of a does not go through a minimum. In many applications, n has been set to unity.

Other temperature functions have been proposed. These have often been power series in T_r (e.g., see [70]) or in $(1 - T_r)$ (e.g., see [59]). Such functions must be used with caution, because they may extrapolate poorly. For example, Trebble and Bishnoi [129] found that Kubic's equation of state [70] gave poor volumetric properties at low T_r due to the presence of a T_r^{-7} term in the α expression.

Adachi and Lu [7] showed that specification of an appropriate temperature dependency for a is a major factor in vapor–liquid equilibrium (VLE) calculations[3]. By using the Heyen form (Equation 2.25), even the van der Waals equation of state can give VLE results comparable to more modern equations of state. They concluded that the form of the equation of state (i.e., its values of u and w) does not significantly affect VLE performance. The major requirement is to have a temperature dependency for a that gives accurate representation of P^s.

Nevertheless, in a subsequent study, Adachi et al. [12] found that the form of the equation of state has a major effect on the performance of various functional forms for α. They made a thorough study of the Soave and

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[3] In the literature, VLE calculations usually deal with the values of P, T, liquid mole fractions x and vapor mole fractions y at equilibrium. Many other properties, particularly volumetric properties, are not normally included in the term VLE.

Heyen temperature functions (with $n = 1$ in the latter) for the representation of P^s with various equations of state. They found that the performance of each function depends strongly on the value of the characteristic constant Ω_{ac}[4] of the equation of state with which it is used, which in turn depends on the values of u and w. The Soave form is particularly suitable for equations of state with Ω_{ac} near 0.45 (e.g., the Peng-Robinson equation), and the Heyen form with $n = 1$ is best for equations with Ω_{ac} near 0.42 (e.g., the Redlich-Kwong and van der Waals equations). Thus, equations of state which use these temperature dependent functions will have reduced abilities to predict P^s if their Ω_{ac} values are substance dependent and/or are significantly different from the values above. Such equations have had to employ variations of these temperature functions in order to achieve good prediction of P^s (and hence good VLE performance). An example of this is the Schmidt-Wenzel equation, with substance-dependent Ω_{ac}, in which the Soave form is used with a temperature dependence in m.

Since the accurate prediction of vapor pressure seems to be the most important consideration in the determination of α, it may be advantageous to calculate α directly from vapor pressure, rather than simply attempting to correlate vapor pressure. Normally, this involves a complicated iterative procedure. Soave [117] developed a polynomial approximation which allows α to be calculated directly from vapor pressure for the van der Waals, Redlich-Kwong and Peng-Robinson equations. Adachi [6] extended this to apply to any cubic equation of state. These expressions have the disadvantage of being complex polynomials (with 10 coefficients in Soave's case, and 50 coefficients in Adachi's case). Sugie et al. [125] therefore developed a streamlined, efficient iterative procedure to perform this calculation for any cubic equation of state[5]. Trebble [127] calculated constants in the temperature-dependent functions in the Trebble-Bishnoi equation of state by direct calculation from vapor pressure; however, he did not specify a systematic approach.

So far, only temperature dependency in a has been discussed. The other equation of state constants are often considered independent of temperature. Their temperature dependency, if any, is weak in comparison to that

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[4] $\Omega_{ac} = a_c P_c/(RT_c)^2$. It results from application of the classical critical point conditions. See §3.1.2.

[5] This procedure is used in two of the equations of state developed in this work, and is described in §3.2.2.

in a, and most workers have chosen to ignore it. Trebble and Bishnoi have used a temperature-dependent b in their equation of state. If a temperature dependency is specified, its form must be chosen with care, otherwise physically unrealistic results may be obtained. For example, Trebble and Bishnoi [129] showed that the Heyen equation of state [60] produced crossing enthalpy isotherms and negative heat capacities under some conditions, due to the form of the temperature dependence of b. They showed that the second derivative of b with respect to T must remain negative to avoid this.

2.2.4 Effects of Varying the Form

As mentioned in §2.2.1, the form of a cubic equation of state is determined by the values of u and w used. This is equivalent to specifying the two remaining quantities at the critical point (§2.2.2).

From the previous section, it is clear that the form of cubics of state has little effect on their VLE behavior. This is primarily determined by the temperature dependency of the constant a. However, the values of u and w do have a major effect on other properties, particularly volumetric properties. Yu et al.[148,149] showed that optimum values of u and w could be found for individual substances for the prediction of volumetric properties. They found that the quality of the predictions depended strongly on the values of u and w, particularly for liquid volumes.

The simplest cubics have constant values of u and w, and are often called "two-constant" equations of state. The major equations in this category are the van der Waals equation ($u = w = 0$), the Redlich-Kwong and related equations [99] ($u = 1$, $w = 0$), and the Peng-Robinson equation [89] ($u = 2$, $w = -1$). The last two currently are the most popular equations of state in process calculations. Many equations have been proposed which are modifications of these, primarily in the temperature dependence of the constants. The best known example is the Soave modification of the Redlich-Kwong equation [118]. Of these equations, the Peng-Robinson gives the best volumetric results, especially for the liquid phase and near the critical region. As shown by Yu [148], it has u and w values close to the optima for several fluids. Equations with fixed u and w are completely determined; other than temperature dependencies of the constants, no additional quantities need to be specified.

Equations with fixed values of u and w cannot give good volumetric prediction for a wide range of substances, as shown by Yu et al. [148,149]. They found that the values of u and w for optimum volumetric performance vary significantly from substance to substance. In many equations of state, the values of u and w are not fixed. The simplest case is where only one can vary independently, i.e., when there is a functional relationship between them. These are known as "three-constant" equations of state. Schmidt and Wenzel [111] proposed the relationship $u = 1 - w$ in their equation of state. Their main justification was that this locus includes both the Redlich-Kwong and Peng-Robinson equations. Many researchers subsequently used this relationship, including Patel and Teja [87], and Toghiani and Viswanath [126]. Other relationships have been used; for example, Yu et al. suggested $u = w - 3$, based on the locus followed by the optimum values of u and w for normal paraffins. Unlike the two-constant equations, these equations of state are not completely determined; one additional quantity at the critical point must be specified. This is usually done through the fitting of an empirical relationship for one of the undetermined constants, often to saturated liquid molar volume data.

Martin [80] suggested that volume predictions of two-constant equations can be improved by a simple volume translation, which is substance dependent.

$$v' = v - c \tag{2.26}$$

v' is the volume after translation, v is the original predicted volume, and c is the translation. This is simply a special case of the three-constant equations above. Translated versions of the van der Waals [9,79], Soave-Redlich-Kwong [27,88] and the Peng-Robinson equation [66,150] have been developed. Yu and Lu [148,150] have generalized the technique of volume translation, showing that there is a simple quadratic relationship between u and w. A translated equation of state has a value of Ω_{ac} identical to the original two-constant equation from which it is derived, and gives identical vapor pressure and VLE predictions. Any three-constant equation of state with a constant value of Ω_{ac} can be interpreted as a volume translation of a two-constant equation.

In some cubics of state, u and w are allowed to vary independently ("four-constant" equations of state). A recent example is the equation of Trebble and Bishnoi [130]. It uses the Schmidt-Wenzel expression as a basis, but modifies it by adding another independent constant; hence u

and w vary independently. Other examples are the equations of Adachi et al. [8] and Sugie et al. [125]. These equations are more flexible, but have the disadvantage that two quantities at the critical point must be specified. They are usually described by empirical relationships fitted to experimental data. However, Sugie et al. determined the quantities directly from liquid molar volume correlations, using an iterative procedure. Trebble [127] used a single value of liquid density in the calculation of constants for the Trebble-Bishnoi equation of state.

2.3 Corresponding-States Theory

The theory of corresponding states is crucial for the practical application of equations of state. Its use permits a general equation of state to be formulated which can apply to a wide range of substances. An extended corresponding states approach is required for application of cubic equations of state to polar fluids.

The theory of corresponding states can be discussed on both a microscopic and macroscopic basis.

2.3.1 Microscopic Corresponding-States

The microscopic theory of corresponding states is well established, and is discussed in many books. The discussion here is based in part on Hirschfelder et al. [61], Reed and Gubbins [100], and Prausnitz et al. [95].

The microscopic principle of corresponding states is based on an equation of state from statistical mechanics, which is derived from the canonical partition function Q.

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{2.27}$$

k is Boltzmann's constant, and V is the total volume of the fluid. It is commonly assumed that the partition function can be expressed as a product of independent contributions due to molecular translation and internal molecular effects (e.g., rotation, vibration), and that the translation can be expressed by classical (as opposed to quantum) mechanics. These assumptions result in a "semiclassical" partition function [100],

$$Q = \frac{Q_{\text{in}}}{N!} \int e^{-\Phi/kT} d\mathbf{r}^N \tag{2.28}$$

Q_{in} is the internal contribution, and Φ is the potential energy of the system of N molecules. The integral is a multiple integral over all molecular coordinates, denoted as $\mathbf{r}^N$. Substituting Equation 2.28 into Equation 2.27 gives the pressure of a fluid as a function of the total potential energy of the system.

$$P = kT \frac{\partial}{\partial V} \ln \int e^{-\Phi/kT} d\mathbf{r}^N \tag{2.29}$$

A principle of corresponding states can be developed from Equation 2.29 if it is assumed that the potential energy for any substance can be expressed as a universal function of characteristic molecular parameters. Models suitable for describing the potential of a system of nonspherical polar molecules usually incorporate an energy parameter ϵ, a molecular diameter σ, a further diameter l (expressing the nonsphericity of the molecule) and dipole moment μ. An example of a pair potential of this type is given by Halm and Stiel [57].

The functional dependence of the overall potential on these parameters can be expressed as

$$\Phi = \Phi[\mathbf{r}^N, \epsilon, \sigma, l, \mu] \tag{2.30}$$

Substituting this into Equation 2.29 results in the following functional dependence for pressure.

$$P = P(V, kT, \epsilon, \sigma, l, \mu) \tag{2.31}$$

Two constraints on this relationship result from requiring dimensional consistency. Therefore, Equation 2.31 can be rewritten as a dimensionless equation involving five dimensionless groups. The groups commonly chosen (because they arise naturally from many fluid models) are

$$P^* = P\sigma^3/\epsilon \tag{2.32}$$

$$v^* = V/N\sigma^3 \tag{2.33}$$

$$T^* = kT/\epsilon \tag{2.34}$$

$$l^* = l/\sigma \tag{2.35}$$

$$\mu^* = \mu/\sqrt{\epsilon\sigma^3} \tag{2.36}$$

The dimensionless equation of state is thus

$$P^* = P^*(T^*, v^*, l^*, \mu^*) \tag{2.37}$$

Substances with identical values of four of these groups will have identical values of the fifth. This is a molecular principle of corresponding states for nonspherical, polar molecules. The use of this principle allows the equation of state to be expressed as a universal function for a wide range of substances, with each substance characterized by a small number of parameters.

For spherical, nonpolar molecules, only two parameters enter into the corresponding-states description, σ and ϵ. This reflects the fact that two-parameter models (e.g., the Lennard-Jones potential) are sufficient to describe potentials between such molecules. Two-parameter models cannot describe the potential energy of systems of nonspherical molecules; a substance-dependent parameter (l^*) must be added [91]. The description of polar fluids requires the addition of a fourth substance-dependent parameter (μ^*) [56]. The groups l^* and μ^* are functions only of the properties of individual molecules. For nonpolar molecules $\mu^* = 0$, and for spherical molecules $l^* = 1$.

The microscopic theory of corresponding states has had two major uses. It can be used directly in equations for equations of state in statistical mechanics (§2.1.4). Of more practical importance, it is useful in the development of macroscopic corresponding-states principles.

2.3.2 Macroscopic Corresponding-States

The macroscopic principle of corresponding states was originally formulated by van der Waals [133], and was based on his equation of state. If all substances are represented by a universal, two-constant equation of state, then

$$P = P(T, V, a, b) \tag{2.38}$$

The substance-dependent constants a and b can be replaced by any other substance-dependent quantities, through a change of the form of the function. If T_c and P_c are chosen, the resulting dimensionless equation is

$$Z = Z(P_r, T_r) \tag{2.39}$$

This bears a clear relationship to the microscopic two-parameter corresponding-states principle. An equation of this form arises naturally from cubic equations of state when they are subjected to the classical derivative conditions (see the development of Equation 3.6 in §3.1.1).

The macroscopic two-parameter corresponding-states principle works well for substances made up of spherical, nonpolar molecules, but not for other substances. The reason is clear from the microscopic corresponding-states principle: additional substance-dependent parameters must be introduced to account for these effects. Researchers have therefore attempted to find dimensionless macroscopic properties which are measures of each of these effects.

Various quantities have been considered for use as a third corresponding-states parameter to account for nonspherical effects. These include Riedel's factor [93], Pitzer's acentric factor [91] and critical compressibility factor. The parameter that has come to be accepted to account for non-sphericity is Pitzer's acentric factor, ω.

$$\omega = -\log P_r^s|_{T_r=0.7} - 1 \qquad (2.40)$$

It is nearly zero for spherical molecules such as argon, and increases for increasingly nonspherical substances. It is easily determined for most substances. However, ω also rises with polarity; therefore, the acentric factor also reflects polar effects.

The three-parameter corresponding-states principle using acentric factor has been very widely applied. At first, it was used to construct tables of properties (e.g., see Pitzer et al. [92]), or generalized correlations for properties such as virial coefficient (e.g., see Tsonopoulos [132]). Acentric factor is clearly related to vapor pressure, and is thus a sensible choice for correlation of the temperature dependence of a in cubic equations. Soave [118] first applied it to cubic equations of state, in the correlation of the quantity m in his temperature function for different substances. Subsequent researchers have used it extensively in cubics, to correlate both constants in temperature dependencies (§2.2.3) and undetermined constants at the critical point (§2.2.4) for a wide range of nonpolar fluids. Many examples are given in §4.2.

Three-parameter corresponding-states principles have consistently failed to describe many properties of polar fluids. Polarity must be accounted for by a fourth dimensionless quantity. There has not been a clear choice for a fourth macroscopic corresponding-states parameter. Two quantities have been used in cubic equations of state to account for polar effects: the critical compressibility factor Z_c, in the equations of Trebble and Bishnoi [130] and Iwai et al. [65]; and Halm and Stiel's polar factor χ [56,57,58], in the equations of Toghiani and Viswanath [126] and Bazuá and Negrete [27]. As with acentric factor, the Halm-Stiel factor is defined in terms of vapor pressure.

$$\chi = \log P_r|_{T_r=0.6} + 1.7\omega + 1.552 \tag{2.41}$$

Its value can change due to nonspherical effects; therefore, it does not uniquely represent polar effects.

A corresponding-states principle does not have to be restricted to four parameters. For example, Trebble [127] developed an extended corresponding-states principle to calculate some of the quantities in the Trebble-Bishnoi equation of state, using six or seven parameters. However, his selection of parameters cannot be made dimensionless, so it does not represent a true corresponding-states approach.

2.4 Mixing Rules

To describe mixtures with an equation of state, mixing rules are required. Given the equation of state for pure fluids, rules for obtaining the equation of state for the mixture must be defined. Many such mixing rules have been proposed in the literature. For this survey, they are classified into two types: the conventional, or random mixing rules, and the local composition mixing rules.

Another approach has been recently proposed, in which the chemical association between species in a mixture is taken into consideration [16,15,69]. This approach is also useful for pure fluids which tend to associate (e.g., where dimer formation is important). It gives highly accurate results for nonideal mixtures, but is relatively complex. Although not further considered in this work, equations of state incorporating association may be an important source of new developments.

A well-known restriction on mixing rules comes from the virial equation of state. At the low density limit, the mixing rule for the second virial coefficient must be quadratic in mole fraction (e.g., see [100]). Application to van der Waals-type cubic equations of state gives the following restriction at low densities.

$$B = \sum_i \sum_j x_i x_j B_{ij} = b - a/RT \tag{2.42}$$

The summations are over all the components i and j in the mixture. Therefore, both a and b should be quadratic functions of mole fraction at low density. However, it is not clear that violation of this restriction would result in significant error in practice, and several successful mixing rules have not obeyed Equation 2.42.

2.4.1 Conventional Mixing Rules

Conventional mixing rules are generally simple. They are assumed to represent mixtures in which the molecules are randomly mixed, although this is not strictly true [41].

The best known mixing rules are

$$a = \sum \sum x_i x_j a_{ij} \tag{2.43}$$

$$b = \sum \sum x_i x_j b_{ij} \tag{2.44}$$

They were originally proposed by van der Waals. Generally, a geometric mean is used to calculate a_{ij}, and an arithmetic mean to calculate b_{ij},

$$a_{ij} = (a_i a_j)^{1/2} \tag{2.45}$$

$$b_{ij} = (b_i + b_j)/2 \tag{2.46}$$

where a_i and b_i are the constants for pure i and j respectively[6]. These mixing rules were originally based on purely empirical arguments, but later were found to have secure theoretical justification. As summarized by Copeman and Mathias [41], the van der Waals mixing rules can be justified several ways: from simulations of non-polar and slightly polar fluids, using simple fluid models (e.g., the Lennard-Jones and square-well potentials); from radial distribution functions, using reasonable assumptions which are best obeyed by nonpolar and slightly polar fluids; from regular solution theory,

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[6] The mixing rules for b are usually also used for the remaining substance-dependent constants in cubic equations of state.

which again applies to nonpolar or slightly polar fluids. The above justifications imply that the van der Waals mixing rules should be best for nonpolar or slightly polar fluids. This is indeed the case in practice.

The van der Waals mixing rules can be considerably improved by the addition of a binary interaction coefficient to the mixing rule for a.

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{2.47}$$

where k_{ij} $(= k_{ji})$ is the binary interaction coefficient between components i and j. k_{ij} is normally determined from fitting of binary VLE data, and is usually found to be weakly dependent on temperature. This concept was introduced by Stotler and Benedict [120] for the BWR equation, and was extended to the van der Waals mixing rules by Zudkevitch and Joffe [152]. The binary interaction coefficient was initially considered an empirical modification, but was later shown by Prausnitz and Gunn [94] to have some theoretical justification, based on the theory of intermolecular forces. Binary interaction coefficients are usually weak functions of temperature.

As mentioned above, the van der Waals mixing rules work quite well for nonpolar or slightly polar fluids. However, they often fail badly for polar fluids, and for highly asymmetric mixtures (i.e., mixtures of dissimilar molecules, such as polar–nonpolar mixtures). Therefore, many attempts have been made to improve them.

Evelein and Moore [50] suggested introducing a binary interaction coefficient for b_{ij}, i.e.,

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{2.48}$$

This form has been tested by Yu [148], Iwai et al. [64,65], and Trebble [128], and was found to give good VLE results for mixtures of polar fluids, but not for highly asymmetric mixtures. It also gave values for excess molar volume which were much too large. Most mixing rules do not introduce an interaction coefficient for b.

Another approach has been to modify the form of the mixing rules. For example, Radosz et. al.[97] have used

$$\frac{a}{b^{0.75}} = \sum\sum x_i x_j \frac{a_{ij}}{b_{ij}^{0.75}} \tag{2.49}$$

$$b = \sum\sum x_i x_j b_{ij} \tag{2.50}$$

Copeman and Mathias [41] have generalized this approach to include other mixing rules from the literature. This type of mixing rule improves predictions for some mixtures, but not for highly asymmetric mixtures.

Several researchers have retained the van der Waals form, but have effectively made k_{ij} composition dependent. Mixing rules of this type do not obey the low-density limit (Equation 2.42), but have achieved considerable success. They generally describe polar mixtures well, and can significantly improve predictions for asymmetric mixtures. Some of these have been local composition models, to be discussed in the next section. Others have been empirical modifications, such as that by Panagiotopoulos and Reid [86], and Stryjek and Vera [122,124].

$$a_{ij} = (a_i a_j)^{1/2}[1 - k_{ij} + (k_{ij} - k_{ji})x_i] \tag{2.51}$$

where the assumption that $k_{ij} = k_{ji}$ has been relaxed. Other approaches are derived from activity coefficient expressions. For example, Adachi and Sugie [10,11] used the Redlich-Kister expression, reduced to two binary coefficients, to obtain

$$a_{ij} = (a_i a_j)^{1/2}[1 - k_{ij} - l_{ij}(x_i - x_j)] \tag{2.52}$$

where k_{ij} $(= k_{ji})$ and l_{ij} $(= -l_{ji})$ are the binary interaction coefficients. Equations 2.51 and 2.52 are equivalent.

Adachi and Sugie [10] found that increasing the number of binary coefficents beyond two in the Redlich-Kister expansion does not result in significant improvement. However, Schwartzentruber and coworkers [112,113] gave an extension of Equation 2.52, which significantly improves the description of some highly asymmetric mixtures.

$$a_{ij} = (a_i a_j)^{1/2}\left[1 - k_{ij} - l_{ij}\frac{m_{ij}x_i - m_{ji}x_j}{m_{ij}x_i + m_{ji}x_j}(x_i + x_j)\right] \tag{2.53}$$

There are three binary interaction coefficients, k_{ij} $(= k_{ji})$, l_{ij} $(= -l_{ji})$ and m_{ij} $(= 1 - m_{ji})$. This mixing rule prevented false liquid-phase splitting for some highly asymmetric systems, which is a common problem of cubic equations of state with most mixing rules.

Wilczek-Vera and Vera [145] also derived a series of mixing rules based on activity coefficient expressions. These did obey the low-density limit (Equation 2.42), but were density-dependent.

2.4.2 Local Composition Mixing Rules

Wilson [146] was the first to use the concept of local composition, in the formulation of his activity coefficient model, to describe highly asymmetric mixtures. The concept is simple: it is assumed that there exist in a mixture local areas whose composition is different from the bulk composition, due to effects of interactions between molecules. Actual description of local composition effects differ widely, and are still the subject of much applied and theoretical research. Important subsequent models have included the NRTL [104] and the UNIQUAC [5] activity coefficient expressions.

The local composition concept has recently been applied to mixing rules for cubic equations of state. A history of local composition and its application to mixing rules is given by Danner and Gupte [44]. The most important formulations have been those of Huron and Vidal [63], Mollerup [82] and Whiting and Prausnitz [144]. The mixing rule of Huron and Vidal is based on the NRTL model.

$$a = b\left(\sum x_i \frac{a_i}{b_i} - \Lambda \frac{\sum x_j b_j E_{ji} C_{ji}}{\sum x_k C_{ki}}\right) \tag{2.54}$$

where

$$E_{ji} = \exp(-\alpha_{ji} C_{ji}/RT) \tag{2.55}$$

where Λ is a constant depending on the equation of state[7], and C_{ji} $(= C_{ij})$ and α_{ji} $(= \alpha_{ij})$ are binary interaction coefficients. This expression does not obey the low-density limit (Equation 2.42). Huron and Vidal have shown that this mixing rule can prevent the prediction of false liquid-phase splitting in some cases, if a three-coefficient version (with $C_{ji} \neq C_{ij}$) is used.

If a local composition mixing rule is to obey Equation 2.42, it must incorporate a density dependence, such that it provides a local composition description at high densities, and the quadratic mixing rule at low densities. An example of this is the mixing rule of Mollerup, based on the UNIQUAC equation,

$$a = \sum x_i q_i \frac{\sum x_j (a_{ji}/q_{ji}) E_{ji}}{\sum x_k E_{ki}} \tag{2.56}$$

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[7] This expression only applies to cubic equations of state with fixed values of u and w.

where

$$a_{ji}/q_{ji} = \sqrt{a_j a_i / q_j q_i}(1 - k_{ij}) \tag{2.57}$$

$$E_{ji} = \exp{(a_{ji}/q_{ji})}\Lambda \tag{2.58}$$

where Λ is now a volume-dependent term varying according to the equation of state used, and the q_i are pure component UNIQUAC constants. The mixing rules of Whiting and Prausnitz are similar.

Obviously, local composition mixing rules are complex. The density-dependent mixing rules result in non-cubic equations of state for mixtures, and require additional iteration to obtain the correct density in the mixing rule. Additionally, some local composition mixing rules overestimate the effect of local composition in nonpolar mixtures [81]. They have nevertheless been extensively investigated because they appear to have some theoretical basis, and because they have been successful in describing polar and asymmetric mixtures.

A study by Adachi and Sugie [10] has shown that the success of local composition mixing rules may simply be due to an increased number of interaction coefficients, and hence increased flexibility in fitting VLE data. They found that a simple two-coefficient Redlich-Kister mixing rule (see above) can describe polar and asymmetric mixtures as well as many recent local composition mixing rules. They concluded that the number of interaction coefficients is more important than the form of the mixing rule.

Another problem with density-dependent local-composition mixing rules is that statistical mechanical theory and recent simulations of mixtures have not agreed with the form of their density dependence (this is summarized and discussed by Danner and Gupte [44]). In particular, it appears that local composition effects are strongest at low densities, and decrease (but do not disappear) at higher densities. This trend is opposite to that of most density-dependent local-composition mixing rules. More recent models (e.g., see Sandler [108] and Adachi et al. [13]) have attempted to reproduce the correct density dependence and may be an important basis for future developments.

2.5 Concluding Remarks

A considerable amount of information has been presented in this literature review. Particular points that are important to this work are summarized here.

There have been many different types of equations of state developed, of varying degrees of complexity and flexibility (§2.1). They have had both practical and theoretical importance. While some of these may perform well in specific areas, none combine the simplicity, accuracy and range of applicability of cubic equations of state.

The general forms for cubic equations of state (§2.2.1) are important. General expressions, useful for any cubic equation of state, can be developed from them. Equation 2.15 is simpler to manipulate; it is therefore adopted for the formulation of general expressions. Equation 2.12 is adopted for studies of the effect of the form of the equation of state (i.e., the effect of the values of u and w) on volumetric performance. The two forms are simply related through Equations 2.16–2.19.

The classical derivative conditions (Equations 2.20 and 2.21) are essential, because they greatly simplify the determination of constants in cubics, and because they naturally transform the equation of state into two-parameter corresponding-states form (§2.2.2). The equations of state developed in this work therefore use the classical derivative conditions.

Only temperature dependency in the constant a is considered in this work. It is more significant than temperature dependencies in the other constants, and is better understood (§2.2.3). The Soave and Heyen forms for α (Equations 2.24 and 2.25) are simple and are known to perform well; they are therefore further considered here. The direct calculation of α from vapor pressure is reliable and accurate; therefore, it is also considered.

The form of a cubic equation of state, as given by its u and w values, is important for its volumetric performance (2.2.4). The approach of Yu et al. [148,149] is a powerful method for determining appropriate choices for values of u and w, and is used in this work.

Corresponding-states theory is required for the efficient application of an equation of state to a wide variety of substances (§2.3). The macroscopic corresponding-states principle is naturally introduced into cubic equations of state by application of the classical derivative conditions. It can be extended to cover nonspherical and polar fluids from considerations from microscopic corresponding-states. Substance-dependent quantities in cubic equations of state have been widely correlated or generalized using extended corresponding-states principles; this approach is used in this work. Alternatives to generalization, such as direct calculation from corresponding-states parameters or from properties, are also used.

Several mixing rules have been proposed for polar and asymmetric mixtures, some of which are examined in this work. The two-coefficient Redlich-Kister mixing rule (Equation 2.52) is simple and describes many such systems. The extended Redlich-Kister mixing rule [112,113] and the Huron-Vidal local-composition mixing rule (Equation 2.54) may prevent the prediction of false liquid-phase splitting for highly asymmetric systems.

Chapter 3

Theory and Methods

In this Chapter, relationships required in this work are given and/or derived. Some of the computational methods used are also described. Most of the expressions and methods given here are applicable to any cubic equation of state of the type discussed in §2.2.1. They are also applicable to any mixing rule which is not density dependent.

3.1 Useful Expressions

A study of this size is greatly simplified if some effort is made to develop expressions which are generally applicable. For cubic equations of state, this is possible if the general forms of the cubic equation are used as a starting point. These have been introduced and discussed to some length (§2.2). Here, dimensionless expressions based on these general forms are derived.

As discussed previously, the Schmidt and Wenzel form for cubic equations of state (Equation 2.12) is useful for examining the effect of the form of the equation of state. However, Equation 2.15 is more suitable for algebraic manipulation, and gives simpler expressions. Therefore, most of the equations used in this work are derived from Equation 2.15. The main use of equation 2.12 will be in establishing relationships between the constants u and w, which are then expressed in terms of Equation 2.15.

3.1.1 The Dimensionless Cubic Equation

Computations involving cubic equations of state are simplified if dimensionless equations are used. A dimensionless general form for cubics is developed here. Instead of being a cubic equation in volume, this is a cubic equation in compressibility factor.

Equation 2.15 can be rewritten in a dimensionless form after dividing through by P.

$$1 = \frac{1}{Z-B} - \frac{A}{(Z-C)(Z-D)} \tag{3.1}$$

The dimensionless constants A, B, C and D are defined as

$$A = \frac{aP}{(RT)^2} \tag{3.2}$$

$$B = \frac{bP}{RT} \tag{3.3}$$

$$C = \frac{cP}{RT} \tag{3.4}$$

$$D = \frac{dP}{RT} \tag{3.5}$$

Equation 3.1 can be rearranged to yield a cubic in Z.

$$Z^3 + pZ^2 + qZ + r = 0 \tag{3.6}$$

The coefficients are given by the following.

$$p = -1 - B - C - D \tag{3.7}$$

$$q = A + C + D + BC + BD + CD \tag{3.8}$$

$$r = -AB - CD - BCD \tag{3.9}$$

3.1.2 Relationships at the Critical Point

As discussed in §2.2.2, almost all cubic equations of state have been subjected to the classical critical point conditions (Equations 2.20 and 2.21). Imposition of the classical critical point conditions on Equation 3.6 leads to several useful relationships at the critical point.

Let the values of A, B, C and D at the critical point be given by Ω_{ac}, Ω_{bc}, Ω_{cc} and Ω_{dc} respectively. Furthermore, consider only a to be temperature dependent, with the temperature dependence given by α, as defined in Equation 2.22. The following expressions for A, B, C and D can therefore be written.

$$A = \Omega_{ac}(\alpha/T_r)(P_r/T_r) \tag{3.10}$$
$$B = \Omega_{bc}(P_r/T_r) \tag{3.11}$$
$$C = \Omega_{cc}(P_r/T_r) \tag{3.12}$$
$$D = \Omega_{dc}(P_r/T_r) \tag{3.13}$$

The expressions for the coefficients of Equation 3.6 can now be written in terms of the critical point constants.

$$p = -(P_r/T_r)(\Omega_{bc} + \Omega_{cc} + \Omega_{dc}) - 1 \tag{3.14}$$
$$\begin{aligned} q = {} & (P_r/T_r)^2(\Omega_{bc}\Omega_{cc} + \Omega_{bc}\Omega_{dc} + \Omega_{cc}\Omega_{dc}) \\ & + (P_r/T_r)[(\alpha/T_r)\Omega_{ac} + \Omega_{cc} + \Omega_{dc}] \end{aligned} \tag{3.15}$$
$$r = -(P_r/T_r)^3\Omega_{bc}\Omega_{cc}\Omega_{dc} - (P_r/T_r)^2[(\alpha/T_r)\Omega_{ac}\Omega_{bc} + \Omega_{cc}\Omega_{dc}] \tag{3.16}$$

Application of the critical point conditions leads to the following set of three equations.

$${\zeta_c}^3 + p_c{\zeta_c}^2 + q_c\zeta_c + r_c = 0 \tag{3.17}$$
$$3{\zeta_c}^2 + 2p_c\zeta_c + q_c = 0 \tag{3.18}$$
$$6\zeta_c + 2p_c = 0 \tag{3.19}$$

ζ_c is the compressibility factor at the critical point predicted by the equation of state. Equations 3.17–3.19 can be expressed in a more convenient form. Substituting for p_c, q_c and r_c and rearranging gives the following expressions.

$$-p_c = 1 + \Omega_{bc} + \Omega_{cc} + \Omega_{dc} = 3\zeta_c \tag{3.20}$$
$$q_c = \Omega_{ac} + \Omega_{cc} + \Omega_{dc} + \Omega_{bc}\Omega_{cc} + \Omega_{bc}\Omega_{dc} + \Omega_{cc}\Omega_{dc} = 3{\zeta_c}^2 \tag{3.21}$$
$$-r_c = \Omega_{ac}\Omega_{bc} + \Omega_{cc}\Omega_{dc} + \Omega_{bc}\Omega_{cc}\Omega_{dc} = {\zeta_c}^3 \tag{3.22}$$

The quantities f, g and h are now defined.

$$f = \zeta_c - \Omega_{bc} \tag{3.23}$$
$$g = \zeta_c - \Omega_{cc} \tag{3.24}$$
$$h = \zeta_c - \Omega_{dc} \tag{3.25}$$

Substituting these into Equations 3.20–3.22 gives

$$\begin{aligned} f+g+h-1 &= 0 && (3.26)\\ fg+gh+fh-(g+h)+\Omega_{ac} &= 0 && (3.27)\\ fgh-gh+f\Omega_{ac} &= 0 && (3.28) \end{aligned}$$

Expressing f, g and h in terms of Ω_{ac} gives the desired expressions.

$$\begin{aligned} f &= \zeta_c-\Omega_{bc}=1-{\Omega_{ac}}^{1/3} && (3.29)\\ g &= \zeta_c-\Omega_{cc}=({\Omega_{ac}}^{1/3}+\sqrt{4\Omega_{ac}-3{\Omega_{ac}}^{2/3}})/2 && (3.30)\\ h &= \zeta_c-\Omega_{dc}=({\Omega_{ac}}^{1/3}-\sqrt{4\Omega_{ac}-3{\Omega_{ac}}^{2/3}})/2 && (3.31) \end{aligned}$$

Note that specification of Ω_{ac} only is needed to determine f, g and h. Specification of one more constraint would determine the value of all remaining critical point quantities.

3.1.3 Relationships between the Standard Forms

As discussed in §2.2.2, imposition of the critical point conditions leaves two quantities to be specified at the critical point. This is apparent in Equations 3.29–3.31, which are a system of three equations in five unknowns. Two approaches are used in this work: the specification of Ω_{ac} and Ω_{bc}; the specification of u and w. The first approach is the most practical for general calculations; the second approach is used only when examining the effects of the form of the equation of state on volumetric performance. The relationships necessary to determine all other critical point constants from these are given here.

The simplest approach is to specify Ω_{ac} and Ω_{bc}. Ω_{cc} and Ω_{dc} are then easily determined from Equations 3.29–3.31. u and w are given by

$$\begin{aligned} u &= -\frac{\Omega_{cc}+\Omega_{dc}}{\Omega_{bc}} && (3.32)\\ w &= \frac{\Omega_{cc}\Omega_{dc}}{{\Omega_{bc}}^2} && (3.33) \end{aligned}$$

which follow from Equations 2.18 and 2.19, and from the definitions of Ω_{bc}, Ω_{cc} and Ω_{dc}.

A more difficult approach is to specify u and w. A complicated cubic equation must then be solved to obtain Ω_{ac}. This is developed below.

First, the quantities $f - g$ and $2(f - h)$ are formulated from Equations 3.29–3.31.

$$\begin{aligned} g - h &= \Omega_{dc} - \Omega_{cc} \\ &= \sqrt{4\Omega_{ac} - 3{\Omega_{ac}}^{2/3}} \qquad (3.34) \\ 2(f - g) &= 2(\Omega_{cc} - 1) \\ &= 2 - {\Omega_{ac}}^{1/3} - 3\sqrt{4\Omega_{ac} - 3{\Omega_{ac}}^{2/3}} \qquad (3.35) \end{aligned}$$

Ω_{cc} and Ω_{dc} are related to u and w as follows.

$$\Omega_{cc} = \frac{\Omega_{bc}}{2}(-u - \sqrt{u^2 - 4w}) \qquad (3.36)$$

$$\Omega_{dc} = \frac{\Omega_{bc}}{2}(-u + \sqrt{u^2 - 4w}) \qquad (3.37)$$

This follows from Equations 3.32 and 3.33. Substituting into Equations 3.34 and 3.35 gives

$$\begin{aligned} g - h &= \Omega_{bc}\sqrt{u^2 - 4w} \\ &= \sqrt{4\Omega_{ac} - 3{\Omega_{ac}}^{2/3}} \qquad (3.38) \\ 2(f - g) &= -2 - u - \sqrt{u^2 - 4w} \\ &= 2 - {\Omega_{ac}}^{1/3} - 3\sqrt{4\Omega_{ac} - 3{\Omega_{ac}}^{2/3}} \qquad (3.39) \end{aligned}$$

Finally, eliminating Ω_{bc} from Equations 3.38 and 3.39 and rearranging gives the desired expression.

$$\Omega_{ac} - 3\frac{u^2 + u + 1}{u^2 + 4u + 4}{\Omega_{ac}}^{2/3} + 3\frac{u^2 - 4w}{u^2 + 4u + 4}{\Omega_{ac}}^{1/3} - \frac{u^2 - 4w}{u^2 + 4u + 4} = 0 \qquad (3.40)$$

Now, if u and w are specified, then the smallest positive root of Equation 3.40 is the cube root of Ω_{ac}. Equations 3.29–3.31 can then be solved for f, g and h. Ω_{bc} is given by

$$\Omega_{bc} = \frac{g - h}{\sqrt{u^2 - 4w}} \qquad (3.41)$$

which follows from Equation 3.38. Ω_{bc} and Ω_{dc} are given by Equations 3.36 and 3.37 (they can also be obtained from Equations 3.29–3.31).

3.1.4 Determination of β_c

A quantity which will be important in subsequent discussions is β_c, the ratio of covolume to molar volume at the critical point predicted by the equation of state.

$$\beta_c = b_c/v_c = \Omega_{bc}/\zeta_c \tag{3.42}$$

It is significant, because it is the only quantity arising in macroscopic corresponding-states for cubics which is directly related to a quantity in microscopic corresponding-states, v_c^* (see §2.3.1 and §5.1.2).

An expression is now developed relating β_c to u and w. From Equations 3.30 and 3.31,

$$g + h = 2\zeta_c + \Omega_{cc} + \Omega_{dc} = {\Omega_{ac}}^{1/3} \tag{3.43}$$

Substituting for Ω_{cc} and Ω_{dc} from Equations 3.36 and 3.37 gives

$$g + h = 2\zeta_c + u\Omega_{bc} = {\Omega_{ac}}^{1/3} \tag{3.44}$$

Dividing Equations 3.29, 3.34 and 3.44 by ζ_c and substituting β_c from Equation 3.42 gives the following set of three equations.

$$\begin{aligned} 1 - \beta_c &= (1 - {\Omega_{ac}}^{1/3})/\zeta_c && (3.45)\\ \beta_c\sqrt{u^2 - 4w} &= \sqrt{4\Omega_{ac} - 3{\Omega_{ac}}^{2/3}}/\zeta_c && (3.46)\\ 2 + u\beta_c &= {\Omega_{ac}}^{1/3}/\zeta_c && (3.47) \end{aligned}$$

ζ_c and Ω_{ac} can be eliminated from this set of equations to yield the desired expression, given here as a cubic in β_c.

$$(u^2 + uw - w){\beta_c}^3 + 3(u + w){\beta_c}^2 + 3\beta_c - 1 = 0 \tag{3.48}$$

This is the same as the expression used by Yu et al. [148,149], although their development was different.

3.1.5 Expressions for $u = -w$

If a constraint is placed on the critical point constants, then only one additional relationship needs to be specified. In §5, the relationship $u = -w$

is imposed as a constraint. This results in several simplifications. The required expressions are developed here, to avoid interrupting the discussion later.

An expression giving Ω_{bc} as a function of Ω_{ac} is here derived. From Equations 3.29–3.31, with $u = -w$,

$$\begin{aligned} f - g &= (s-1)\Omega_{bc} && (3.49) \\ f - h &= (t-1)\Omega_{bc} && (3.50) \end{aligned}$$

where

$$\begin{aligned} s &= (-u - \sqrt{u^2 + 4u})/2 && (3.51) \\ t &= (-u + \sqrt{u^2 + 4u})/2 && (3.52) \end{aligned}$$

u can be eliminated from Equations 3.51 and 3.52 to give the following relationship between s and t.

$$\frac{s^2}{1-s} = \frac{t^2}{1-t} \qquad (3.53)$$

s and t can now be eliminated from Equations 3.49–3.53 to give an expression for Ω_{bc}.

$$\Omega_{bc} = \frac{(f-g) - \sqrt{(f-g)(f-h)}}{\sqrt{(f-g)/(f-h)} - 1} \qquad (3.54)$$

From Equations 3.29–3.31,

$$(f-g)(f-h) = f^3 \qquad (3.55)$$

Equation 3.54 can thus be simplified to give the final result,

$$\Omega_{bc} = f^{3/2} = (1 - {\Omega_{ac}}^{1/3})^{3/2} \qquad (3.56)$$

which is a very simple expression that does not involve u.

An expression for u from Ω_{ac} can also be developed. u is given by

$$u = \frac{1-3f}{f^3} - 2 \qquad (3.57)$$

which follows from Equations 3.51, 3.49 and 3.55.

From these relationships, it is apparent that specification of Ω_{ac} allows the simple calculation of all the other constants. In such a case, Ω_{bc} is determined from Equation 3.56, and Ω_{cc} and Ω_{dc} are then determined from Equations 3.29–3.31. u is calculated from Equation 3.57, and w from $w = -u$.

3.1.6 Fugacity Coefficient

Fugacity is an important quantity in phase equilibrium calculations, since equality of fugacities in each phase for each component is the criterion for equilibrium. A general expression for fugacity coefficient is developed below. The expression will be applicable to: pure components and components in mixtures; any cubic equation of state conforming to Equation 2.15; any mixing rule independent of density.

Cubic equations of state are explicit in pressure. The following expression is useful for obtaining fugacity coefficient from pressure, for each component i in a mixture.

$$\ln \phi_i = \ln \frac{f_i}{x_i P} = \int_V^\infty \left[\frac{1}{RT} \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j(j \neq i)} - \frac{1}{V} \right] dV - \ln Z \tag{3.58}$$

f_i and ϕ_i are the fugacity and fugacity coefficient of component i in the mixture. n_i is the total number of moles in a volume V of the mixture. Equation 3.58 is derived in a variety of chemical engineering thermodynamics texts (e.g., see [95]). An expression for fugacity coefficient from Equation 2.15 is best obtained if it is rewritten as follows.

$$P = \frac{nRT}{V - nb} - \frac{na}{nc - nd} \left(\frac{n}{V - nc} - \frac{n}{V - nd} \right) \tag{3.59}$$

The derivative in Equation 3.58 is easily evaluated from Equation 3.59. The integration is also straightforward. Rearrangement and conversion to dimensionless quantities yields:

$$\begin{aligned} \ln \phi_i &= \frac{\hat{B}_i}{Z - B} - \ln (Z - B) + \left(\frac{\hat{C}_i - \hat{D}_i}{C - D} - 1 - \frac{\hat{A}_i}{A} \right) \frac{A}{C - D} \ln \frac{Z - D}{Z - C} \\ &\quad - \frac{A}{C - D} \left(\frac{\hat{C}_i}{Z - C} - \frac{\hat{D}_i}{Z - D} \right) \end{aligned} \tag{3.60}$$

This equation is indeterminate for $C = D$. In this case, it becomes

$$\ln \phi_i = \frac{\hat{B}_i}{Z - B} - \ln(Z - B) - \frac{A + \hat{A}_i}{Z - C} - \frac{A\hat{C}_i}{(Z - C)^2} \tag{3.61}$$

The quantity $\hat{A}_i$ is given by the derivative

$$\hat{A}_i = [\partial(nA)/\partial n_i]_{T,V,n_j(j \neq i)} \tag{3.62}$$

The quantities $\hat{B}_i$, $\hat{C}_i$ and $\hat{D}_i$ are obtained from similar expressions. The expressions resulting from this will vary according to the mixing rule used.

The conventional van der Waals mixing rule is used for the constants b, c and d. After simplifying and converting to dimensionless form, Equations 2.44 and 2.46 give

$$B = \sum_i x_i B_i \tag{3.63}$$

$$C = \sum_i x_i C_i \tag{3.64}$$

$$D = \sum_i x_i D_i \tag{3.65}$$

Applying Equation 3.62 gives the following expressions.

$$\hat{B}_i = B_i \tag{3.66}$$

$$\hat{C}_i = C_i \tag{3.67}$$

$$\hat{D}_i = D_i \tag{3.68}$$

For the attractive constant a, several mixing rules are used in this work. The two-coefficient Redlich-Kister mixing rule of Adachi and Sugie (Equation 2.52) results in the following expressions for A and $\hat{A}_i$.

$$A = \sum_i \sum_j x_i x_j (A_i A_j)^{1/2} [1 - k_{ij} - l_{ij}(x_i - x_j)] \tag{3.69}$$

$$\begin{aligned} \hat{A}_i &= 2 \sum_j x_j (A_i A_j)^{1/2} [1 - k_{ij} - l_{ij}(2x_i - x_j)] \\ &\quad + \sum_j \sum_k x_j x_k (A_j A_k)^{1/2} l_{jk} (x_j - x_k) - A \qquad (3.70) \\ & \qquad (3.71) \end{aligned}$$

Note that $k_{ij} = k_{ji}$, and $l_{ij} = -l_{ji}$. For pure fluids, $k_{ij} = l_{ij} = 0$.

The augmented Redlich-Kister mixing rule of Schwartzentruber and coworkers (Equation 2.53) gives the following for A and $\hat{A}_i$.

$$A = \sum_i \sum_j x_i x_j (A_i A_j)^{1/2} \left[1 - k_{ij} - l_{ij} \frac{m_{ij} x_i - m_{ji} x_j}{m_{ij} x_i + m_{ji} x_j} (x_i + x_j)\right] \tag{3.72}$$

$$\begin{aligned} \hat{A}_i &= 2 \sum_j x_j A_{ij} + \sum_j \sum_k x_j x_k (A_j A_k)^{1/2} (1 - k_{jk}) - 2A - \qquad (3.73) \\ &\quad 2 \sum_j x_i x_j (A_i A_j)^{1/2} l_{ij} \left[\frac{m_{ij} x_i - m_{ji} x_j}{m_{ij} x_i + m_{ji} x_j} + 2 m_{ij} m_{ji} x_j \frac{x_i + x_j}{(m_{ij} x_i + m_{ji} x_j)^2}\right] \end{aligned}$$

Note that $k_{ij} = k_{ji}$, $l_{ij} = -l_{ji}$ and $m_{ij} = 1 - m_{ji}$. If $m_{ij} = 0.5$, then the two-coefficient Redlich-Kister mixing rule is recovered. For pure fluids, $k_{ii} = l_{ii} = 0$.

The Huron-Vidal mixing rule (Equation 2.54) must be modified for equations of state with variable u and w. Yu [148] derived an appropriate expression for his equation of state; it is easily extended to the general equation of state (Equation 2.15) to give

$$A = \frac{1}{\Lambda}\sum_i x_i\left(A_i\Lambda_i - \frac{S_{1i}}{S_{2i}}\right) \tag{3.74}$$

where

$$\begin{aligned}
\Lambda &= \frac{1}{C-D}\ln\frac{B-D}{B-C} && (3.75)\\
S_{1i} &= \sum_j x_j B_j E_{ji}(C_{ji}/RT) && (3.76)\\
S_{2i} &= \sum_j x_j B_j E_{ji} && (3.77)\\
E_{ji} &= \exp[\alpha_{ji}(C_{ji}/RT)] && (3.78)
\end{aligned}$$

Note that $\alpha_{ij} = \alpha_{ji}$, but that in general $C_{ij} \neq C_{ji}$. For pure fluids, $C_{ii} = 0$. Application of Equation 3.62 gives the following expression for $\hat{A}_i$.

$$\begin{aligned}
\hat{A}_i = {}& A\left\{\frac{1}{C-D}\left[\hat{C}_i - \hat{D}_i - \frac{1}{\Lambda}\left(\frac{\hat{B}_i - \hat{D}_i}{B-D} - \frac{\hat{B}_i - \hat{C}_i}{B-C}\right)\right] - 1\right\}\\
& + \frac{1}{\Lambda}\left[A_i\Lambda_i - \frac{S_{1i}}{S_{2i}} - B_i\sum_j x_j\frac{E_{ij}}{S_{2j}^2}\left(\frac{C_{ij}}{RT}S_{2j} - S_{1j}\right)\right] \qquad (3.79)
\end{aligned}$$

Note that these expressions involve the mixing rules for the other constants B, C and D.

For pure fluids, Equations 3.60 and 3.61 can be used directly, with the mixture derivatives set equal to the pure fluid constants (e.g., $\hat{A}_i = A_i = A$). The resulting expressions, after some simplification, are

$$\ln\phi = Z - 1 - \ln(Z-B) - \frac{A}{C-D}\ln\frac{Z-C}{Z-D} \tag{3.80}$$

for $C \neq D$, and

$$\ln\phi = Z - 1 - \ln(Z-B) + \frac{A}{Z-C} \tag{3.81}$$

for $C = D$.

3.2 Methods

Calculations and numerical methods used in this work are described here. These are general procedures, applicable to most cubic equations with most mixing rules. The only procedures that are not given here are those which pertain directly to the development of the new equation of state (§5). FORTRAN subroutines implementing many of these methods are given in §B.

3.2.1 The Direct Solution of Cubic Equations

Cubic equations arise frequently in calculations involving cubic equations of state. Many researchers have resorted to iterative methods to find the roots of such equations; however, any cubic can be solved explicitly. It is given here (from Press et al. [96]), using Equation 3.6 as an example.

The following two quantities are calculated from the coefficients of Equation 3.6.

$$Q = (p^2 - 3q)/9 \tag{3.82}$$

$$R = (2p^3 - 9pq + 27r)/54 \tag{3.83}$$

If $R^2 - Q^3$ is negative, there are three real roots Z_1, Z_2 and Z_3, given by

$$Z_i = -2\sqrt{Q}\cos\left[\frac{\theta + 2\pi(i-1)}{3}\right] - \frac{p}{3} \tag{3.84}$$

where $\theta = \arccos(R/Q^{3/2})$. Otherwise, there is one real root, given by

$$Z = -\operatorname{sgn}(R)(S + Q/S) - p/3 \tag{3.85}$$

where $S = (\sqrt{R^2 - Q^3} + |R|)^{1/3}$.

3.2.2 Determination of α

The temperature dependency of the constant a is usually determined from vapor pressure (§2.2.3). Sugie et al. [125] give a method for the calculation of α from vapor pressure P^s. It is efficient, and is applicable to any cubic equation of state conforming to Equation 2.15. It is derived from the criteria for equilibrium between vapor and liquid phases.

The quantity λ is defined as

$$\lambda = Z - B \tag{3.86}$$

The following identities can be written, using Equations 3.11–3.13, 3.29–3.31, and 3.86.

$$\begin{aligned} Z - C &= \lambda + (P_r/T_r)(g - f) & (3.87) \\ Z - D &= \lambda + (P_r/T_r)(h - f) & (3.88) \end{aligned}$$

Also, the following identities are obtained from Equations 3.29–3.31.

$$\begin{aligned} g + h &= 1 - f & (3.89) \\ gh &= f(1 - f)^2 & (3.90) \end{aligned}$$

Using Equations 3.86–3.90 allows the dimensionless equation of state (Equation 3.6) to be rewritten in terms of λ.

$$\lambda^3 + S_2\lambda^2 + S_1\lambda + S_0 = 0 \tag{3.91}$$

The coefficients S_0, S_1 and S_2 are given by

$$\begin{aligned} S_0 &= (P_r^s/T_r)^2 f^3 & (3.92) \\ S_1 &= (P_r^s/T_r)^2 f^3 - (P_r^s/T_r)(1 - 3f - \Omega_{ac}\alpha/T_r) & (3.93) \\ S_2 &= (P_r^s/T_r)(1 - 3f) - 1 & (3.94) \end{aligned}$$

The vapor and liquid values for λ are the minimum and maximum roots respectively of this equation.

At saturation, the fugacities of the liquid and vapor phases are equal. Using Equation 3.80, and introducing λ through Equations 3.86–3.88, yields

$$\frac{\alpha}{T_r} = \frac{(h - g)[(\lambda_L - \lambda_V) + \ln(\lambda_V/\lambda_L)}{\Omega_{ac} \ln \frac{[\lambda_V + (P_r^s/T_r)(g-f)][\lambda_L + (P_r^s/T_r)(h-f)]}{[\lambda_V + (P_r^s/T_r)(h-f)][\lambda_L + (P_r^s/T_r)(g-f)]}} \tag{3.95}$$

Equation 3.95 is indeterminate for $C = D$. A form suitable for the case $C = D$ can be obtained by using l'Hôpital's rule, or by using Equation 3.61

instead of Equation 3.60 in the derivation.

$$\frac{\alpha}{T_r} = \frac{[\lambda_L - \lambda_V + \ln(\lambda_V/\lambda_L)][\lambda_L + (P_r^s/T_r)(g-f)][\lambda_V + (P_r^s/T_r)(g-f)]}{\Omega_{ac}(P_r^s/T_r)(\lambda_L - \lambda_V)} \tag{3.96}$$

Thus, α/T_r is a function only of Ω_{ac} and P_r^s/T_r. Once the value of Ω_{ac} is known, α/T_r can be determined iteratively from Equations 3.91–3.96 at given values of P_r^s/T_r.

Equations 3.95 and 3.96 are solved iteratively, using the method of successive substitution. The procedure is as follows.

- Calculate f, g and h from Equations 3.29–3.31.
- Calculate S_0 and S_2 from Equations 3.92 and 3.94.
- Obtain an initial estimate for α. Sugie et al. suggested

$$\frac{\alpha}{T_r} = 1 - \frac{f}{1-f}\ln\frac{P_r^s}{T_r}$$

- Repeat the following until $|\alpha - \alpha^{est}|$ is sufficiently small.
  - Set α^{est} equal to α.
  - Calculate S_1 from Equation 3.93.
  - Calculate λ_l and λ_v from Equation 3.91. They are the smallest and largest roots respectively. The method given in §3.2.1 is used.
  - Calculate α from Equation 3.95 or 3.96.

The procedure requires about five iterations to converge to a high degree of accuracy.

3.2.3 Solution of Cubic Equations of State

Most calculations in this thesis require determining volume from cubic equations of state at some point. The procedure used, which is applicable to all cubic equations of state, is described here.

The temperature T, pressure P and mole fractions x_i of the phase are given. The compressibility factor Z is obtained as follows.

- For each component i, calculate the dimensionless equation of state constants as follows[1].
    - Calculate P_{ri}, T_{ri}.
    - Determine Ω_{aci}, Ω_{bci} and α_i for the equation of state under consideration.
    - Calculate Ω_{cci} and Ω_{dci} from Equations 3.29–3.31.
    - Calculate A_i, B_i, C_i, and D_i from Equations 3.2–3.5.
- Calculate B, C and D from the mixing rules (Equations 3.63–3.63).
- Calculate A using the appropriate mixing rule (Equation 3.69, 3.72 3.74).
- Calculate p, q and r from Equations 3.7–3.9.
- Solve the cubic (Equation 3.6) for Z (see §3.2.1). Volume is obtained using $v = ZRT/P$.

The pure fluid case is obtained by considering a single component with mole fraction 1. If more than one root is found, the appropriate one must be selected. For a pure fluid, the smallest root corresponds to the liquid phase, and the largest root corresponds to the vapor phase. This is not necessarily true for mixtures, although it did apply to all cases in this study.

3.2.4 Calculation of Fugacity Coefficient

Phase equilibrium calculations require evaluation of the fugacity coefficient for each component in each phase. Given temperature T, pressure P, and phase mole fractions x_i, fugacity coefficient is calculated as follows.

- Find the compressibility factor of the phase by solving the cubic equation of state, using the method in §3.2.3. This also gives values of A_i, B_i, C_i, D_i, A, B, C and D.
- Calculate the derivatives $\hat{B}_i$, $\hat{C}_i$ and $\hat{D}_i$ from Equations 3.66–3.68.

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[1] The procedure for the Trebble-Bishnoi equation of state differs slightly, because it has a temperature dependent b.

- Calculate the derivative $\hat{A}_i$ using the appropriate mixing rule (Equation 3.70, 3.74 or 3.79).
- Calculate ϕ_i values from Equation 3.60 (or Equation 3.61).

The pure fluid case is obtained by considering a single component with mole fraction 1.

3.2.5 Pure Fluid Calculations

In this section, the calculation of pure fluid properties along the saturation curve is described. From the phase rule, the state of a pure saturated fluid is completely specified if a single thermodynamic variable is fixed. In this study, temperature T is assumed to be fixed and known, thus allowing all other properties to be calculated. Specifically, saturated pressure P^s, saturated liquid molar volume v_l^s, and saturated vapor molar volume v_v^s are calculated.

The following condition must be satisfied at saturation.

$$\begin{aligned} F(P) &= \phi_v - \phi_l \\ &= 0 \end{aligned} \tag{3.97}$$

The values of ϕ are calculated using the procedure in §3.2.4. An iterative procedure must be used to find the value of P which will satisfy Equation 3.97; this is P^s. Of the methods tested, the best (fastest and most stable) is the secant method. The search is for the value of $\ln(1 - P_r^s)$ which satisfies Equation 3.97. This improves stability (compared to a direct search for P^s) by preventing searches at supercritical pressures.

The complete procedure is as follows.

- Obtain two estimates of P^s, P_1 and P_2. P_1 is taken as the experimental P^s, and P_2 is taken as 95 % of this value.
- Calculate $X_1 = \ln(1 - P_1/P_c)$, and $X_2 = \ln(1 - P_2/P_c)$.
- Calculate $F_1 = F(P_1)$ and $F_2 = F(P_2)$.
- If $|F_1|$ is smaller than $|F_2|$, values of X_1 and X_2, and F_1 and F_2 are interchanged.

- Repeat the following until $|\Delta X|$ is sufficiently small.
  - Calculate $\Delta X = F_2(X_1 - X_2)/(F_2 - F_1)$.
  - Substitute the values of X_2 and F_2 for those of X_1 and F_1.
  - Calculate the new value of X_2, using $X_2 = X_2 + \Delta X$.
  - The new value of P_2 is thus $P_2 = P_c(1 - e^{X_2})$.
  - Calculate the new value of F_2, using $F_2 = F(P_2)$.
- The saturated vapor pressure is $P^s = P_2$.

The values of v_l^s and v_v^s are available from the calculation of ϕ values.

3.2.6 Mixture Calculations

Calculations for saturated mixtures are described here. Mixture calculations are more complex than pure component calculations, because they involve solving a system of nonlinear equations in more than one variable. In the following, it is assumed that the values of the binary interaction coefficients are known. The determination of these coefficients is discussed later.

From the phase rule, the state of a two-phase system of N_c components at saturation is completely specified if N_c thermodynamic variables are fixed. In this study, temperature T and the mole fractions of the liquid phase x_i are considered fixed and known. P^s is thus calculated as the bubble-point pressure of the liquid phase; the vapor mole fractions y_i, saturated liquid molar volume v_l^s and saturated vapor molar volume v_v^s can also be calculated.

At saturation, the following condition must be satisfied for all components.

$$f_{il} = f_{iv} \tag{3.98}$$

From the definition of fugacity coefficient for a component in a mixture ($\phi_i = f_i/x_iP$), these equations can be rewritten as follows

$$\begin{aligned} K_i &= \frac{y_i}{x_i} \\ &= \frac{\phi_{il}}{\phi_{iv}} \end{aligned} \tag{3.99}$$

K_i is the equilibrium ratio for component i. This is a system of N_c nonlinear equations. A problem of this type is generally quite difficult to solve. The method used here follows.

From these equations, and the mole fraction constraint on the vapor phase, the following equation can be written.

$$\begin{aligned} F(P) &= \sum_i x_i K_i - 1 \\ &= 0 \end{aligned} \tag{3.100}$$

This will be satisfied at the correct values of P^s and y_i. For an estimated value of P^s, F is calculated as follows.

- Obtain initial estimates of vapor mole fractions, y_i^{est}. These are usually the experimental values, or the values from a previous iteration.
- Repeat the following until $y_i - y_i^{est}$ is sufficiently small for all i.
  - Set $y_i^{est} = y_i$.
  - Calculate ϕ_{il} and ϕ_{iv} values from the procedure in §3.2.4.
  - Calculate K_i values from Equation 3.99.
  - Calculate new y_i values from Equation 3.99.
  - Normalize y_i values, i.e., $y_i \leftarrow y_i / \sum_j y_j$.
- Calculate $F(P)$ from Equation 3.100.

This will also return values of y_i corresponding to the estimate of P^s. If P^s is correct, then these y_i values will be correct. The value of P^s is found using the secant method. The algorithm for this follows.

- Obtain two estimates of P^s, P_1 and P_2. P_1 is taken as the experimental P^s, and P_2 is taken as 95 % of this value.
- Calculate $F_1 = F(P_1)$ and $F_2 = F(P_2)$.
- If $|F_1|$ is smaller than $|F_2|$, values of P_1 and P_2, and F_1 and F_2 are interchanged.
- Repeat the following until $|\Delta P|$ is sufficiently small.

  - Calculate $\Delta P = F_2(P_1 - P_2)/(F_2 - F_1)$.
  - Substitute the values of P_2 and F_2 for those of P_1 and F_1.
  - Calculate the new value of P_2, using $P_2 = P_2 + \Delta P$.
  - Calculate the new value of F_2, using $F_2 = F(P_2)$.
- The saturated vapor pressure is $P^s = P_2$.

This procedure yields values of P^s and y_i (from the calculation of F), as well as v_l^s and v_v^s (from the calculation of fugacity coefficient).

3.2.7 Modelling Techniques

Many of the calculations in this work require the determination of adjustable parameters by fitting to data, and/or the comparison of different models (i.e., equations of state, mixing rules). The modelling techniques used in this work are summarized here. Further details can be found in Bates and Watts [26].

A good parameter estimation technique should give accurate (unbiased) and precise (minimum variance) estimates of the parameters. This is satisfied by least-squares estimation (or Box-Draper estimation for multivariate responses) using appropriate residuals (normally distributed, unbiased, homoscedastic, independent), with known and fixed operating variables.

In this work, the Box-Draper multiresponse technique, which simplifies to least squares for a single response, is used and is summarized here. In general, at each of N data points, there will be M quantities (or responses) which are to be predicted by a model. Define the $M \times N$ residual matrix $\mathbf{Z}$, where element Z_{ij} is the difference between predicted and measured response i at data point j. The model predictions are functions of the P parameters p_i, represented here by the vector $\mathbf{p}$ of length P. Therefore, each element of $\mathbf{Z}$ will be a function of $\mathbf{p}$. The parameter estimates are those which minimize the determinant

$$S(\mathbf{p}) = |\mathbf{Z}^{\mathrm{T}}\mathbf{Z}| \tag{3.101}$$

The estimates at the minimum are denoted by $\hat{\mathbf{p}}$. The actual residuals used for each case in $\mathbf{Z}$ are specified later.

The minimization of objective functions in this work is done by the Nelder-Mead simplex method. A modified version of the implementation of Press et al. [96] is used. It was found to be preferable to other methods because it is simple, it does not require derivatives of the objective function with respect to the parameters (analytical derivatives are unavailable in all cases in the present work), it is self-scaling, and it is very robust. It does not converge as rapidly as some other methods (e.g., Levenberg-Marquardt minimization with numerical derivatives), but the difference is not large for one, two or three-parameter models, as is the case in this work.

It is useful to have some indication of the quality or precision of the estimated parameters. Approximate information on the precision of parameter estimates can be calculated from the Hessian $\mathbf{H}(\mathbf{p})$, a $P \times P$ matrix with element i, j given by $\partial^2 S(\mathbf{p})/\partial p_i \partial p_j$.

A $100(1-\alpha)\,\%$ confidence region for the parameter estimates is approximated by

$$(\mathbf{p}-\hat{\mathbf{p}})^{\mathrm{T}}\mathbf{H}(\hat{\mathbf{p}})(\mathbf{p}-\hat{\mathbf{p}}) \;\leq\; \frac{2P}{N-P}S(\hat{\mathbf{p}})F(P, N-P; \alpha) \qquad (3.102)$$

where $F(P, N-P; \alpha)$ denotes the upper α quantile of Fisher's F distribution with P and $N-P$ degrees of freedom. Equation 3.102 describes a P-dimensional ellipsoid in parameter space, the size of which gives some indication of the precision of the determined parameters.

An approximate $100(1-\alpha)\,\%$ confidence interval for parameter p_i is

$$\hat{p}_i \;\pm\; t(N-P; \alpha/2)\frac{P}{N-P}S(\hat{\mathbf{p}})\sqrt{2A_{ii}} \qquad (3.103)$$

where $t(N-P; \alpha/2)$ is the upper $\alpha/2$ quantile of the Student-t distribution with $N-P$ degrees of freedom, and A_{ij} denotes element i, j of $\mathbf{H}^{-1}(\hat{\mathbf{p}})$ Equation 3.103 gives approximate bounds on the estimate of a parameter.

Correlations between the parameter estimates are also calculated from the Hessian. They are given by

$$r_{ij} \;=\; \frac{A_{ij}}{\sqrt{A_{ii}A_{jj}}} \qquad (3.104)$$

The correlation is a dimensionless value between -1 and 1. A value of correlation close to these bounds is indicative of dependency between the parameters, which is undesirable.

All parameter confidence regions, confidence intervals and correlations are calculated from approximate Hessians, obtained by finite difference at the minima. Appropriate step sizes are returned by the minimization routine.

Several quantities are calculated to compare overall results from parameter estimation and/or from different models. The most direct method for comparison of predictions from parameter estimation is through the values of $S(\hat{\mathbf{p}})$. However, this does not take into account the number of parameters. A more meaningful quantity is the standard error, σ.

$$\sigma = \sqrt{\frac{S(\hat{\mathbf{p}})}{N-P}} \tag{3.105}$$

Overall deviations in particular quantities are expressed by the square-root of the mean squared deviations (RMS), or by the square-root of the mean squared percent deviations (%RMS). Overall RMS deviation is calculated for vapor mole fractions only.

$$RMS = \sqrt{\frac{1}{N_c N}\sum_{i=1}^{N_c}\sum_{j=1}^{N}(y_i^{\mathrm{calc}} - y_i)_j^2} \tag{3.106}$$

Overall %RMS deviation is calculated for other quantities. Using P^s as an example, it is given by

$$\%RMS = 100\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\frac{(P^s)^{\mathrm{calc}} - P^s}{P^s}\right]_i^2} \tag{3.107}$$

Chapter 4

Data and Equation Sources

A study of this type requires many types of data from a wide variety of sources. It also makes use of many different correlations and equations of state. Rather than presenting these as they are introduced, they are given here.

4.1 Data Sources

Several types of data are used in this study. These are presented below, classified in terms of pure component properties, pure component data, and mixture data. The actual data used are not given, since it would require a prohibitive amount of space. The references are given instead, along with some characteristics of the data where appropriate.

4.1.1 Properties

Most pure fluid properties are obtained from Reid et al. [102], fourth edition. Specifically, the ones used in this study are molecular weight W, boiling temperature T_b, critical temperature T_c, critical pressure P_c, critical compressibility factor Z_c, acentric factor ω, and dipole moment μ. Note that there are significant differences in many cases between values in the third [103] and the fourth editions.

The critical compressibility factor Z_c for methyl ethyl ether is not available. The Joback method, as presented in Reid et al. [102], is used to estimate Z_c for this substance.

The Halm-Stiel polar factor χ (see §2.3.2) is not available for most substances. Therefore, in all cases it is estimated from P^s correlations (see below), using Equation 2.41. Severe errors can result if these values of χ are used in calculations with acentric factors which are inconsistent with the P^s correlations. Therefore, for use in Equation 2.41 and for any other calculations involving χ, ω is calculated from Equation 2.40, using the same P^s correlations.

In this study, saturated pressures P^s and saturated liquid molar volumes v_l^s are sometimes represented by correlations. The following correlations are used for P^s.

1. Gomez-Nieto and Thodos (GT and GGT):

$$\ln P^s{}_r = \beta(T_r^{-m} - 1) + \gamma(T_r^7 - 1)$$

   This involves three constants (m, β and γ), which are either obtained from the tabulation of Gomez-Nieto and Thodos [54] (GT) or from the generalized expressions given by them (GGT). The latter requires W, T_b, T_c and P_c as input quantities.

2. Wagner (W):

$$\ln P_r^s = T_r^{-1}(ax + bx^{1.5} + cx^3 + dx^6)$$

   $x = 1 - T_r$. This requires four constants (a, b, c and d), which are tabulated in the compilation of Reid et al. [102].

3. Frost-Kalwarf-Thodos (FKT):

$$\ln P_r^s = a - b/T + c \ln T + dP^s/T^2$$

   This requires four constants (a, b, c and d), which are tabulated in the compilation of Reid et al. [102]. Note that this correlation requires iterative solution, and dimensional consistency between the constants, P^s and T.

For saturated liquid volumes, the following correlations are used.

1. Campbell and Thodos (CT and GCT):

$$\rho_r = 1 + \alpha(1 - T_r)^{3/8} + \beta(1 - T_r)^n$$

This requires three constants (n, α and β) which are either obtained from the tabulation of Campbell and Thodos [36] (CT) or from the generalized expressions given by them (GCT). The latter require W, T_b, T_c, P_c, v_c and μ as input quantities.

2. Hankinson-Thomson (HBT):

$$v_l^s = V^* V_R^{(0)}(1 - \omega_{\mathrm{SRK}} V_R^{(\delta)})$$

$V_R^{(0)}$ and $V_R^{(\delta)}$ are given by polynomials in T_R.

$$\begin{aligned} V_R^{(0)} &= 1 + ax^{1/3} + bx^{2/3} + cx + dx^{4/3} \\ V_R^{(\delta)} &= (e + fT_r + gT_r^2 + hT_r^3)/(T_r - 1.00001) \end{aligned}$$

where $x = 1 - T_r$. This requires two constants (ω_{SRK} and V^*), tabulated in the compilation of Reid et al. [102]. The constants a–h are the same for all substances, and are given in Reid et al. [102]. This correlation does not predict actual v_c, so it may be slightly inaccurate near the critical point.

The correlations selected are among the most accurate available. They reproduce the shapes of the saturation curves accurately up to the critical point. The correlations are given in order of preference. The lowest numbered one for which fitted constants for a particular substance are available is used. The only exceptions are in the cases of hydrogen sulfide, ethanol, cyclopropane and 1-propanol, for which the GT correlation gave poor results[1]. If no tabulated constants are available for a given substance, the generalized correlations (GGT or GCT) are used. Table 4.1 indicates which equation is used for each substance in this study.

4.1.2 Pure Fluids

An extensive compilation of data for pure fluids is made to assist in the formulation and evaluation of new equations of state. This consists of data on the vapor–liquid saturation curve, and compressed liquid data. A wide variety of substances, from nonpolar to highly polar, are included.

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[1] The critical properties used by Gomez and Thodos for these substances differed significantly from those used in this study.

A compilation of data for 97 polar and nonpolar fluids at saturation is made, comprising a total of 2925 data points. The data consists of P^s, v_l^s and v_v^s for each substance at a number of temperatures between the triple point and critical point. The substances are the following, classified into the shown categories for the purpose of presenting results compactly.

noble gases (5 substances, 255 points):
argon, helium, krypton, neon, xenon.

diatomics (5 substances, 260 points):
chlorine, fluorine, hydrogen, nitrogen, oxygen.

inorganics (6 substances, 339 points):
hydrogen chloride, water, hydrogen sulfide, ammonia, sulfur dioxide, sulfur trioxide.

paraffins (13 substances, 398 points):
methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, neopentane, isopentane, *n*-hexane, *n*-heptane, *n*-octane, isooctane, *n*-decane.

olefins (5 substances, 213 points):
ethylene, propylene, 1-butene, 1,2-butadiene, 1,3-butadiene.

alkynes (2 substances, 39 points):
acetylene, propyne.

naphthenes (2 substances, 37 points):
cyclopropane, cyclohexane.

aromatics (7 substances, 104 points):
benzene, toluene, *m*-xylene, *o*-xylene, *p*-xylene, ethyl benzene, naphthalene.

ethers (5 substances, 81 points):
dimethyl ether, methyl ethyl ether, diethyl ether, ethyl propyl ether, diphenyl ether.

alcohols (6 substances, 85 points):
methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, *t*-butanol.

carboxylic acids (1 substance, 31 points):
acetic acid.

esters and ketones (11 substances, 214 points):
methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, *n*-propyl formate, *n*-propyl acetate, ethyl propionate, methyl butyrate, methyl isobutyrate, acetone.

nitrogen compounds (3 substances, 39 points):
acetonitrile, diethyl amine, aniline.

sulfur compounds (4 substances, 80 points):
methyl mercaptan, ethyl mercaptan, dimethyl sulfide, diethyl sulfide.

oxides (4 substances, 89 points):
carbon monoxide, carbon dioxide, ethylene oxide, propylene oxide.

halogenated paraffins (13 substances, 553 points):
phosgene, carbon tetrachloride, carbon tetrafluoride, chloroform, freon-13 (chlorotrifluoromethane), freon-12 (dichlorodifluoromethane), freon-11 (trichlorofluoromethane), freon-22 (chlorodifluoromethane), freon-21 (dichlorofluoromethane), methyl chloride, freon-114 (1,2-dichlorotetrafluo-roethane), freon-113 (1,2,2-trichlorotrifluoroethane), ethyl chloride.

halogenated naphthenes (1 substance, 53 points):
perfluorocyclobutane.

halogenated aromatics (4 substances, 55 points):
bromobenzene, chlorobenzene, fluorobenzene, iodobenzene.

Table 4.1 gives the sources for the data, the number of points used, and the T_r range covered by the data. Only points which have temperatures below the critical temperature given in Reid et al. [102] are used.

A compilation of compressed liquid molar volume data for 13 polar and nonpolar fluids is made, comprising a total of 1712 data points. Each data point consists of temperature T, pressure P, and compressed liquid molar volume v_l. The number of data points, the T_r and P_r ranges covered by the data, and the reference for each substance are given in Table 4.2.

Table 4.1: Pure fluid saturation data. Sources and characteristics

substance	data source			correlations	
	N	T_r range	ref.	P^s	v_l^s
argon	68	0.556–0.995	[17]	GT	CT
chlorine	51	0.413–0.995	[18]	GT	CT
fluorine	20	0.658–0.988	[136]	GT	CT
helium	55	0.420–0.973	[23]	GT	CT
hydrogen chloride	15	0.579–0.995	[141]	GT	CT
hydrogen	22	0.424–0.985	[136]	GT	CT
water	213	0.422–1.000	[1]	GT	CT
hydrogen sulfide	30	0.565–0.997	[119]	FKT	HBT
ammonia	29	0.602–0.986	[37]	GT	CT
krypton	47	0.553–0.993	[136]	GT	CT
nitrogen	65	0.500–0.998	[24]	GT	CT
neon	20	0.563–0.991	[136]	GT	CT
oxygen	102	0.352–0.996	[136]	GT	CT
sulfur dioxide	37	0.593–0.996	[37]	GT	CT
sulfur trioxide	15	0.647–0.984	[141]	GT	HBT
xenon	65	0.557–0.994	[136]	GT	CT
phosgene	19	0.618–0.996	[141]	GT	GCT
carbon tetrachloride	21	0.635–0.994	[141]	GT	CT
carbon tetrafluoride	16	0.393–0.967	[77]	GGT	GCT
carbon monoxide	24	0.513–0.981	[37]	GT	CT
carbon dioxide	47	0.712–1.000	[20]	GT	CT
chloroform	9	0.624–0.941	[2]	GT	HBT
freon-13	69	0.540–0.991	[136]	W	HBT
freon-12	78	0.528–0.995	[136]	GT	HBT
freon-11	62	0.452–0.877	[136]	FKT	HBT
freon-22	73	0.469–0.994	[136]	W	HBT
freon-21	119	0.472–0.999	[136]	FKT	HBT
methyl chloride	25	0.512–0.800	[136]	W	CT
methane	52	0.476–0.998	[21]	GT	CT
methanol	20	0.659–0.991	[141]	GT	CT
methyl mercaptan	20	0.594–0.985	[141]	W	HBT

Table 4.1: Pure fluid saturation data. Sources and characteristics (continued).

substance	data source			correlations	
	N	T_r range	ref.	P^s	v_l^s
freon-114	21	0.557–0.795	[136]	W	HBT
freon-113	23	0.499–0.725	[136]	W	HBT
acetylene	22	0.624–0.991	[37]	GT	HBT
acetonitrile	12	0.547–0.996	[51]	FKT	CT
ethylene	76	0.507–0.999	[19]	GT	CT
ethylene oxide	9	0.604–0.938	[2]	W	HBT
acetic acid	31	0.495–0.984	[141]	GT	CT
methyl formate	19	0.626–0.992	[141]	W	GCT
ethyl chloride	18	0.620–0.984	[141]	W	HBT
ethane	35	0.436–0.991	[119]	GT	CT
dimethyl ether	18	0.624–0.995	[141]	W	HBT
ethanol	18	0.684–0.999	[141]	GT	HBT
ethyl mercaptan	20	0.616–0.988	[141]	W	HBT
dimethyl sulfide	20	0.614–0.980	[141]	W	HBT
propyne	17	0.803–1.000	[140]	GT	HBT
propylene	45	0.370–0.959	[22]	GT	CT
acetone	19	0.648–0.990	[141]	GT	CT
propylene oxide	9	0.638–0.954	[2]	W	HBT
ethyl formate	20	0.644–0.989	[141]	W	GCT
methyl acetate	19	0.652–0.993	[141]	W	HBT
cyclopropane	21	0.737–0.988	[75]	W	CT
propane	38	0.495–0.984	[119]	GT	CT
1-propanol	19	0.658–0.993	[141]	GT	CT
2-propanol	9	0.700–0.980	[2]	W	HBT
methyl ethyl ether	17	0.641–0.989	[141]	W	HBT
perfluorocyclobutane	53	0.600–0.991	[136]	GGT	GCT
1,2-butadiene	9	0.640–0.902	[2]	GT	HBT
1,3-butadiene	47	0.407–0.977	[136]	GT	HBT
1-butene	26	0.651–0.979	[37]	GT	HBT
ethyl acetate	19	0.670–0.990	[141]	W	HBT
methyl propionate	21	0.665–0.995	[141]	W	GCT
n-propyl formate	19	0.658–0.991	[141]	W	GCT
n-butane	29	0.627–0.993	[119]	GT	CT
isobutane	39	0.469–0.993	[119]	GT	CT

Table 4.1: Pure fluid saturation data. Sources and characteristics (continued).

substance	data source			correlations	
	N	T_r range	ref.	P^s	v_l^s
1-butanol	10	0.694–0.993	[2]	GT	CT
t-butanol	9	0.702–0.948	[2]	GGT	HBT
diethyl ether	18	0.659–0.992	[141]	GT	CT
diethyl sulfide	20	0.653–0.993	[141]	GGT	HBT
diethyl amine	18	0.662–0.993	[141]	W	HBT
n-propyl acetate	19	0.682–0.998	[141]	W	GCT
ethyl propionate	20	0.682–0.995	[141]	W	GCT
methyl butyrate	20	0.678–0.998	[141]	W	GCT
methyl isobutyrate	19	0.676–0.995	[141]	W	GCT
n-pentane	30	0.638–0.981	[119]	GT	CT
isopentane	31	0.470–0.989	[119]	GT	CT
neopentane	9	0.652–0.945	[2]	GT	HBT
1-pentanol				W	HBT
ethyl propyl ether	17	0.669–0.986	[141]	W	GCT
bromobenzene	12	0.646–0.811	[141]	W	HBT
chlorobenzene	14	0.653–0.859	[141]	GT	HBT
fluorobenzene	20	0.648–0.988	[141]	GT	HBT
iodobenzene	9	0.642–0.753	[141]	GGT	GCT
benzene	47	0.553–0.998	[37]	GT	CT
aniline	9	0.655–0.966	[2]	GT	HBT
cyclohexane	16	0.639–0.981	[141]	GT	CT
n-hexane	42	0.525–0.985	[119]	GT	CT
toluene	9	0.648–0.972	[2]	GT	CT
n-heptane	30	0.545–0.987	[119]	GT	CT
n-octane	27	0.488–0.976	[119]	GT	CT
isooctane	27	0.502–0.998	[136]	GGT	HBT
m-xylene	9	0.668–0.980	[2]	GT	CT
o-xylene	9	0.662–0.960	[2]	GT	CT
p-xylene	9	0.669–0.982	[2]	GT	CT
ethyl benzene	10	0.663–0.993	[2]	GT	HBT
n-nonane				GT	HBT
naphthalene	11	0.659–0.793	[136]	GT	HBT
n-decane	9	0.724–0.971	[2]	GT	HBT
diphenyl ether	11	0.696–0.827	[136]	GGT	GCT

Table 4.2: Pure fluid compressed liquid volume data. Sources and characteristics

substance	N	T_r range	P_r range	ref.
argon	73	0.796–0.995	0.312–4.161	[46]
water	81	0.541–0.927	0.002–4.521	[90]
hydrogen sulfide	65	0.744–0.922	0.154–7.712	[107]
ammonia	346	0.764–0.986	0.179–9.820	[47]
nitrogen	157	0.713–0.990	0.149–119.558	[48]
carbon dioxide	55	0.800–0.997	0.206–8.238	[47]
acetonitrile	102	0.501–0.959	1.035–51.760	[51]
propylene	63	0.761–0.943	0.300–14.989	[107]
propane	227	0.622–0.973	0.024–9.536	[46]
1-butene	85	0.741–0.979	0.343–17.151	[107]
isobutane	82	0.721–0.966	0.189–5.667	[37]
n-pentane	90	0.662–0.993	1.023–6.138	[37]
n-nonane	286	0.523–0.859	0.602–30.108	[107]

4.1.3 Mixtures

One of the most important applications for equations of state is in mixture calculations. Therefore, compilations are made of various types of data for mixtures. These are mixtures involving polar compounds, which have typically been difficult to describe with conventional equations of state.

Vapor-liquid equilibrium (VLE) data and volumetric data for mixtures are compiled. Four sets of data are described below: binary VLE data for normal alkanes and 1-alkanols; VLE data for ternary systems and their constituent binary systems; VLE and saturated volume data for binary systems; compressed liquid volume data for binary systems.

A compilation is made of VLE data for binary systems of normal alkanes and 1-alkanols. This consists of 15 systems, comprising 233 data points. Each data point includes temperature T, saturated pressure P^s, liquid mole fractions x_i and (unless otherwise indicated) vapor mole fractions y_i. The data are described in Table 4.3.

A compilation is made of VLE data for ternary systems, along with the data for the constituent binary systems. The binary data consist of 16 systems, comprising 21 isotherms and 277 data points. The data are described in Table 4.4. The ternary data consist of 6 systems, comprising 7 isotherms and 184 data points. These data are described in Table 4.5. Each data point includes temperature T, saturated pressure P^s, liquid mole fractions x_i and (unless otherwise indicated) vapor mole fractions y_i.

A compilation is made of binary VLE data and saturated volume data. This consists of 7 systems, comprising 27 isotherms and 274 data points. Each data point includes temperature T, saturated pressure P^s, liquid mole fractions x_i and saturated liquid molar volume v_l^s for all systems, as well as vapor mole fraction y_i and saturated vapor molar volume v_v^s for most systems. Table 4.6 lists the systems, sources and some characteristics, including the presence of a critical point. As described in §6.2.3, some data near critical points had to be excluded. Table 4.6 lists only the data points actually used.

A final compilation is made of compressed molar volume data for binary mixtures. This consists of 3 systems, comprising 12 isotherms and 1962 data points. Each data point consists of temperature T, pressure P, mole fractions x_i, and compressed liquid molar volume v_l. The data are described in Table 4.7. All of these systems correspond to systems in the compilation of binary VLE and saturated volume data (see Table 4.6).

Table 4.3: VLE data for systems of normal alkanes and 1-alkanols. Sources and characteristics.

system	T /K	N	P range /bar	y data	ref.
1-C_4H_9OH–n-C_5H_{12}	303.15	15	0.013–0.821	yes	[105]
CH_3OH–n-C_6H_{14}	323.15	24	0.540–1.029	yes	[147]
C_2H_5OH–n-C_6H_{14}	323.14	20	0.294–0.739	yes	[45]
1-C_4H_9OH–n-C_6H_{14}	298.15	11	0.008–0.200	yes	[116]
1-$C_5H_{11}OH$–n-C_6H_{14}	323.15	15	0.018–0.540	no	[116]
C_2H_5OH–n-C_7H_{16}	343.15	11	0.406–1.004	yes	[98]
1-C_3H_7OH–n-C_7H_{16}	348.15	14	0.495–0.713	yes	[53]
1-C_4H_9OH–n-C_7H_{16}	323.15	8	0.143–0.200	yes	[25]
1-$C_5H_{11}OH$–n-C_7H_{16}	363.27	14	0.154–0.789	no	[131]
C_2H_5OH–n-C_8H_{18}	328.15	21	0.084–0.406	yes	[32]
1-C_3H_7OH–n-C_8H_{18}	313.15	17	0.041–0.093	no	[85]
1-C_4H_9OH–n-C_8H_{18}	313.15	14	0.025–0.058	no	[85]
1-$C_5H_{11}OH$–n-C_8H_{18}	363.27	15	0.154–0.380	no	[131]
1-C_4H_9OH–n-$C_{10}H_{22}$	373.15	21	0.098–0.515	yes	[72]
1-$C_5H_{11}OH$–n-$C_{10}H_{22}$	363.27	13	0.064–0.166	no	[131]

Table 4.4: VLE data for several binary systems. Sources and characteristics. These are the constituent binaries of the ternary systems in Table 4.5, and are grouped and ordered to correspond with the latter.

system	T /K	N	P range /bar	y data	ref.
C_3H_6O–CH_3OH	373.15	14	3.523–4.027	yes	[55]
C_3H_6O–H_2O	373.15	22	1.110–3.689	yes	[55]
CH_3OH–H_2O	373.15	16	1.041–3.372	yes	[55]
C_3H_6O–CH_3OH	328.15	28	0.723–1.011	yes	[52]
C_3H_6O–2-C_3H_7OH	328.15	14	0.344–0.943	yes	[52]
CH_3OH–2-C_3H_7OH	328.15	20	0.329–0.660	yes	[52]
n-C_6H_{14}–C_2H_5OH	328.15	17	0.460–0.902	yes	[62]
C_6H_6–n-C_6H_{14}	328.15	14	0.495–0.648	yes	[62]
C_2H_5OH–C_6H_6	328.15	9	0.478–0.628	yes	[62]
C_2H_5OH–C_2H_3N	293.15	8	0.097–0.109	yes	[139]
C_2H_5OH–C_6H_6	318.15	12	0.271–0.413	yes	[34]
C_2H_3N–C_6H_6	318.15	12	0.300–0.371	yes	[33]
CH_3OH–CCl_4	308.15	9	0.345–0.434	yes	[110]
CH_3OH–C_6H_6	308.15	9	0.271–0.390	yes	[110]
CCl_4–C_6H_6	313.15	8	0.254–0.283	yes	[110]
CH_3OH–CCl_4	328.15	6	0.758–0.995	yes	[109]
CH_3OH–C_6H_6	328.15	9	0.621–0.905	yes	[110]
CCl_4–C_6H_6	323.14	16	0.362–0.409	yes	[151]
N_2–CO_2	273.15	2	50.00–75.00	yes	[143]
N_2–CH_3OH	273.15	4	50.00–125.00	no	[143]
CO_2–CH_3OH	273.15	28	4.48–33.51	no	[143]

Table 4.5: VLE data for several ternary systems. Sources and characteristics. The constituent binary systems for these are listed in Table 4.4.

system	T /K	N	P range /bar	ref.
C_3H_6O–CH_3OH–H_2O	373.15	51	1.234–3.923	[55]
C_3H_6O–CH_3OH–isoC_3H_7OH	328.15	27	0.355–0.995	[52]
n-C_6H_{14}–C_2H_5OH–C_6H_6	328.15	43	0.542–0.893	[62]
C_2H_5OH–C_2H_3N–C_6H_6	318.15	21	0.342–0.431	[83]
CH_3OH–CCl_4–C_6H_6	308.15	6	0.388–0.411	[109]
CH_3OH–CCl_4–C_6H_6	328.15	8	0.887–0.956	[109]
N_2–CO_2–CH_3OH	273.15	28	50.00–125.00	[143]

Table 4.6: VLE and saturated volume data for binary systems. Sources and characteristics. The column headed "crit." indicates if the isotherm in question has a critical point.

system	T /K	N	P range /bar	crit.	ref.
N_2–H_2S	256.43	12	17.72–207.05	yes	[30]
	277.65	13	11.65–206.84	yes	
	300.04	12	20.68–206.84	yes	
	321.87	12	34.68–206.84	yes	
	344.26	8	71.22–177.19	yes	
CH_4–H_2S	277.59	24	11.65–131.00	yes	[107]
	310.93	21	27.17–127.55	yes	
	344.26	13	53.70–113.76	yes	
H_2S–n-C_5H_{12}	277.59	9	0.30–11.65	no	[107]
	310.93	9	1.08–27.17	no	
	344.26	9	2.93–53.70	no	
	377.59	11	6.54–68.95	yes	
	410.93	10	12.80–68.95	yes	
H_2S–n-C_7H_{16}	310.93	13	1.60–24.20	no	[84]
	352.59	11	2.79–55.64	no	
	394.26	12	6.05–84.18	yes	
H_2S–n-$C_{10}H_{22}$	344.26	6	20.68–53.70	no	[107]
	377.59	5	27.58–82.74	yes	
	410.93	6	27.58–96.53	yes	
	444.26	7	13.79–96.53	yes	
C_2H_4–$CHCl_3$[a]	298.15	5	10.13–50.66	yes	[115]
	323.15	7	10.13–70.93	yes	
	348.15	9	10.13–91.19	yes	
	373.15	9	10.13–91.19	yes	
C_2H_6–CH_4O[b]	323.15	7	0.54–60.79	yes	[78]
	348.15	7	1.51–60.79	yes	
	373.15	7	3.50–60.79	yes	

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[a] No v_v^s data

[b] No y or v_l^s data

Table 4.7: Compressed liquid volume data for binary mixtures.

system	T K	N	P range bar	x_1 range
CH_4 -H_2S	277.59	106	69–689	0.1–0.7
	310.93	75	86–689	0.1–0.5
	344.26	31	103-689	0.1–0.2
H_2S -C_5H_{12}	277.59	198	14–689	0.1–0.9
	310.93	193	14–689	0.1–0.9
	344.26	184	14–689	0.1–0.9
	377.59	173	14–689	0.1–0.9
	410.93	132	28–689	0.1–0.7
H_2S -$C_{10}H_{22}$	344.26	187	14–689	0.1–0.9
	377.59	179	14–689	0.1–0.9
	410.93	169	14–689	0.1–0.9
	444.26	162	14–689	0.1–0.9

4.2 Summary of Equations of State

In this work, comparisons are made to several equations of state from the literature. These equations are given in full below. These are all cubic equations of the van der Waals form, and they conform to the general forms given in §2.2.1. Furthermore, they are all subjected to the classical critical point conditions (§2.2.2). Therefore, they can be completely specified by giving two further conditions at the critical point, and by giving any temperature dependencies for the constants.

For each equation of state shown here, the values of the critical point constants Ω_{ac} and Ω_{bc} are specified. The temperature-dependent portion of a (α) is also given. In the case of the Trebble-Bishnoi equation only, expressions for A, B, C and D are given (this is necessary because it has a temperature-dependent b). FORTRAN programs which calculate the constants in these equations of state are given in §B.

Soave-Redlich-Kwong (SRK) [118]

The SRK equation has $u = 1$ and $w = 0$. The critical constants are given by

$$\begin{aligned} \Omega_{ac} &= 0.42747 \\ \Omega_{bc} &= 0.08664 \end{aligned}$$

The temperature dependency of a is of the Soave type.

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

For $\omega \leq 0.5$, m is given by

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

For $\omega > 0.5$, m is given by

$$\begin{aligned} m &= 0.47978 + 1.57624\omega - 0.19394\omega^2 + 0.02779\omega^3 \\ &\quad - 0.0016577\omega^4 - 0.00013153\omega^5 \end{aligned}$$

Peng-Robinson (PR) [89]

The PR equation has $u = 2$ and $w = -1$. The critical constants are given by

$$\begin{aligned} \Omega_{ac} &= 0.45724 \\ \Omega_{bc} &= 0.07780 \end{aligned}$$

The temperature dependency of a is of the Soave type.

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

For $\omega < 0.5$, m is given by

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

For $0.2 \leq \omega \leq 0.5$, m is given by

$$m = 0.37964 + 1.48503\omega - 0.16442\omega^2 + 0.01667\omega^3$$

Schmidt-Wenzel (SW) [111]

The SW equation has $u = 1 - w$. The critical constants are given by

$$\begin{aligned} \Omega_{ac} &= [1 - \zeta_c(1 - \beta_c)]^3 \\ \Omega_{bc} &= \beta_c\zeta_c \end{aligned}$$

β_c and ζ_c are determined from the following correlations.

$$\begin{aligned} \beta_c &= 0.25989 - 0.0217\omega + 0.0375\omega^2 \\ \zeta_c &= \frac{1}{3(1 + \beta_c\omega)} \end{aligned}$$

The temperature dependency of a is of the Soave type.

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

m is a complicated function of T_r and ω. For $\omega \leq 0.4$, m is given by

$$m = \kappa_1 = \kappa_0 + (5T_r - 3\kappa_0 - 1)^2/70$$

For $\omega \geq 0.55$, m is given by

$$m = \kappa_2 = \kappa_0 + 0.71(T_r - 0.779)^2$$

For $0.4 < \omega < 0.55$, m is given by

$$m = \frac{\omega - 0.4}{0.15}\kappa_1 + \frac{0.55 - \omega}{0.15}\kappa_2$$

κ_0 is calculated from

$$\kappa_0 = 0.465 + 1.347\omega - 0.528\omega^2$$

for $\omega \leq 0.3671$ and from

$$\kappa_0 = 0.5361 + 0.9593\omega$$

for $\omega > 0.3671$. If $T_r > 1$, m is evaluated at $T_r = 1$.

Patel-Teja (PT) [87]

The PT equation has $u = 1 - w$. Ω_{ac} is given by

$$\Omega_{ac} = 3{\zeta_c}^2 + 3(1 - 2\zeta_c)\Omega_{bc} + {\Omega_{bc}}^2 + 1 - 3\zeta_c$$

Ω_{bc} is the smallest positive root of the following equation.

$${\Omega_{bc}}^3 + (2 - 3\zeta_c){\Omega_{bc}}^2 + 3{\zeta_c}^2\Omega_{bc} - {\zeta_c}^3 = 0$$

ζ_c is determined from the following correlation.

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2$$

The temperature dependency of a is of the Soave type

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

where m is given by

$$m = 0.452413 + 1.30982\omega - 0.295937\omega^2$$

Translated Peng-Robinson (TPR) [150]

For the TPR equation, $w = (u^2 - 4u - 4)/8$. It is identical to the PR equation, except that Ω_{bc} is given by

$$\Omega_{bc} = \frac{0.3112}{2 - u}$$

with

$$u = 1.5251 + 1.1146\omega + 1.1538\omega^2$$

The original TPR equation of Yu and Lu uses a correlation involving ω to determine Ω_{bc}. This correlation is redundant and results in inconsistencies at high values of ω. It is therefore replaced by the relationship given above, which was derived by the author.

Toghiani-Viswanath (TV) [126]

The TV equation has $u = 1 - w$. The critical constants are given by

$$\begin{aligned} \Omega_{ac} &= [1 - \zeta_c(1 - \eta_c)]^3 \\ \Omega_{bc} &= \eta_c \zeta_c \end{aligned}$$

ζ_c is determined from the following correlation.

$$\zeta_c = B_1 + B_2\omega + B_3\omega^2 + B_4\chi + B_5\chi^2 + B_6\omega\chi + B_7\omega^3 + B_8\chi^3$$

η_c is the smallest positive root of the following equation.

$$\eta_c^3 + (2/\zeta_c - 3)\eta_c^2 + 3\eta_c - 1 = 0$$

The temperature dependency of a is of the Soave type.

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

where m is given by

$$m = A_1 + A_2\omega + A_3\omega^2 + A_4\chi + A_5\chi^2 + A_6\omega\chi + A_7\omega^3 + A_8\chi^3$$

The values of A_1–A_8 and B_1–B_8 are given by Toghiani and Viswanath [126].

Trebble-Bishnoi (TB) [130]

The TB equation does not have a unique relation between u and w. Ω_{ac} is given by

$$\Omega_{ac} = 3{\zeta_c}^2 + 2\Omega_{bc}(1 - 3\zeta_c) + \Omega_{bc} + (1 - 3\zeta_c) + B_c^2 + D_c^2$$

Ω_{bc} is the smallest positive root of the following equation.

$$\Omega_{bc}{}^3 + (2 - 3\zeta_c)\Omega_{bc}{}^2 + 3{\zeta_c}^2\Omega_{bc} - {\zeta_c}^3 - D_c^2 = 0$$

ζ_c and D_c are determined from the following correlations.

$$\begin{aligned} \zeta_c &= 1.075 Z_c \\ D_c &= 0.341 Z_c - (0.005\,\mathrm{m}^3/\mathrm{gmol}) P_c/RT_c \end{aligned}$$

The temperature dependency for a is of the Heyen form (Equation 2.25), but with $n = 1$.

$$\alpha = \exp[m_1(1 - T_r)]$$

m_1 is given by

$$m_1 = 0.66208 + 4.63961\omega + 7.45183\omega^2$$

for $\omega < -0.1$, by

$$m_1 = -0.31913$$

for $\omega < -0.35$ (helium) and $T_r < 1$, by

$$m_1 = 0.35 + 0.7924\omega + 0.1875\omega^2$$

for $-0.10 \leq \omega \leq 0.40$, and by

$$0.32 + 0.9424\omega - 28.93(0.3 - Z_c)^2$$

for $\omega > 0.40$. There is also a temperature dependency for b, given by

$$\beta = 1 + m_2(1 - T_r + \ln T_r)$$

where m_2 is given by

$$m_2 = 0$$

for $\omega < -0.0423$, by

$$m_2 = 0.05246 + 1.15058\omega - 1.99348\omega^2 + 1.59490\omega^3 - 1.39267\omega^4$$

for $-0.0423 \leq \omega \leq 0.30$, and by

$$m_2 = 0.17959 + 0.23471\omega$$

for $\omega > 0.30$. For $T > T_c$, $\beta = 1$.

Because of the temperature dependency in b, specific formulae must be given for A, B, C and D, the dimensionless equation of state constants. They are given by

$$\begin{aligned} A &= \alpha\Omega_{ac}P_r/T_r^2 \\ B &= \beta\Omega_{bc}P_r/T_r \\ C &= -B(1 + X + 0.5\sqrt{1 + 6X + X^2 + 4Y^2} \\ D &= -B(1 + X - 0.5\sqrt{1 + 6X + X^2 + 4Y^2} \end{aligned}$$

where X and Y are given by

$$\begin{aligned} X &= (1 - 3\zeta_c)/(\beta\Omega_{bc}) \\ Y &= D_c/(\beta\Omega_{bc}) \end{aligned}$$

Sugie-Iwahori-Lu (SIL) [125]

The SIL equation does not have a unique relation between u and w. Ω_{ac} and Ω_{bc} are determined iteratively from P^s and v_l^s correlations, using the following procedure. It is assumed that values of $P_r^s(T_r)$ and $Z_l^s(T_r)$ are available from correlations. The P^s and v_l^s correlations used for all substances in this study are given in Table 4.1, and are described in §4.1.1.

- Assume initial value(s) of Ω_{ac}. Almost all substances have $0.421875 < \Omega_{ac} <\approx 0.7$ for this equation of state.

- Determine the actual value of Ω_{ac} iteratively. Each iteration involves the following.

    - Calculate f, g, and h from Equations 3.29–3.31

  - Use the procedure of §3.2.2 to obtain $\alpha(0.7)$ and $\alpha(0.9)$. This will also give the values of $\lambda_L(0.7)$ and $\lambda_L(0.9)$.
  - The condition to be satisfied is

$$\frac{0.7}{P_r^s(0.7)}[Z_l^s(0.7) - \lambda_L(0.7)] = \frac{0.9}{P_r^s(0.9)}[Z_l^s(0.9) - \lambda_L(0.9)]$$

- Ω_{bc} is calculated from

$$\Omega_{bc} = \frac{0.7}{P_r^s(0.7)}[Z_l^s(0.7) - \lambda_L(0.7)]$$

In this work, the iterative solution is by Brent's algorithm, as presented by Press et al. [96]. This combines bissection and false position to obtain rapid and robust determination of roots. It requires about 5 iterations to converge to a high degree of accuracy.

At subcritical temperatures, the value of α is determined from P^s correlations using the procedure of §3.2.2. At supercritical temperatures, Soave's expression is used,

$$\alpha = [1 + m(1 - T_r^{1/2})]^2$$

where m is determined from α at $T_r = 0.9$.

Chapter 5

Development of a New Equation of State

In this Chapter, the effect of the form of cubic equations of state on volumetric property predictions is investigated. Based on this investigation, a new equation of state is proposed. Three different methods of evaluating the constants in the equation of state are developed.

5.1 The Relationship between u and w

In §2.2.4, it is shown that the form of a cubic equation of state is important for its volumetric performance. This is best understood in terms of the relationship between u and w. The general cubic equation proposed by Schmidt and Wenzel (Equation 2.12) is therefore used as a basis for consideration.

As discussed in §2.2.3, the temperature dependency of b is considerably less significant than that in a. In addition, the effects of temperature dependency in b on the equation of state are not well understood. Therefore, for simplicity, only temperature dependency in a is considered in this work.

In this section, it is shown how experimental data for saturated molar volumes clearly follow a trend, approximated by the relationship $u = -w$. Physical support for this relationship is given. Previous equations of state are discussed with respect to these results.

5.1.1 u and w from Volumetric Data

Pure fluid saturation data, described in §4.1.2, are used to determine u and w values for 97 polar and nonpolar fluids. These values are examined for any systematic relationships. The approach of Yu et al. [148,149] was shown to be quite powerful for the determination of such relationships; it is therefore adopted in this work.

For each substance, values of P^s, v_l^s and v_v^s are available at several temperatures. For given values of u and w, liquid molar volume v_l^s and vapor molar volume v_v^s are calculated as follows.

- Calculate the value of Ω_{ac} from Equation 3.40. The equation is solved directly, using the method described in §3.2.1.
- Calculate Ω_{bc} from Equation 3.41.
- At each temperature T, do the following.
  - Select α to give exact prediction of P^s, using the method given in §3.2.2.
  - Calculate predicted values of Z_l^s and Z_v^s from λ_L and λ_V (obtained in the previous step), using the definition of λ, Equation 3.86.
- Calculate objective function from saturated volumes (see below).

The optimum u and w values for each substance are determined by minimizing Equation 3.101, using residuals in v_l^s and Z_v^s (residuals in Z_v^s are used instead of those in v_l^s, because the latter are strongly heteroscedastic). Three combinations of residuals are considered.

1. Only use the residuals in v_l^s. Thus $\mathbf{Z}$ is an $1 \times N$ matrix with elements $Z_{1j} = [(v_l^s)^{\text{calc}} - v_l^s]_j$.
2. Only use the residuals in Z_v^s. Thus $\mathbf{Z}$ is an $1 \times N$ matrix with elements $Z_{1j} = [(Z_v^s)^{\text{calc}} - Z_v^s]_j$.
3. Use residuals in v_l^s and Z_v^s. Thus $\mathbf{Z}$ is a $2 \times N$ matrix with elements $Z_{1j} = [(v_l^s)^{\text{calc}} - v_l^s]_j$, and $Z_{2j} = [(Z_v^s)^{\text{calc}} - Z_v^s]_j$.

Note that cases 1 and 2 are equivalent to minimizing the sum of squared residuals in v_l^s and Z_v^s respectively. See §3.2.7 for further details of parameter estimation.

Estimation of u and w using residuals in Z_v^s (case 2 and 3) worked poorly. Equation 3.101 had multiple minima, and often a realistic minimum could not be found. The reason for this is clear upon inspection of the denominator of the attractive term in the general equation of state, Equation 2.12. This has the form $v^2 + ubV + wb^2$ (or $Z^2 + uBZ + wB^2$). Clearly, for large v (or Z), the equation of state will be insensitive to u and w. This is the case for the vapor phase, since $v_v^s \gg v_l^s$ except quite near the critical point. Only high precision data has any possibility of yielding meaningful values of u and w. Even if meaningful values could be obtained, this would be of minimal use, since it would have little effect on the vapor phase. Clearly, it is better to fit u and w values to v_l^s alone, in order to obtain the best possible description of the liquid phase. Again, this will have little effect on the vapor phase.

The results for a fit to v_l^s for all substances are summarized in Table 5.1. This gives standard error σ corresponding to the minimum value of Equation 3.101, and the fitted values of u and w with some of their characteristics (95 % confidence intervals, correlations). In all cases, the parameters u and w are significant and well-determined. Only propylene oxide has unusually large confidence intervals for the parameters. Correlations between the parameters are generally moderate.

The deviations in v_l^s for several polar and nonpolar fluids are plotted versus T_r in Figure 5.1. These are typical of the deviations for other substances in this study. The same general behavior is observed for each substance. High positive deviations occur at low T_r (less than 0.6) and at high T_r (greater than 0.95). The later is expected, because a cubic equation of state subjected to the classical critical point conditions cannot simultaneously describe critical region volumes and volumes elsewhere (§2.2.2). In the region $0.6 < T_r < 0.95$, there are moderate negative deviations in v_l^s, with the best predictions occurring near the limits. Over most of the T_r range shown, the absolute deviations in v_l^s are less than 4 %.

There is clearly a consistent trend[1] in the deviations for v_l^s. At T_r away

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[1] This trend indicates that there is some lack of fit of v_l^s for the general cubic equation of state model. Inferences drawn from the model (e.g., confidence regions for the parameters) should therefore be viewed with caution.

from the critical point, this could be reduced by an appropriate temperature dependency in b. However, for most substances, at most values of T_r, deviations in v_l^s are less than 3 %; thus, only a moderate gain in accuracy would be achieved in most cases by the introduction of a temperature-dependency in b. This must be balanced against increased complexity in the equation of state.

Overall deviations in v_l^s and v_v^s are summarized in Table 5.2, in terms of the classes of compounds described in §4.1.2 (more detailed results, for each substance, are given in Table A.1). All classes of substances appear to have similar deviations in v_l^s, close to the overall average of 2.43 %. Both polar and nonpolar fluids give similar overall deviations. The inorganics have the highest deviation, due largely to a poor fit for sulfur trioxide (7.16 %). The halogenated aromatics have the lowest overall deviation (0.76 %).

There is considerably more variation in the overall deviations for v_v^s. The average is 7.82 %, but most classes of substances have lower deviations than this. Ethers, carboxylic acids and sulfur compounds have very high deviations. In the case of the ethers, this is due to a very high deviation for ethyl propyl ether (73.12 %). For the sulfur compounds, this is due to high deviations for mercaptans and to alkyl sulfides. The average is 5.28 % excluding these groups. Alcohols and nitrogen compounds have moderately high deviations. It appears that high deviations in v_v^s are occuring for some polar and hydrogen-bonding fluids. However, this is not a consistent result; for example, water is strongly polar and hydrogen bonding, but does not have a high overall deviation in v_v^s.

The u and w values from Table 5.1 are plotted on Figure 5.2. The plot is repeated in Figure 5.3, but with 95 % confidence intervals for the estimates of u and w. The line $u = -w$ is shown on both plots. The small size of the confidence intervals in most cases confirms that the parameters are well determined. Values far from these result in significantly higher deviations in v_l^s.

It is obvious from Figures 5.2 and 5.3 that the u and w values follow a trend, close to the line $u = -w$. For values of u less than about 2.5, the u and w values are slightly above this line. These correspond mostly (but not exclusively) to nonpolar fluids with low acentric factors, such as methane, noble gases and freons. Most substances have u values between 2.5 and 4, and are somewhat below the line $u = -w$. The confidence intervals overlap this line in many cases. A few substances have u values greater than 4.

These are all highly polar and/or associating fluids, such as water, acetone, acetonitrile and alcohols. The u and w values are significantly below the line $u = -w$ for $4 < u < 5$, and are closer to this line for higher u values.

5.1.2 Physical Justification

The fit to saturated molar volumes clearly indicates that a relationship between u and w, close to $u = -w$, is followed. This is an empirical result, but there is physical justification for it, which is discussed here.

Figure 5.4 is a plot of w versus u, showing the $u = -w$ relationship along with loci of constant β_c. The loci of constant β_c are obtained from Equation 3.48. It is obvious that the $u = -w$ relationship corresponds closely to a locus of constant β_c (near $\beta_c = 0.30$).

Physically, β_c is the ratio of critical covolume b_c to critical molar volume v_c (Equation 3.42). The covolume is related to the molecular radius σ.

$$b = \frac{2\pi}{3} N_a \sigma^3 \tag{5.1}$$

Therefore, β_c can be written as follows

$$\begin{aligned} \beta_c &= \frac{2\pi}{3} \frac{N_a \sigma^3}{v_c} \\ &= \frac{2\pi}{3} \frac{1}{v_c^*} \end{aligned} \tag{5.2}$$

where v_c^* is the critical point value of the dimensionless volume v^* from microscopic corresponding-states theory (Equation 2.33). Therefore, β_c, a quantity arising from application of the macroscopic corresponding-states principle to cubic equations of state, is simply related to v_c^*, a quantity from the microscopic corresponding-states principle.

Corresponding-states theory is discussed in §2.3. The vapor-liquid critical point is unique for a given substance; in terms of corresponding-states theory, the critical points of substances with the same dimensionless properties must be given by the same, constant values of the dimensionless groups corresponding to temperature, pressure and volume. Therefore, for given values of l^* and μ^*, the values of T_c^*, P_c^* and v_c^* must be constant. For example, all spherical, nonpolar fluids (i.e., $l^* = 0$ and $\mu^* = 0$) should have the same values of T_c^*, P_c^* and v_c^*. The variation in these quantities with l^* and

μ^* has been studied. Rowlinson [106] found that the variation with μ^* is not large. In particular, the variation in v_c^* is over a range of approximately $\pm 50\,\%$, and is considerably less than this for most substances. Calculations by Reed and Gubbins [100] for a limited number of polar fluids, using a corresponding-states theory for polar fluids, determined that deviations in these quantities due to l^* are not large; in the case of v_c^*, the variation is over a range of approximately $\pm 15\,\%$.

Therefore, v_c^* is expected to vary over a range of no more than $\pm 50\,\%$, and considerably less than this for most substances. From Equation 5.2, β_c is expected to vary over a similar range. Comparison of Figures 5.2 and 5.4 shows that ***this is the result obtained empirically in** §5.1.1.* The fitted values of u and w are approximately bounded by $\beta_c = 0.25$ and $\beta_c = 0.50$, corresponding to a variation of about $\pm 30\,\%$. Most substances are represented by a much narrower range of β_c values, $0.3 < \beta_c < 0.4$.

Calculated and experimental v_c^* values, from potential models such as the Lennard-Jones potential, are widely reported in the literature. These generally fall in the range corresponding to $0.6 < \beta_c < 1$, which is somewhat higher than that found above. Part of this deviation is probably due to the different natures of the diameters from the van der Waals model and from potential functions; for potential functions, σ represents a point of zero potential values, but for the van der Waals model it represents the radius of a hard sphere. Most of the deviation is probably due to the approximate nature of the van der Waals model.

It is therefore clear that the fitted u and w values follow a trend, close to $u = -w$, because of underlying physical reasons. A cubic equation of state following this relationship would therefore be somewhat justified on physical grounds. This is an important point, because few, if any, cubic equations of state since van der Waals have had physical justification for the form of the attractive term.

5.1.3 Comparison to Previous Equations

For good description of volumetric properties, a cubic equation of state should have u and w values close to the optimum for the substance in question. The u and w values for several equations of state are shown in Figure 2.1. These can be compared with the optimum values shown in Figure 5.2 and 5.3.

Consider the equations of state with fixed values of u and w, namely the van der Waals equation, the Redlich-Kwong and related equations (such as Soave's modification), and the Peng-Robinson equation. The van der Waals equation is well known to give poor volumetric performance. This is clearly because it has $u = w = 0$, which is far from optimum values for the substances considered here. The Redlich-Kwong and related equations (such as Soave's modification) give somewhat improved volumetric performance, but nevertheless overpredict volumes significantly (e.g., see [129,148]); the values of $u = 1$ and $w = 0$ are still far from those of most substances. The Peng-Robinson equation gives better volumetric results, especially for low molecular weight, nonpolar fluids (e.g., see [129,148]); this is explained by its values of $u = 2$ and $w = -1$, which are close to those of such substances. However, most substances have optimum u and w far from the Peng-Robinson values. A better choice of fixed u and w for the description of a wider variety of substances would appear to be near $u = 3$ and $w = -3$, which would be near the optimum values for a large number of substances. However, no such equation has been proposed to date.

Several workers have attempted to improve the above equations by the technique of volume translation (§2.2.4). For translated equations, u and w are variable, but are quadratically related. The loci for such equations are shown in Figure 2.1. Comparison with Figure 5.2 and 5.3 shows that volume translation does not result in the best values of u and w for volumetric performance for most substances. This is particularly true for polar fluids, whose optimum u and w values are far from the loci of the translated equations of state. Comparison with Figure 5.4 shows that translated equations do not follow loci of constant β_c; this is not physically realistic (§5.1.2).

The Schmidt-Wenzel and related equations of state (such as the Patel-Teja and Toghiani-Viswanath equations) follow the line $u = 1 - w$. This has two advantages: it is closer to the optimum values of u and w for most substances than the equations discussed above; it approximates a locus of constant β_c, which is physically realistic. Nevertheless, the locus followed by these equations is significantly displaced from the trend followed by the optimum values of u and w.

Trebble and Bishnoi attempted to improve the Schmidt-Wenzel approach by introducing a new parameter d, such that $u_c = 1 - w_c - d/b_c^2$ (Trebble and Bishnoi have temperature-dependent b, u and w, so critical-point values are shown here). This is equivalent to having effective values of u and w that are independently variable. Figure 5.5 shows the u and w values at the critical point for the Trebble-Bishnoi equation of state, for the same substances listed in Table 5.1. These are calculated by determining Ω_{ac} and Ω_{bc} values from the equations in §4.2, and then applying the equations of 3.1.3. Clearly, there is a strong tendency to follow the line $u = -w$, i.e., the extra parameter d is effectively given by $d = b_c^2$. Trebble and Bishnoi generalized the constants in their equation by fitting to saturated pressure and volume data, and to single phase volumetric data. It is therefore not surprising that their equation of state exhibits this relationship.

The Sugie-Iwahori-Lu equation also has independently variable u and w. In Figure 5.6, values of u and w from this equation are plotted (calculated as above for the Trebble-Bishnoi equation). Clearly, these follow the same trend as above. Again, the relationship appears to be well represented by $u = -w$. This is not surprising, since the equation is designed for good description of v_l^s, and its constants are directly determined from v_l^s data.

Obviously, both of the previous equations could have been formulated with $u = -w$, without substantially changing their performance. The determination of their constants would then have been considerably simplified.

Table 5.1: Results for the estimation of u and w from v_l^s data. The standard error σ is shown for each substance. The values of u and w, their 95 % confidence intervals, and the correlation between them (r_{uw}) are also shown.

substance	σ gmol/mL	u	w	r_{uw}
argon	0.8306	2.29 ± 0.07	−2.70 ± 0.12	−0.959
chlorine	1.8939	2.41 ± 0.11	−2.56 ± 0.20	−0.931
fluorine	0.6629	2.40 ± 0.11	−2.91 ± 0.19	−0.952
helium	0.1591	1.90 ± 0.02	−2.69 ± 0.03	−0.994
hydrogen chloride	2.0576	3.48 ± 0.33	−3.98 ± 0.51	−0.941
hydrogen	0.6136	1.97 ± 0.10	−2.56 ± 0.15	−0.973
water	0.7575	5.10 ± 0.04	−5.31 ± 0.06	−0.842
hydrogen sulfide	2.2678	2.78 ± 0.22	−3.29 ± 0.35	−0.957
ammonia	0.7838	3.72 ± 0.12	−3.63 ± 0.25	−0.869
krypton	1.0437	2.36 ± 0.09	−2.75 ± 0.16	−0.956
nitrogen	1.3732	2.40 ± 0.10	−2.80 ± 0.17	−0.960
neon	0.1905	1.43 ± 0.06	−1.65 ± 0.13	−0.969
oxygen	1.1220	2.25 ± 0.12	−2.47 ± 0.20	−0.977
sulfur dioxide	5.0131	3.50 ± 0.28	−4.13 ± 0.39	−0.933
sulfur trioxide	2.7543	3.39 ± 0.31	−3.76 ± 0.56	−0.926
xenon	1.3098	2.47 ± 0.07	−2.89 ± 0.13	−0.957
phosgene	2.6812	2.72 ± 0.17	−3.19 ± 0.28	−0.951
carbon tetrachloride	5.5156	3.29 ± 0.21	−3.89 ± 0.32	−0.955
carbon tetrafluoride	2.2981	2.44 ± 0.11	−2.54 ± 0.17	−0.735
carbon monoxide	0.4895	1.93 ± 0.07	−1.96 ± 0.15	−0.957
carbon dioxide	1.0797	2.96 ± 0.07	−3.53 ± 0.11	−0.918
chloroform	2.5355	2.96 ± 0.33	−3.35 ± 0.58	−0.974
freon-13	1.9211	2.59 ± 0.08	−2.86 ± 0.14	−0.954
freon-12	2.3999	2.54 ± 0.09	−2.74 ± 0.17	−0.970
freon-11	0.8278	1.84 ± 0.07	−1.29 ± 0.16	−0.991
freon-22	2.4591	3.07 ± 0.08	−3.39 ± 0.14	−0.907
freon-21	3.0017	2.88 ± 0.08	−3.11 ± 0.14	−0.948
methyl chloride	0.2424	2.04 ± 0.08	−1.22 ± 0.19	−0.993
methane	1.2337	2.37 ± 0.10	−2.71 ± 0.17	−0.959
methanol	1.3372	4.94 ± 0.13	−5.38 ± 0.20	−0.896
methyl mercaptan	1.5450	2.91 ± 0.14	−3.26 ± 0.24	−0.947

Table 5.1: Results for the estimation of u and w from v_l^s data (continued).

substance	σ gmol/mL	u	w	r_{uw}
freon-114	0.5154	1.98 ± 0.09	-1.49 ± 0.20	−0.995
freon-113	0.3105	1.53 ± 0.04	-0.51 ± 0.10	−0.993
acetylene	1.4474	2.98 ± 0.15	-3.39 ± 0.26	−0.948
acetonitrile	3.4841	8.07 ± 0.42	-8.18 ± 0.49	−0.762
ethylene	2.4924	2.84 ± 0.10	-3.33 ± 0.16	−0.947
ethylene oxide	1.7276	3.58 ± 0.37	-3.87 ± 0.67	−0.961
acetic acid	2.8237	5.59 ± 0.21	-5.68 ± 0.36	−0.918
methyl formate	2.4685	3.62 ± 0.17	-4.06 ± 0.29	−0.928
ethyl chloride	2.0559	3.09 ± 0.15	-3.43 ± 0.26	−0.940
ethane	2.6308	2.89 ± 0.16	-3.33 ± 0.26	−0.954
dimethyl ether	2.3908	3.21 ± 0.14	-3.73 ± 0.23	−0.921
ethanol	4.8831	4.72 ± 0.36	-5.49 ± 0.44	−0.975
ethyl mercaptan	3.2259	3.14 ± 0.19	-3.63 ± 0.32	−0.953
dimethyl sulfide	2.3598	3.09 ± 0.16	-3.46 ± 0.29	−0.954
propyne	2.2837	2.95 ± 0.10	-3.54 ± 0.12	−0.562
propylene	1.8123	2.22 ± 0.13	-2.02 ± 0.26	−0.970
acetone	4.4580	4.51 ± 0.25	-5.06 ± 0.37	−0.932
propylene oxide	7.1861	3.38 ± 0.98	-3.04 ± 2.50	−0.909
ethyl formate	2.9458	3.54 ± 0.14	-3.98 ± 0.23	−0.916
methyl acetate	3.4661	3.70 ± 0.18	-4.15 ± 0.30	−0.930
cyclopropane	1.7146	3.15 ± 0.10	-3.76 ± 0.17	−0.939
propane	1.3693	2.57 ± 0.06	-2.81 ± 0.11	−0.937
1-propanol	2.4029	3.54 ± 0.14	-3.92 ± 0.24	−0.936
2-propanol	3.9182	4.14 ± 0.38	-4.76 ± 0.56	−0.962
methyl ethyl ether	3.5155	3.29 ± 0.21	-3.87 ± 0.32	−0.959
perfluorocyclobutane	3.2788	2.78 ± 0.09	-3.11 ± 0.14	−0.963
1,2-butadiene	1.6566	2.83 ± 0.29	-3.00 ± 0.57	−0.980
1,3-butadiene	2.4808	2.80 ± 0.03	-3.00 ± 0.08	−0.586
1-butene	2.2503	2.68 ± 0.11	-3.01 ± 0.21	−0.954
ethyl acetate	3.8717	3.71 ± 0.16	-4.16 ± 0.26	−0.920
methyl propionate	4.0117	3.61 ± 0.14	-4.09 ± 0.22	−0.907
n-propyl formate	4.0744	3.47 ± 0.17	-3.93 ± 0.29	−0.935
n-butane	3.9456	2.86 ± 0.15	-3.19 ± 0.28	−0.934
isobutane	0.8926	2.03 ± 0.03	-1.63 ± 0.08	−0.927

Table 5.1: Results for the estimation of u and w from v_l^s data (continued).

substance	σ gmol/mL	u	w	r_{uw}
1-butanol	2.7874	2.79 ± 0.17	−2.94 ± 0.35	−0.902
t-butanol	1.7959	3.05 ± 0.20	−3.27 ± 0.39	−0.966
diethyl ether	3.1889	3.18 ± 0.13	−3.61 ± 0.22	−0.918
diethyl sulfide	4.0111	1.00 ± 0.13	−1.42 ± 0.23	−0.981
diethyl amine	2.5796	3.19 ± 0.11	−3.54 ± 0.20	−0.921
n-propyl acetate	6.4234	3.91 ± 0.19	−4.49 ± 0.28	−0.924
ethyl propionate	4.9430	3.61 ± 0.15	−4.06 ± 0.24	−0.908
methyl butyrate	4.9795	3.57 ± 0.14	−4.08 ± 0.23	−0.909
methyl isobutyrate	4.9692	3.48 ± 0.16	−3.98 ± 0.25	−0.921
n-pentane	3.1623	2.69 ± 0.11	−2.78 ± 0.24	−0.935
isopentane	3.8090	2.93 ± 0.16	−3.16 ± 0.28	−0.968
neopentane	2.1741	2.52 ± 0.20	−2.76 ± 0.40	−0.970
ethyl propyl ether	2.6687	2.50 ± 0.12	−2.72 ± 0.24	−0.951
bromobenzene	0.2595	2.43 ± 0.07	−1.99 ± 0.15	−0.995
chlorobenzene	0.4964	2.51 ± 0.08	−2.27 ± 0.18	−0.991
fluorobenzene	3.4434	3.20 ± 0.15	−3.66 ± 0.26	−0.945
iodobenzene	0.1470	2.23 ± 0.07	−1.60 ± 0.17	−0.998
benzene	5.0171	3.12 ± 0.15	−3.55 ± 0.25	−0.951
aniline	2.8636	2.96 ± 0.25	−3.18 ± 0.49	−0.949
cyclohexane	3.2573	2.85 ± 0.14	−3.31 ± 0.26	−0.948
n-hexane	6.4801	2.43 ± 0.18	−1.90 ± 0.45	−0.919
toluene	4.2108	3.31 ± 0.28	−3.77 ± 0.47	−0.949
n-heptane	4.3186	3.28 ± 0.13	−3.53 ± 0.23	−0.963
n-octane	12.2737	2.28 ± 0.36	−0.98 ± 1.07	−0.905
isooctane	9.3591	3.02 ± 0.21	−3.37 ± 0.35	−0.946
m-xylene	2.3197	2.83 ± 0.13	−2.77 ± 0.29	−0.895
o-xylene	3.1168	2.96 ± 0.22	−3.15 ± 0.44	−0.953
p-xylene	5.8571	3.48 ± 0.31	−3.94 ± 0.51	−0.936
ethyl benzene	6.6653	3.47 ± 0.27	−4.05 ± 0.41	−0.932
naphthalene	0.3170	3.48 ± 0.09	−3.71 ± 0.16	−0.998
n-decane	5.4501	3.54 ± 0.21	−3.77 ± 0.43	−0.926
diphenyl ether	0.7762	2.67 ± 0.15	−2.20 ± 0.36	−0.996

Table 5.2: Overall deviations in v_l^s and v_v^s from the estimation of u and w values from v_l^s data. The entries in the table are averages of %RMS deviations for the substances in the indicated group.

group	v_l^s	v_v^s
noble gases	1.58	3.82
diatomics	2.61	3.95
inorganics	4.16	6.39
paraffins	2.42	3.85
olefins	2.39	4.50
acetylenes	2.19	4.95
naphthenes	1.96	6.92
aromatics	2.18	7.18
ethers	1.97	24.48
alcohols	2.73	9.57
carboxylic acids	3.62	59.37
esters and ketones	2.95	6.12
nitrogen compounds	2.70	8.00
sulfur compounds	2.28	29.32
oxides	2.87	4.72
halogenated paraffins	2.07	4.34
halogenated naphthenes	2.20	3.80
halogenated aromatics	0.76	2.13
overall	2.43	7.82

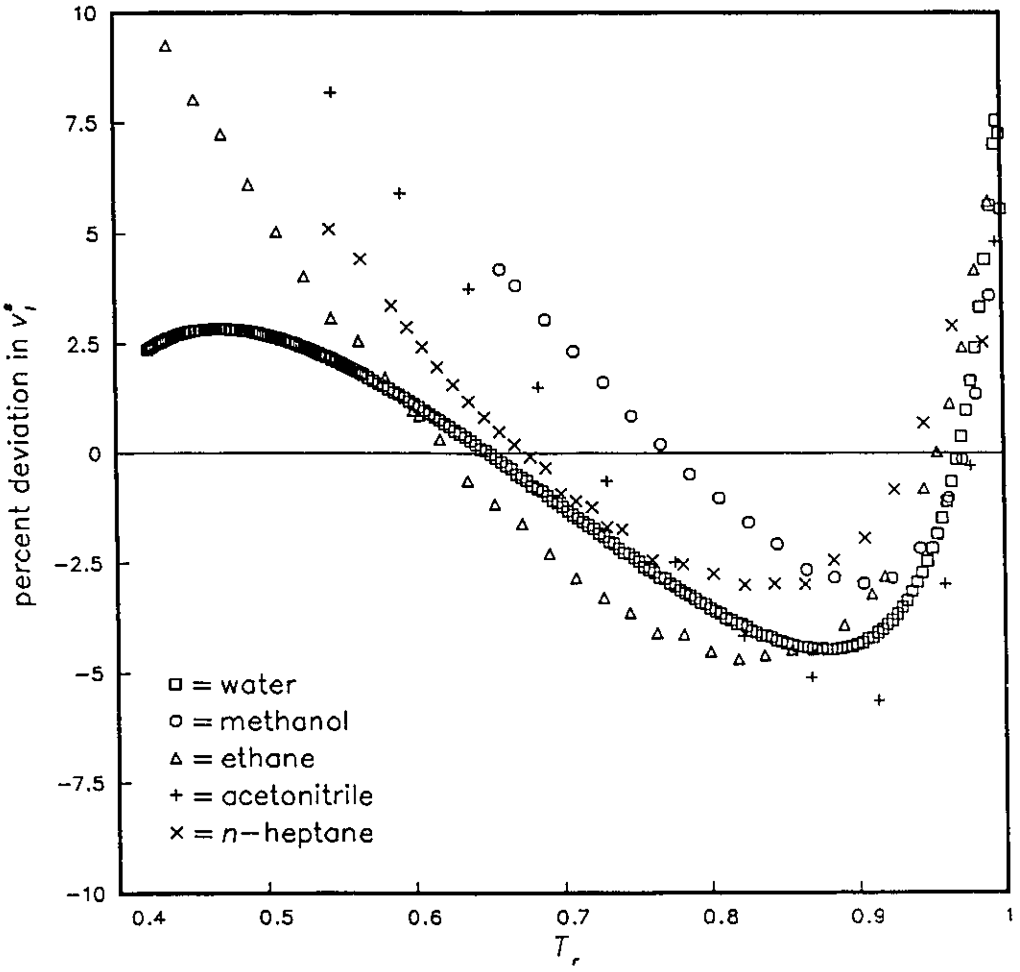

Figure 5.1: Deviations in v_l^s from the estimation of u and w, for selected polar and nonpolar fluids.

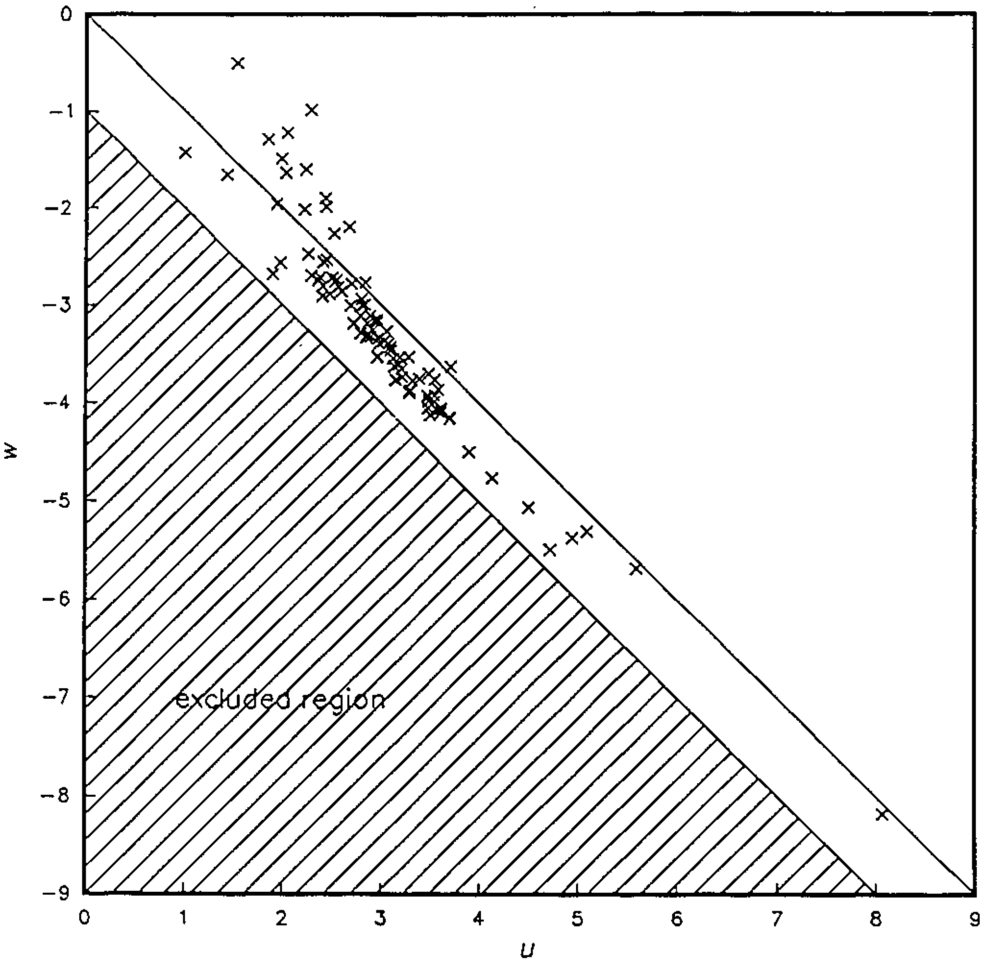

Figure 5.2: u and w values estimated from a fit to v_l^s data, from Table 5.1.

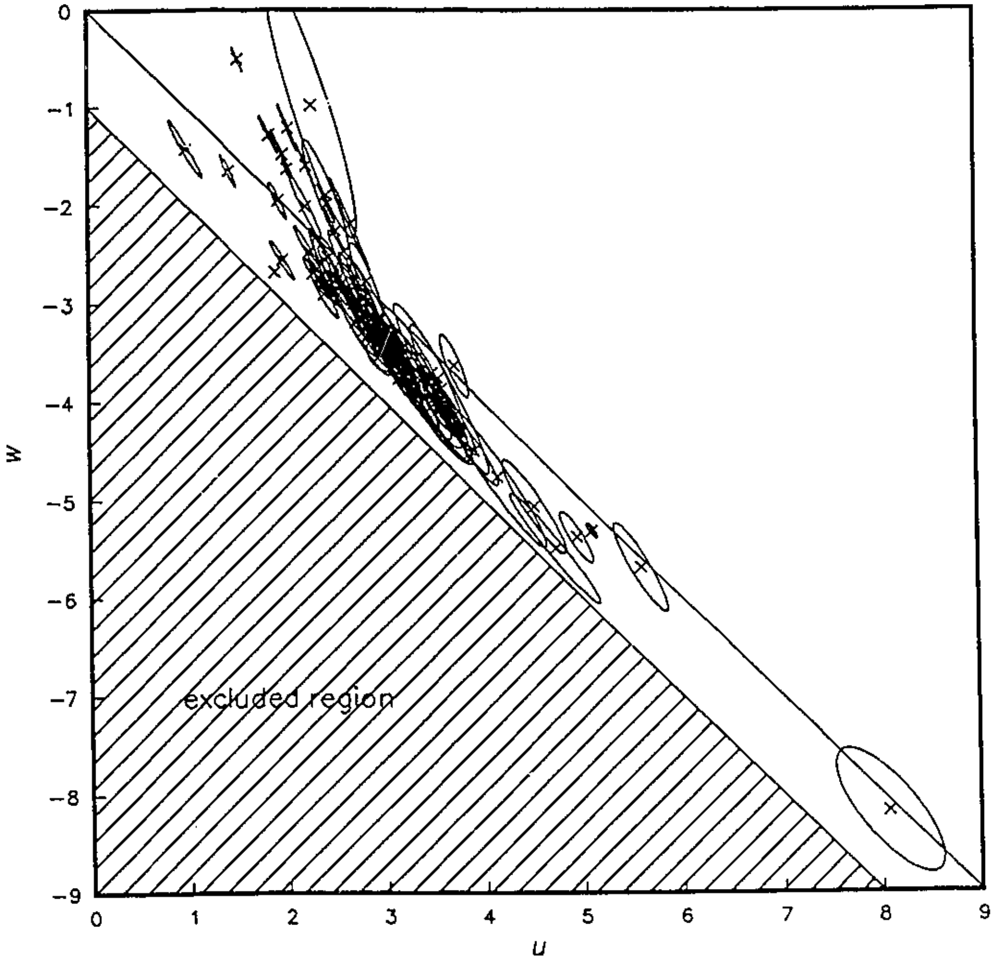

Figure 5.3: 95 % confidence regions for u and w values estimated from a fit to v_l^s data. Points denote estimated values of u and w, from Table 5.1.

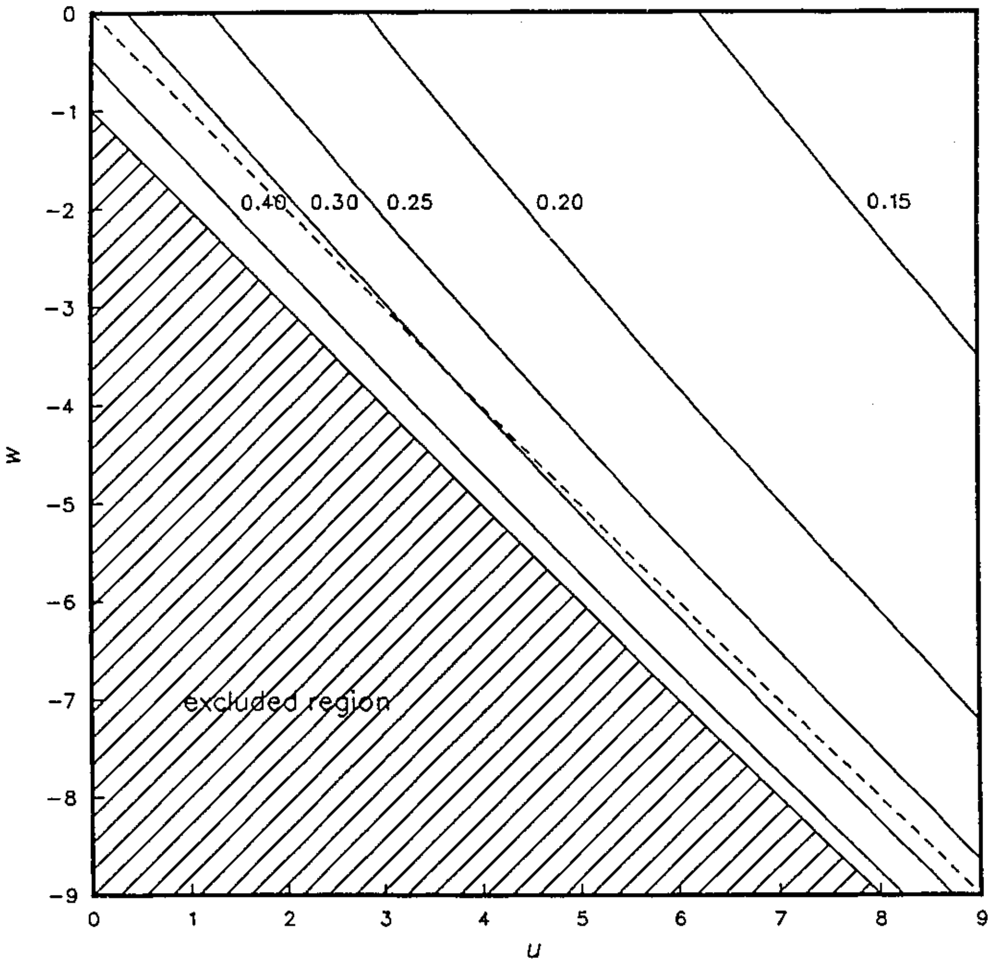

Figure 5.4: Loci of constant β_c on a plot of w versus u. The locus $u = -w$ is also shown, as a dashed line.

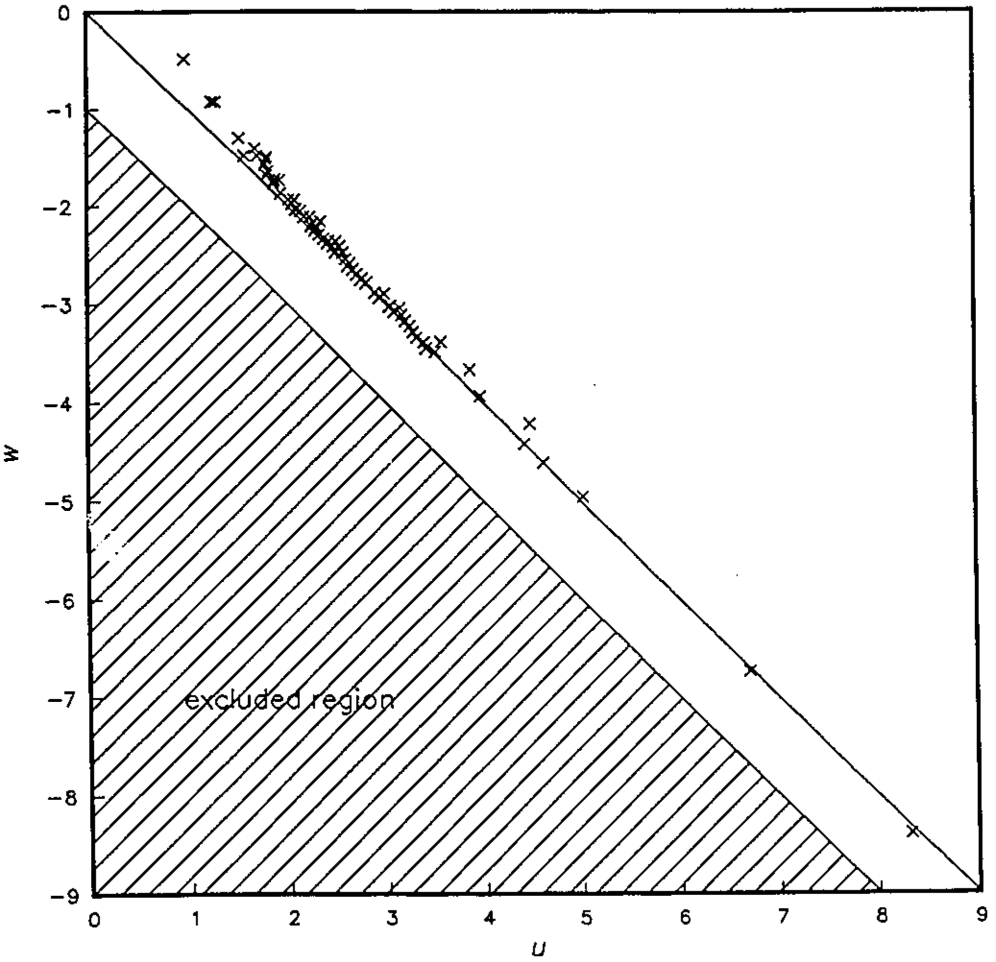

Figure 5.5: u and w values from the Trebble-Bishnoi equation, evaluated at the critical point. Calculated for the same substances as in Table 5.1.

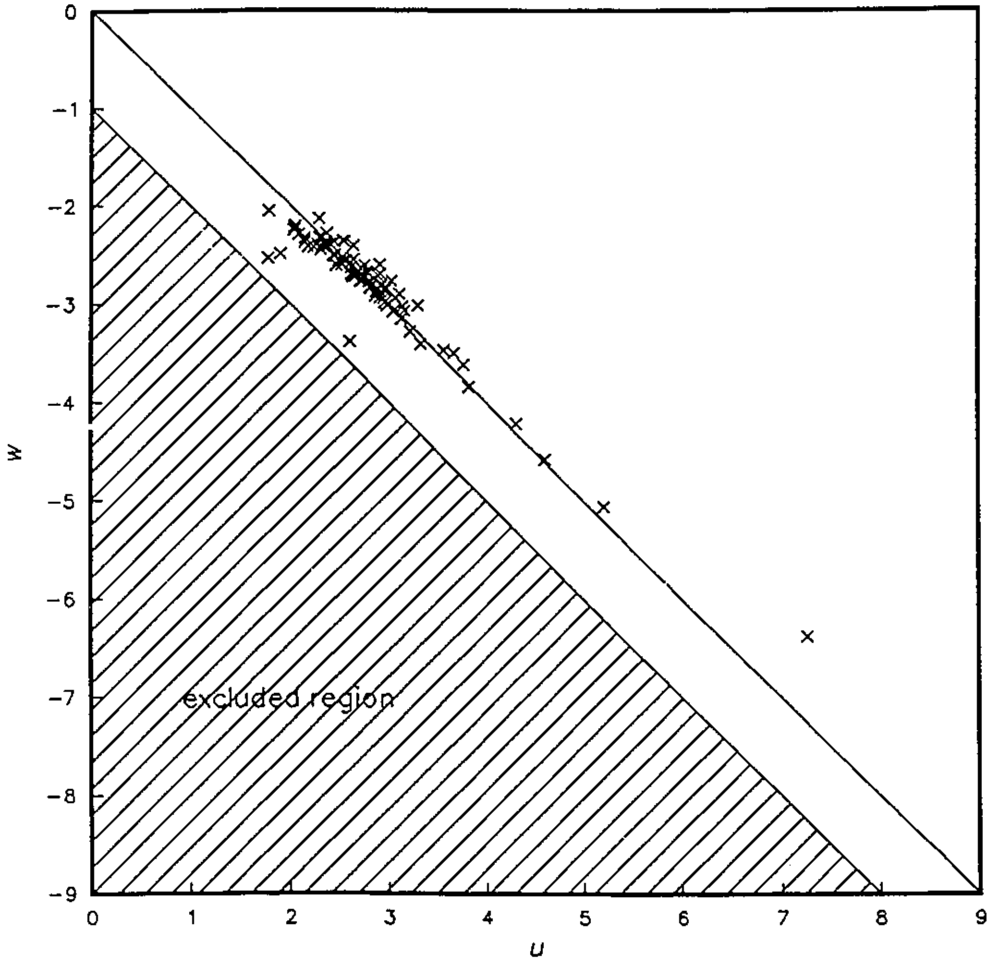

Figure 5.6: u and w values from the Sugie-Iwahori-Lu equation. Calculated for the same substances as in Table 5.1.

5.2 New Equation of State

Based on the previous discussion, the relationship $u = -w$ is fundamentally important, and is selected for a new equation of state. The new equation is expected to be very good at predicting volumetric properites.

In §5.1, only temperature dependency in the attractive parameter a is considered. However, as pointed out in §5.1.1, an appropriate temperature dependency in b could result in small improvements in volumetric performance. The incorporation of such a temperature dependency would clearly increase the complexity of the equation of state. In addition, an appropriate form for the temperature dependency is not clear, and the effects of it on other aspects of equation of state performance are not well understood. Therefore, only temperature dependency in a is considered in the new equation of state.

The new equation of state has the following form.

$$P = \frac{RT}{v-b} - \frac{a_c\alpha}{v^2+ubv-ub^2} \tag{5.3}$$

Only one quantity at the critical point needs to be determined. In addition, the temperature dependency α must be specified. Three versions of Equation 5.3 are presented below, based on three different methods of determining α and the quantity at the critical point. The methods are formulated to give values of Ω_{ac}, Ω_{bc} and α for a given substance at a given temperature, so that they can be used directly in the procedures described in §3.2. FORTRAN programs which calculate the constants for the different versions of the new equation of state are given in §B.

5.2.1 Generalized Constants

From §2.3, it is clear that at least a four-parameter corresponding-states principle is required to describe fluids of polar, nonspherical molecules. Most equations of state have used a three-parameter corresponding-states principle (T_c, P_c and ω), and have thus had limited success in describing polar fluids.

The author and coworkers have previously presented a generalized equation of state for polar fluids, based on Equation 5.3, which uses Z_c as a fourth corresponding-states parameter (Iwai et al. [64,65]). The development of correlations for the equation of state constants is briefly described below[2].

Optimum values of u were obtained from least squares fitting of v_l^s, using the same procedure as in 5.1.1, but with $u = -w$. Comparison with Z_c for several polar and nonpolar fluids showed a clear relationship. An empirical relationship between the two was determined by least squares fitting.

$$u = \frac{0.333}{Z_c^2} - 1.95 \tag{5.4}$$

The value of Ω_{ac} is obtained by solving Equation 3.40. The value of Ω_{bc} follows from Equation 3.56. A less direct but equivalent procedure was given in the original papers.

The fitting of u values described above gave α values at each data point as secondary quantities. A corresponding-states correlation for α was developed by fitting these values. A variation of the Soave expression was used. For $T_r \geq 0.7$,

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 / T_r^{0.4} \tag{5.5}$$

and for $T_r < 0.7$,

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 / (0.57667 T_r^{0.8} + 0.43352) \tag{5.6}$$

where m is given by

$$m = -0.25\omega^2 + 1.31\omega - 0.209/Z_c + 0.5275 \tag{5.7}$$

The two expressions for α give identical α and $d\alpha/dT_r$ values at $T_r = 0.7$.

It should be noted that these correlations were developed using much less extensive data than used in this work, and that different property values were used in many cases.

5.2.2 Constants from Property Correlations

Generalized correlations have several drawbacks[3]. Generalized correlations are mostly empirical; hence, they do not extrapolate well outside the range

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[2] The generalization procedure is not given in full because it was not performed by the author.

[3] Some good examples of the points made here are given in §6.1.

of values used in their generation. The constants in the correlations are usually determined from fitting to pure fluid data; if this data is inaccurate, or if the properties originally used are inaccurate, this will be reflected in the correlation. For best accuracy, the original properties used to generate the correlation should be used [102]. This is clearly inconvenient, and does not make best use of available information.

Sugie et al. [125] proposed an alternative approach: instead of generalizing equation of state constants by the fitting of pure component properties, they calculated the constants directly from accurate pure fluid property correlations. There are some disadvantages: the constants for the property correlations must be retained; the equation of state constants must be calculated iteratively. However, there are two major advantages: generalization of the equation of state constants and the associated problems are avoided; the constants are very accurately determined. An extension of the approach of Sugie et al. is therefore used here.

The value of α is determined from vapor pressure using the iterative procedure presented in §3.2.2. This method obviously cannot be used in the supercritical region. For this region, the expression of Soave (Equation 2.24) is used. The coefficient m is obtained from the α value at $T_r = 0.9$.

Sugie et al. determined Ω_{ac} and Ω_{bc} for the Sugie-Iwahori-Lu equation by requiring exact prediction of v_l^s values at $T_r = 0.7$ and $T_r = 0.9$. For the new equation, only Ω_{ac} needs to be determined, since Ω_{bc} can be calculated from Ω_{ac} using Equation 3.56. The value of Ω_{ac} is determined here by requiring exact prediction of saturated liquid molar volume *at all temperatures*. Ω_{ac} is now a function of temperature. From Equation 3.86, the following equation can be written.

$$Z_l^s - \Omega_{bc}(P_r^s/T_r) = \lambda_L \tag{5.8}$$

The value of Ω_{ac} is chosen to satisfy this equation at the given temperature, vapor pressure and saturated liquid compressibility factor. Note that this is an iterative procedure.

In the region $0.9 < T_r < 1.0$ this method gives excessive deviations for compressed liquid molar volume. This is because of an inherent limitation of cubic equations of state: they cannot describe the critical region and compressed regions simultaneously (see §2.2.2). Therefore, the Ω_{ac} value calculated at $T_r = 0.9$ is used for all $T_r > 0.9$. Note that this also defines

Ω_{ac} values for the supercritical region, which cannot be obtained from the above method.

The complete procedure for the determination of constants in Equation 5.3 from pure fluid property correlations is given here. It is assumed that values of $P_r^s(T_r)$ and $Z_l^s(T_r)$ are available from correlations. The P^s and v_l^s correlations used for all substances in this study are given in Table 4.1, and are described in §4.1.1.

- Specify T_r and P_r for which constants are required.
- Obtain appropriate values of P_r^s and Z_l^s.
    - If $T_r < 0.9$, obtain $P_r^s(T_r)$ and $Z_l^s(T_r)$.
    - If $0.9 \leq T_r \leq 1$, obtain $P_r^s(T_r)$, $P_r^s(0.9)$ and $Z_l^s(0.9)$.
    - If $T_r > 1$, obtain $P_r^s(0.9)$ and $Z_l^s(0.9)$.
- Assume initial value(s) of Ω_{ac}. Almost all substances have $0.421875 < \Omega_{ac} <\approx 0.7$ for this equation of state.
- Determine the actual value of Ω_{ac} iteratively, so as to satisfy Equation 5.8. The procedure for solving Equation 5.8 is as follows.
    1. $T_r < 0.9$.
        - Calculate f, g, and h from Equations 3.29–3.31
        - Calculate Ω_{bc} from Equation 3.56.
        - Use the procedure of §3.2.2 to obtain α. This will also give the value of λ_L.
        - Check Equation 5.8.
    2. $T_r \geq 0.9$. Do the same as above, but at $T_r = 0.9$.
- Calculate α.
    - $T_r \leq 0.9$. α is already available from above.
    - $0.9 < T_r \leq 1.0$. Solve for α as above, but with of §3.2.2.
    - $T_r > 1.0$. α at $T_r = 0.9$ is already available from above. Solve Equation 2.24 to obtain m, then apply it using the actual value of T_r.

Equation 5.8 was solved for Ω_{ac} using Brent's algorithm, as presented by Press et al. [96]. This combines bisection and false position to obtain rapid and robust determination of roots. It required about 5 iterations to converge to a high degree of accuracy.

If calculations are being made at several different temperatures, the entire procedure must be repeated at each temperature. However, for isothermal calculations, the critical constants and α do not have to be recalculated. Therefore, the iterative portion of the procedure need only be done once at each temperature for each substance.

5.2.3 Constants from Selected Properties

The method of §5.2.2 is potentially a very accurate and reliable way of determining the constants of Equation 5.3. However, the calculation is involved. Also, many constants (for the property correlations) must be retained. A simplified approach, which uses pure fluid properties at selected temperatures, is developed in this section.

Sugie et al. [125] used v_l^s data at $T_r = 0.7$ and $T_r = 0.9$ to determine Ω_{ac} and Ω_{bc} for the Sugie-Iwahori-Lu equation. This equation has already been noted to be close to having a $u = -w$ relationship (§5.1.3). If this relationship is imposed, only one critical point parameter needs to be determined. Therefore, it should be possible to fix accurately the value of Ω_{ac} from a single v_l^s value near $T_r = 0.7$ or $T_r = 0.9$, using a procedure similar to that in §5.2.2. This is confirmed by the plot of deviations in v_l^s versus T_r in Figure 5.1, which shows that deviations are close to zero near these values of T_r.

In order to determine the appropriate temperature at which v_l^s should be fixed, overall deviations in v_l^s are calculated using the pure fluid saturated data described in 4.1.2. The Ω_{ac} and Ω_{bc} values are determined as in §5.2.2, but at a single reduced temperature; they are thus constant for a given substance. At a given temperature, α (and thus λ_L) is determined from vapor pressure as before; predicted v_l^s values are then obtained using equation 5.8. The results are summarized in Table 5.3. As expected the best results occur when the constants are calculated using v_l^s at $T_r = 0.7$ and at $T_r = 0.9$, with slightly better results at $T_r = 0.9$. However, v_l^s values at elevated T_r are often difficult to obtain accurately. The reference temperature is therefore at $T_r = 0.7$, where values of v_l^s are more accessible.

Note that only the acetylenes and the sulfides give unusually high deviations in v_l^s. In the formei case, this is due entirely to propyne, while in the later case it is due entirely to diethyl sulfide. This is because the v_l^s data for these substances are not well described by the v_l^s correlation used here (see §6.1).

The next step is to find a method of reliably determining α without calculating it from vapor pressure at each temperature. As discussed in §2.2.3, Soave [118] determined the coefficient m in his α expression directly from vapor pressure at a fixed temperature (i.e., from acentric factor, which corresponds to vapor pressure at $T_r = 0.7$). Soave's approach is followed, i.e., an α correlation with a coefficient determined from vapor pressure at a fixed reduced temperature is considered. Two correlations are considered, Soave's (Equation 2.24), and Heyen's (Equation 2.25, with $n = 1$). The values of m are determined from $\alpha(0.7)$ calculated from acentric factor using the method outlined in 3.2.2. Unfortunately, neither correlation gave consistently good results for all substances; in fact, neither gave as good results for P^s as the Peng-Robinson equation of state.

The reason for the above behavior was explained by Adachi et al. [12]. As discussed in §2.2.3, they showed that the Soave and Heyen ($n = 1$) correlations have optimum performance for equations of state with $\Omega_{ac} \approx 0.45$ and $\Omega_{ac} \approx 0.42$ respectively, and that their performance deteriorates rapidly for Ω_{ac} different from these values. Since the equations considered here can have values significantly different from these (depending on the substance), it is obvious why they cannot have consistent performance for all substances with these α correlations.

Therefore, the full form of Heyen's equation (with variable n) is adopted (another possible choice is Stryjek and Vera's modification of Soave's function [121,123]). There are now two constants, m and n, to be determined. In order to avoid the use of generalized correlations, m and n are determined from P^s at $T_r = 0.6$ and $T_r = 0.7$. These correspond to Halm and Stiel's polar factor and to Pitzer's acentric factor respectively, two well-known, easily accessible quantities. Also, the choice of a low temperature fixed point (at $T_r = 0.6$) should lead to improved extrapolation to low temperatures, a common area of failure.

A modification is made to Equation 2.25 in order to simplify the calcu-

Table 5.3: Overall deviations in v_l^s for different choices of reference T_r. The entries in the table are averages of %RMS deviations for the substances in the indicated group.

group	T_r				
	0.60	0.65	0.70	0.75	0.90
noble gases	3.93	3.87	3.91	3.99	4.68
diatomics	3.80	3.69	3.67	3.65	3.40
inorganics	5.77	5.48	5.39	5.47	5.17
paraffins	3.23	2.99	3.19	3.57	3.27
olefins	3.17	2.96	3.01	3.26	2.85
acetylenes	14.24	14.05	13.81	13.35	7.80
naphthenes	2.89	2.81	3.14	3.57	3.44
aromatics	3.88	3.06	2.60	2.56	2.57
ethers	5.09	4.45	4.04	3.79	3.43
alcohols	5.41	4.86	4.77	5.17	5.32
carboxylic acids	4.04	3.70	4.04	4.71	4.75
esters and ketones	4.01	3.80	4.08	4.59	4.44
nitrogen compounds	4.48	3.52	3.23	3.61	4.43
sulfur compounds	9.39	9.34	9.44	9.57	9.12
oxides	3.86	3.53	3.58	3.78	3.53
halogenated paraffins	2.88	2.68	2.88	3.19	2.79
halogenated naphthenes	6.86	5.59	4.51	3.68	3.43
halogenated aromatics	2.71	1.77	1.51	1.82	1.45
overall	4.33	3.98	3.98	4.20	3.93

lation of the constants. A power series expansion of the term T_r^n gives

$$T_r^n = 1 + n\ln T_r + (n\ln T_r)^2 + \cdots \tag{5.9}$$

Truncating after the second term, substituting into Equation 2.25 and redefining the constants gives a new functional form for α.

$$\alpha = T_r^{m(1+n\ln T_r)} \tag{5.10}$$

This expression gives nearly identical results to Equation 2.25[4].

The procedure to calculate m and n is as follows. First, the values $\alpha(0.6)$ and $\alpha(0.7)$ are determined from P^s using the method of §3.2.2. From Equation 5.10, the following expressions for m and n can be derived,

$$n = \frac{1-X}{X\ln 0.6 - \ln 0.7} \tag{5.11}$$

$$m = \frac{\ln\alpha(0.7)}{(1+n\ln 0.7)\ln 0.7} \tag{5.12}$$

where

$$X = \frac{\ln 0.6 \ln\alpha(0.7)}{\ln 0.7 \ln\alpha(0.6)} \tag{5.13}$$

Note that it would not have been possible to obtain explicit expressions for m and n had Equation 2.25 been used.

The complete procedure to obtain the constants of the new equation from selected pure fluid properties is described below. The input parameters are T_c, P_c, $Z_l^s(0.7)$, $P_r^s(0.6)$ (or χ) and $P_r^s(0.7)$ (or ω). The required values of P^s and Z_l^s for all substances in this study are obtained from the correlations given in Table 4.1, and described in §4.1.1.

- Assume initial value(s) of Ω_{ac}. Almost all substances have $0.421875 < \Omega_{ac} <\approx 0.7$ for this equation of state.

- Determine the actual value of Ω_{ac} iteratively, so as to satisfy Equation 5.8, using the input parameters at $T_r = 0.7$. Equation 5.8 is solved as follows.

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[4] Note that $m = -0.5$ and $n = 0$ gives the original temperature function of Redlich and Kwong.

1. Calculate f, g, and h from Equations 3.29–3.31
2. Calculate Ω_{bc} from Equation 3.56.
3. Use the procedure of §3.2.2 to obtain α. This will also give the value of λ_L.
4. Check Equation 5.8.

- Obtain $\alpha(0.6)$ from $P_r^s(0.6)$ using the procedure of §3.2.2. Note that $\alpha(0.7)$ is already available from the previous step.
- Calculate n and m from Equations 5.11 and 5.12.

Note that Ω_{ac}, m and n need only be calculated once for each substance, i.e., the iterative procedure need only be performed once for each substance. This is a considerable simplification over the previous equation and the Sugie-Iwahori-Lu equation.

This formulation of the new equation of state effectively uses a five-parameter corresponding-states principle. Four of these parameters (T_c, P_c, ω and χ) have been previously used in corresponding-states descriptions of polar fluids. $Z_l^s(0.7)$ is a fifth corresponding-states parameter.

Chapter 6

Evaluation and Comparison

In this Chapter, the three versions of the new cubic equation of state developed in §5 are evaluated, using the data presented in §4.1. The effectiveness of various mixing rules is also tested.

The three formulations of the new equation of state are represented here by roman numerals. The generalized formulation, given in §5.2.1, is called equation I. The formulation in §5.2.2, which uses pure fluid property correlations to determine the constants, is called equation II. The formulation in §5.2.3, which uses selected pure fluid properties to determine the constants, is called equation III.

Comparisons are made to previous equations of state. The Soave modification of the Redlich-Kwong equation (SRK) and the Peng-Robinson equation (PR) are selected because they are simple, well known equations of state, and are thus good standards of comparison. The Schmidt-Wenzel (SW) and Patel-Teja (PT) equations represent the $u = 1 - w$ family of equations, which have received much attention recently. The translated Peng-Robinson equation (TPR) of Yu and Lu is included to test the effectiveness of volume translation for improvement of volumetric performance. The Toghiani-Viswanath (TV) and Trebble-Bishnoi (TB) equations represent recent attempts to achieve good overall performance for polar and non-polar fluids by the inclusion of a fourth parameter. The TB equation uses Z_c as a fourth parameter, whereas the TV equation uses Halm and Stiel's χ. Finally, the Sugie-Iwahori-Lu equation (SIL) is included because it is related to the new equation of state. All these equations of state are fully described in §4.2. In addition, some of them are discussed in §2.2 and

§5.1.3.

It should be noted that more accurate modifications of some of these equations exist, for example Stryjek and Vera's modification of the Peng-Robinson equation (PRSV). The primary improvement obtained with these equations is in the prediction of vapor pressure.

6.1 Pure Fluids

An equation of state should give good prediction of important properties of pure fluids. In this section, the equations listed above are used to predict properties on the vapor–liquid saturation curve, and liquid-phase volumes. Their performance is compared and discussed.

6.1.1 Saturated Properties

The data for pure fluids at saturation, described in §4.1.2, are used to compare equations of state for their ability to predict saturated properties. Predicted values of saturated pressure P^s, saturated liquid molar volume v_l^s, and saturated vapor molar volume v_v^s are obtained using the procedure described in 3.2.5. Overall %RMS deviations are calculated for the various classes of substances defined in §4.1.2; results for P^s, v_l^s and v_v^s are given in Table 6.1, Table 6.2 and Table 6.3 respectively. More extensive results for each substance for each of the equations of state are given in Tables A.2–A.12.

The performance of the various equations of state in the prediction of P^s (Table 6.1) is discussed first. The equations with the best overall performance by far are the SIL equation, and equations II and III. This is expected, because they use actual vapor pressure data to determine α. The SIL equation and equation II give identical results; they both have α calculated directly from vapor pressure correlations at each temperature. The predicted P^s values for these equations are therefore identical to those of the vapor pressure correlations used. These correlations are generally more accurate for the prediction of vapor pressure than are generalized equations of state. Equation III is nearly as accurate as Equation II even though it uses only two points on the vapor pressure curve to fix the constants m and n in its α expression. This approach is considerably simpler, and evidently results in only slight losses in accuracy. Note that the SRK equation uses a similar approach (m is selected to predict α at $T_r = 0.7$); however, it only uses a single point on the vapor pressure curve, and tends to deviate badly at low reduced pressure.

Except for the aromatics, the SIL equation, and equations II and III had the lowest or close to the lowest deviations in P^s for each of the groups of substances tested. The high deviations for the aromatics is entirely due to ethyl benzene; the vapor pressure correlation used for ethyl benzene did not fit the data used here very well. The magnitudes of the overall deviations are roughly similar, for both polar and nonpolar groups of compounds. All the other equations of state give significantly higher deviations for some groups. The SIL equation, and equations II and III have the advantage of avoiding the use of generalized correlations: they can therefore be reliably extended to most substances, as long as accurate input data is available.

All of the other equations use generalized correlations to determine α. They have similar overall deviations in P^s to each other, except for the TV and TB equations. The TB equation has the highest deviation; Trebble and Bishnoi [130] also reported high deviations for P^s in comparison with other equations of state, when the generalized version of their equation was used. The TB equation uses the Heyen expression for α, with $n = 1$. As discussed in §2.2.3, this form is suited for equations of state with Ω_{ac} near 0.42, such as the van der Waals equation. For equations with variable Ω_{ac}, a variable n is desirable, such as in equation III. The TV equation also has high deviations, although it performed quite well for some classes of substances. Its generalized correlations are very sensitive to the values of ω and χ used (they are third order polynomials in these quantities; see §4.2). The values used here are evidently not all the same as those used by Toghiani and Viswanath. This illustrates one of the drawbacks to the use of generalized correlations. They often work best using the parameters used in their creation, which can change as new experimental work is done.

Comparisons in terms of groups of substances show that most groups have similar deviations in P^s for a given generalized equation of state. Exceptions occur for the noble gases, inorganic compounds, alcohols and carboxylic acids, for which deviations are high in most cases. The noble gases include helium and neon, which, because of quantum effects, have negative acentric factors. This causes severe problems with some equations of state (notably the SW, PT and TV), whose generalized correlations do not account for this eventuality. A similar reason accounts for the inorganic compounds, which include hydrogen, another substance with negative acentric factor due to quantum effects. The high deviations for alcohols and carboxylic acids are probably because of the strong hydrogen bonding that occurs with these substances. Equation I has high deviation for nitrogen compounds, because of a very high deviation for acetonitrile. Acetonitrile was not included among the substances used in the generalization of equation I; it has an extremely low Z_c value which is outside the range of applicability of the generalized correlations of the equation I. These examples illustrate another drawback to generalized correlations; they do not extrapolate well to substances which were not included in their generation.

The deviations in P^s as a function of T_r for some substances are shown for several equations of state in Figures 6.1–6.3.

Of the substances tested, water has the highest deviations in P^s at low T_r (Figure 6.1). Only equations such as equation II, which uses an accurate vapor pressure correlation to determine α, adequately describe this region. Equations I and III gave reasonable prediction (less than 2.5 % absolute deviation) down to $T_r = 0.55$. The PR and TB equations could only give reasonable prediction down to about $T_r = 0.65$; their expressions for α extrapolate poorly to low reduced temperature. Equation III gives reasonable deviations in P^s down to about $T_r = 0.50$; it extrapolates better because a vapor pressure at relatively low temperature ($T_r = 0.6$) is used in the calculation of the coefficients of its α expression. Equation I describes P^s for water even better, over a similar range; it uses the Soave expression for α, but modified by a function of T_r specifically to improve low temperature performance.

The deviations in P^s for methanol are shown in Figure 6.2. This data does not extend to low temperatures. Nevertheless, the TB equation deviations are large below $T_r = 0.7$. The PR equation overpredicts P^s by more than 2.5 % over most of the T_r range. Equations I, II and III have lower deviations than these at almost all points.

The deviations in P^s for n-heptane (Figure 6.3) are typical of those for nonpolar fluids. Equations II and III describe the data well over the entire T_r range. Note that the predictions for equations II and III are almost identical, even though the latter is simpler. At low T_r, the PR and TB equations have deviations exceeding 2.5 %.

Table 6.2 summarizes overall deviations in v_l^s. The lowest overall deviation is given by equation II. This is not surprising, since its Ω_{ac} value is calculated directly from accurate v_l^s correlations at each temperature up to $T_r = 0.9$. The SIL equation also has a low overall deviation, because its Ω_{ac} and Ω_{bc} values are calculated from the same correlations, at $T_r = 0.7$ and $T_r = 0.9$. Also, it follows the $u = -w$ relationship closely, which is desirable for volumetric predictions. The results for equation III are not far from those of the SIL equation, even though the former uses only one volume to determine Ω_{ac} and Ω_{bc}, at $T_r = 0.7$. The choices made in the design of equation III (§5.2.3) therefore appear appropriate. Equation I also has low deviations; it follows the $u = -w$ relationship, and it was generalized using saturated volume data. The TB equation is the only other one to have an overall deviation under 5 %. As noted in §5.1.3, although it is based on the $u = 1 - w$ relationship, it effectively follows $u = -w$. Since it was generalized using volumetric data, it can therefore be expected to have good volumetric performance. Note, however, that it does not give an overall deviation in v_l^s as low as equations I, II or III, even though it incorporates an extra constant and has a temperature dependency in b.

The remaining equations give very poor predictions of v_l^s, with at least twice the overall deviations as equations I, II or III. The deviations for these equations are very high for polar compounds in particular. They have u and w values which are far from optimum for good volumetric performance for most substances (§5.1.3). Even the volume translation used in the TPR equation did not result in large overall improvements, because its locus is still far from the optimum u and w values for most substances.

For the PR, SRK, SW, PT and TPR equations, additional deviation in the prediction of v_l^s for polar fluids result from their generalized correlations, which are based on three-parameter corresponding-states, and are designed for nonpolar fluids. This does not occur with the TV and TB equations, and equation I, because they use four-parameter corresponding-states, and included polar fluids in their generalization. It also does not occur for the SIL equation, and equations II and III, because of the direct methods they use to calculate their constants. There is a similar problem with the noble gases and the inorganic compounds, because they include substances with negative acentric factors due to quantum effects. Only the TB equation has generalized correlations taking this into account. These substances present no special difficulty for the SIL equation, and equations II and III, again because of the direct methods of constant determination.

There are two substances in particular that had high deviations in v_l^s, propyne and diethyl sulfide. They are major sources of the high deviations for the acetylenes and the sulfur compounds. This occurs even with the equations of state that use v_l^s correlations. The volumetric data for these substances may be inaccurate.

The deviations in v_l^s as a function of T_r for water, methanol and n-heptane are shown for several equations of state in Figures 6.4, 6.5 and 6.6 respectively. All substances have high positive deviations in v_l^s for all equations of state above $T_r = 0.95$. This is expected, because cubic equations of state cannot simultaneously give accurate volumes in the critical region and in other regions, as discussed in §2.2.2. Equation II clearly gives low deviations over the whole T_r range below the critical region for all three substances. Ω_{ac} values for equation II are calculated directly from accurate v_l^s correlations below $T_r = 0.9$; it therefore gives the same predictions for v_l^s as the correlations below $T_r = 0.9$. Equation III also gives reasonable predictions over the same range, although deviations become high for n-heptane below $T_r = 0.6$. The deviations are close to zero near $T_r = 0.7$ and $T_r = 0.9$, as expected. The TB equation and equation I give high deviations for the polar fluids water and methanol. This is surprising, since they use a four-parameter corresponding-states principle, and were generalized using volumetric data for polar fluids. The PR equation gives very poor predictions of v_l^s, except for n-heptane below $T_r = 0.8$ (it is not shown for water and methanol, because the deviations are off the scale of the plots).

Note that the shapes of the curves followed by the v_l^s deviations for equations I and III are almost the same for all three substances. Equation III gives better results because its Ω_{ac} value is calculated from v_l^s at $T_r = 0.7$, thus "shifting" the deviations to give good overall results. The curve followed by the deviations for the TB equation has a different shape; this is because the TB equation has a temperature dependency in b. This does not result in an improvement in v_l^s predictions; in fact, in the case of water and methanol, it results in larger deviations at low T_r. Of course, the shapes of the curves for the deviations from equation II are simply those of the liquid molar volume correlations used to determine its Ω_{ac} values below $T_r = 0.9$.

The deviations in v_v^s are summarized in Table 6.3. As noted in §5.1.1, these should not be affected greatly by the values of u and w. Instead, the constant a is expected to have the greatest effect. Therefore, the performance in v_v^s prediction should be related to the performance in P^s prediction. Inspection of the results and comparison with Table 6.1 shows that this is indeed the case. For further discussion, see the section on P^s deviations above. Some substances have very high deviations in v_v^s; this is discussed in §5.1.1.

Table 6.1: Overall deviations in pure fluid P^s predictions for several equations of state. The entries in the table are averages of %RMS deviations for the substances in the indicated group.

group	SRK	PR	SW	PT	TPR	TV	TB	SIL	I	II	III
noble gases	5.51	2.87	4.41	4.68	2.87	7.09	6.67	1.14	2.57	1.14	1.41
diatomics	4.20	2.46	2.51	2.68	2.46	2.52	2.74	1.99	1.74	1.99	2.53
inorganics	5.53	4.54	5.24	4.93	4.54	3.16	5.32	1.28	3.95	1.28	2.26
paraffins	1.85	1.85	0.89	1.47	1.85	2.28	2.12	1.13	1.38	1.13	1.21
olefins	2.28	3.36	1.75	2.80	3.36	3.93	3.41	1.74	3.28	1.74	2.58
acetylenes	1.42	0.82	0.65	0.90	0.82	0.93	0.71	0.44	0.64	0.44	0.84
naphthenes	0.50	0.64	1.03	0.35	0.64	0.70	2.58	2.61	0.51	2.61	1.10
aromatics	1.65	1.84	1.88	2.10	1.84	2.22	2.95	3.27	1.89	3.27	3.19
ethers	2.82	2.62	2.67	2.31	2.62	1.87	3.75	2.28	2.55	2.28	1.96
alcohols	3.49	3.84	4.21	4.43	3.84	4.69	5.07	2.99	3.86	2.99	3.72
carboxylic acids	10.39	7.51	9.92	7.71	7.51	3.78	3.33	5.13	7.59	5.13	4.57
esters & ketones	1.08	0.67	0.70	0.98	0.67	1.01	2.43	0.82	0.85	0.82	0.76
nitr. comp.	3.65	2.79	3.00	2.72	2.79	3.72	4.23	1.35	7.83	1.35	1.19
sulfur comp.	2.20	2.06	2.20	2.09	2.06	2.30	3.78	2.07	1.82	2.07	2.09
oxides	2.93	2.66	3.00	2.74	2.66	3.71	4.77	1.60	2.65	1.60	1.70
halog. paraf.	2.34	3.05	2.22	2.56	3.05	3.75	3.23	1.10	2.50	1.10	1.59
halog. naphth.	0.50	1.01	0.90	1.38	1.01	1.53	10.02	0.98	1.14	0.98	0.86
halog. arom.	1.00	0.57	0.56	0.67	0.57	0.75	2.93	0.65	0.77	0.65	0.63
overall	2.64	2.39	2.27	2.45	2.39	2.84	3.51	1.60	2.33	1.60	1.81

Table 6.2: Overall deviations in pure fluid v_l^s predictions for several equations of state. The entries in the table are averages of %RMS deviations for the substances in the indicated group.

group	SRK	PR	SW	PT	TPR	TV	TB	SIL	I	II	III
noble gases	9.47	12.61	8.08	8.00	7.13	10.87	5.61	2.29	5.24	2.57	4.04
diatomics	8.14	9.98	6.98	6.70	5.00	7.60	4.22	2.77	3.68	2.50	3.70
inorganics	24.33	13.04	14.51	13.81	13.63	13.53	6.56	5.25	5.82	4.88	5.40
paraffins	14.79	6.71	6.30	5.97	5.65	7.08	3.78	3.17	3.50	2.80	3.25
olefins	13.00	5.62	6.65	6.11	5.45	8.98	3.21	2.86	2.85	2.08	3.14
acetylenes	19.65	9.47	12.21	11.51	10.88	14.50	6.54	5.24	5.22	8.40	14.20
naphthenes	17.07	6.85	10.49	9.78	8.82	9.90	4.36	3.41	3.72	3.36	3.91
aromatics	18.53	6.81	7.58	7.00	7.20	7.88	3.65	2.72	3.47	2.44	2.62
ethers	17.42	7.22	7.51	7.21	7.10	14.26	5.73	3.75	4.69	3.45	4.21
alcohols	26.75	13.74	10.24	10.38	11.74	8.10	5.40	5.51	4.58	5.18	4.45
carboxylic acids	50.67	33.66	28.75	28.15	28.40	6.93	11.45	4.29	7.02	3.18	3.95
esters & ketones	25.20	12.34	12.13	11.52	12.02	14.28	4.36	4.64	3.89	4.38	4.06
nitr. comp.	42.00	27.24	27.31	26.66	27.12	13.54	6.93	4.12	6.48	3.10	3.98
sulfur comp.	16.08	11.15	13.13	12.75	12.18	12.46	9.11	9.14	8.76	9.08	9.59
oxides	18.38	10.16	10.82	10.28	10.07	9.60	5.85	3.66	4.65	3.21	3.65
halog. paraf.	11.83	5.80	5.77	5.71	5.24	8.58	3.57	2.79	3.30	1.99	2.87
halog. naphth.	10.94	6.71	7.05	7.55	7.46	8.84	3.96	4.48	2.75	4.36	4.51
halog. arom.	14.93	2.61	4.93	3.97	4.27	5.65	1.59	1.45	1.45	1.05	1.49
overall	18.13	9.64	9.45	9.06	8.89	10.00	4.73	3.77	4.20	3.44	4.05

Table 6.3: Overall deviations in pure fluid v_v^s predictions for several equations of state. The entries in the table are averages of %RMS deviations for the substances in the indicated group.

group	SRK	PR	SW	PT	TPR	TV	TB	SIL	I	II	III
noble gases	8.16	5.05	6.71	7.12	4.46	14.60	7.06	3.97	8.00	2.92	2.89
diatomics	6.16	4.15	4.10	4.03	3.74	6.06	3.83	3.96	4.15	3.36	4.25
inorganics	9.71	7.78	9.07	8.30	7.73	5.23	7.85	4.79	6.33	4.72	5.89
paraffins	2.24	2.61	1.87	2.31	2.46	3.11	3.40	3.26	3.76	3.14	3.40
olefins	1.89	2.85	1.68	2.31	2.76	3.45	3.93	2.59	3.63	2.46	3.64
acetylenes	6.38	3.72	4.88	4.20	4.05	6.10	3.32	4.47	3.24	3.44	6.18
naphthenes	1.35	1.89	2.16	1.37	1.72	2.75	3.61	4.30	3.63	4.06	3.29
aromatics	3.37	3.10	3.04	3.03	3.07	3.11	4.12	5.77	4.42	5.78	5.73
ethers	23.32	22.87	22.96	23.73	22.89	23.75	22.78	23.38	22.68	23.30	23.49
alcohols	9.75	9.47	9.40	10.02	9.07	10.27	8.63	6.36	8.29	6.45	8.09
carboxylic acids	75.99	68.42	74.70	71.06	68.33	55.14	55.17	51.27	47.25	51.17	52.59
esters & ketones	4.43	2.92	3.00	3.38	2.86	3.70	4.01	3.13	3.61	3.27	3.66
nitr. comp.	9.41	8.01	8.17	8.44	7.97	6.32	7.95	8.75	9.41	8.39	7.91
sulfur comp.	26.67	27.09	26.64	27.02	26.99	27.02	26.37	27.99	28.42	27.90	28.03
oxides	4.37	3.18	4.04	3.51	3.27	4.78	5.28	3.36	3.76	3.30	2.85
halog. paraf.	3.89	4.35	3.66	3.92	4.31	5.06	4.72	3.28	4.47	3.19	3.78
halog. naphth.	1.42	1.52	1.31	2.19	1.56	2.39	8.99	2.07	2.51	2.34	2.82
halog. arom.	1.95	1.47	1.81	1.79	1.49	1.93	4.19	1.68	1.60	1.66	1.60
overall	7.42	6.74	6.79	6.96	6.64	7.52	7.33	6.44	6.90	6.29	6.77

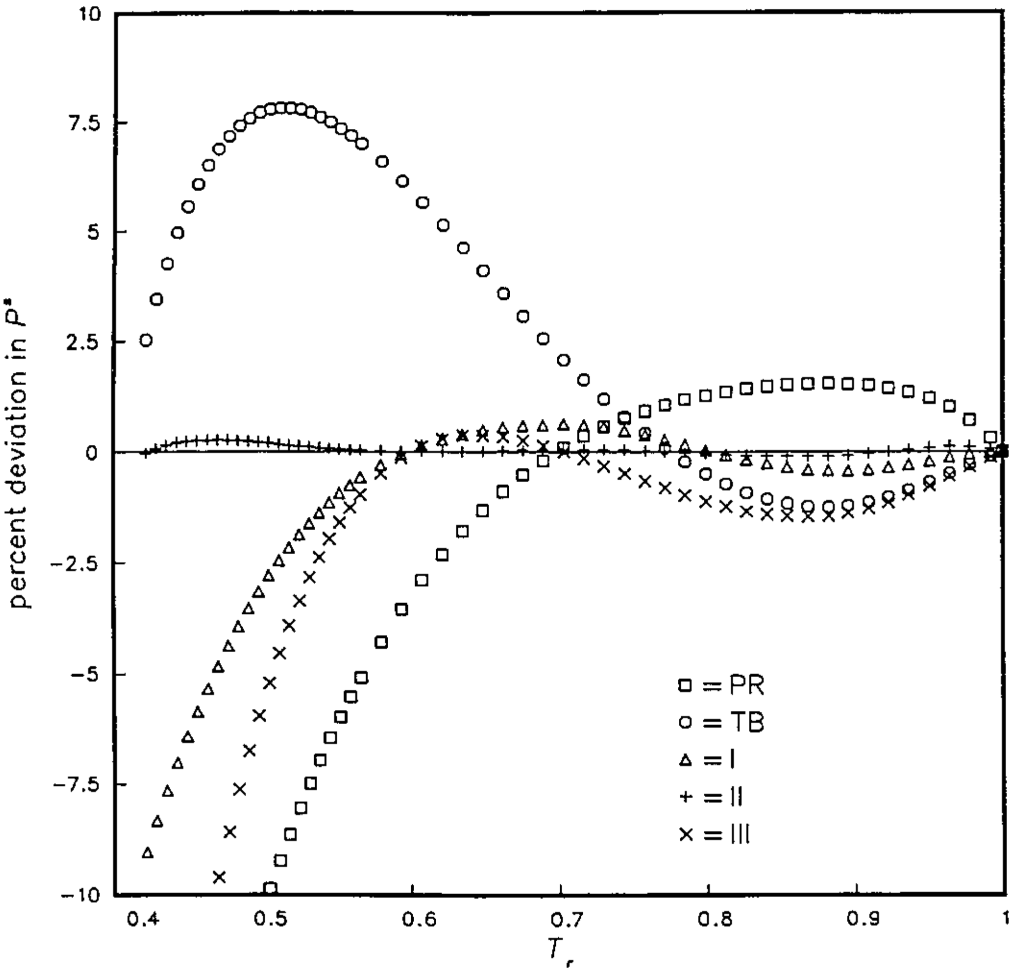

Figure 6.1: Deviations in P^s for water for several equations of state.

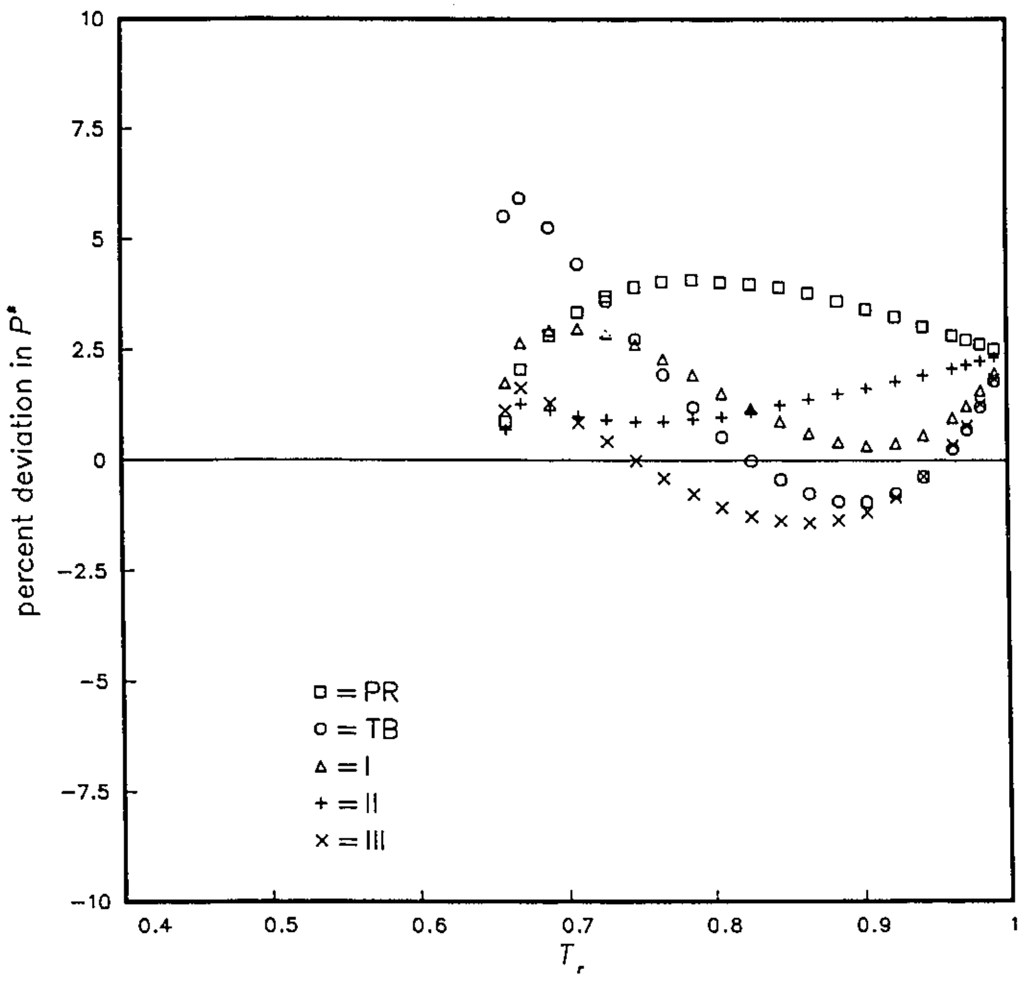

Figure 6.2: Deviations in P^s for methanol for several equations of state.

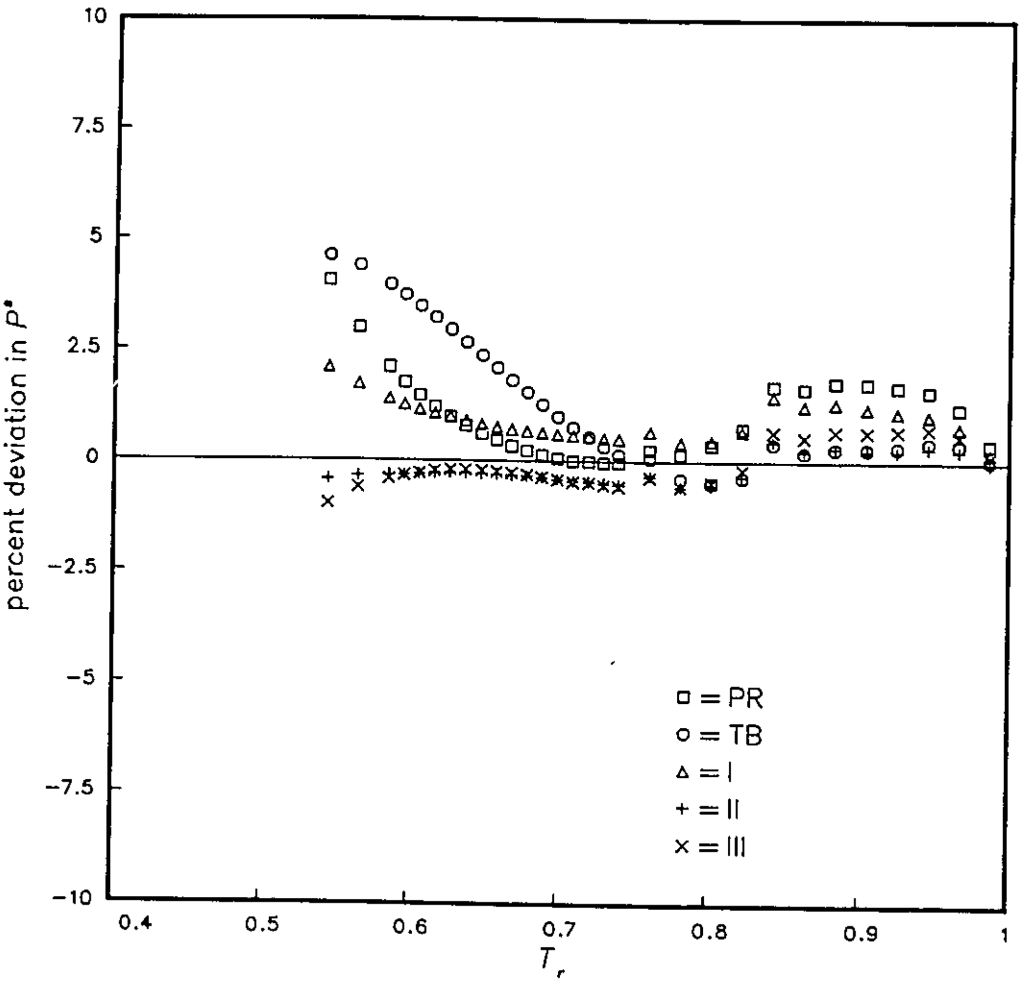

Figure 6.3: Deviations in P^s for n-heptane several equations of state.

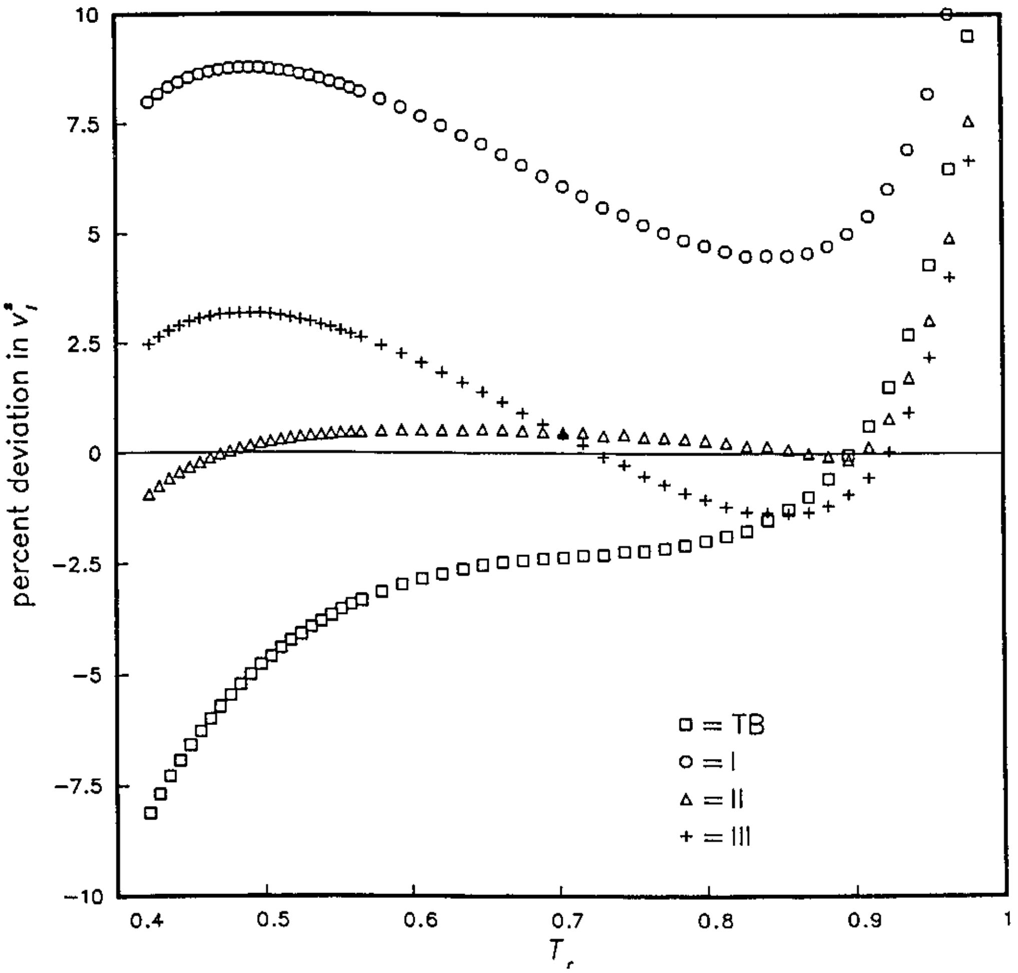

Figure 6.4: Deviations in v_l^s for water for several equations of state.

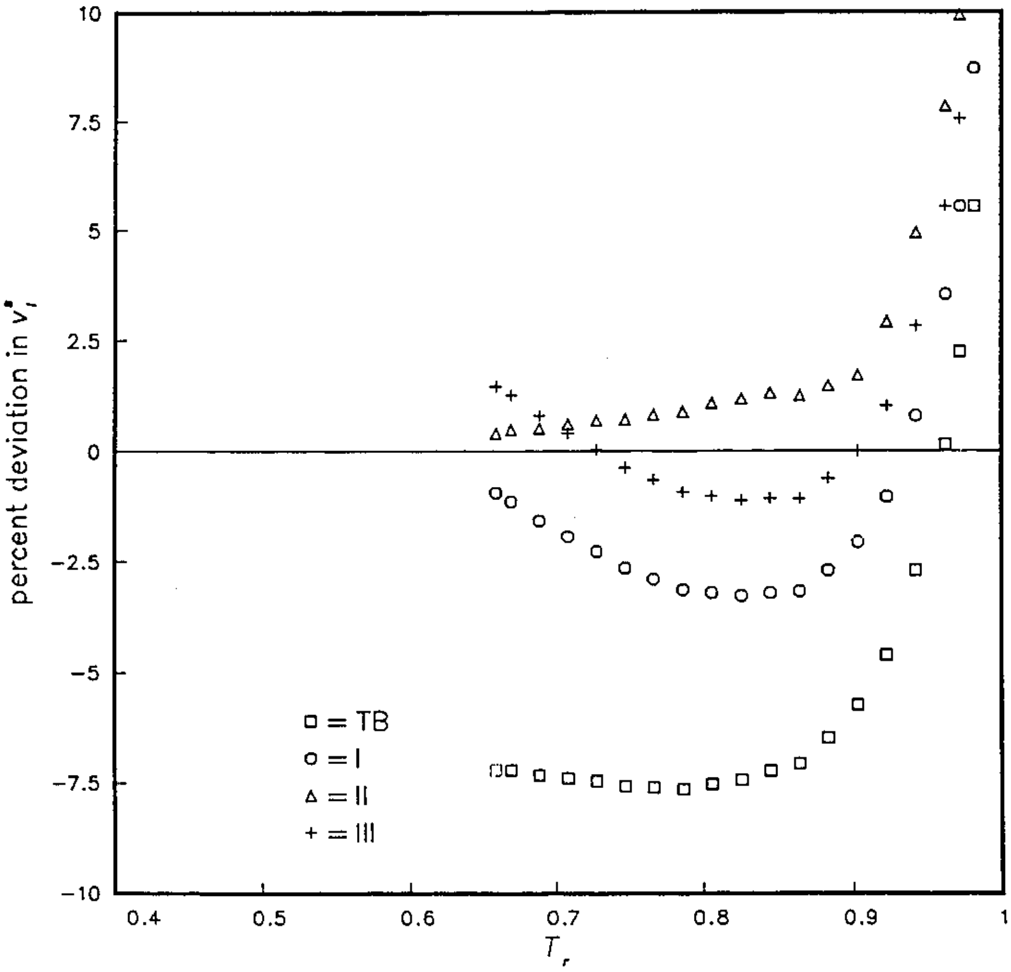

Figure 6.5: Deviations in v_l^s for methanol for several equations of state.

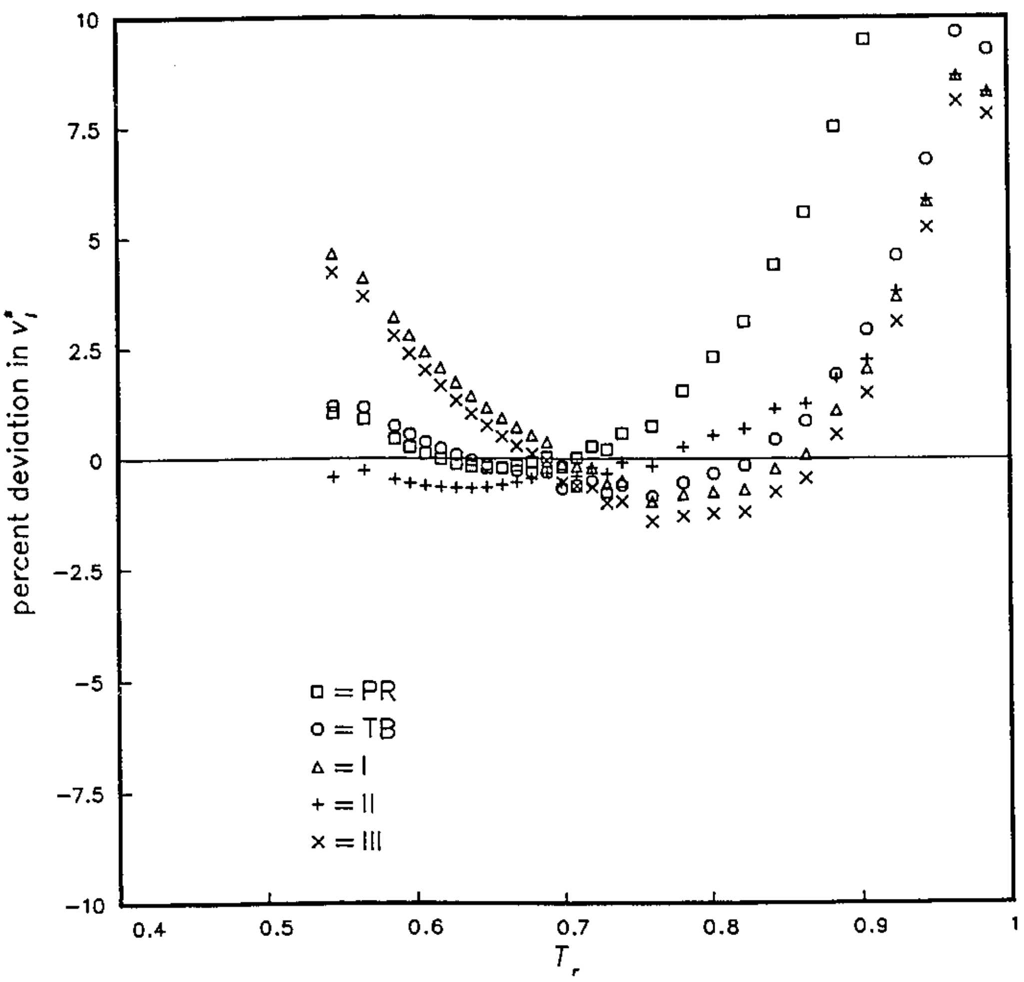

Figure 6.6: Deviations in v_l^s for n-heptane several equations of state.

6.1.2 Single Phase Region

The equations of state are further evaluated by testing their performance in prediction of compressed liquid molar volumes, v_l, using the data described in Table 4.2. Overall deviations in v_l are given in Table 6.4.

The best performance is by the SIL equation, and equations II and III. They give good predictions of v_l^s; since liquid volume varies slowly with P, this leads to good predictions of v_l. The next best performance is by the TB equation, which is now significantly better than equation I; this is the reverse of the results for overall v_l^s deviations. The TB equation was generalized using single phase data as well as saturated data, unlike equation I, which used only saturated data. It appears that the improvement in v_l prediction is at the cost of increased v_l^s deviations. All of the remaining equations have much higher deviations. For water, ammonia and acetonitrile, the deviations are especially large. These equations have u and w values which are far from the optima for highly polar fluids.

Acetonitrile has overall deviations in v_l that are significantly higher than for other substances, for all the equations of state tested. Most of this is due to large deviations at higher pressures. This happens to a lesser extent with other substances as well, particularly the polar ones.

Table 6.4: Overall deviations in pure fluid v_l predictions for several equations of state. The entries in the table are averages of %RMS deviations for the indicated substances.

substance	SRK	PR	SW	PT	TPR	TV	TB	SIL	I	II	III
argon	4.38	8.55	4.00	3.31	2.35	6.72	1.72	0.99	2.43	1.60	1.02
water	37.70	22.31	21.83	20.90	21.27	2.29	2.13	3.13	8.53	2.41	3.15
hydrogen sulfide	6.23	6.30	3.17	2.42	1.57	32.67	0.88	2.17	0.83	2.15	2.34
ammonia	27.62	13.72	16.75	15.67	16.11	5.79	2.46	1.57	2.91	2.73	1.61
nitrogen	5.96	9.69	5.32	5.30	4.37	8.53	4.40	5.74	4.00	4.50	5.25
carbon dioxide	11.37	3.94	3.92	3.71	3.50	7.55	2.23	1.76	1.91	1.48	1.69
acetonitrile	79.37	60.56	60.83	59.64	60.13	11.03	7.09	6.80	10.98	8.89	10.06
propylene	5.82	6.67	2.44	2.87	2.21	6.07	2.40	1.05	3.03	1.25	0.97
propane	8.04	5.27	2.95	2.67	2.17	5.32	2.18	1.26	1.24	1.20	1.11
1-butene	6.26	6.49	3.15	3.79	3.17	6.80	1.37	1.98	1.96	2.14	1.89
isobutane	6.74	5.93	2.40	2.94	2.55	8.98	3.06	1.97	1.61	1.99	1.82
n-pentane	9.99	4.07	3.15	3.31	3.01	8.23	3.83	1.60	3.91	1.51	1.60
n-nonane	15.34	3.22	1.60	1.85	2.57	2.75	4.51	3.36	6.06	2.53	4.27
overall	17.29	12.06	10.12	9.73	9.61	8.67	2.94	2.57	3.80	2.64	2.83

6.2 Mixtures

Prediction of properties for mixtures is considerably more difficult than for pure fluids. This is particularly true for mixtures involving polar fluids, and for highly asymmetric mixtures.

The vapor-liquid equilibrium (VLE) and volumetric data for mixtures described in §4.1.3 is used to further examine the performance of the new equation of state. Comparisons are made with the PR equation, because it has good VLE performance, and because it is well-known and is thus a good standard for comparison. Comparisons are also made with the TB equation, because it has been designed for polar fluids, and has good volumetric performance. Note that other equations, (such as the PRSV), which accurately predicts vapor pressure, would give better VLE results than the PR or TB equations.

The optimum values of binary interaction coefficients for each system at each temperature are determined by minimizing Equation 3.101, using residuals in P^s and y_1 from VLE calculations. Two cases are considered.

1. No y data are available. Therefore only residuals in P^s are used. Thus $\mathbf{Z}$ is an $1 \times N$ matrix with elements $Z_{1j} = [(P^s)^{\text{calc}} - P^s]_j$.
2. Both P^s and y data are available. Residuals in P^s and y_1 are used. Thus $\mathbf{Z}$ is a $2 \times N$ matrix with elements $Z_{1j} = [(P^s)^{\text{calc}} - P^s]_j$, and $Z_{2j} = [(y_1)^{\text{calc}} - y_1]_j$.

Note that case 1 is equivalent to minimizing the sum of squared residuals in P^s. See §3.2.7 for further details of parameter estimation.

6.2.1 Mixing Rules

Alcohol–alkane mixtures are particularly difficult to describe with cubic equations of state. A frequent problem, especially at low temperatures, is the false prediction of liquid-phase splitting. This can sometimes be prevented by the use of an appropriate mixing rule (§2.4). Various mixing rules are therefore considered here. Comparisons are also made between the equations of state listed above.

For the attractive constant a, several mixing rules are considered. The simplest is the two-coefficient Redlich-Kister mixing rule (RK2) of Adachi et al.[11]. The augmented form of this mixing rule (RK2+), proposed by Schartzentruber et al. [112,113], is also considered. It has been shown to prevent false liquid-phase splitting in some cases. The local-composition mixing rule of Huron and Vidal [63] (HV) has also been shown to prevent false liquid-phase splitting; it is also considered. All these mixing rules are discussed in §2.4, and are given in full in §3.1.6.

The results for the estimation of the binary interaction coefficients are summarized for the PR and TB equations, and for equations I, II and III, in Tables 6.5–6.9 respectively. Overall deviations in P^s and y are summarized in Table 6.10.

The values of the interaction coefficients are shown with 95 % confidence intervals, except for those cases where strong correlations between parameters cause near-singular Hessians[1]. This occurred only with the PR equation using the HV mixing rule, for the systems 1-butanol–*n*-heptane, 1-butanol–*n*-octane and 1-pentanol–*n*-decane. However, these and many other systems using the HV mixing rule have strong correlations between the parameters C_{ij} and C_{ji} (not shown), and have very large confidence intervals for the parameters (indicating that they could not be precisely determined). Reasonable parameter estimates could not be obtained for the 1-pentanol–*n*-decane system with the TB equation of state using the HV mixing rule, apparently because of a very strong dependency between C_{ij} and C_{ji}. Large confidence intervals also occur for some cases using the RK2+ mixing rule, namely the 1-butanol–*n*-heptane system for the PR equation and equation I, and the 1-pentanol–*n*-decane system with the PR and TB equations, and equation I.

The RK2+ and HV mixing rules are complex models, each with three binary interaction coefficients. They obviously have difficulties describing some systems (the HV equation in particular), as indicated by the problems in parameter determination listed above. For all systems considered here, equations II and III do not have these problems. In addition, the parameters determined with equations II and III have smaller confidence intervals (i.e., are more precisely determined) than those determined with the other equations. As subsequently shown, equations II and III give better descriptions of the VLE of the mixtures considered here, due to better predictions of pure fluid P^s; equations such as the PRSV, which also accurately pre-

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[1] In such cases, the confidence intervals cannot be calculated.

dicts pure fluid P^s would show similar results. It therefore appears that an equation of state giving good performance for pure fluid properties is necessary for the successful application of complex mixture models, such as the RK2+ and HV mixing rules.

The RK2 mixing rule predicts false liquid-phase splitting for highly asymmetric systems (low molecular-weight alcohols with high molecular weight alkanes). This occurs for the systems methanol–*n*-hexane, ethanol–*n*-hexane, and ethanol–*n*-octane for all the equations of state. It also occurs for the system 1-propanol–*n*-heptane with the TB equation and equation II, and for the 1-butanol–*n*-heptane system with equation II. The RK2+ and HV mixing rules eliminate false liquid–phase splitting for most of these systems. Neither could eliminate it for the very asymmetric methanol–*n*-hexane system. The HV mixing rule could not eliminate false liquid-phase splitting for the ethanol–*n*-octane system, although the RK2+ mixing rule is successful. Finally, false liquid-phase splitting still occurs for the 1-propanol–*n*-heptane system with the TB equation using the RK2+ and HV mixing rules, although it is eliminated with equation II.

Comparison of the standard errors shows that the RK2+ mixing rule gives a better fit than the HV mixing rule in almost all cases. It also gives lower deviations in P^s and y. For most systems where no false liquid-phase splitting is predicted, the RK2 mixing rule, with only two binary interaction coefficients, gives almost as good results as the three-coefficient mixing rules (RK2+ and HV). Indeed, in terms of the standard error, the RK2 mixing rule is actually better in many cases. The extra complexity of the RK2+ and HV mixing rules therefore appears unnecessary for systems where the RK2 mixing rule does not predict false liquid-phase splitting.

Comparisons of the standard errors and overall deviations can also be made in terms of the equations of state. The results for equations II and III are nearly the same (with equation II being slightly better), and are almost always better than those for the other equations. Equation I gives somewhat higher standard errors and overall deviations, and is comparable to the PR equation. The TB equation has significantly higher standard errors and deviations in almost all cases.

Plots of P versus x and y are shown for several systems in Figures 6.7–6.10. The predicted curves for the PR and TB equations, and for equation II are shown. In all cases, Equation III gives nearly the same results as equation II.

Figure 6.7 shows the ethanol–n-hexane system, using the RK2+ mixing rule (the RK2 mixing rule causes false liquid-phase splitting for this system). Clearly, the system is very well described by the PR equation and Equation II, with equation II giving very slightly better description for the vapor phase. The TB equation significantly overpredicts pressure, because it gives a value for ethanol vapor pressure which is too high.

Figure 6.8 shows the 1-propanol–n-hexane system, using the RK2+ mixing rule (again, the RK2 mixing rule predicts false liquid-phase splitting for this system). Equation II describes the system well. The PR equation is not as good in this case, because it overpredicts the vapor pressures of both 1-propanol and n-octane. The TB equation overpredicts these quantities even more, and gives false liquid-phase splitting. The curve for the TB equation shown here is not physically meaningful. It is typical of the curves obtained when false liquid-phase splitting occurs, with irregularities and with multiple local extrema in P^s. As noted above, none of the mixing rules considered here could eliminate the false liquid-phase splitting predicted by the TB equation for this system. This appears to be due to the overprediction of P^s for 1-propanol; it is too high for a realistic description of this mixture.

Figure 6.9 shows the 1-butanol–n-decane system using the RK2 mixing rule (the three-coefficient mixing rules are not significantly better for this system). Equation II again gives the best description of the data, in this case because it accurately predicts the vapor pressure of 1-butanol. Note especially the significant deviations for the PR and TB equations for 1-butanol mole fractions greater than 0.8.

Figure 6.10 shows the 1-pentanol–n-decane system using the RK2 mixing rule (again, the three-coefficient mixing rules are not significantly better for this system). Equation II gives much better description of this system. The PR and TB have very significant deviations for 1-pentanol mole fractions above 0.7; most notably, they fail to predict the azeotrope. Once again, this is because the PR and TB equations do not predict pure fluid vapor pressures as well as equation II.

Trebble [128] studied alcohol–n-hexane systems, using the PR and TB equations. He used conventional van der Waals mixing rules, but with binary interaction coefficients for both a and b (see §2.4). This mixing rule was not as successful as those considered here. For systems where false liquid-phase splitting was obtained, Trebble adjusted the binary interaction coefficients "manually" to obtain normal VLE. However, P^s for mixtures was significantly underpredicted in such cases. Schwartzentruber et al. [112,113] observed false liquid-phase splitting for some systems with both the RK2+ and HV mixing rules. They avoided this by imposing a stability constraint on the liquid phase (this is essentially a formalized version of Trebble's approach). Again, underprediction of mixture P^s resulted. Such an approach could have been used in this study to prevent false liquid-phase splitting for systems such as methanol–*n*-hexane; however, it would not have changed the fact that these mixing rules have difficulty describing very highly asymmetric systems.

In summary, the RK2 mixing rule is sufficient for most of the mixtures studied here. For highly asymmetric mixtures, the RK2+ mixing rule prevents false liquid-phase splitting in all but one case. The HV mixing rule is not as successful, despite being more complex and despite using the local-composition concept. Equations II and III give the best descriptions of the mixtures considered here, because they give the best predictions of pure fluid P^s. In addition, the complex mixing rules (RK2+ and HV) work better with equations II and III.

Table 6.5: VLE for alcohol–alkane systems, using the PR equation of state with different mixing rules.

system	mixing rule	σ 100 Pa	interaction coefficients with 95 % confidence intervals		
	RK2 RK2+ HV		k_{ij} k_{ij} C_{ji}/RT	l_{ij} l_{ij} C_{ij}/RT	 m_{ij} α_{ji}
1-C_4H_9OH–	RK2	1.2991	0.068 ± 0.010	−0.011 ± 0.011	
n-C_5H_{12}	RK2+	0.1982	0.248 ± 0.032	−0.191 ± 0.032	0.946 ± 0.008
at 303.15 K	HV	0.2673	0.840 ± 0.044	0.451 ± 0.013	−1.684 ± 0.175
CH_3OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+		false liquid-phase splitting		
at 323.15 K	HV		false liquid-phase splitting		
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+	0.1007	0.110 ± 0.003	−0.081 ± 0.002	0.706 ± 0.015
at 323.14 K	HV	0.0753	1.578 ± 0.034	0.519 ± 0.014	−0.821 ± 0.032
1-C_4H_9OH–	RK2	0.3616	0.047 ± 0.006	−0.032 ± 0.008	
n-C_6H_{14}	RK2+	0.1987	0.098 ± 0.079	−0.059 ± 0.065	0.863 ± 0.180
at 298.15 K	HV	0.2280	0.994 ± 0.164	0.452 ± 0.093	−1.164 ± 0.489
1-$C_5H_{11}OH$–	RK2	10.4359	0.058 ± 0.003	−0.030 ± 0.006	
n-C_6H_{14}	RK2+	3.9323	0.080 ± 0.007	−0.042 ± 0.006	0.770 ± 0.053
at 323.15 K	HV	4.4451	0.895 ± 0.107	0.306 ± 0.062	−1.182 ± 0.314
C_2H_5OH–	RK2	1.9230	0.096 ± 0.006	−0.059 ± 0.010	
n-C_7H_{16}	RK2+	0.4251	0.156 ± 0.018	−0.104 ± 0.017	0.759 ± 0.045
at 343.15 K	HV	0.2972	1.376 ± 0.072	0.660 ± 0.013	−1.214 ± 0.134
1-C_3H_7OH–	RK2	1.7295	0.073 ± 0.004	−0.047 ± 0.008	
n-C_7H_{16}	RK2+	1.2599	0.118 ± 0.026	−0.077 ± 0.021	0.814 ± 0.088
at 348.15 K	HV	1.4892	1.237 ± 0.378	0.432 ± 0.100	−0.980 ± 0.644
1-C_4H_9OH–	RK2	0.3671	0.039 ± 0.018	−0.034 ± 0.022	
n-C_7H_{16}	RK2+	0.3082	−0.023 ± 0.063	−0.083 ± 0.056	0.174 ± 0.147
at 323.15 K	HV	0.4110	3.782	−1.921	−0.120
1-$C_5H_{11}OH$–	RK2	9.3461	0.055 ± 0.002	−0.039 ± 0.005	
n-C_7H_{16}	RK2+	8.0103	0.067 ± 0.012	−0.042 ± 0.007	0.635 ± 0.119
at 363.27 K	HV	8.0562	1.608 ± 4.172	−0.487 ± 4.655	−0.446 ± 1.665
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_8H_{18}	RK2+	0.2470	0.113 ± 0.004	−0.099 ± 0.003	0.703 ± 0.015
at 328.15 K	HV		false liquid-phase splitting		
1-C_3H_7OH–	RK2	2.9192	0.041 ± 0.004	−0.066 ± 0.009	
n-C_8H_{18}	RK2+	2.5905	0.060 ± 0.020	−0.073 ± 0.013	0.646 ± 0.129
at 313.15 K	HV	2.6020	1.618 ± 0.672	0.215 ± 0.330	−0.822 ± 0.602
1-C_4H_9OH–	RK2	2.4068	0.036 ± 0.006	−0.049 ± 0.017	
n-C_8H_{18}	RK2+	2.5136	0.036 ± 0.039	−0.050 ± 0.020	0.508 ± 0.400
at 313.15 K	HV	2.5291	3.361	−1.521	−0.219
1-$C_5H_{11}OH$–	RK2	7.0606	0.052 ± 0.004	−0.042 ± 0.009	
n-C_8H_{18}	RK2+	7.1932	0.059 ± 0.021	−0.043 ± 0.010	0.582 ± 0.249
at 363.15 K	HV	7.2152	1.358 ± 2.827	−0.099 ± 2.322	−0.643 ± 2.214
1-C_4H_9OH–	RK2	0.9423	0.071 ± 0.005	−0.066 ± 0.010	
n-$C_{10}H_{22}$	RK2+	0.9489	0.079 ± 0.021	−0.069 ± 0.014	0.558 ± 0.138
at 373.15 K	HV	0.9631	1.609 ± 0.570	0.175 ± 0.280	−0.761 ± 0.487
1-$C_5H_{11}OH$–	RK2	7.9742	0.040 ± 0.009	−0.052 ± 0.020	
n-$C_{10}H_{22}$	RK2+	7.8340	0.011 ± 0.069	−0.063 ± 0.051	0.252 ± 0.387
at 363.27 K	HV	8.5066	5.197	−3.006	−0.116

Table 6.6: VLE for alcohol–alkane systems, using the TB equation of state with different mixing rules.

system	mixing rule	σ 100 Pa	interaction coefficients with 95 % confidence intervals		
	RK2 RK2+ HV		k_{ij} k_{ij} C_{ji}/RT	l_{ij} l_{ij} C_{ij}/RT	 m_{ij} α_{ji}
1-C_4H_9OH– n-C_5H_{12} at 303.15 K	RK2	2.9005	0.067 ± 0.013	−0.010 ± 0.015	
	RK2+	1.3936	0.117 ± 0.025	−0.081 ± 0.022	0.876 ± 0.049
	HV	0.7870	0.877 ± 0.066	0.458 ± 0.023	−1.887 ± 0.279
CH_3OH– n-C_6H_{14} at 323.15 K	RK2		false liquid-phase splitting		
	RK2+		false liquid-phase splitting		
	HV		false liquid-phase splitting		
C_2H_5OH– n-C_6H_{14} at 323.14 K	RK2		false liquid-phase splitting		
	RK2+	0.4806	0.093 ± 0.006	−0.076 ± 0.005	0.675 ± 0.023
	HV	0.6485	1.827 ± 0.080	0.520 ± 0.022	−0.699 ± 0.069
1-C_4H_9OH– n-C_6H_{14} at 298.15 K	RK2	0.5355	0.042 ± 0.006	−0.034 ± 0.008	
	RK2+	0.2835	0.095 ± 0.074	−0.061 ± 0.060	0.860 ± 0.165
	HV	0.3400	1.040 ± 0.182	0.438 ± 0.116	−1.159 ± 0.497
1-$C_5H_{11}OH$– n-C_6H_{14} at 323.15 K	RK2	11.0408	0.052 ± 0.003	−0.031 ± 0.006	
	RK2+	5.5565	0.073 ± 0.010	−0.042 ± 0.008	0.757 ± 0.074
	HV	5.9312	0.942 ± 0.161	0.277 ± 0.098	−1.144 ± 0.419
C_2H_5OH– n-C_7H_{16} at 343.15 K	RK2	1.9412	0.082 ± 0.005	−0.056 ± 0.011	
	RK2+	1.1066	0.107 ± 0.017	−0.070 ± 0.015	0.662 ± 0.087
	HV	1.4996	1.711 ± 0.383	0.563 ± 0.099	−0.897 ± 0.389
1-C_3H_7OH– n-C_7H_{16} at 348.15 K	RK2	2.6165	0.054 ± 0.005	−0.044 ± 0.009	
	RK2+	2.6897	0.060 ± 0.026	−0.046 ± 0.014	0.569 ± 0.265
	HV	2.6923	1.619 ± 1.703	0.218 ± 0.814	−0.575 ± 1.142
1-C_4H_9OH– n-C_7H_{16} at 323.15 K	RK2	0.9196	0.048 ± 0.012	−0.033 ± 0.018	
	RK2+	0.5931	0.099 ± 0.036	−0.064 ± 0.029	0.795 ± 0.105
	HV	0.7152	1.076 ± 0.198	0.462 ± 0.141	−1.254 ± 0.574
1-$C_5H_{11}OH$– n-C_7H_{16} at 363.27 K	RK2	14.8301	0.044 ± 0.004	−0.035 ± 0.008	
	RK2+	15.4646	0.046 ± 0.021	−0.035 ± 0.009	0.524 ± 0.280
	HV	16.0844	1.085 ± 1.071	−0.034 ± 0.952	−0.807 ± 1.374
C_2H_5OH– n-C_8H_{18} at 328.15 K	RK2		false liquid-phase splitting		
	RK2+	1.3347	0.096 ± 0.019	−0.103 ± 0.010	0.712 ± 0.081
	HV		false liquid-phase splitting		
1-C_3H_7OH– n-C_8H_{18} at 313.15 K	RK2		false liquid-phase splitting		
	RK2+		false liquid-phase splitting		
	HV		false liquid-phase splitting		
1-C_4H_9OH– n-C_8H_{18} at 313.15 K	RK2	4.0196	0.018 ± 0.010	−0.053 ± 0.028	
	RK2+	4.1531	0.001 ± 0.084	−0.054 ± 0.039	0.336 ± 0.677
	HV	4.3241	1.710 ± 4.496	−0.531 ± 4.524	−0.666 ± 2.537
1-$C_5H_{11}OH$– n-C_8H_{18} at 363.15 K	RK2	13.9336	0.033 ± 0.007	−0.039 ± 0.017	
	RK2+	14.4372	0.027 ± 0.044	−0.041 ± 0.023	0.417 ± 0.536
	HV	14.8330	1.210 ± 2.104	−0.215 ± 1.976	−0.761 ± 2.057
1-C_4H_9OH– n-$C_{10}H_{22}$ at 373.15 K	RK2	3.3364	0.054 ± 0.012	−0.065 ± 0.015	
	RK2+	3.0699	0.100 ± 0.043	−0.080 ± 0.027	0.714 ± 0.143
	HV	3.0687	1.199 ± 0.264	0.346 ± 0.149	−1.284 ± 0.581
1-$C_5H_{11}OH$– n-$C_{10}H_{22}$ at 363.27 K	RK2	16.4897	0.015 ± 0.018	−0.065 ± 0.039	
	RK2+	15.5016	−0.071 ± 0.212	−0.121 ± 0.193	0.125 ± 0.298
	HV		did not converge		

Table 6.7: VLE for alcohol–alkane systems, using equation of state I with different mixing rules.

system	mixing rule	σ 100 Pa	interaction coefficients with 95 % confidence intervals		
	RK2		k_{ij}	l_{ij}	
	RK2+		k_{ij}	l_{ij}	m_{ij}
	HV		C_{ji}/RT	C_{ij}/RT	α_{ji}
1-C_4H_9OH– n-C_5H_{12} at 303.15 K	RK2	1.1805	0.064 ± 0.009	-0.011 ± 0.010	
	RK2+	0.1848	0.215 ± 0.070	-0.161 ± 0.069	0.942 ± 0.018
	HV	0.2363	0.846 ± 0.042	0.446 ± 0.012	-1.643 ± 0.163
CH_3OH– n-C_6H_{14} at 323.15 K	RK2		false liquid-phase splitting		
	RK2+		false liquid-phase splitting		
	HV		false liquid-phase splitting		
C_2H_5OH– n-C_6H_{14} at 323.14 K	RK2		false liquid-phase splitting		
	RK2+	0.0792	0.095 ± 0.002	-0.076 ± 0.002	0.690 ± 0.013
	HV	0.0853	1.687 ± 0.040	0.526 ± 0.014	-0.806 ± 0.035
1-C_4H_9OH– n-C_6H_{14} at 298.15 K	RK2	0.3448	0.045 ± 0.005	-0.031 ± 0.007	
	RK2+	0.1746	0.091 ± 0.066	-0.055 ± 0.053	0.857 ± 0.171
	HV	0.2064	1.015 ± 0.167	0.441 ± 0.096	-1.152 ± 0.467
1-$C_5H_{11}OH$– n-C_6H_{14} at 323.15 K	RK2	10.2218	0.055 ± 0.003	-0.028 ± 0.005	
	RK2+	3.8979	0.076 ± 0.007	-0.039 ± 0.005	0.765 ± 0.053
	HV	4.3811	0.904 ± 0.108	0.301 ± 0.063	-1.167 ± 0.310
C_2H_5OH– n-C_7H_{16} at 343.15 K	RK2	1.7549	0.084 ± 0.005	-0.058 ± 0.010	
	RK2+	0.3595	0.131 ± 0.015	-0.093 ± 0.014	0.731 ± 0.046
	HV	0.3915	1.473 ± 0.099	0.674 ± 0.019	-1.171 ± 0.155
1-C_3H_7OH– n-C_7H_{16} at 348.15 K	RK2	1.8077	0.064 ± 0.004	-0.044 ± 0.007	
	RK2+	1.4371	0.104 ± 0.029	-0.071 ± 0.024	0.799 ± 0.112
	HV	1.6163	1.298 ± 0.440	0.418 ± 0.127	-0.923 ± 0.664
1-C_4H_9OH– n-C_7H_{16} at 323.15 K	RK2	0.3707	0.037 ± 0.017	-0.033 ± 0.020	
	RK2+	0.3139	-0.025 ± 0.059	-0.082 ± 0.052	0.174 ± 0.146
	HV	0.4353	1.065 ± 0.235	0.439 ± 0.165	-1.232 ± 0.681
1-$C_5H_{11}OH$– n-C_7H_{16} at 363.27 K	RK2	9.5986	0.051 ± 0.002	-0.036 ± 0.005	
	RK2+	8.9105	0.060 ± 0.012	-0.038 ± 0.006	0.614 ± 0.139
	HV	8.9243	1.393 ± 7.278	-0.258 ± 7.374	-0.550 ± 4.509
C_2H_5OH– n-C_8H_{18} at 328.15 K	RK2		false liquid-phase splitting		
	RK2+	0.3398	0.098 ± 0.005	-0.095 ± 0.004	0.693 ± 0.023
	HV		false liquid-phase splitting		
1-C_3H_7OH– n-C_8H_{18} at 313.15 K	RK2	3.1114	0.036 ± 0.004	-0.064 ± 0.009	
	RK2+	2.8780	0.053 ± 0.021	-0.069 ± 0.013	0.633 ± 0.143
	HV	2.8849	1.720 ± 0.896	0.174 ± 0.453	-0.763 ± 0.687
1-C_4H_9OH– n-C_8H_{18} at 313.15 K	RK2	2.3448	0.034 ± 0.006	-0.049 ± 0.015	
	RK2+	2.4472	0.036 ± 0.036	-0.049 ± 0.019	0.520 ± 0.366
	HV	2.4614	3.019 ± 4.380	-1.207 ± 3.955	-0.259 ± 0.513
1-$C_5H_{11}OH$– n-C_8H_{18} at 363.15 K	RK2	7.8167	0.047 ± 0.004	-0.040 ± 0.009	
	RK2+	8.0448	0.052 ± 0.022	-0.041 ± 0.010	0.568 ± 0.284
	HV	8.0757	1.473 ± 3.919	-0.230 ± 3.469	-0.561 ± 2.355
1-C_4H_9OH– n-$C_{10}H_{22}$ at 373.15 K	RK2	1.3397	0.057 ± 0.006	-0.065 ± 0.011	
	RK2+	1.3709	0.061 ± 0.025	-0.066 ± 0.014	0.532 ± 0.173
	HV	1.3717	2.470 ± 5.674	-0.416 ± 3.622	-0.364 ± 1.309
1-$C_5H_{11}OH$– n-$C_{10}H_{22}$ at 363.27 K	RK2	8.9796	0.031 ± 0.010	-0.051 ± 0.021	
	RK2+	8.7593	-0.002 ± 0.078	-0.066 ± 0.061	0.227 ± 0.379
	HV	9.9350	1.574 ± 3.750	-0.338 ± 3.085	-0.637 ± 2.304

Table 6.8: VLE for alcohol–alkane systems, using equation of state II with different mixing rules.

system	mixing rule	σ 100 Pa	interaction coefficients with 95 % confidence intervals		
	RK2 RK2+ HV		k_{ij} k_{ij} C_{ji}/RT	l_{ij} l_{ij} C_{ij}/RT	 m_{ij} α_{ji}
1-C_4H_9OH–	RK2	0.1100	0.041 ± 0.004	-0.018 ± 0.005	
n-C_5H_{12}	RK2+	0.0072	0.062 ± 0.003	-0.039 ± 0.003	0.762 ± 0.016
at 303.15 K	HV	0.0130	0.978 ± 0.027	0.311 ± 0.008	-1.044 ± 0.090
CH_3OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+		false liquid-phase splitting		
at 323.15 K	HV		false liquid-phase splitting		
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+	0.0353	0.098 ± 0.002	-0.078 ± 0.002	0.693 ± 0.014
at 323.14 K	HV	0.0546	1.712 ± 0.033	0.531 ± 0.013	-0.789 ± 0.027
1-C_4H_9OH–	RK2	0.0664	0.047 ± 0.003	-0.029 ± 0.008	
n-C_6H_{14}	RK2+	0.0158	0.079 ± 0.008	-0.052 ± 0.007	0.822 ± 0.035
at 298.15 K	HV	0.0203	1.048 ± 0.053	0.463 ± 0.024	-1.184 ± 0.136
1-$C_5H_{11}OH$–	RK2	12.8467	0.035 ± 0.004	-0.036 ± 0.007	
n-C_6H_{14}	RK2+	3.5920	0.060 ± 0.006	-0.049 ± 0.005	0.760 ± 0.038
at 323.15 K	HV	4.3238	0.968 ± 0.063	0.362 ± 0.029	-1.367 ± 0.195
C_2H_5OH–	RK2	2.0234	0.085 ± 0.006	-0.058 ± 0.010	
n-C_7H_{16}	RK2+	0.4066	0.142 ± 0.018	-0.099 ± 0.017	0.762 ± 0.046
at 343.15 K	HV	0.3550	1.468 ± 0.088	0.683 ± 0.016	-1.147 ± 0.142
1-C_3H_7OH–	RK2	1.8671	0.069 ± 0.004	-0.045 ± 0.008	
n-C_7H_{16}	RK2+	1.4083	0.105 ± 0.031	-0.070 ± 0.024	0.789 ± 0.134
at 348.15 K	HV	1.5692	1.293 ± 0.356	0.442 ± 0.088	-0.953 ± 0.558
1-C_4H_9OH–	RK2	0.1833	0.046 ± 0.010	-0.039 ± 0.018	
n-C_7H_{16}	RK2+	0.1143	0.063 ± 0.020	-0.042 ± 0.015	0.690 ± 0.162
at 323.15 K	HV	0.1034	1.055 ± 0.327	0.416 ± 0.211	-1.143 ± 0.737
1-$C_5H_{11}OH$–	RK2	8.9732	0.045 ± 0.002	-0.042 ± 0.004	
n-C_7H_{16}	RK2+	3.5530	0.062 ± 0.005	-0.047 ± 0.003	0.668 ± 0.041
at 363.27 K	HV	3.4175	1.069 ± 0.099	0.247 ± 0.059	-1.103 ± 0.202
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_8H_{18}	RK2+	0.2423	0.100 ± 0.003	-0.093 ± 0.003	0.703 ± 0.016
at 328.15 K	HV		false liquid-phase splitting		
1-C_3H_7OH–	RK2		false liquid-phase splitting		
n-C_8H_{18}	RK2+	0.4327	0.073 ± 0.004	-0.065 ± 0.003	0.711 ± 0.020
at 313.15 K	HV	0.6939	1.453 ± 0.122	0.497 ± 0.038	-0.954 ± 0.156
1-C_4H_9OH–	RK2		false liquid-phase splitting		
n-C_8H_{18}	RK2+	0.8609	0.068 ± 0.012	-0.055 ± 0.009	0.661 ± 0.086
at 313.15 K	HV	0.8432	1.509 ± 0.312	0.336 ± 0.147	-0.788 ± 0.328
1-$C_5H_{11}OH$–	RK2	3.1287	0.051 ± 0.001	-0.041 ± 0.003	
n-C_8H_{18}	RK2+	1.0076	0.062 ± 0.003	-0.044 ± 0.002	0.638 ± 0.028
at 363.15 K	HV	1.0194	1.238 ± 0.087	0.277 ± 0.044	-0.904 ± 0.120
1-C_4H_9OH–	RK2	0.5386	0.067 ± 0.003	-0.056 ± 0.006	
n-$C_{10}H_{22}$	RK2+	0.3281	0.093 ± 0.014	-0.072 ± 0.011	0.679 ± 0.066
at 373.15 K	HV	0.3384	1.334 ± 0.177	0.365 ± 0.064	-1.017 ± 0.275
1-$C_5H_{11}OH$–	RK2	1.0764	0.053 ± 0.001	-0.033 ± 0.002	
n-$C_{10}H_{22}$	RK2+	0.8339	0.058 ± 0.004	-0.034 ± 0.002	0.585 ± 0.061
at 363.27 K	HV	0.8280	1.443 ± 0.199	0.399 ± 0.070	-0.697 ± 0.188

Table 6.9: VLE for alcohol–alkane systems, using the equation of state III with different mixing rules.

system	mixing rule	σ 100 Pa	interaction coefficients with 95 % confidence intervals		
	RK2 RK2+ HV		k_{ij} k_{ij} C_{ji}/RT	l_{ij} l_{ij} C_{ij}/RT	 m_{ij} α_{ji}
1-C_4H_9OH–	RK2	0.1518	0.037 ± 0.004	−0.017 ± 0.005	
n-C_5H_{12}	RK2+	0.0171	0.057 ± 0.003	−0.036 ± 0.003	0.745 ± 0.016
at 303.15 K	HV	0.0206	0.952 ± 0.029	0.284 ± 0.011	−1.035 ± 0.086
CH_3OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+		false liquid-phase splitting		
at 323.15 K	HV		false liquid-phase splitting		
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_6H_{14}	RK2+	0.0328	0.099 ± 0.002	−0.078 ± 0.001	0.696 ± 0.010
at 323.14 K	HV	0.0486	1.683 ± 0.032	0.525 ± 0.012	−0.801 ± 0.028
1-C_4H_9OH–	RK2	0.1242	0.047 ± 0.005	−0.035 ± 0.010	
n-C_6H_{14}	RK2+	0.0192	0.084 ± 0.007	−0.057 ± 0.007	0.841 ± 0.028
at 298.15 K	HV	0.0194	1.015 ± 0.033	0.491 ± 0.018	−1.276 ± 0.090
1-$C_5H_{11}OH$–	RK2	13.6221	0.039 ± 0.004	−0.033 ± 0.007	
n-C_6H_{14}	RK2+	2.8010	0.067 ± 0.005	−0.050 ± 0.004	0.791 ± 0.029
at 323.15 K	HV	4.0835	0.924 ± 0.058	0.354 ± 0.028	−1.428 ± 0.200
C_2H_5OH–	RK2	1.9859	0.086 ± 0.006	−0.059 ± 0.010	
n-C_7H_{16}	RK2+	0.3733	0.139 ± 0.017	−0.097 ± 0.016	0.753 ± 0.046
at 343.15 K	HV	0.3353	1.461 ± 0.081	0.679 ± 0.016	−1.163 ± 0.132
1-C_3H_7OH–	RK2	1.8266	0.069 ± 0.004	−0.045 ± 0.007	
n-C_7H_{16}	RK2+	1.3298	0.109 ± 0.030	−0.072 ± 0.022	0.805 ± 0.124
at 348.15 K	HV	1.5296	1.285 ± 0.360	0.441 ± 0.089	−0.964 ± 0.573
1-C_4H_9OH–	RK2	0.2108	0.048 ± 0.011	−0.040 ± 0.018	
n-C_7H_{16}	RK2+	0.1312	0.064 ± 0.022	−0.043 ± 0.016	0.697 ± 0.169
at 323.15 K	HV	0.1137	1.008 ± 0.288	0.450 ± 0.192	−1.252 ± 0.757
1-$C_5H_{11}OH$–	RK2	8.9590	0.047 ± 0.002	−0.041 ± 0.004	
n-C_7H_{16}	RK2+	3.4152	0.064 ± 0.005	−0.046 ± 0.003	0.673 ± 0.040
at 363.27 K	HV	3.3450	1.059 ± 0.105	0.227 ± 0.064	−1.091 ± 0.212
C_2H_5OH–	RK2		false liquid-phase splitting		
n-C_8H_{18}	RK2+	0.2765	0.100 ± 0.004	−0.095 ± 0.003	0.699 ± 0.019
at 328.15 K	HV		false liquid-phase splitting		
1-C_3H_7OH–	RK2	2.2618	0.050 ± 0.003	−0.053 ± 0.006	
n-C_8H_{18}	RK2+	0.5806	0.076 ± 0.005	−0.065 ± 0.004	0.713 ± 0.027
at 313.15 K	HV	0.8152	1.487 ± 0.104	0.513 ± 0.030	−0.933 ± 0.130
1-C_4H_9OH–	RK2	1.4783	0.053 ± 0.003	−0.047 ± 0.008	
n-C_8H_{18}	RK2+	1.0452	0.073 ± 0.015	−0.058 ± 0.012	0.673 ± 0.103
at 313.15 K	HV	1.0192	1.521 ± 0.367	0.362 ± 0.165	−0.810 ± 0.398
1-$C_5H_{11}OH$–	RK2	3.0240	0.052 ± 0.001	−0.041 ± 0.003	
n-C_8H_{18}	RK2+	1.1012	0.062 ± 0.003	−0.043 ± 0.002	0.635 ± 0.032
at 363.15 K	HV	1.1105	1.229 ± 0.111	0.262 ± 0.057	−0.894 ± 0.153
1-C_4H_9OH–	RK2	0.5582	0.068 ± 0.003	−0.058 ± 0.006	
n-$C_{10}H_{22}$	RK2+	0.3974	0.092 ± 0.015	−0.071 ± 0.012	0.666 ± 0.079
at 373.15 K	HV	0.4062	1.399 ± 0.245	0.337 ± 0.092	−0.960 ± 0.332
1-$C_5H_{11}OH$–	RK2	0.9841	0.052 ± 0.001	−0.034 ± 0.002	
n-$C_{10}H_{22}$	RK2+	0.8281	0.057 ± 0.004	−0.035 ± 0.002	0.568 ± 0.061
at 363.27 K	HV	0.8321	1.506 ± 0.238	0.368 ± 0.089	−0.653 ± 0.198

Table 6.10: Overall deviations in P^s and y for alcohol–alkane systems using various equations of state with different mixing rules. Entries are %RMS deviation for P^s and RMS×100 for y.

system	mixing rule	PR		TB		I		II		III	
		P^s	y	P^s	y	P^s	y	P^s	y	P^s	y
1-C_4H_9OH–n-C_5H_{12} at 303.15 K	RK2	23.43	0.58	34.16	0.94	22.38	0.55	5.30	0.08	8.15	0.09
	RK2+	25.59	0.31	17.89	3.26	24.28	0.31	3.44	0.02	6.57	0.08
	HV	19.92	0.60	29.16	0.97	19.07	0.57	3.62	0.02	6.79	0.07
CH_3OH–n-C_6H_{14} at 323.15 K	RK2										
	RK2+										
	HV										
C_2H_5OH–n-C_6H_{14} at 323.14 K	RK2										
	RK2+	0.60	0.61	3.34	1.36	0.72	0.44	0.37	0.35	0.45	0.30
	HV	0.68	0.66	3.12	1.51	0.99	0.54	0.72	0.55	0.75	0.45
1-C_4H_9OH–n-C_6H_{14} at 298.15 K	RK2	17.91	2.86	24.79	3.95	17.05	2.76	4.80	0.76	5.59	0.78
	RK2+	17.51	2.02	24.51	2.87	16.40	1.95	1.11	0.60	2.08	0.68
	HV	17.14	2.28	24.14	3.22	16.14	2.20	2.13	0.70	3.73	0.84
1-$C_5H_{11}OH$–n-C_6H_{14} at 323.15 K	RK2	11.74		17.39		11.36		4.73		6.29	
	RK2+	12.31		18.24		11.90		1.84		2.73	
	HV	12.36		18.22		11.96		1.86		2.86	
C_2H_5OH–n-C_7H_{16} at 343.15 K	RK2	5.28	1.41	5.71	1.55	5.00	1.32	5.20	1.35	5.06	1.34
	RK2+	1.16	1.48	4.52	0.80	1.42	1.27	1.05	1.48	1.13	1.37
	HV	0.49	2.02	2.58	2.22	0.55	2.32	0.60	2.00	0.50	2.11
1-C_3H_7OH–n-C_7H_{16} at 348.15 K	RK2	2.76	2.92	3.51	4.46	2.84	3.06	2.79	3.01	2.79	2.96
	RK2+	3.36	1.63	3.75	4.22	3.50	1.79	3.01	1.86	3.12	1.75
	HV	3.11	2.18	3.73	4.24	3.24	2.39	3.03	2.30	3.04	2.24
1-C_4H_9OH–n-C_7H_{16} at 323.15 K	RK2	1.90	3.29	9.72	4.75	1.84	3.32	2.62	1.29	2.91	1.48
	RK2+	3.04	1.57	17.96	4.78	3.20	1.54	1.97	0.90	1.92	1.05
	HV	1.83	3.40	16.64	5.28	10.11	3.20	2.15	0.76	2.25	0.83
1-$C_5H_{11}OH$–n-C_7H_{16} at 363.27 K	RK2	4.27		8.42		4.75		1.16		1.16	
	RK2+	4.23		8.43		4.73		0.57		0.55	
	HV	4.23		8.46		4.73		0.54		0.53	
C_2H_5OH–n-C_8H_{18} at 328.15 K	RK2										
	RK2+	2.04	1.82	4.36	2.29	2.29	1.81	2.27	1.67	2.38	1.67
	HV										
1-C_3H_7OH–n-C_8H_{18} at 313.15 K	RK2	3.70				3.92				2.51	
	RK2+	3.35				3.65		0.50		0.69	
	HV	3.36				3.65		0.76		0.91	
1-C_4H_9OH–n-C_8H_{18} at 313.15 K	RK2	8.47		14.20		8.31				3.40	
	RK2+	8.47		14.10		8.31		1.88		2.59	
	HV	8.51		14.40		8.34		1.84		2.54	
1-$C_5H_{11}OH$–n-C_8H_{18} at 363.15 K	RK2	4.09		8.19		4.58		0.85		0.82	
	RK2+	4.08		8.17		4.57		0.30		0.32	
	HV	4.09		8.25		4.58		0.30		0.32	
1-C_4H_9OH–n-$C_{10}H_{22}$ at 373.15 K	RK2	3.42	1.69	10.78	1.75	4.41	1.76	2.77	1.42	2.82	1.43
	RK2+	3.26	1.60	14.43	1.13	4.38	1.71	1.93	1.02	2.14	1.06
	HV	3.26	1.54	14.43	1.16	4.39	1.70	2.00	1.02	2.20	1.07
1-$C_5H_{11}OH$–n-$C_{10}H_{22}$ at 363.27 K	RK2	4.80		9.89		5.39		1.14		1.10	
	RK2+	4.51		8.89		5.03		1.03		1.02	
	HV	4.86				5.69		1.03		1.02	

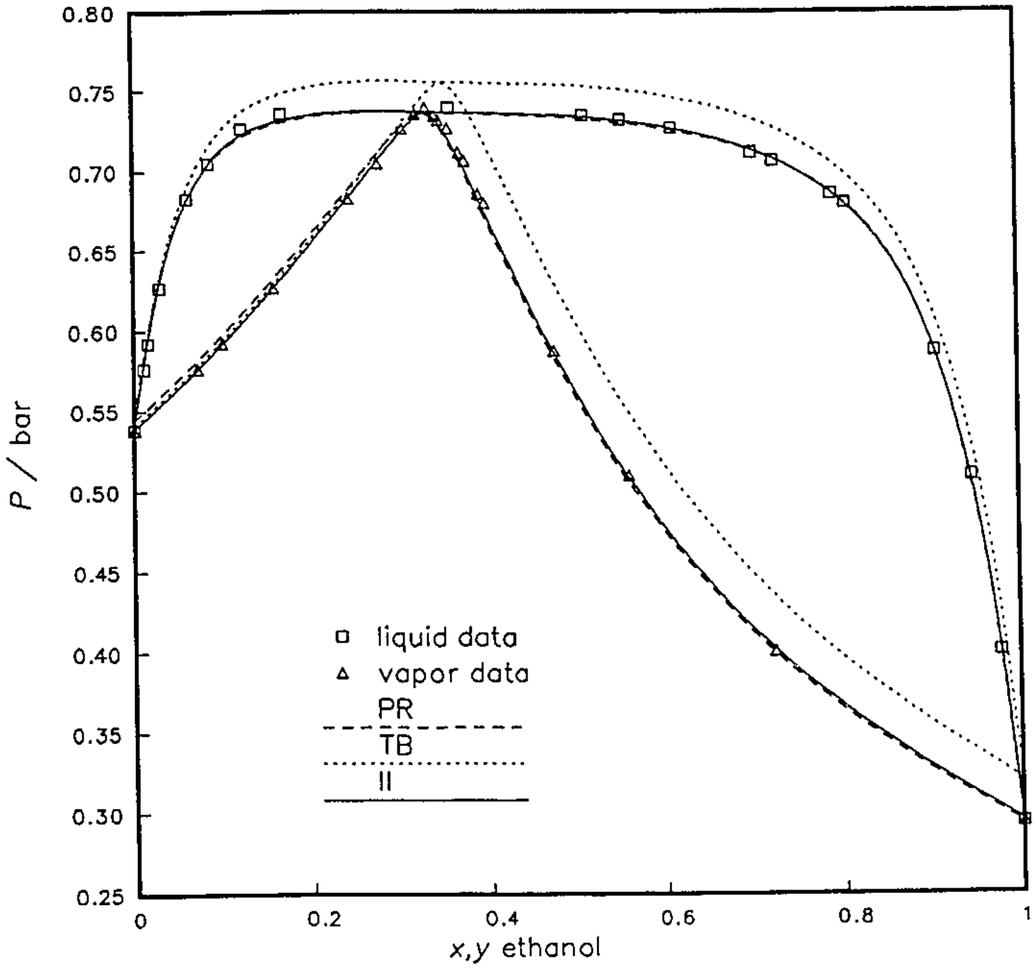

Figure 6.7: VLE for the ethanol–n-hexane system at 323.14 K using the RK2+ mixing rule with different equations of state.

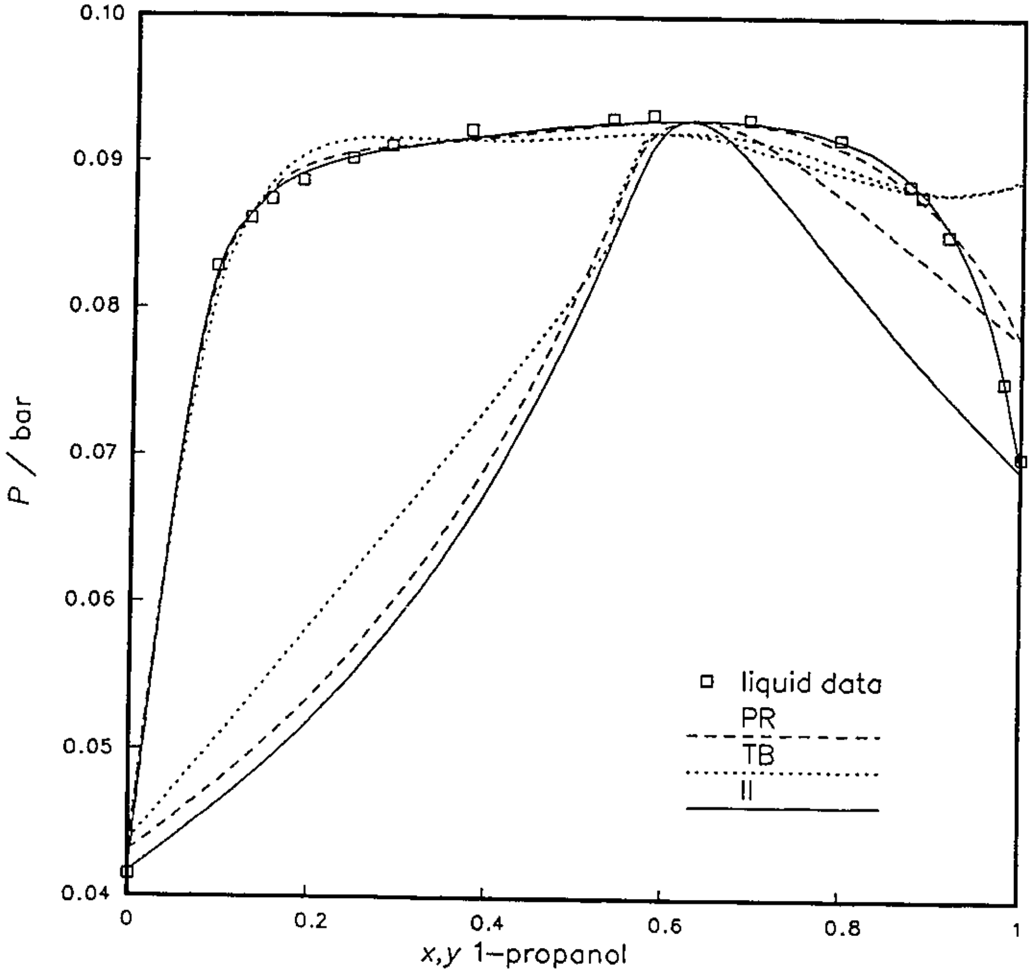

Figure 6.8: VLE for the 1-propanol–n-octane system at 313.15 K, using the RK2+ mixing rule with different equations of state.

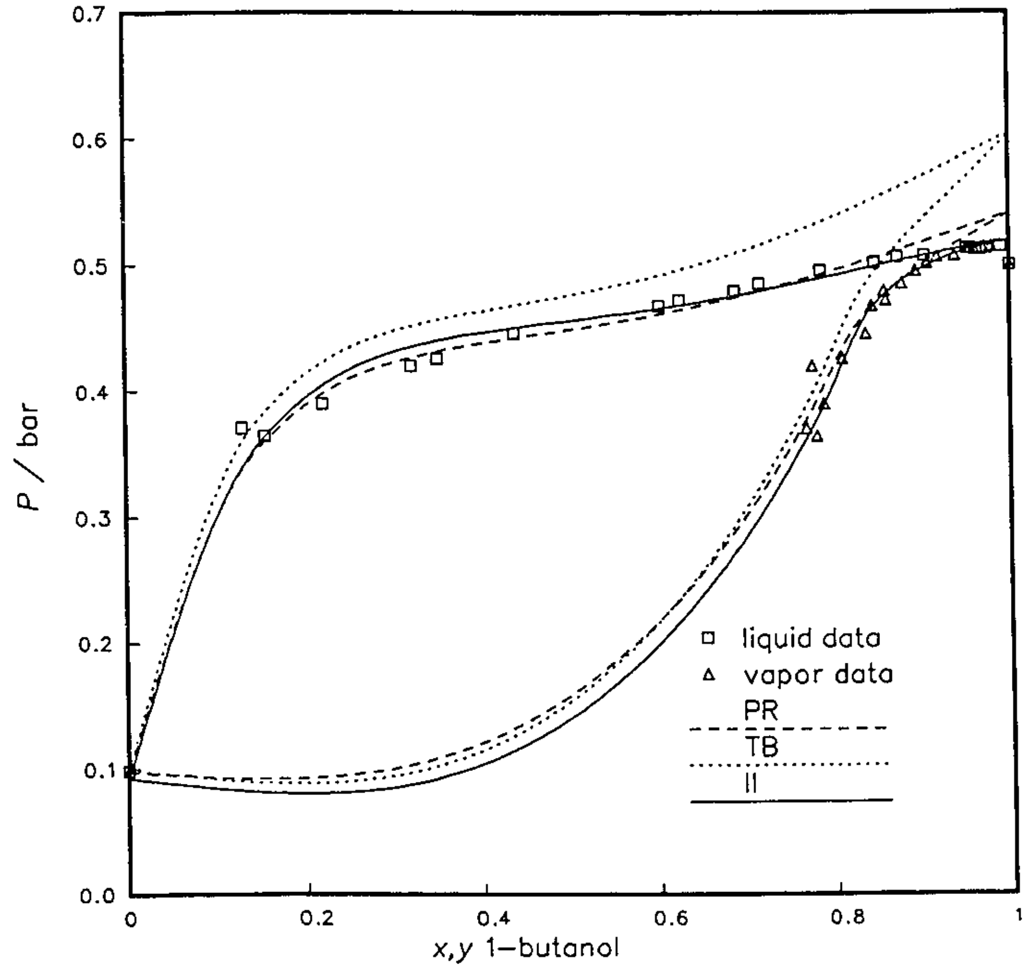

Figure 6.9: VLE for the 1-butanol–*n*-decane system at 373.15 K, using the RK2 mixing rule with different equations of state.

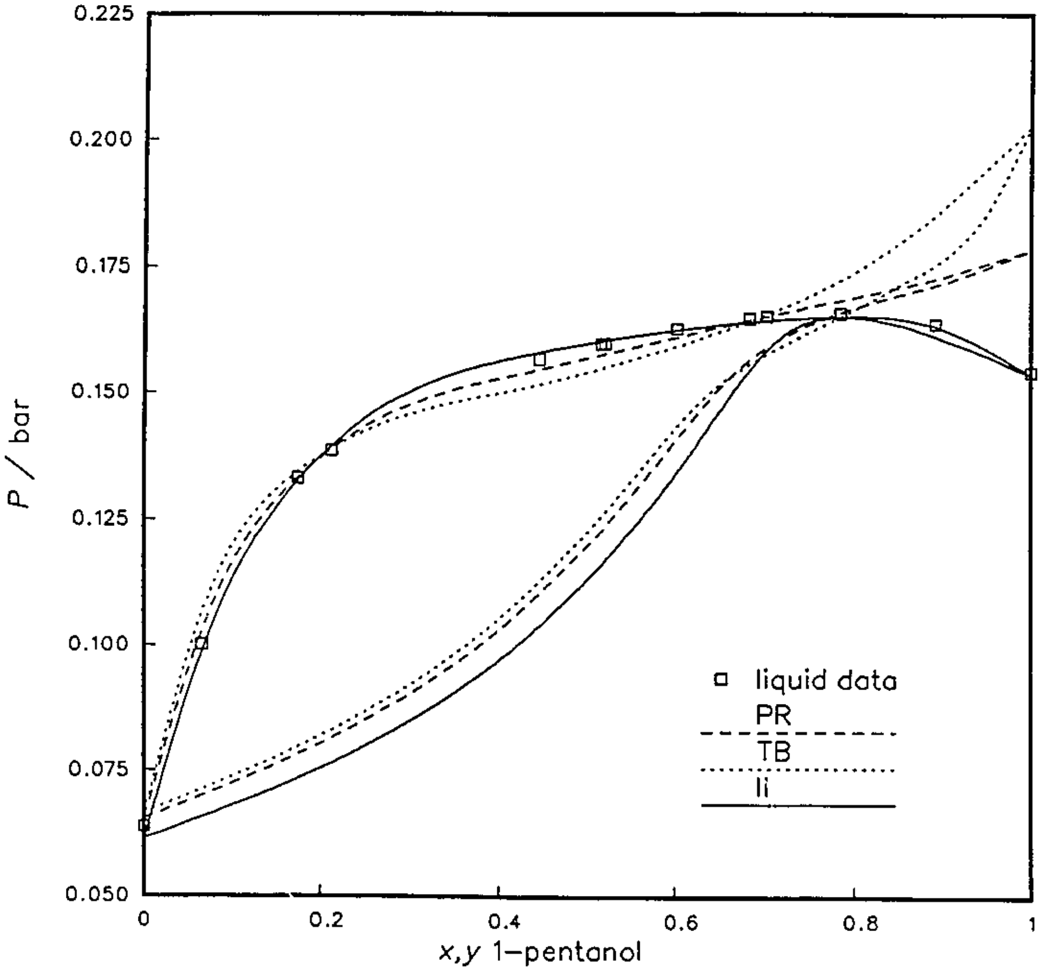

Figure 6.10: VLE for the 1-pentanol–n-decane system at 363.27 K, using the RK2 mixing rule with different equations of state.

6.2.2 Ternary VLE

A good test of the suitability of an equation of state model for mixtures using binary interaction coefficients is to see how well it extends to ternary mixtures. The systems given in Tables 4.4 and 4.5 are therefore used to evaluate the new equation of state. This will also allow further evaluation with binary mixtures.

Binary interaction coefficients are first determined, for the systems given in Table 4.4. Since the RK2 mixing rule performs well for most systems, it is used again here. Some systems show false liquid-phase splitting; in these cases, the RK2+ mixing rule is used. There are only two data points for the nitrogen–carbon dioxide system. Since a two-parameter model cannot be meaningfully fitted to this data, l_{ij} is set to zero[2]. Except for the PR equation, this resulted in exceedingly low values of the objective function, and very small confidence intervals for the parameters.

The binary interaction coefficients are then used to calculate VLE for the ternary systems given in Table 4.5. The results for the ternary systems and their constituent binaries are summarized by system in Tables 6.11–6.17.

The binary interaction coefficients are shown, with estimated 95 % confidence intervals. They are precisely determined in most cases. Some of the binary interaction coefficients are quite small, and have confidence intervals which are larger than the parameter values. However, correlations between the parameters (not shown) are moderate in all such cases. As before, the confidence intervals tend to be smaller for equations II and III. Large confidence intervals (indicating uncertainty in the parameter estimates) occur only for the nitrogen–methanol system. This may be due to the lack of fit occuring near the critical point exhibited by this system.

Equations II and III give the lowest standard error and overall deviations for most of the binary systems. Conversely, the TB equation gives the highest standard errors and overall deviations for most of the binary systems, although it performs well for a few systems. The PR equation and equation I generally give intermediate values. Equation I has particularly high deviations for binary systems containing acetonitrile; as noted in §6.1, the Z_c value for acetonitrile is outside the range of applicability of the generalized correlations used in equation I. As before, these results are

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[2] The RK2 mixing rule is equivalent to the conventional mixing rule for $l_{ij} = 0$.

explained by the relative accuracies of the equations of state in predicting pure fluid P^s.

A plot of P^s versus mole fraction is shown for the methanol–2-propanol system in 6.11, for the PR and TB equation, and equation II (equation III gives results simliar to those for equation II). Equation II clearly fits the data very well. The PR equation shows considerable deviations from the data; the TB has even larger deviations. Once again, this appears to be because pure fluid vapor pressure is better predicted by equation II.

The methanol–benzene system at 308.15 K is shown in Figure 6.12. This system requires the RK2+ mixing rule to prevent false liquid-phase splitting. Equation II again gives the best description of this system, particularly for the vapor phase. Note that this system can be represented by the RK2 mixing rule at 328.15 K, without any false phase-splitting. Clearly, the RK2 model, with these equations of state, predicts an upper temperature for liquid–liquid equilibrium between 308.15 K and 328.15 K for this system.

The overall deviations for the ternary systems are now considered. Except for the *n*-hexane–ethanol–benzene and the nitrogen–carbon dioxide–methanol systems, equations II and III give the lowest deviations for P^s and/or y. For the acetone–methanol–2-propanol they are particularly good, with much lower deviations than the other equations.

The deviations in $P^s$for the nitrogen–carbon dioxide–methanol system are much higher than for any of the other systems, especially for the PR equation. Comparisons may therefore not be meaningful for this system.

The TB equation gives the best performance for the *n*-hexane–ethanol–benzene system, although the difference between the various equations is not large. The differences in deviations for the constituent binaries are generally also not large; the TB equation generally does not give the best predictions for the constituent binaries.

Equation I gives reasonable performance for most systems, except for ethanol–acetonitrile–benzene. This is because of the presence of acetonitrile, as noted above.

Averaging the overall deviations for the ternary systems gives the following results (excluding nitrogen–carbon dioxide–methanol) for deviations in P^s and y respectively: 3.06 and 1.69 for the PR equation; 3.73 and 2.36 for the TB equation; 4.69 and 2.24 for equation I; 2.32 and 1.57 for equation II; 2.29 and 1.65 for equation III. Note that the deviations for equation I are high mainly because of the ethanol–acetonitrile–benzene system. Once again, equations II and III give significantly better performance compared to the other equations. The reason is as before: because they predict pure fluid P^s more accurately, they can describe mixtures better. Other equations which give accurate pure fluid P^s, such as the PRSV, would also give good VLE results.

Table 6.11: VLE for the acetone–methanol–water system at 373.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients		deviation	
		100 Pa	k_{ij}	l_{ij}	P^s	y
C_3H_6O	PR	3.5195	0.005 ± 0.006	0.012 ± 0.007	3.57	1.00
-CH_3OH	TB	2.1512	0.002 ± 0.004	0.023 ± 0.005	2.40	0.73
at 373.15 K	I	3.1493	0.000 ± 0.005	0.010 ± 0.006	3.42	1.13
	II	1.9669	0.001 ± 0.004	0.010 ± 0.005	2.03	1.20
	III	1.7203	0.002 ± 0.003	0.010 ± 0.005	1.68	1.21
C_3H_6O	PR	4.6400	-0.165 ± 0.003	0.079 ± 0.004	2.76	1.38
-H_2O	TB	7.0996	-0.157 ± 0.005	0.081 ± 0.007	3.53	1.99
at 373.15 K	I	3.4727	-0.167 ± 0.003	0.071 ± 0.004	2.56	0.92
	II	3.6555	-0.163 ± 0.003	0.076 ± 0.004	2.39	1.10
	III	3.0511	-0.162 ± 0.003	0.075 ± 0.004	2.15	1.02
CH_3OH	PR	6.0921	-0.094 ± 0.007	-0.003 ± 0.010	3.99	1.76
-H_2O	TB	5.0785	-0.085 ± 0.008	0.008 ± 0.011	4.99	1.02
at 373.15 K	I	3.3038	-0.089 ± 0.005	0.000 ± 0.009	2.34	1.37
	II	1.6550	-0.083 ± 0.003	-0.001 ± 0.006	1.19	1.37
	III	1.4197	-0.082 ± 0.002	-0.001 ± 0.004	1.03	1.50
C_3H_6O	PR				3.42	2.76
-CH_3OH	TB				2.00	2.77
-H_2O	I				2.70	2.50
at 373.15 K	II				1.97	2.65
	III				2.00	2.70

Table 6.12: VLE for the acetone–methanol–2-propanol system at 328.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients		deviation	
		100 Pa	k_{ij}	l_{ij}	P^s	y
C_3H_6O -CH_3OH at 328.15 K	PR	0.0671	0.002 ± 0.000	0.010 ± 0.001	0.35	0.54
	TB	1.5462	0.004 ± 0.002	0.034 ± 0.005	1.53	2.39
	I	0.3366	−0.008 ± 0.001	0.006 ± 0.003	0.88	0.95
	II	0.0645	−0.001 ± 0.000	0.012 ± 0.001	0.32	0.43
	III	0.0547	−0.002 ± 0.000	0.012 ± 0.001	0.25	0.49
C_3H_6O 2-C_3H_7OH at 328.15 K	PR	0.5315	0.043 ± 0.003	0.001 ± 0.003	3.67	1.33
	TB	3.4167	0.041 ± 0.010	0.013 ± 0.009	5.37	3.98
	I	0.8138	0.040 ± 0.002	0.001 ± 0.003	6.67	1.19
	II	0.1404	0.038 ± 0.001	−0.001 ± 0.003	1.01	0.62
	III	0.1495	0.038 ± 0.002	−0.001 ± 0.004	0.93	0.64
CH_3OH -2-C_3H_7OH at 328.15 K	PR	0.3527	−0.020 ± 0.003	0.005 ± 0.002	3.47	1.47
	TB	1.0495	−0.017 ± 0.002	0.004 ± 0.002	12.92	1.57
	I	0.5171	−0.020 ± 0.002	0.003 ± 0.002	5.91	1.43
	II	0.1121	−0.021 ± 0.001	−0.002 ± 0.002	1.01	0.48
	III	0.1574	−0.022 ± 0.002	−0.001 ± 0.002	1.27	0.53
C_3H_6O -CH_3OH -2-C_3H_7OH at 328.15 K	PR				2.98	1.20
	TB				7.10	2.41
	I				4.80	1.33
	II				0.85	0.74
	III				1.13	0.79

Table 6.13: VLE for the *n*-hexane–ethanol–benzene system at 328.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients			deviation	
		100 Pa	k_{ij}	l_{ij}	m_{ij}	P^s	y
n-C_6H_{14} -C_2H_5OH at 328.15 K	PR	0.8941	0.124 ± 0.006	0.092 ± 0.006	0.275 ± 0.032	1.17	2.86
	TB	0.4859	0.104 ± 0.007	0.086 ± 0.006	0.278 ± 0.029	1.27	1.32
	I	0.7431	0.108 ± 0.006	0.086 ± 0.005	0.283 ± 0.029	0.99	2.44
	II	0.8468	0.111 ± 0.006	0.089 ± 0.005	0.284 ± 0.031	1.10	2.75
	III	0.7723	0.112 ± 0.006	0.088 ± 0.005	0.281 ± 0.030	1.03	2.59
C_6H_6 $-n$-C_6H_{14} at 328.15 K	PR	0.0539	0.009 ± 0.001	-0.002 ± 0.002		0.47	0.80
	TB	0.0271	0.010 ± 0.001	-0.001 ± 0.001		0.40	0.37
	I	0.0577	0.007 ± 0.001	-0.001 ± 0.002		0.44	0.82
	II	0.0271	0.012 ± 0.001	-0.001 ± 0.001		0.39	0.33
	III	0.0270	0.012 ± 0.001	-0.001 ± 0.001		0.39	0.34
C_2H_5OH $-C_6H_6$ at 328.15 K	PR	0.4022	0.094 ± 0.003	-0.036 ± 0.005		2.11	1.85
	TB	0.7443	0.080 ± 0.004	-0.044 ± 0.008		2.15	2.27
	I	0.3354	0.082 ± 0.002	-0.037 ± 0.004		1.92	1.67
	II	0.6537	0.088 ± 0.004	-0.041 ± 0.008		2.13	1.82
	III	0.6322	0.088 ± 0.004	-0.041 ± 0.008		2.08	1.78
n-C_6H_{14} $-C_2H_5OH$ $-C_6H_6$ at 328.15 K	PR					3.85	2.83
	TB					3.55	2.43
	I					4.01	2.79
	II					3.77	2.72
	III					3.65	2.68

Table 6.14: VLE for the ethanol–acetonitrile–benzene system at 318.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients		deviation	
		100 Pa	k_{ij}	l_{ij}	P^s	y
C_2H_5OH	PR	0.0718	0.075 ± 0.003	−0.016 ± 0.009	2.60	2.02
$-C_2H_3N$	TB	0.6345	0.022 ± 0.009	−0.006 ± 0.008	17.71	3.01
at 293.15 K	I	2.7272	0.017 ± 0.030	0.018 ± 0.023	29.14	8.39
	II	0.0128	0.024 ± 0.001	−0.008 ± 0.003	0.45	1.43
	III	0.0118	0.027 ± 0.001	−0.011 ± 0.002	0.59	1.17
C_2H_5OH	PR	0.2980	0.087 ± 0.001	−0.030 ± 0.003	1.93	2.33
$-C_6H_6$	TB	0.5135	0.075 ± 0.003	−0.038 ± 0.004	2.92	2.61
at 318.15 K	I	0.2405	0.077 ± 0.001	−0.031 ± 0.002	1.84	2.19
	II	0.4542	0.083 ± 0.003	−0.036 ± 0.005	2.16	1.75
	III	0.4580	0.084 ± 0.003	−0.037 ± 0.006	2.15	1.75
C_2H_3N	PR	0.1318	0.065 ± 0.001	0.011 ± 0.003	0.69	1.77
$-C_6H_6$	TB	1.2066	−0.024 ± 0.013	−0.034 ± 0.013	5.03	3.35
at 318.15 K	I	3.7565	−0.003 ± 0.011	−0.028 ± 0.010	17.48	5.60
	II	0.0197	0.005 ± 0.001	−0.018 ± 0.002	0.44	0.44
	III	0.0157	0.006 ± 0.001	−0.017 ± 0.001	0.41	0.41
C_2H_5OH	PR				1.26	1.26
$-C_2H_3N$	TB				4.43	2.81
$-C_6H_6$	I				8.39	4.11
at 318.15 K	II				1.82	0.83
	III				1.39	0.90

Table 6.15: VLE for the methanol–carbon tetrachloride–benzene system at 308.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients			deviation	
		100 Pa	k_{ij}	l_{ij}	m_{ij}	P^s	y
CH_3OH	PR	0.2144	0.117 ± 0.006	-0.081 ± 0.005	0.704 ± 0.027	5.97	4.78
$-CCl_4$	TB	0.8155	0.117 ± 0.010	-0.106 ± 0.008	0.772 ± 0.053	2.00	1.74
at 308.15 K	I	0.4958	0.085 ± 0.008	-0.074 ± 0.006	0.625 ± 0.047	7.26	6.04
	II	0.3275	0.128 ± 0.007	-0.102 ± 0.004	0.795 ± 0.036	1.60	1.55
	III	0.3745	0.128 ± 0.008	-0.103 ± 0.005	0.794 ± 0.038	1.72	1.69
CH_3OH	PR	0.0994	0.107 ± 0.006	-0.058 ± 0.004	0.694 ± 0.035	1.68	3.08
$-C_6H_6$	TB	0.1742	0.084 ± 0.008	-0.070 ± 0.007	0.663 ± 0.064	1.38	1.51
at 308.15 K	I	0.1371	0.083 ± 0.012	-0.059 ± 0.008	0.643 ± 0.079	1.98	2.85
	II	0.0839	0.099 ± 0.006	-0.067 ± 0.005	0.693 ± 0.043	1.02	1.04
	III	0.1037	0.098 ± 0.007	-0.068 ± 0.005	0.688 ± 0.049	1.08	1.11
CCl_4	PR	0.0052	0.006 ± 0.000	0.002 ± 0.000		2.29	0.45
$-C_6H_6$	TB	0.0123	0.008 ± 0.001	0.002 ± 0.001		1.78	0.50
at 313.15 K	I	0.0034	0.006 ± 0.000	0.001 ± 0.000		2.43	0.29
	II	0.0118	0.010 ± 0.001	0.002 ± 0.003		0.39	0.44
	III	0.0030	0.006 ± 0.000	0.001 ± 0.000		1.60	0.13
CH_3OH	PR					2.84	1.05
$-CCl_4$	TB					2.25	2.03
$-C_6H_6$	I					3.75	1.29
at 308.15 K	II					1.53	1.32
	III					1.91	1.66

Table 6.16: VLE for the methanol–carbon tetrachloride–benzene system at 328.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS × 100 for y.

system		σ	interaction coefficients			deviation	
		100 Pa	k_{ij}	l_{ij}	m_{ij}	P^s	y
CH_3OH $-CCl_4$ at 328.15 K	PR	0.2404	0.149 ± 0.010	-0.094 ± 0.007	0.748 ± 0.043	1.91	1.96
	TB	0.5838	0.130 ± 0.017	-0.102 ± 0.013	0.735 ± 0.051	3.95	3.41
	I	0.3585	0.124 ± 0.011	-0.090 ± 0.009	0.730 ± 0.055	2.19	2.45
	II	0.2020	0.131 ± 0.008	-0.094 ± 0.006	0.732 ± 0.036	1.94	1.68
	III	0.2110	0.131 ± 0.008	-0.095 ± 0.006	0.730 ± 0.037	1.99	1.72
CH_3OH $-C_6H_6$ at 328.15 K	PR	1.1996	0.098 ± 0.003	-0.050 ± 0.007		4.90	4.03
	TB	0.7565	0.078 ± 0.003	-0.060 ± 0.006		4.06	2.47
	I	0.8491	0.080 ± 0.002	-0.053 ± 0.005		4.58	3.76
	II	0.9715	0.087 ± 0.003	-0.056 ± 0.007		4.15	2.58
	III	0.9256	0.087 ± 0.003	-0.057 ± 0.007		4.09	2.51
CCl_4 $-C_6H_6$ at 323.14 K	PR	0.0738	0.007 ± 0.001	0.002 ± 0.001		2.68	0.59
	TB	0.0202	0.012 ± 0.000	0.007 ± 0.001		0.25	0.59
	I	0.0743	0.007 ± 0.001	0.001 ± 0.001		2.91	0.47
	II	0.0111	0.008 ± 0.000	0.004 ± 0.001		0.20	0.34
	III	0.0105	0.009 ± 0.000	0.004 ± 0.001		0.19	0.34
CH_3OH $-CCl_4$ $-C_6H_6$ at 328.15 K	PR					4.05	1.03
	TB					3.10	1.76
	I					4.46	1.43
	II					3.99	1.17
	III					3.66	1.18

Table 6.17: VLE for the nitrogen–carbon dioxide–methanol system at 273.15 K with various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and RMS×100 for y.

system		σ	interaction coefficients			deviation	
		100 Pa	k_{ij}	l_{ij}	m_{ij}	P^s	y
N_2	PR	1.8158	0.017 ± 0.080			1.58	1.57
$-CO_2$	TB	0.0000	−0.052 ± 0.000			0.36	0.54
at 273.15 K	I	0.0000	0.058 ± 0.000			0.49	0.52
	II	0.0000	−0.003 ± 0.000			0.33	0.74
	III	0.0000	0.029 ± 0.000			0.26	0.66
N_2	PR	722.3573	−0.130 ± 0.147	0.046 ± 0.162		0.58	
$-CH_3OH$	TB	738.2750	−0.307 ± 0.138	0.284 ± 0.152		0.59	
at 273.15 K	I	744.0430	−0.176 ± 0.117	0.008 ± 0.130		0.60	
	II	750.9993	−0.200 ± 0.128	0.078 ± 0.141		0.60	
	III	742.7314	−0.179 ± 0.127	0.039 ± 0.140		0.59	
CO_2	PR	251.7538	0.102 ± 0.020	0.065 ± 0.019	0.079 ± 0.029	2.89	
$-CH_3OH$	TB	454.4271	−0.007 ± 0.007	0.059 ± 0.004	0.355 ± 0.051	3.81	
at 273.15 K	I	362.3645	0.047 ± 0.011	0.049 ± 0.009	0.190 ± 0.055	3.45	
	II	359.6776	0.034 ± 0.008	0.047 ± 0.006	0.247 ± 0.055	3.40	
	III	326.1472	0.051 ± 0.010	0.046 ± 0.008	0.187 ± 0.053	3.27	
N_2	PR					37.66	3.04
$-CO_2$	TB					9.28	1.04
$-CH_3OH$	I					11.13	0.98
at 273.15 K	II					13.31	1.13
	III					14.98	1.24

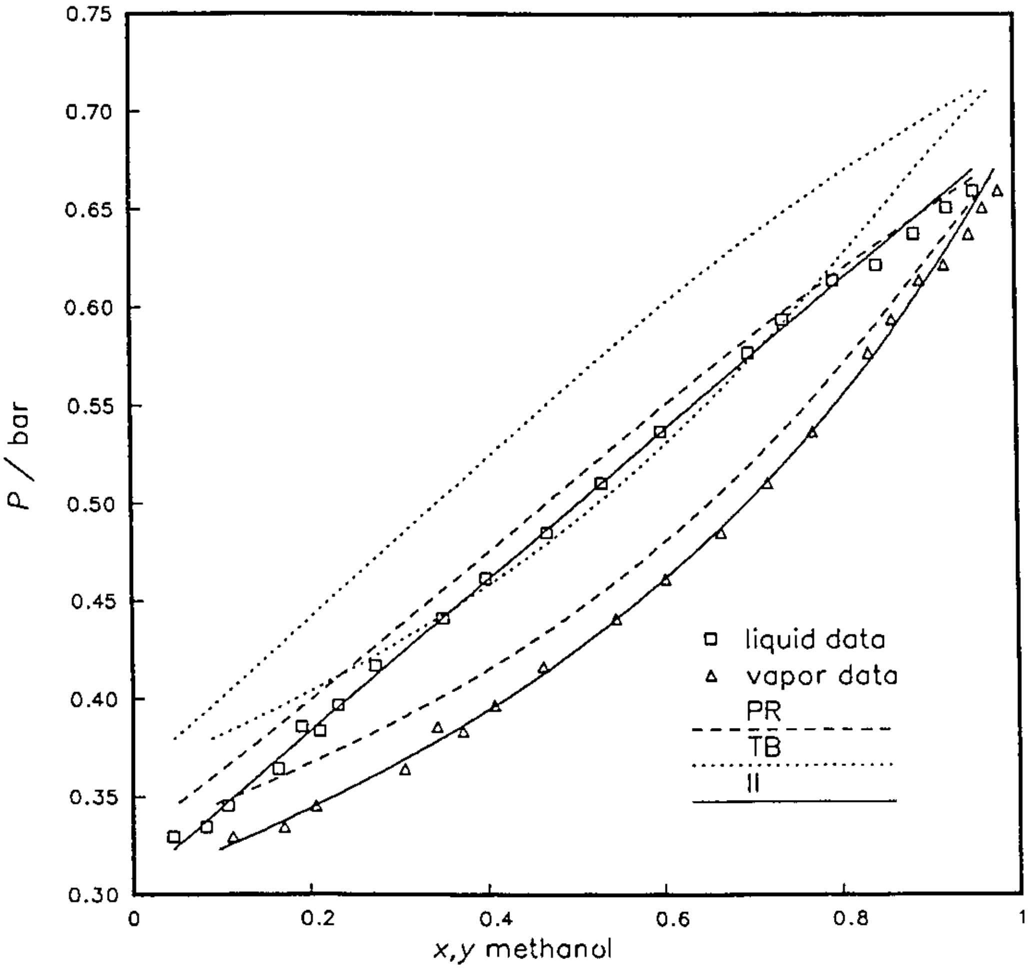

Figure 6.11: VLE for the methanol–2-propanol system at 328.15 K, using the RK2 mixing rule with different equations of state.

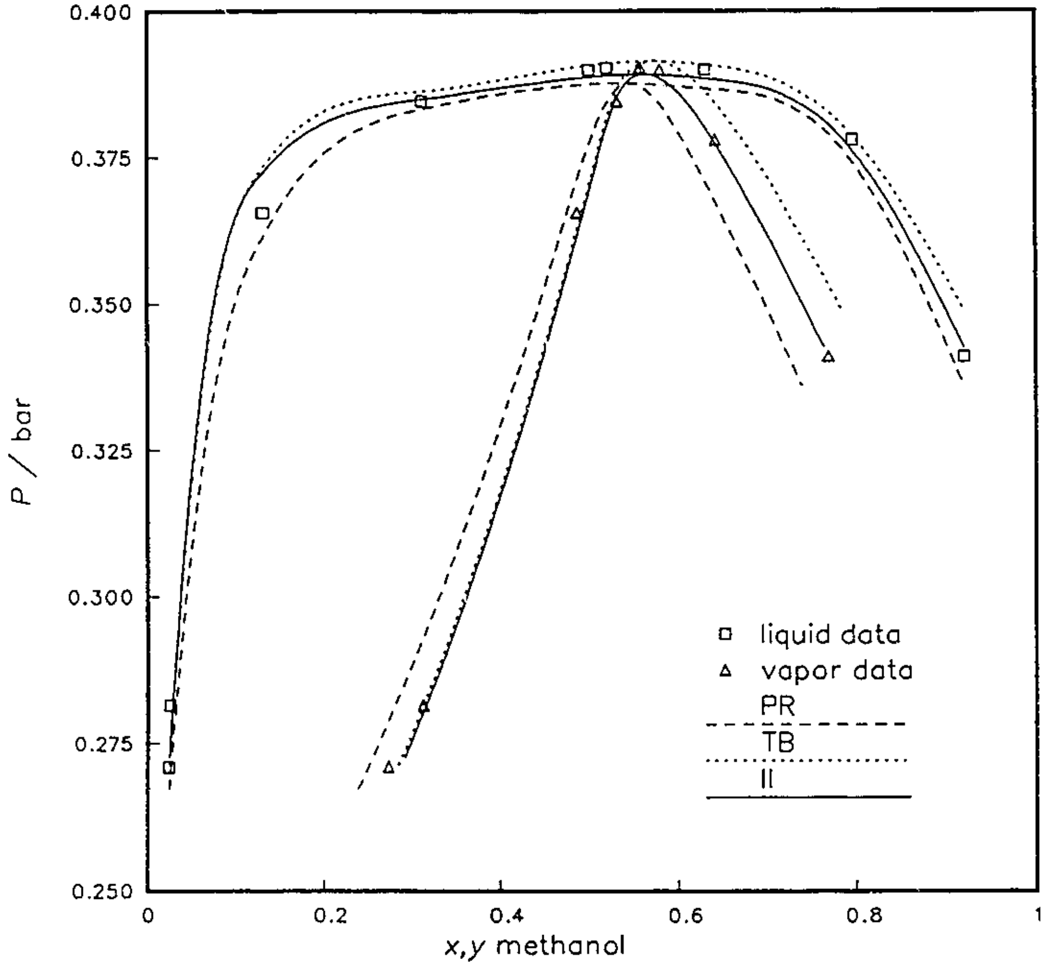

Figure 6.12: VLE for the methanol–benzene system at 308.15 K, using the RK2 mixing rule with different equations of state.

6.2.3 Mixture VLE and Volumes

The new equation of state predicts pure fluid volumes more accurately than any other equation of state tested (§6.1); it also gives VLE results superior to the other equations tested (§6.2.1, §6.2.2). Therefore, the data given Tables 4.6 and 4.7 are used to evaluate the VLE and volumetric performance of the new equation for binary mixtures.

The results for the saturated systems listed in Table 4.6 are summarized by system in Tables 6.18–6.24. In all cases the RK2 mixing rule is used, because none of these systems show false liquid-phase splitting.

The systems exhibiting critical points (see Table 4.6) have significant lack of fit. This is particularly severe near the critical points. Errors near the critical points are major contributions to the standard error and to the overall deviations given in the tables, and tend to obscure the differences between the different equations of state. Parameter estimation is also difficult for these systems, due to convergence problems with bubble-point calculations near the critical point. This is avoided by obtaining good initial estimates for the binary interaction coefficients. These are obtained by first performing VLE calculations using low-pressure data points only; data points at higher pressures are progressively added, and the VLE calculations repeated, until the full data set is fitted. Data points near the critical point often have to be dropped (see §4.1.3), when the equations of state underpredict the critical-point pressure for all values of the binary interaction coefficients.

For systems exhibiting critical points, no equation of state considered here gives consistently superior VLE performance. There are several reasons for this. The systems are dominated by errors near the critical point, thus obscuring any differences. Also, the temperature-dependent functions in the equations of state are being extrapolated into the critical region for one of the components in the mixture. Therefore, equations of state which have good performance for subcritical properties (such as the new equation) may not necessarily achieve superior performance in the supercritical region. It may be necessary to develop temperature-dependent functions specifically for extrapolation into supercritical regions.

The prediction of v_l^s for systems exhibiting critical points is somewhat more consistent. The new equation gives lower deviations in v_l^s compared to the PR equation for many systems (e.g., the nitrogen–hydrogen sulfide system, the ethane–methanol system). There does not appear to be a consistent difference between the new equation and the TB equation; a notable exception is the ethane–methanol system, where all three versions of the new equation are significantly better than the TB equation for prediction of v_l^s.

The prediction of v_v^s for mixtures is related to VLE performance (for the same reasons pure fluid v_v^s is related to P^s performance). Therefore, no equation seems to be consistently better for prediction of v_v^s for systems exhibiting critical points.

The results for systems not exhibiting critical points show more obvious differences between the equations of state. Equations II and III give better VLE for many of these systems (e.g., hydrogen sulfide–n-pentane at 277.59, 310.93 and 344.26 K), with correspondingly good v_v^s prediction. v_l^sprediction is significantly better, compared to the PR equation, in most cases. The new equation is better than the TB equation for prediction of v_l^s for the hydrogen sulfide–n-pentane at 277.59, 310.93 and 344.26 K; other systems do not show a consistent difference.

Typical results for these systems are shown in Figures 6.13 and 6.14, for the PR and TB equations, and equation II. Figure 6.13 is a plot of P^s versus x and y for the ethylene–chloroform system at 348.15 K, which exhibits a critical point. All equations seem to give reasonable description of the data, but there is increasing deviation as the critical point is approached, especially for the PR equation. Figure6.14 shows the saturated molar volumes of the liquid and vapor phases for the system nitrogen–hydrogen sulfide at 321.87 K. This system also exhibits a critical point. The volumes appear to be well described, except the PR equation gives high deviations for the liquid molar volume; there are also high deviations in v_v^s for all three equations of state near the critical point.

Table 6.25 shows overall deviations in compressed liquid molar volume v_l, for the systems given in Table 4.7. Binary interaction coefficients are obtained from the VLE calculations for the corresponding saturated systems (Table 6.19, 6.19 and 6.22). The TB equation gives the best performance for the methane–hydrogen sulfide and the hydrogen sulfide–n-decane systems. As noted in §6.1.2, the TB equation performs well for pure fluid compressed v_l, because such data was used in its generalization. This is clearly reflected in its performance here. Nevertheless, the new equation gives deviations which are not much larger than those for the TB equation, and which are almost all lower than those for the PR equation. Equation I gives the best results for the hydrogen sulfide–*n*-pentane system; equation II and the TB equation have the next highest deviations, and give nearly the same results.

In summary, the results here are not as clear as previously, due to the presence of critical points in most of the binary systems considered. Errors in the critical region tend to obscure any differences between the equations of state. Nevertheless, the new equation has good performance in most cases, particularly for liquid molar volumes.

Table 6.18: VLE and saturated volumes for nitrogen–hydrogen sulfide systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s, v_l^s and v_v^s, and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations			
K		100 Pa	k_{ij}	l_{ij}	P^s	y	v_l^s	v_v^s
256.43	PR	245.1530	0.216 ± 0.044	0.014 ± 0.047	7.97	1.44	8.02	5.77
	TB	264.9472	0.195 ± 0.045	0.033 ± 0.048	8.07	1.48	0.63	6.57
(c.p.)	I	181.8928	0.259 ± 0.030	0.030 ± 0.032	6.72	1.30	0.38	5.53
	II	238.9058	0.213 ± 0.040	0.020 ± 0.043	7.04	1.50	1.73	5.44
	III	214.2032	0.228 ± 0.036	0.016 ± 0.038	6.71	1.44	1.92	5.25
277.65	PR	236.8928	0.207 ± 0.064	0.033 ± 0.070	5.69	2.53	7.03	7.23
	TB	249.1768	0.192 ± 0.070	0.064 ± 0.078	5.45	2.67	0.51	7.74
(c.p.)	I	168.5769	0.241 ± 0.033	0.027 ± 0.036	4.91	1.97	0.78	7.29
	II	207.8592	0.205 ± 0.045	0.036 ± 0.049	4.65	2.46	1.85	7.53
	III	194.0173	0.216 ± 0.044	0.022 ± 0.048	4.43	2.36	1.56	7.61
300.04	PR	141.5804	0.148 ± 0.044	-0.030 ± 0.043	3.41	1.28	6.12	3.68
	TB	127.5382	0.125 ± 0.030	-0.001 ± 0.029	3.25	1.33	0.65	3.54
(c.p.)	I	319.9375	0.225 ± 0.052	0.006 ± 0.053	4.83	2.33	1.36	4.12
	II	177.6063	0.171 ± 0.038	0.003 ± 0.037	4.01	1.57	1.29	3.48
	III	146.4104	0.216 ± 0.016	-0.016 ± 0.018	10.16	0.68	0.94	9.19
321.87	PR	87.3075	0.064 ± 0.023	-0.143 ± 0.023	4.32	0.59	5.38	7.68
	TB	112.4366	0.047 ± 0.116	-0.100 ± 0.115	4.53	0.67	1.69	5.68
(c.p.)	I	178.4461	0.207 ± 0.041	-0.014 ± 0.043	3.29	2.09	1.87	2.87
	II	162.6315	0.122 ± 0.035	-0.077 ± 0.034	6.90	0.51	1.78	8.07
	III	117.7922	0.179 ± 0.038	-0.021 ± 0.037	3.16	1.46	1.47	1.83
344.26	PR	164.5195	-0.348 ± 0.061	-0.553 ± 0.060	3.75	3.47	6.13	15.21
	TB	112.0692	-0.434 ± 0.010	-0.568 ± 0.008	3.03	4.47	4.12	15.85
(c.p.)	I	202.7807	-0.061 ± 0.052	-0.281 ± 0.053	3.40	4.26	3.00	9.95
	II	150.2054	-0.305 ± 0.035	-0.486 ± 0.034	3.57	4.86	4.56	17.83
	III	207.5050	-0.184 ± 0.073	-0.421 ± 0.073	4.77	4.10	4.36	16.26

Table 6.19: VLE and saturated volumes for methane–hydrogen sulfide systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s, v_l^s and v_v^s, and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations			
K		100 Pa	k_{ij}	l_{ij}	P^s	y	v_l^s	v_v^s
277.59	PR	148.3730	0.068 ± 0.003	-0.028 ± 0.006	4.86	2.45	7.90	8.22
	TB	151.5856	0.047 ± 0.003	-0.032 ± 0.005	4.59	2.63	2.76	7.12
(c.p.)	I	222.3531	0.083 ± 0.003	-0.027 ± 0.004	4.99	3.40	3.56	10.63
	II	155.3559	0.067 ± 0.000	-0.033 ± 0.000	4.27	2.93	2.64	9.35
	III	161.7180	0.074 ± 0.000	-0.031 ± 0.004	4.28	3.04	2.38	9.60
310.93	PR	26.9883	0.062 ± 0.005	-0.063 ± 0.004	1.03	1.28	5.25	6.32
	TB	32.2955	0.031 ± 0.001	-0.068 ± 0.001	1.06	1.64	1.91	6.55
(c.p.)	I	66.4862	0.083 ± 0.005	-0.047 ± 0.012	1.10	2.53	2.90	8.12
	II	44.5693	0.061 ± 0.000	-0.062 ± 0.000	1.31	1.93	2.23	8.85
	III	43.8178	0.075 ± 0.000	-0.057 ± 0.001	1.30	1.82	2.05	8.66
344.26	PR	40.8723	0.013 ± 0.008	-0.130 ± 0.006	0.84	2.14	0.88	6.73
	TB	26.5529	-0.013 ± 0.001	-0.110 ± 0.002	0.34	2.30	2.86	6.62
(c.p.)	I	47.2075	0.072 ± 0.004	-0.076 ± 0.009	0.83	2.72	1.10	6.95
	II	30.2354	0.031 ± 0.065	-0.088 ± 0.103	0.40	2.55	1.33	6.42
	III	27.9639	0.051 ± 0.020	-0.087 ± 0.031	0.37	2.43	2.86	6.38

Table 6.20: VLE and saturated volumes for hydrogen sulfide–n-pentane systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s, v_l^s and v_v^s, and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations			
K		100 Pa	k_{ij}	l_{ij}	P^s	y	v_l^s	v_v^s
277.59	PR	1.1673	0.057 ± 0.004	-0.003 ± 0.006	2.34	0.25	3.47	1.91
	TB	0.8355	0.021 ± 0.002	0.002 ± 0.004	3.86	0.24	2.78	4.01
	I	1.5970	0.035 ± 0.004	-0.003 ± 0.007	2.88	0.27	0.81	2.36
	II	0.5672	0.035 ± 0.002	-0.002 ± 0.004	1.87	0.28	0.97	1.67
	III	0.5559	0.039 ± 0.002	-0.002 ± 0.004	1.86	0.28	2.32	1.71
310.93	PR	2.7331	0.039 ± 0.006	0.007 ± 0.005	3.17	0.50	2.49	3.63
	TB	1.6709	0.015 ± 0.006	0.004 ± 0.007	1.87	1.06	2.85	2.41
	I	2.7815	0.014 ± 0.005	0.006 ± 0.005	3.00	0.37	1.95	3.47
	II	1.0452	0.026 ± 0.004	0.002 ± 0.006	0.85	0.79	1.65	1.71
	III	1.0016	0.028 ± 0.004	0.002 ± 0.005	0.85	0.78	1.90	1.71
344.26	PR	11.8096	0.041 ± 0.012	0.018 ± 0.012	3.83	1.83	3.75	4.97
	TB	7.5436	0.012 ± 0.013	0.016 ± 0.014	3.44	2.19	4.66	4.92
	I	11.0539	0.015 ± 0.010	0.017 ± 0.010	3.67	1.58	3.79	5.57
	II	6.0082	0.028 ± 0.010	0.013 ± 0.012	2.73	1.88	3.77	4.74
	III	5.4970	0.026 ± 0.010	0.012 ± 0.012	2.52	1.92	4.46	4.45
377.59	PR	17.5737	0.071 ± 0.007	0.006 ± 0.015	0.89	1.53	10.87	9.73
	TB	24.5961	0.031 ± 0.008	0.005 ± 0.018	1.43	1.98	10.24	11.97
(c.p.)	I	22.8906	0.038 ± 0.006	0.002 ± 0.014	0.90	2.20	9.60	12.81
	II	21.3401	0.047 ± 0.006	0.002 ± 0.014	0.80	2.02	10.61	12.17
	III	21.8752	0.042 ± 0.006	0.002 ± 0.015	0.82	2.06	10.84	12.05
410.93	PR	15.9891	0.091 ± 0.007	0.056 ± 0.010	1.43	2.13	10.76	4.27
	TB	26.1082	0.032 ± 0.011	0.053 ± 0.016	3.28	3.06	7.62	6.58
(c.p.)	I	33.9220	0.045 ± 0.007	0.060 ± 0.008	2.69	3.70	7.46	8.07
	II	27.5127	0.052 ± 0.008	0.054 ± 0.010	2.63	3.30	8.91	6.99
	III	29.4317	0.049 ± 0.008	0.057 ± 0.011	2.60	3.41	9.04	7.01

Table 6.21: VLE and saturated volumes for hydrogen sulfide–n-heptane systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s, v_l^s and v_v^s, and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations			
K		100 Pa	k_{ij}	l_{ij}	P^s	y	v_l^s	v_v^s
310.93	PR	2.3815	0.068 ± 0.006	-0.027 ± 0.008	3.72	0.13	3.65	22.61
	TB	2.1305	0.024 ± 0.005	-0.023 ± 0.007	4.37	0.12	3.59	23.01
	I	2.3468	0.034 ± 0.006	-0.026 ± 0.007	3.65	0.12	5.42	22.70
	II	1.9883	0.022 ± 0.005	-0.020 ± 0.007	2.81	0.12	3.27	22.36
	III	1.9645	0.031 ± 0.005	-0.020 ± 0.007	2.70	0.12	5.79	22.31
352.59	PR	4.0563	0.058 ± 0.005	-0.017 ± 0.007	3.58	0.20	6.40	7.51
	TB	8.3216	0.008 ± 0.007	-0.016 ± 0.009	3.15	0.36	5.82	8.19
	I	6.5802	0.021 ± 0.006	-0.018 ± 0.008	3.64	0.35	5.64	7.93
	II	6.8307	0.015 ± 0.006	-0.016 ± 0.008	4.06	0.34	5.02	7.57
	III	6.8281	0.015 ± 0.006	-0.016 ± 0.008	4.03	0.33	6.38	7.48
394.26	PR	104.4892	0.081 ± 0.022	-0.008 ± 0.022	5.86	2.99	12.01	6.06
	TB	136.2473	0.018 ± 0.020	0.002 ± 0.021	6.93	3.71	10.69	8.05
(c.p.)	I	141.5352	0.036 ± 0.018	0.001 ± 0.019	7.04	3.82	10.20	8.91
	II	132.4177	0.034 ± 0.019	-0.001 ± 0.020	6.97	3.66	10.45	8.64
	III	136.2636	0.029 ± 0.020	0.001 ± 0.021	7.08	3.69	10.68	8.56

Table 6.22: VLE and saturated volumes for hydrogen sulfide–n-decane systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s, v_l^s and v_v^s, and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations			
K		100 Pa	k_{ij}	l_{ij}	P^s	y	v_l^s	v_v^s
344.26	PR	0.0446	0.056 ± 0.004	-0.043 ± 0.011	3.08	0.05	7.67	4.05
	TB	0.0259	-0.070 ± 0.003	0.001 ± 0.008	1.89	0.01	3.18	3.68
	I	0.1080	-0.037 ± 0.020	0.002 ± 0.031	0.86	0.01	4.30	5.99
	II	0.0440	-0.036 ± 0.009	-0.011 ± 0.018	1.75	0.01	3.00	5.21
	III	0.0314	-0.020 ± 0.008	-0.015 ± 0.016	1.94	0.01	6.46	5.17
377.59	PR	0.4186	0.026 ± 0.004	0.002 ± 0.005	2.84	0.22	11.68	1.37
	TB	0.4541	-0.088 ± 0.002	0.019 ± 0.003	4.55	0.35	7.87	1.74
(c.p.)	I	0.1848	-0.048 ± 0.001	0.010 ± 0.001	4.31	0.36	7.93	2.59
	II	0.2398	-0.051 ± 0.001	0.008 ± 0.002	4.08	0.35	7.71	2.33
	III	0.1528	-0.045 ± 0.001	0.007 ± 0.001	3.96	0.33	9.73	1.93
410.93	PR	2.5421	0.012 ± 0.006	0.031 ± 0.008	3.03	0.39	11.47	2.25
	TB	17.9896	-0.117 ± 0.000	0.064 ± 0.000	5.22	0.85	6.11	4.98
(c.p.)	I	16.9602	-0.073 ± 0.000	0.054 ± 0.000	4.96	0.87	6.42	5.29
	II	11.6440	-0.070 ± 0.050	0.045 ± 0.075	4.68	0.82	6.89	4.14
	III	11.9499	-0.071 ± 0.000	0.047 ± 0.000	4.69	0.79	8.05	4.04
444.26	PR	8.6875	0.012 ± 0.012	0.056 ± 0.011	3.50	0.77	10.21	3.96
	TB	32.5690	-0.119 ± 0.018	0.081 ± 0.017	6.58	1.69	4.14	6.99
(c.p.)	I	30.4132	-0.072 ± 0.016	0.072 ± 0.015	6.14	1.70	4.36	7.41
	II	23.4235	-0.069 ± 0.015	0.066 ± 0.013	5.76	1.50	5.78	6.45
	III	25.1551	-0.075 ± 0.016	0.069 ± 0.014	5.99	1.51	5.71	6.58

Table 6.23: VLE and saturated volumes for ethylene–chloroform systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for P^s and v_l^s and RMS×100 for y. Isotherms exhibiting a critical point are denoted by (c.p.).

T K		σ 100 Pa	interaction coefficients k_{ij}	l_{ij}	deviations P^s	y	v_l^s
298.15	PR	1.7440	-0.012 ± 0.003	-0.002 ± 0.005	0.35	0.84	3.23
	TB	2.2710	-0.004 ± 0.003	0.000 ± 0.003	0.29	1.07	7.81
(c.p.)	I	2.3529	0.005 ± 0.003	-0.002 ± 0.006	1.32	0.84	6.93
	II	2.1985	-0.010 ± 0.003	-0.001 ± 0.005	0.97	0.89	1.05
	III	2.4698	-0.007 ± 0.004	-0.002 ± 0.006	1.40	0.86	2.50
323.15	PR	15.7550	-0.014 ± 0.008	-0.013 ± 0.008	5.16	1.05	4.26
	TB	18.3559	-0.040 ± 0.013	0.002 ± 0.013	9.78	0.46	8.16
(c.p.)	I	12.3744	0.009 ± 0.006	-0.008 ± 0.006	4.50	1.04	6.90
	II	16.3138	-0.008 ± 0.007	-0.011 ± 0.008	4.98	1.03	2.99
	III	10.8810	-0.004 ± 0.005	-0.007 ± 0.006	4.21	0.99	3.66
348.15	PR	17.2838	-0.035 ± 0.008	-0.010 ± 0.009	4.45	0.97	5.33
	TB	76.6420	-0.015 ± 0.021	-0.028 ± 0.014	4.90	1.59	11.40
(c.p.)	I	17.5703	-0.003 ± 0.008	-0.010 ± 0.007	4.26	0.99	7.99
	II	30.5476	-0.023 ± 0.011	-0.017 ± 0.009	4.66	1.17	5.00
	III	22.3191	-0.014 ± 0.022	-0.012 ± 0.018	3.73	1.12	5.64
373.15	PR	79.5146	-0.023 ± 0.012	-0.027 ± 0.017	5.55	1.91	6.37
	TB	121.5613	-0.013 ± 0.015	-0.030 ± 0.017	6.89	2.52	13.85
(c.p.)	I	78.9168	0.014 ± 0.009	-0.021 ± 0.013	5.42	2.13	10.38
	II	98.8260	-0.011 ± 0.011	-0.026 ± 0.015	5.83	2.37	6.76
	III	81.9669	-0.002 ± 0.009	-0.019 ± 0.012	5.40	2.29	7.06

Table 6.24: VLE and saturated volumes for ethane–methanol systems using various equations of state. Interaction coefficients are shown with 95 % confidence intervals. Deviations are %RMS for $P^s$and v_l^s. Isotherms exhibiting a critical point are denoted by (c.p.).

T		σ	interaction coefficients		deviations	
K		100 Pa	k_{ij}	l_{ij}	P^s	v_l^s
323.15	PR	2394.8278	0.034 ± 0.007	-0.021 ± 0.022	5.23	11.47
	TB	1089.8899	-0.016 ± 0.001	0.045 ± 0.008	4.53	8.57
(c.p.)	I	1999.8500	0.010 ± 0.005	0.005 ± 0.018	3.78	3.92
	II	2031.7972	0.013 ± 0.005	0.001 ± 0.017	3.99	3.81
	III	2138.2236	0.013 ± 0.005	0.001 ± 0.018	4.25	2.71
323.15	PR	372.0000	0.062 ± 0.003	-0.024 ± 0.007	2.22	13.16
	TB	379.8921	0.014 ± 0.003	0.046 ± 0.006	1.97	8.34
(c.p.)	I	358.2374	0.039 ± 0.003	0.006 ± 0.006	1.94	3.71
	II	365.6173	0.039 ± 0.003	-0.002 ± 0.006	2.05	2.55
	III	363.7114	0.040 ± 0.003	0.001 ± 0.006	2.00	2.07
323.15	PR	782.3810	0.065 ± 0.016	-0.065 ± 0.025	5.67	14.43
	TB	758.1425	0.024 ± 0.014	0.012 ± 0.022	5.27	8.72
(c.p.)	I	781.0250	0.045 ± 0.014	-0.029 ± 0.022	5.57	4.46
	II	805.9777	0.042 ± 0.014	-0.041 ± 0.022	5.73	2.33
	III	808.5172	0.044 ± 0.014	-0.035 ± 0.022	5.74	2.65

Table 6.25: Compressed liquid volumes for binary mixtures using various equations of state. Entries are %RMS deviations in v_l.

system	T	equation of state				
	K	PR	TB	I	II	III
CH_4	277.59	8.30	1.82	3.24	2.49	2.13
$-H_2S$	310.93	7.03	1.11	2.58	1.46	1.24
	344.26	5.45	1.07	1.23	0.89	1.23
	overall	7.50	1.51	2.80	1.99	1.74
H_2S	277.59	3.97	1.69	0.93	2.07	3.54
$-C_5H_{12}$	310.93	4.12	2.02	1.31	1.94	2.35
	344.26	3.94	2.34	2.03	1.85	2.20
	377.59	4.81	4.00	3.57	3.98	4.12
	410.93	6.03	4.67	4.68	4.98	5.17
	overall	4.53	3.02	2.69	3.06	3.52
H_2S	344.26	5.85	1.95	4.91	2.53	6.96
$-C_{10}H_{22}$	377.59	5.60	2.32	3.94	3.19	5.90
	410.93	5.64	2.97	3.52	4.13	5.31
	444.26	6.25	4.06	3.92	5.44	5.42
	overall	5.84	2.89	4.13	3.92	5.97

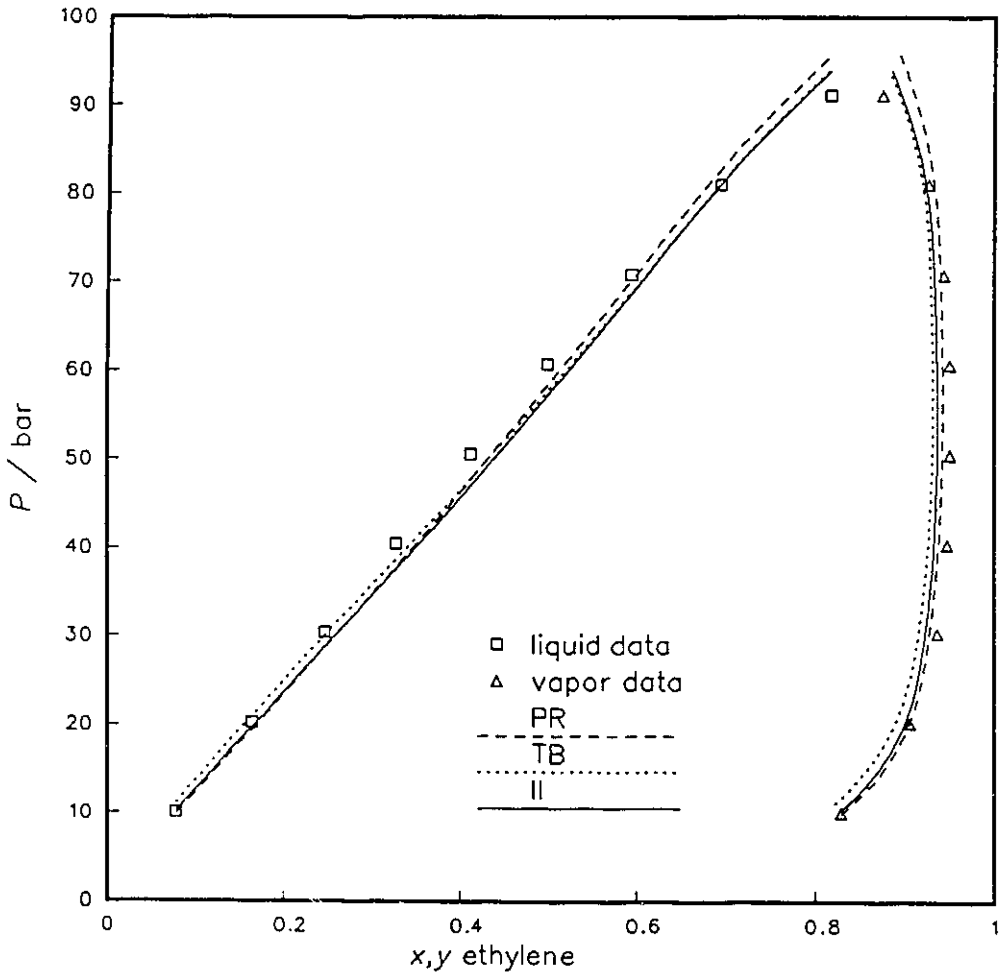

Figure 6.13: VLE for the ethylene–chloroform system at 348.15 K, using the RK2 mixing rule with different equations of state.

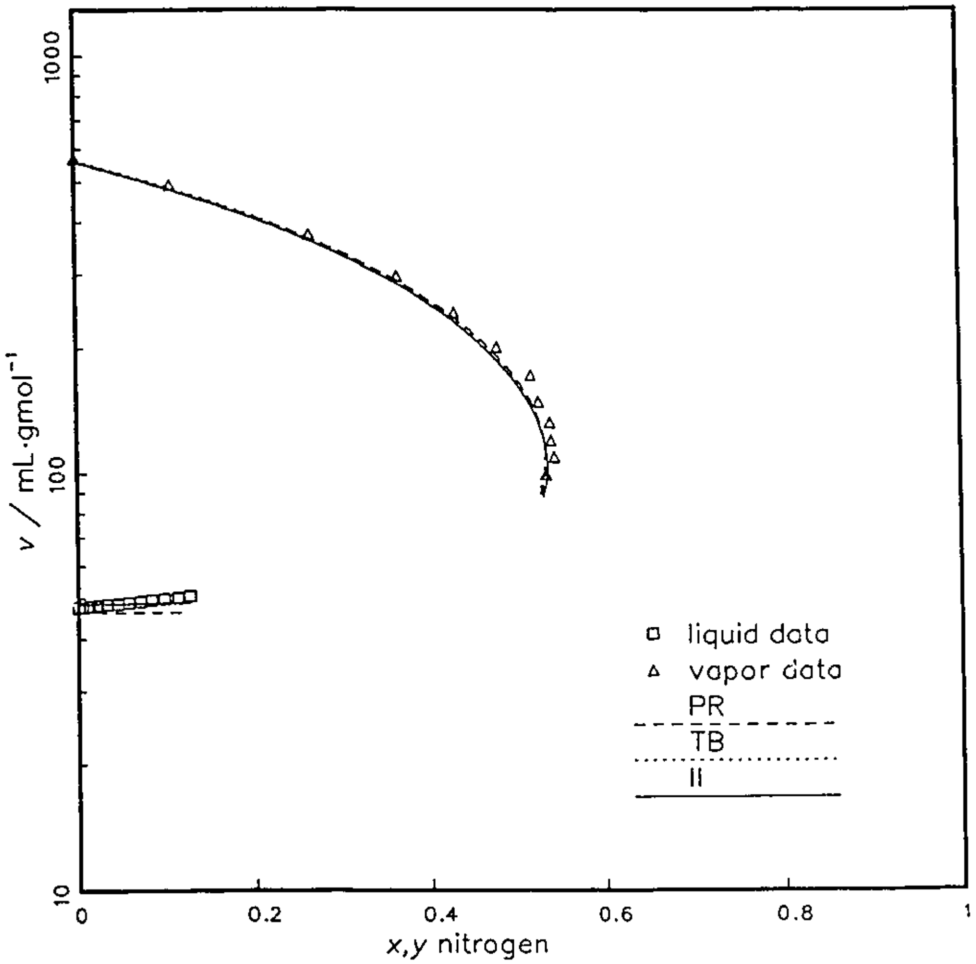

Figure 6.14: Volumes for the nitrogen–hydrogen sulfide system at 321.87 K, using the RK2 mixing rule with different equations of state.

Chapter 7

Conclusion

A new equation of state for polar fluids has been successfully developed.

Several important considerations in cubic equation of state design are identified in the literature review. Among these are the importance of the form of the equation of state, which has a strong effect on volumetric performance, and the temperature dependence of the constant a, which has a strong effect on vapor pressure prediction and VLE performance.

Based on the literature review, a general form for cubic equations of state is adopted, with temperature dependency in the parameter a only. General expressions and methods based on this and one other form are developed. These are very useful because they are applicable to most cubic equations of state, and to most mixing rules.

An extensive study of the effect of the form of cubic equations of state on the prediction of saturated volumes is made, using an extensive compilation of data for pure polar and nonpolar fluids. The optimum u and w values for volumetric performance are determined for each substance, and are found to be close to the locus $u = -w$. This finding is supported by considerations from microscopic corresponding-states theory: the line $u = -w$ is close to a locus of constant $\beta_c = b_c/v_c$, which is the expected behavior for real fluids. Comparison with other equations of state shows that few have come close to this relationship. Those that do come close have done so by the unnecessary introduction of an extra constant.

A new equation of state is therefore adopted, with $u = -w$. Two quantities (the temperature dependency of a, and one constant at the critical point) must then be specified. Three approaches are used. Equation I uses generalized correlations based on a four-parameter corresponding-states theory. In equation II, the constants are calculated directly from accurate correlations for pure fluid vapor pressure and saturated liquid molar volume. Equation III uses a new functional form for α, involving two constants per substance. All constants are then calculated from selected pure substance properties, using what is effectively a five-parameter corresponding-states principle.

The various versions of the new equation are first evaluated by comparing them to several other equations for the prediction of pure fluid properties, for polar and nonpolar fluids. The new equation gives the best performance in almost every case, in particular for volumetric properties. Equations II and III are found to be very reliable for a wide range of substances, because they avoid the use of generalized correlations.

Mixing rules are then evaluated, with the new equation and with some previous equations. The evaluation is extensive, using mixtures of alcohols and alkanes, which are difficult to describe with cubic equations of state. The simplest mixing rule, a two-coefficient Redlich-Kister expression, describes most systems well, but predicts false liquid-phase splitting in highly asymmetric systems. An augmented version of this mixing rule, with three binary interaction coefficients, prevents the false liquid phase-splitting in most cases. It performs better than the local composition mixing rule of Huron and Vidal.

The new equation of state gives the best VLE performance for a wide variety of mixtures containing polar components among the equations tested. This is due to its ability to accurately predict pure fluid vapor pressure, particularly for the versions using direct methods to obtain the constants. The new equation also gives good predictions of the volumes of mixtures.

Several areas for further research can be identified from the findings in this work.

Temperature dependency in b is not considered here, for a variety of reasons. However, it is evident that introduction of a temperature dependency for b has the potential for further improvements in volumetric performance. Research should be done to determine what effects such a temperature dependency has on various aspects of equation of state performance, and to determine an accurate and reliable form for the temperature dependency.

Good description is obtained for most of the mixtures in this study; however, false phase-splitting still occurred in some cases. Improved mixing rules could reduce the tendency of cubic equations of state to predict false phase-splitting for highly asymmetric systems.

The description of the critical regions of most mixtures is poor, for all equations of states examined here. This is believed to be due to errors in the extrapolation of temperature-dependent functions of supercritical components. Further study should be made of this, to determine if this is actually occurring, and to determine an appropriate temperature function for extrapolation into supercritical regions.

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Appendix A

Tables of Results

This section contains tables summarizing deviations in saturated pressure P^s, saturated liquid molar volume v_l^s and saturated vapor molar volume v_v^s for the pure fluids considered in this study.

In addition to %RMS deviations for each of these properties, the overall percent biases (%bias) and the overall averages of absolute percent deviations (%AAD) are shown. These are defined as follows, using P^s as an example.

$$\%bias = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{(P^s)^{\text{calc}} - P^s}{P^s}\right]_i \tag{A.1}$$

$$\%AAD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(P^s)^{\text{calc}} - P^s}{P^s}\right|_i \tag{A.2}$$

Table A.1: Overall deviations in v_l^s and v_v^s from the estimation of u and w.

	v_l^s			v_v^s		
	%bias	%RMS	%AAD	bias	RMSD	AAD
argon	0.05	2.15	1.84	−2.39	4.21	2.97
chlorine	0.12	3.28	2.80	−0.78	1.64	0.88
fluorine	0.04	1.87	1.60	−2.62	4.92	3.02
helium	0.00	0.46	0.39	−2.39	4.19	2.91
hydrogen chloride	0.20	4.37	3.88	−0.63	7.64	5.89
hydrogen	0.03	1.88	1.42	−3.55	5.14	3.60
water	0.11	2.86	2.55	−0.60	2.61	1.46
hydrogen sulfide	0.17	4.15	3.38	−6.52	9.62	6.52
ammonia	0.04	1.91	1.53	2.77	3.19	2.79
krypton	0.05	2.22	1.90	−3.34	4.94	3.46
nitrogen	0.09	2.97	2.57	−2.94	4.55	2.98
neon	0.01	0.89	0.77	0.91	1.19	0.92
oxygen	0.10	3.03	2.55	−1.65	3.50	1.96
sulfur dioxide	0.46	7.25	5.23	−4.40	6.76	4.74
sulfur trioxide	0.20	4.41	3.55	−6.09	8.54	7.66
xenon	0.05	2.18	1.83	−3.29	4.59	3.34
phosgene	0.08	2.71	2.36	−9.23	13.21	11.80
carbon tetrachloride	0.13	3.59	3.04	−5.19	7.95	5.47
carbon tetrafluoride	0.13	3.48	2.99	−1.87	3.69	1.87
carbon monoxide	0.02	1.19	0.98	1.56	4.15	3.26
carbon dioxide	0.05	2.18	1.91	−4.77	6.39	4.99
chloroform	0.05	2.10	1.81	−4.93	8.04	5.07
freon-13	0.06	2.26	1.96	−2.03	3.68	2.49
freon-12	0.06	2.27	1.93	−1.30	2.04	1.37
freon-11	0.01	0.83	0.68	0.02	0.14	0.09
freon-22	0.11	3.25	2.73	−2.88	4.66	3.15
freon-21	0.11	3.15	2.70	−0.92	3.14	1.88
methyl chloride	0.00	0.44	0.38	1.55	1.77	1.55
methane	0.06	2.45	2.13	−2.12	3.52	2.26
methanol	0.06	2.35	2.04	1.17	4.22	3.90
methyl mercaptan	0.04	1.99	1.66	−30.37	34.38	30.37
freon-114	0.00	0.43	0.37	0.12	0.59	0.46
freon-113	0.00	0.25	0.21	0.19	0.24	0.22
acetylene	0.06	2.45	2.18	−1.63	3.40	2.03
acetonitrile	0.24	4.39	3.78	5.86	9.56	6.94
ethylene	0.14	3.66	3.10	−2.69	4.97	3.58
ethylene oxide	0.07	2.59	2.28	−4.25	6.72	4.61
acetic acid	0.15	3.62	3.10	54.89	59.37	54.89
methyl formate	0.08	2.80	2.44	−2.99	4.66	3.03
ethyl chloride	0.05	2.14	1.87	−4.51	7.21	5.40
ethane	0.16	4.04	3.42	−3.10	5.76	3.38
dimethyl ether	0.08	2.68	2.36	−4.23	6.55	4.90
ethanol	0.27	5.36	4.79	−6.75	11.09	6.82
ethyl mercaptan	0.09	3.03	2.62	−17.30	18.20	17.30
dimethyl sulfide	0.06	2.31	2.04	−19.02	21.92	19.46
propyne	0.04	1.94	1.68	−5.58	6.50	5.58
propylene	0.06	2.29	1.95	−0.45	1.21	0.67
acetone	0.16	3.95	3.42	−13.67	16.25	15.70
propylene oxide	0.35	5.53	3.37	−1.21	1.61	1.39

Table A.1: Overall deviations in v_l^s and v_v^s from the estimation of u and w (continued).

	v_l^s			v_v^s		
	%bias	%RMS	%AAD	bias	RMSD	AAD
ethyl formate	0.07	2.56	2.24	−3.64	5.30	3.64
methyl acetate	0.09	2.93	2.55	−3.43	4.94	3.45
cyclopropane	0.04	1.89	1.62	−6.37	8.13	6.37
propane	0.03	1.57	1.32	−2.20	4.11	2.67
1-propanol	0.05	2.14	1.88	0.33	2.69	2.11
2-propanol	0.11	3.43	3.11	−1.13	13.16	9.61
methyl ethyl ether	0.09	3.02	2.63	3.70	21.20	18.18
perfluorocyclobutane	0.05	2.20	1.89	−1.61	3.80	1.96
1,2-butadiene	0.02	1.43	1.21	−2.71	7.61	4.86
1,3-butadiene	0.07	2.63	2.07	−2.07	3.75	2.85
1-butene	0.04	1.95	1.72	−3.11	4.98	3.85
ethyl acetate	0.08	2.67	2.37	−2.61	4.70	2.94
methyl propionate	0.09	2.83	2.46	−2.97	5.62	3.85
n-propyl formate	0.08	2.73	2.35	−3.16	5.17	3.39
n-butane	0.04	2.16	1.42	−2.66	4.17	2.85
isobutane	0.00	0.72	0.62	−1.38	3.00	1.85
1-butanol	0.04	1.87	1.67	12.82	21.97	13.83
t-butanol	0.02	1.24	1.09	−1.17	4.32	3.66
diethyl ether	0.05	2.23	1.95	−1.75	4.52	3.40
diethyl sulfide	0.03	1.78	1.54	−42.30	42.78	42.30
diethyl amine	0.04	1.78	1.56	−10.93	12.18	11.64
n-propyl acetate	0.13	3.50	3.07	−4.58	6.73	4.67
ethyl propionate	0.08	2.80	2.46	−2.16	4.16	2.59
methyl butyrate	0.09	2.86	2.49	−1.93	5.20	3.96
methyl isobutyrate	0.08	2.81	2.49	−2.28	4.60	3.23
n-pentane	0.02	1.52	1.04	−2.18	3.33	2.28
isopentane	0.09	2.83	2.44	−1.58	3.92	2.15
neopentane	0.02	1.33	1.12	−3.11	4.82	3.58
ethyl propyl ether	0.03	1.60	1.40	52.90	73.12	53.18
bromobenzene	0.00	0.18	0.16	1.90	2.01	1.90
chlorobenzene	0.00	0.36	0.31	0.23	0.51	0.40
fluorobenzene	0.06	2.42	2.07	−3.00	4.56	3.13
iodobenzene	0.00	0.10	0.08	1.34	1.46	1.34
benzene	0.14	3.71	3.14	−4.12	6.29	4.54
aniline	0.04	1.93	1.67	−1.37	2.26	1.55
cyclohexane	0.04	2.04	1.66	−4.34	5.71	4.37
n-hexane	0.05	2.54	1.77	−0.19	1.65	1.17
toluene	0.07	2.54	2.32	−9.71	12.10	9.71
n-heptane	0.06	2.32	1.98	−1.68	3.20	1.82
n-octane	0.12	4.27	3.52	0.56	0.75	0.68
isooctane	0.17	3.93	3.38	−8.70	9.00	8.70
m-xylene	0.01	1.14	1.09	−2.13	2.83	2.32
o-xylene	0.03	1.63	1.46	−2.30	3.02	2.30
p-xylene	0.09	2.87	2.61	−4.21	6.11	4.22
ethyl benzene	0.10	3.19	2.84	−7.84	9.27	7.84
naphthalene	0.00	0.19	0.16	−7.66	10.63	9.24
n-decane	0.03	1.72	1.57	−2.11	2.87	2.27
diphenyl ether	0.00	0.34	0.30	15.25	17.00	15.25

Table A.2: Overall deviations in P^s, v_l^s and v_v^s for the Soave-Redlich-Kwong equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.92	1.99	1.45	4.58	7.52	4.98	2.11	3.09	2.18
chlorine	−1.13	2.28	1.81	6.96	8.82	6.96	2.67	3.03	2.67
fluorine	−0.94	1.03	0.94	5.67	7.13	5.67	3.26	4.68	4.32
helium	−11.42	17.33	11.81	−10.61	14.52	12.98	19.06	28.99	19.37
hydrogen chloride	−0.41	2.92	2.34	19.55	21.19	19.55	5.27	6.99	5.88
hydrogen	−3.17	9.86	6.35	−1.93	10.05	8.91	3.87	13.55	8.83
water	−8.01	13.79	9.62	38.37	39.07	38.37	13.76	19.25	13.76
hydrogen sulfide	3.83	4.76	3.83	10.00	12.22	10.00	−6.17	6.46	6.17
ammonia	1.50	1.61	1.52	29.74	30.05	29.74	5.54	7.23	5.54
krypton	−1.13	2.38	1.76	5.75	8.41	5.75	1.35	3.13	2.56
nitrogen	−0.82	1.82	1.33	4.86	7.94	4.91	1.18	2.38	1.82
neon	2.48	3.94	3.61	−3.04	7.25	6.47	−1.48	3.21	2.81
oxygen	−3.36	6.00	3.97	3.35	6.78	3.95	4.18	7.15	4.78
sulfur dioxide	0.98	1.35	1.21	19.38	22.72	19.38	2.51	5.92	2.67
sulfur trioxide	−7.04	8.73	7.04	19.72	20.65	19.72	8.54	12.41	8.91
xenon	−0.65	1.92	1.47	7.22	9.63	7.22	1.12	2.39	1.85
phosgene	−0.18	0.85	0.51	9.34	11.54	9.34	−4.88	9.71	8.28
carbon tetrachloride	−0.60	1.09	0.86	15.48	16.88	15.48	1.45	3.01	2.32
carbon tetrafluoride	−1.26	2.56	1.94	6.51	8.61	6.51	1.03	2.93	2.30
carbon monoxide	−3.44	4.97	3.87	3.28	5.60	3.66	7.27	8.88	7.61
carbon dioxide	−0.94	1.53	1.12	15.02	16.47	15.02	3.67	4.11	3.67
chloroform	−3.02	3.08	3.02	12.29	13.19	12.29	2.29	3.71	3.53
freon-13	−4.50	6.20	4.52	9.04	10.63	9.04	6.37	8.10	6.37
freon-12	−5.71	7.21	5.76	7.90	9.10	7.90	7.54	8.70	7.54
freon-11	−1.14	1.38	1.26	6.29	6.41	6.29	1.43	1.54	1.43
freon-22	0.03	1.03	0.85	16.98	18.20	16.98	2.31	2.57	2.31
freon-21	−0.56	1.13	1.01	12.49	13.72	12.49	2.72	2.86	2.72
methyl chloride	1.01	1.86	1.44	12.19	12.22	12.19	0.78	1.02	0.96
methane	−0.23	2.60	2.08	5.45	8.70	5.51	0.79	2.81	2.14
methanol	4.00	4.29	4.03	42.66	43.86	42.66	3.97	5.38	3.97
methyl mercaptan	−0.53	1.09	0.96	13.54	14.82	13.54	−26.66	32.27	26.67
freon-114	0.86	1.54	1.31	7.93	7.98	7.93	−0.35	1.23	1.10
freon-113	−1.13	1.23	1.13	7.21	7.21	7.21	1.42	1.52	1.42
acetylene	0.49	1.85	1.68	14.62	16.20	14.62	2.18	2.32	2.18
acetonitrile	1.92	7.40	6.30	87.93	88.53	87.93	13.65	16.45	13.65
ethylene	−0.53	1.46	1.16	10.11	13.00	10.11	2.57	3.15	2.75
ethylene oxide	−1.87	2.35	1.95	22.19	22.89	22.19	1.89	1.93	1.89
acetic acid	−0.59	10.39	7.88	50.03	50.67	50.03	64.56	75.99	64.56
methyl formate	−0.13	0.42	0.30	22.70	23.63	22.70	3.15	4.07	3.15
ethyl chloride	0.85	1.27	1.16	17.06	18.09	17.06	−1.20	3.61	3.08
ethane	−1.41	2.65	1.78	9.88	12.94	9.88	2.43	3.15	2.47
dimethyl ether	0.46	0.89	0.56	16.60	18.28	16.60	2.12	3.64	2.83
ethanol	0.17	0.24	0.19	30.16	32.48	30.16	1.62	2.18	1.70
ethyl mercaptan	−0.01	1.23	0.89	14.87	16.32	14.87	−12.68	14.35	12.93
dimethyl sulfide	−0.19	3.05	2.59	16.44	17.82	16.44	−15.44	19.63	16.54
propyne	0.79	0.98	0.79	22.37	23.11	22.37	7.55	10.44	7.55
propylene	−0.90	1.65	1.40	7.96	8.77	7.96	1.67	1.89	1.67
acetone	0.40	0.96	0.85	32.70	33.23	32.70	−7.51	12.18	11.19

Table A.2: Overall deviations in P^s, v_l^s and v_v^s for the Soave-Redlich-Kwong equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−0.71	2.88	2.49	27.60	28.58	27.60	2.42	2.55	2.42
ethyl formate	−0.11	0.41	0.35	22.33	23.41	22.33	2.85	3.49	2.85
methyl acetate	0.35	0.78	0.70	23.68	24.67	23.68	2.17	3.21	2.17
cyclopropane	0.12	0.32	0.29	17.93	18.95	17.93	1.60	1.70	1.60
propane	0.28	1.42	1.23	9.96	11.95	9.96	0.74	1.49	1.18
1-propanol	−0.73	1.88	1.64	21.63	22.89	21.63	6.34	7.24	6.68
2-propanol	−3.84	5.51	4.63	24.83	26.30	24.83	11.41	15.50	13.57
methyl ethyl ether	−2.10	2.38	2.10	15.25	17.20	15.25	12.23	21.19	15.46
perfluorocyclobutane	−0.12	0.50	0.44	9.15	10.94	9.15	1.21	1.42	1.24
1,2-butadiene	−1.17	5.10	3.49	13.21	13.48	13.21	1.27	1.30	1.27
1,3-butadiene	1.44	2.03	1.75	15.00	16.50	15.00	0.17	1.49	1.22
1-butene	0.92	1.14	1.04	12.15	13.25	12.15	−0.30	1.61	1.39
ethyl acetate	0.81	0.96	0.84	24.59	25.58	24.59	2.85	3.72	2.85
methyl propionate	0.95	1.51	1.02	23.47	24.72	23.47	2.84	3.72	2.84
n-propyl formate	0.64	0.98	0.80	21.12	22.18	21.12	1.86	2.36	1.86
n-butane	0.76	1.00	0.89	14.28	16.01	14.28	0.88	2.14	1.04
isobutane	0.11	1.41	1.27	8.65	9.05	8.65	−0.11	2.11	1.89
1-butanol	2.75	4.80	3.65	16.93	18.19	16.93	12.97	21.70	14.22
t-butanol	−2.61	4.20	2.90	16.37	16.79	16.37	5.74	6.53	5.74
diethyl ether	1.36	1.53	1.38	18.61	20.12	18.61	2.21	2.35	2.21
diethyl sulfide	−3.19	3.44	3.20	−14.68	15.37	14.68	−39.94	40.42	39.94
diethyl amine	1.69	1.99	1.69	19.01	20.05	19.01	−7.96	10.19	8.40
n-propyl acetate	0.68	0.97	0.81	25.95	27.11	25.95	2.76	4.40	2.76
ethyl propionate	1.50	1.81	1.55	24.10	25.25	24.10	2.62	3.67	2.62
methyl butyrate	1.51	1.82	1.56	23.31	24.65	23.31	3.27	4.07	3.27
methyl isobutyrate	0.97	1.26	1.07	21.60	22.82	21.60	3.13	3.86	3.13
n-pentane	0.82	1.12	1.01	14.59	15.42	14.59	0.14	0.85	0.68
isopentane	−0.18	1.57	1.42	11.23	12.92	11.23	0.67	1.98	1.76
neopentane	−0.68	3.41	1.92	10.09	10.98	10.09	0.75	1.12	1.05
ethyl propyl ether	1.93	3.88	3.53	11.64	13.28	11.64	54.55	77.24	54.77
bromobenzene	0.11	0.77	0.69	14.18	14.21	14.18	2.56	2.74	2.56
chlorobenzene	1.41	1.63	1.41	13.93	14.03	13.93	−0.09	0.66	0.55
fluorobenzene	0.79	1.11	0.92	17.50	18.67	17.50	1.41	2.15	1.69
iodobenzene	−0.32	0.51	0.32	12.82	12.83	12.82	2.11	2.24	2.11
benzene	0.38	1.51	1.11	14.46	15.94	14.46	−0.36	2.37	1.65
aniline	1.28	1.55	1.46	16.66	17.42	16.66	0.87	1.60	0.96
cyclohexane	0.46	0.68	0.58	13.83	15.20	13.83	0.36	1.00	0.89
n-hexane	0.54	1.69	1.52	15.49	16.00	15.49	0.75	1.52	1.33
toluene	−1.45	2.44	1.99	16.89	17.82	16.89	−2.78	2.83	2.78
n-heptane	0.38	1.68	1.39	16.93	18.06	16.93	0.53	2.47	1.70
n-octane	0.51	1.80	1.58	19.00	19.70	19.00	0.91	1.78	1.41
isooctane	0.23	1.54	1.33	12.97	14.29	12.97	−5.65	6.06	5.85
m-xylene	0.03	0.88	0.73	17.74	18.11	17.74	1.45	2.35	1.47
o-xylene	0.34	1.31	1.07	16.48	17.19	16.48	0.69	1.19	0.88
p-xylene	0.55	0.92	0.70	20.77	21.76	20.77	1.05	2.28	1.46
ethyl benzene	−1.93	2.10	1.93	18.63	20.13	18.63	1.82	3.91	1.82
naphthalene	−1.93	2.37	1.93	18.69	18.79	18.69	−4.47	8.67	7.71
n-decane	1.48	2.19	2.05	25.74	26.28	25.74	0.85	1.68	0.87
diphenyl ether	5.02	5.40	5.02	18.18	18.22	18.18	10.18	12.19	10.52

Table A.3: Overall deviations in P^s, v_l^s and v_v^s for the Peng-Robinson equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.25	0.47	0.39	−7.28	9.32	8.59	−0.25	2.13	1.77
chlorine	1.39	3.19	1.66	−5.16	7.36	6.94	−0.95	3.04	1.88
fluorine	−1.26	1.43	1.31	−6.41	7.69	6.84	1.63	4.66	3.33
helium	−4.07	9.09	6.01	−19.78	21.82	19.93	5.07	13.19	9.34
hydrogen chloride	−0.43	1.77	1.44	5.98	10.12	5.98	3.67	6.45	5.17
hydrogen	1.20	5.04	4.18	−12.49	15.58	13.70	−3.72	8.12	7.24
water	−4.46	7.81	5.37	22.78	23.76	22.78	7.51	9.89	7.51
hydrogen sulfide	4.03	5.71	4.03	−2.50	7.57	6.16	−7.76	8.42	7.76
ammonia	1.27	1.53	1.29	14.79	15.35	14.79	4.35	5.70	4.54
krypton	−0.41	0.74	0.61	−6.24	8.64	7.97	−1.04	2.81	2.34
nitrogen	0.25	0.79	0.45	−7.06	9.29	8.70	−1.43	2.22	1.56
neon	3.30	3.61	3.31	−13.97	15.36	14.26	−4.03	4.97	4.03
oxygen	0.89	1.86	1.14	−8.29	9.99	9.43	−1.57	2.72	2.00
sulfur dioxide	0.82	0.98	0.88	6.04	13.05	6.86	0.60	3.64	1.24
sulfur trioxide	−7.72	9.42	7.77	5.88	8.38	5.88	7.89	12.58	8.48
xenon	−0.05	0.44	0.39	−4.95	7.92	7.23	−1.14	2.14	1.73
phosgene	−0.40	0.56	0.45	−3.12	7.42	6.53	−6.20	9.98	8.92
carbon tetrachloride	−1.22	1.36	1.22	2.24	6.98	4.79	0.43	3.97	2.46
carbon tetrafluoride	2.76	5.54	2.84	−5.61	7.61	7.26	−3.54	5.44	3.54
carbon monoxide	−2.55	3.18	2.82	−8.53	9.55	8.83	4.85	6.41	5.75
carbon dioxide	−1.68	2.10	1.69	2.03	7.25	5.28	2.23	3.20	2.62
chloroform	−3.35	3.62	3.35	−0.80	4.43	3.52	1.58	3.85	3.34
freon-13	−4.50	5.43	4.51	−3.50	6.38	5.88	5.02	6.68	5.53
freon-12	−5.20	5.90	5.20	−4.54	6.27	5.83	5.88	6.67	5.89
freon-11	1.33	2.78	1.77	−5.89	5.97	5.89	−1.22	2.62	1.71
freon-22	0.49	2.08	0.91	3.70	7.36	4.90	0.15	2.18	1.48
freon-21	0.79	2.71	1.68	−0.34	5.47	4.17	0.29	3.17	2.66
methyl chloride	2.33	2.55	2.33	−0.79	0.99	0.90	−0.83	1.82	1.32
methane	1.42	1.46	1.42	−6.46	9.20	8.50	−2.33	2.77	2.33
methanol	3.23	3.33	3.23	26.33	28.08	26.33	3.10	3.58	3.10
methyl mercaptan	−0.74	1.17	0.97	0.49	5.82	4.46	−27.74	32.56	27.74
freon-114	1.94	3.63	2.88	−4.57	4.62	4.57	−1.64	3.13	2.48
freon-113	1.99	3.11	2.15	−5.02	5.03	5.02	−1.77	2.83	1.90
acetylene	−0.02	1.27	1.04	1.46	6.93	4.79	1.19	2.04	1.93
acetonitrile	2.28	5.77	5.07	66.89	67.72	66.89	11.02	13.10	11.02
ethylene	0.18	1.02	0.70	−2.28	8.35	7.18	0.19	2.01	1.68
ethylene oxide	−1.95	2.83	2.13	7.98	9.43	7.98	0.96	1.32	1.13
acetic acid	0.48	7.51	5.95	32.84	33.66	32.84	59.92	68.42	59.92
methyl formate	−0.49	0.80	0.71	8.64	10.79	8.64	1.97	2.56	2.34
ethyl chloride	0.33	0.42	0.35	3.57	6.83	4.23	−2.10	4.25	3.39
ethane	0.32	1.59	0.99	−2.52	8.31	7.46	−0.72	2.34	1.82
dimethyl ether	0.20	1.58	1.20	3.44	8.35	5.86	0.46	2.05	1.65
ethanol	−0.80	1.02	0.85	15.10	18.80	15.10	0.85	3.72	2.40
ethyl mercaptan	−0.49	0.75	0.57	1.67	6.73	4.54	−13.56	14.93	13.67
dimethyl sulfide	−0.66	2.41	2.03	3.00	7.18	4.51	−16.27	19.86	17.21
propyne	0.30	0.37	0.30	9.97	12.02	10.10	3.16	5.41	3.55
propylene	2.81	6.28	3.24	−4.38	5.48	5.20	−2.46	5.45	3.17
acetone	−0.07	0.89	0.74	17.43	18.36	17.43	−8.56	12.32	11.29

Table A.3: Overall deviations in P^s, v_l^s and v_v^s for the Peng-Robinson equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−1.07	2.53	2.23	12.77	14.43	12.77	1.62	1.78	1.62
ethyl formate	−0.57	0.82	0.70	8.36	10.85	8.36	1.62	1.99	1.83
methyl acetate	−0.16	0.33	0.27	9.50	11.68	9.50	1.14	1.46	1.26
cyclopropane	−0.69	0.72	0.69	4.45	7.58	5.13	0.29	1.65	1.49
propane	0.82	1.38	0.88	−2.58	6.65	6.19	−1.22	2.33	1.91
1-propanol	−1.61	2.90	2.53	7.60	10.52	7.60	5.95	7.11	6.45
2-propanol	−4.94	6.51	5.69	10.33	13.18	10.33	11.45	16.28	14.45
methyl ethyl ether	−2.48	3.01	2.69	2.04	7.95	5.37	11.09	20.90	16.04
perfluorocyclobutane	0.02	1.01	0.76	−3.34	6.71	6.30	0.08	1.52	1.36
1,2-butadiene	−1.62	5.13	3.39	−0.07	2.31	1.97	0.88	1.23	1.10
1,3-butadiene	1.91	3.97	1.91	1.92	6.80	5.38	−1.86	3.12	1.98
1-butene	0.20	0.39	0.32	−0.84	5.17	4.44	−1.02	2.46	1.97
ethyl acetate	0.18	0.27	0.20	10.31	12.42	10.31	1.85	2.05	1.85
methyl propionate	0.39	0.98	0.47	9.46	12.21	9.46	1.55	1.89	1.57
n-propyl formate	0.04	0.45	0.40	7.21	9.79	7.21	0.89	1.36	1.15
n-butane	0.14	0.30	0.24	1.13	6.85	5.51	−0.06	1.44	1.14
isobutane	1.03	2.06	1.03	−3.78	4.51	3.88	−2.13	3.27	2.39
1-butanol	1.77	4.21	3.47	3.57	7.58	4.65	11.99	19.57	13.25
t-butanol	−3.78	5.09	3.85	2.67	4.29	2.88	5.99	6.57	5.99
diethyl ether	0.82	0.90	0.82	5.12	9.13	5.74	0.95	1.83	1.70
diethyl sulfide	−3.74	3.92	3.74	−24.47	24.88	24.47	−40.65	41.03	40.65
diethyl amine	1.13	1.98	1.41	5.38	8.30	5.38	−8.95	10.56	9.20
n-propyl acetate	−0.06	0.33	0.29	11.64	14.11	11.64	1.63	2.09	1.63
ethyl propionate	0.81	0.99	0.81	9.97	12.50	9.97	1.50	1.76	1.50
methyl butyrate	0.81	0.99	0.82	9.34	12.37	9.34	2.04	2.45	2.09
methyl isobutyrate	0.28	0.51	0.43	7.74	10.69	7.74	2.03	2.15	2.03
n-pentane	0.30	0.39	0.31	1.33	4.82	3.83	−0.73	1.47	1.04
isopentane	2.23	3.29	2.23	−1.41	6.11	5.02	−2.50	3.29	2.50
neopentane	−1.44	3.55	1.72	−2.77	4.85	4.44	0.28	1.18	1.09
ethyl propyl ether	1.23	3.15	2.78	−1.23	6.29	5.35	53.65	76.91	55.10
bromobenzene	−0.10	0.23	0.18	0.80	1.07	0.80	2.32	2.38	2.32
chlorobenzene	0.94	0.98	0.94	0.54	1.47	1.12	−0.24	0.48	0.38
fluorobenzene	0.25	0.62	0.49	3.98	7.48	4.70	0.39	1.38	1.15
iodobenzene	−0.12	0.44	0.34	−0.32	0.42	0.37	1.59	1.63	1.59
benzene	0.62	1.46	0.87	1.39	6.75	4.34	−1.89	3.98	2.93
aniline	0.59	0.63	0.59	3.10	5.71	3.51	0.25	0.38	0.31
cyclohexane	−0.17	0.57	0.47	0.74	6.12	4.77	−0.72	2.13	1.63
n-hexane	1.18	1.71	1.22	2.20	4.20	2.72	−0.96	2.33	1.80
toluene	−1.86	2.95	2.10	3.39	6.42	3.82	−3.68	3.95	3.68
n-heptane	1.02	1.40	1.03	3.50	6.82	3.57	−1.01	2.03	1.45
n-octane	1.96	3.27	1.96	5.30	6.80	5.96	−1.34	2.89	1.88
isooctane	1.23	2.09	1.23	0.13	5.92	4.36	−7.77	7.94	7.77
m-xylene	−0.55	0.89	0.78	4.17	5.48	4.17	0.53	0.98	0.86
o-xylene	−0.19	0.97	0.81	2.94	5.42	3.28	0.02	0.92	0.78
p-xylene	−0.03	1.00	0.89	6.88	9.35	6.88	0.11	1.21	0.99
ethyl benzene	−2.45	2.74	2.51	5.17	9.22	5.45	0.53	1.91	1.28
naphthalene	−2.15	2.85	2.35	4.80	5.05	4.80	−4.60	8.73	7.88
n-decane	0.45	1.62	1.43	11.09	12.20	11.09	0.51	0.67	0.56
diphenyl ether	4.18	4.44	4.18	4.27	4.38	4.27	10.60	12.64	10.83

Table A.4: Overall deviations in P^s, v_l^s and v_v^s for the Schmidt-Wenzel equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−1.24	1.32	1.24	4.19	7.00	4.55	2.74	2.79	2.74
chlorine	−0.32	0.60	0.49	3.18	6.03	3.23	1.68	2.33	1.81
fluorine	−1.98	2.12	1.98	3.09	5.07	3.59	4.39	5.94	5.55
helium	−12.51	15.57	12.51	3.22	10.09	7.85	22.25	25.47	22.25
hydrogen chloride	−0.82	1.84	1.31	13.47	15.67	13.47	5.19	6.71	6.04
hydrogen	−2.54	5.87	3.23	6.23	11.26	8.38	4.39	7.32	4.39
water	−7.51	13.03	8.32	22.23	23.21	22.23	12.16	18.13	12.16
hydrogen sulfide	3.45	5.37	3.47	6.37	9.45	6.37	−5.90	6.61	5.90
ammonia	0.88	1.24	0.99	18.00	18.44	18.00	5.25	6.69	5.36
krypton	−1.36	1.51	1.36	5.21	7.78	5.21	1.83	2.10	1.83
nitrogen	−0.61	0.82	0.72	3.01	6.60	3.99	0.93	1.15	0.98
neon	2.06	2.53	2.23	−2.30	6.65	5.85	−0.61	1.43	0.84
oxygen	−1.80	3.13	1.80	2.18	5.95	3.59	2.42	3.74	2.51
sulfur dioxide	0.46	0.66	0.54	8.66	14.42	8.66	1.57	4.19	1.64
sulfur trioxide	−7.76	9.30	7.82	0.74	5.86	4.10	7.31	12.08	8.10
xenon	−0.99	1.11	1.01	6.54	8.88	6.54	1.72	1.77	1.72
phosgene	−0.81	0.97	0.82	1.11	6.70	4.80	−5.12	9.16	8.06
carbon tetrachloride	−1.43	1.52	1.43	7.15	9.65	7.15	1.48	3.65	2.72
carbon tetrafluoride	−1.16	2.30	1.28	−0.44	5.21	3.79	0.60	2.85	1.70
carbon monoxide	−3.30	3.86	3.49	0.46	4.21	3.28	6.97	7.91	6.98
carbon dioxide	−2.03	2.39	2.03	5.15	8.52	5.58	3.41	3.84	3.41
chloroform	−3.76	4.00	3.76	3.19	5.39	3.52	2.52	4.14	3.87
freon-13	−4.83	5.75	4.83	1.05	5.37	3.81	6.01	7.24	6.06
freon-12	−5.88	6.67	5.88	−0.21	4.27	2.95	7.14	7.81	7.14
freon-11	0.07	0.62	0.54	−1.02	1.44	1.34	0.08	0.75	0.65
freon-22	−0.48	0.63	0.56	7.58	9.83	7.58	1.84	2.04	1.87
freon-21	−0.49	1.04	0.89	3.87	6.63	3.87	2.07	2.77	2.29
methyl chloride	1.73	1.77	1.73	5.80	5.83	5.80	−0.07	1.08	0.96
methane	0.33	0.45	0.39	4.75	7.99	4.91	0.36	0.52	0.42
methanol	3.06	3.20	3.06	17.36	19.71	17.36	2.39	2.81	2.40
methyl mercaptan	−1.06	1.38	1.14	6.91	8.96	6.91	−26.72	32.06	26.72
freon-114	1.29	2.81	2.40	−1.63	1.77	1.65	−0.94	2.42	2.10
freon-113	0.21	0.52	0.47	−2.48	2.50	2.48	−0.04	0.41	0.37
acetylene	−0.25	1.11	0.96	6.50	9.33	6.50	2.22	2.42	2.22
acetonitrile	1.84	6.30	5.26	67.06	67.87	67.06	11.72	13.91	11.72
ethylene	−0.47	0.85	0.71	6.22	10.05	6.22	2.28	2.87	2.43
ethylene oxide	−2.42	3.18	2.42	12.97	13.92	12.97	1.98	2.10	1.98
acetic acid	−0.54	9.92	7.21	27.84	28.75	27.84	62.71	74.70	62.71
methyl formate	−0.82	1.04	0.94	11.38	13.03	11.38	2.79	3.44	3.03
ethyl chloride	0.11	0.21	0.17	8.71	10.42	8.71	−1.14	3.23	2.57
ethane	−0.90	1.10	0.91	5.63	9.72	5.75	1.64	1.97	1.78
dimethyl ether	−0.19	1.60	1.38	8.08	10.99	8.08	1.80	3.06	2.70
ethanol	−1.38	1.79	1.52	4.04	11.50	6.51	0.38	4.89	2.86
ethyl mercaptan	−0.71	0.96	0.80	6.70	9.28	6.70	−12.67	14.32	12.78
dimethyl sulfide	−0.89	2.32	1.84	8.12	10.39	8.12	−15.41	19.48	16.36
propyne	0.02	0.18	0.14	13.68	15.09	13.68	5.40	7.34	5.40
propylene	−0.49	1.00	0.75	2.11	3.92	2.19	1.04	1.45	1.21
acetone	−0.27	1.06	0.86	18.48	19.33	18.48	−8.17	12.12	11.11

Table A.4: Overall deviations in P^s, v_l^s and v_v^s for the Schmidt-Wenzel equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−1.39	2.59	2.34	15.21	16.65	15.21	2.27	2.30	2.27
ethyl formate	−0.83	1.04	0.89	10.02	12.11	10.02	2.25	2.65	2.39
methyl acetate	−0.29	0.40	0.35	9.67	11.76	9.67	1.39	1.80	1.56
cyclopropane	−1.19	1.21	1.19	11.84	13.26	11.84	2.43	2.53	2.43
propane	0.18	0.65	0.38	3.58	7.09	5.23	0.35	1.19	1.00
1-propanol	−2.05	3.43	3.00	−2.17	7.27	6.10	5.50	7.11	6.44
2-propanol	−5.64	7.25	6.45	−0.78	7.66	5.79	11.33	16.79	14.99
methyl ethyl ether	−2.81	3.31	2.93	5.08	9.15	5.38	11.99	21.05	15.78
perfluorocyclobutane	0.09	0.90	0.72	−4.12	7.05	6.74	−0.03	1.31	1.14
1,2-butadiene	−1.95	5.29	3.69	2.64	3.50	2.85	1.52	1.76	1.64
1,3-butadiene	1.01	1.22	1.01	6.72	9.31	6.72	−0.22	0.81	0.65
1-butene	−0.05	0.39	0.29	4.09	6.46	4.09	0.00	1.50	1.20
ethyl acetate	0.18	0.44	0.28	9.17	11.43	9.17	1.78	2.09	1.78
methyl propionate	0.35	0.93	0.44	8.76	11.61	8.76	1.59	1.93	1.59
n-propyl formate	−0.14	0.39	0.32	7.81	10.17	7.81	1.26	1.53	1.32
n-butane	−0.06	0.31	0.25	5.83	8.92	6.33	0.92	1.58	1.02
isobutane	0.16	0.28	0.20	1.28	2.68	2.04	−0.69	1.77	1.08
1-butanol	1.42	4.00	3.36	−4.88	8.15	7.67	11.10	18.25	12.96
t-butanol	−4.28	5.61	4.47	−6.49	7.15	6.50	5.87	6.56	5.95
diethyl ether	0.56	0.66	0.56	6.86	10.12	6.86	1.61	2.01	1.79
diethyl sulfide	−3.96	4.14	3.97	-23.49	23.90	23.49	−40.31	40.71	40.31
diethyl amine	0.89	1.98	1.50	6.78	9.20	6.78	−8.43	10.25	8.70
n-propyl acetate	0.03	0.23	0.15	9.47	12.32	9.47	1.28	1.73	1.28
ethyl propionate	0.91	0.94	0.91	7.82	10.80	7.82	1.15	1.53	1.33
methyl butyrate	0.87	0.90	0.87	7.59	11.05	7.59	1.78	2.10	1.85
methyl isobutyrate	0.26	0.34	0.29	6.63	9.84	6.63	1.97	2.04	1.97
n-pentane	−0.04	0.23	0.19	4.13	6.16	4.40	0.08	0.81	0.71
isopentane	0.36	0.40	0.36	2.16	6.31	3.44	−0.38	1.29	0.73
neopentane	−1.68	3.58	1.88	1.91	4.37	3.04	1.19	1.55	1.48
ethyl propyl ether	1.11	2.91	2.54	−1.31	6.21	5.30	53.80	76.70	55.00
bromobenzene	−0.34	0.44	0.34	3.75	3.82	3.75	2.71	2.76	2.71
chlorobenzene	0.64	0.71	0.66	3.53	3.79	3.53	0.27	0.60	0.45
fluorobenzene	−0.09	0.56	0.43	7.09	9.44	7.09	1.30	1.95	1.78
iodobenzene	−0.33	0.53	0.42	2.67	2.69	2.67	1.89	1.93	1.89
benzene	0.05	1.01	0.47	5.53	8.37	5.53	−0.87	3.51	2.57
aniline	0.67	0.72	0.67	1.29	4.85	3.41	0.02	0.35	0.29
cyclohexane	−0.59	0.85	0.66	4.88	7.73	5.18	0.52	1.78	1.65
n-hexane	0.47	0.66	0.50	3.31	4.84	3.49	−0.08	1.64	1.19
toluene	−2.17	3.22	2.31	5.81	7.90	5.81	−2.99	3.19	2.99
n-heptane	0.76	0.85	0.76	2.89	6.43	3.41	−0.76	1.68	1.07
n-octane	1.17	1.31	1.17	2.99	5.09	3.96	−0.77	1.17	0.94
isooctane	0.29	0.37	0.31	0.76	5.08	3.66	−7.63	8.72	7.63
m-xylene	−0.68	1.02	0.91	4.37	5.56	4.37	0.79	1.26	1.15
o-xylene	−0.37	0.96	0.81	3.68	5.78	3.68	0.38	1.09	0.97
p-xylene	−0.17	1.12	1.00	7.26	9.56	7.26	0.41	1.40	1.16
ethyl benzene	−2.63	2.92	2.68	6.16	9.72	6.16	1.00	2.15	1.26
naphthalene	−2.18	2.88	2.37	5.95	6.16	5.95	−4.54	8.66	7.82
n-decane	0.43	1.37	1.17	5.39	7.28	5.39	−0.05	0.47	0.40
diphenyl ether	4.71	4.87	4.71	0.57	1.06	0.68	9.85	11.99	10.14

Table A.5: Overall deviations in P^s, v_l^s and v_v^s for the Patel-Teja equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	0.32	0.80	0.71	2.70	6.52	4.49	0.41	1.41	1.16
chlorine	1.09	1.67	1.09	1.81	5.64	3.30	−0.11	1.82	1.20
fluorine	−0.48	0.86	0.71	1.82	4.67	3.58	2.05	4.13	3.32
helium	−9.85	16.26	10.78	0.52	10.67	8.76	18.24	27.22	18.24
hydrogen chloride	0.01	1.95	1.65	12.14	14.63	12.14	3.88	6.03	5.02
hydrogen	−1.04	8.46	6.01	4.18	10.97	8.67	1.99	10.84	7.19
water	−6.01	9.44	6.52	21.33	22.35	21.33	9.40	12.07	9.40
hydrogen sulfide	4.63	6.02	4.63	5.02	8.75	5.03	−7.49	7.89	7.49
ammonia	0.95	1.09	0.97	16.86	17.36	16.86	4.91	6.10	5.01
krypton	0.13	1.01	0.91	3.70	7.14	4.69	−0.38	1.93	1.72
nitrogen	0.60	0.66	0.61	1.56	6.34	4.36	−0.84	1.20	0.87
neon	3.86	4.37	4.00	−3.74	7.56	6.81	−3.12	3.64	3.29
oxygen	−0.32	1.75	1.27	0.64	5.86	4.16	0.40	2.18	1.73
sulfur dioxide	0.50	0.60	0.56	7.68	13.91	7.68	1.23	3.91	1.38
sulfur trioxide	−8.87	10.51	8.87	0.34	5.89	4.26	8.83	13.78	9.36
xenon	0.54	0.94	0.85	5.03	8.09	5.29	−0.54	1.38	1.22
phosgene	−0.42	0.55	0.44	0.07	6.74	5.21	−5.77	9.86	8.73
carbon tetrachloride	−0.92	1.09	0.92	6.04	8.98	6.04	0.59	3.51	2.12
carbon tetrafluoride	1.92	3.52	1.92	−1.58	5.54	4.59	−2.63	3.83	2.63
carbon monoxide	−2.19	3.14	2.59	−0.90	4.55	3.94	5.26	6.72	5.85
carbon dioxide	−1.71	2.18	1.72	4.19	8.09	5.38	2.69	3.46	2.78
chloroform	−3.43	3.60	3.43	2.10	4.93	3.21	1.93	3.91	3.56
freon-13	−4.36	5.45	4.37	−0.04	5.41	4.27	5.22	6.82	5.50
freon-12	−5.44	6.34	5.45	−1.32	4.57	3.59	6.44	7.31	6.44
freon-11	0.97	1.97	1.18	−2.23	2.47	2.41	−0.83	1.89	1.20
freon-22	0.18	1.28	0.65	6.54	9.15	6.54	0.83	1.78	1.44
freon-21	0.26	1.71	1.19	2.78	6.17	3.36	1.08	2.66	2.30
methyl chloride	2.44	2.52	2.44	4.38	4.43	4.38	−0.85	1.40	1.02
methane	1.55	1.83	1.68	3.19	7.45	4.77	−1.42	1.83	1.62
methanol	1.79	1.96	1.88	17.31	19.71	17.31	3.76	3.82	3.76
methyl mercaptan	−0.32	0.79	0.65	5.69	8.19	5.69	−27.57	32.63	27.57
freon-114	1.17	2.79	2.29	−2.71	2.80	2.71	−0.85	2.39	2.01
freon-113	0.59	1.76	1.28	−3.51	3.52	3.51	−0.39	1.64	1.25
acetylene	0.28	1.33	1.17	5.38	8.70	5.58	1.32	1.77	1.58
acetonitrile	1.44	5.96	5.02	65.77	66.62	65.77	11.96	13.92	11.96
ethylene	0.52	0.68	0.52	4.88	9.47	5.73	0.74	1.76	1.50
ethylene oxide	−2.00	2.69	2.01	11.73	12.83	11.73	1.29	1.45	1.29
acetic acid	−0.97	7.71	5.60	27.23	28.15	27.23	62.16	71.06	62.16
methyl formate	−0.79	0.91	0.86	10.33	12.20	10.33	2.52	2.92	2.59
ethyl chloride	0.63	0.72	0.65	7.56	9.58	7.56	−1.99	4.00	3.15
ethane	0.27	0.62	0.47	4.30	9.22	5.61	0.00	1.01	0.76
dimethyl ether	0.23	1.32	0.97	6.99	10.34	6.99	0.97	2.32	1.96
ethanol	−2.26	2.49	2.26	4.63	12.36	6.73	1.73	4.20	3.43
ethyl mercaptan	−0.20	0.74	0.58	5.57	8.62	5.57	−13.44	14.88	13.55
dimethyl sulfide	−0.37	2.46	2.10	6.96	9.62	6.96	−16.16	19.90	17.11
propyne	0.39	0.47	0.39	12.78	14.32	12.78	4.30	6.64	4.36
propylene	2.08	4.11	2.11	0.84	3.56	2.20	−1.64	3.71	2.06
acetone	−0.62	0.88	0.67	17.47	18.40	17.47	−7.98	12.01	10.91

Table A.5: Overall deviations in P^s, v_l^s and v_v^s for the Patel-Teja equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−1.48	2.95	2.61	14.11	15.66	14.11	2.21	2.40	2.21
ethyl formate	−0.99	1.14	1.00	9.06	11.40	9.06	2.21	2.39	2.21
methyl acetate	−0.82	1.00	0.83	8.78	11.09	8.78	1.82	1.90	1.82
cyclopropane	−0.09	0.19	0.13	10.68	12.32	10.68	0.62	1.00	0.83
propane	1.02	1.21	1.02	2.42	6.77	5.35	−0.89	1.58	1.31
1-propanol	−3.07	4.12	3.60	−1.90	7.28	6.03	6.71	8.09	7.50
2-propanol	−6.40	7.71	6.82	−0.33	7.74	5.63	12.33	17.62	15.65
methyl ethyl ether	−2.69	3.11	2.70	4.07	8.73	5.28	11.65	21.35	16.23
perfluorocyclobutane	−1.09	1.38	1.17	−4.86	7.55	7.30	1.15	2.19	2.00
1,2-butadiene	−1.94	5.20	3.59	1.60	2.85	2.12	1.37	1.55	1.37
1,3-butadiene	1.93	3.34	1.93	5.65	8.70	5.80	−1.46	2.42	1.53
1-butene	0.54	0.65	0.55	3.00	5.97	3.72	−0.95	2.12	1.76
ethyl acetate	−0.62	0.78	0.64	8.36	10.84	8.36	2.55	2.62	2.55
methyl propionate	−0.32	1.10	0.80	7.94	11.07	7.94	2.19	2.48	2.21
n-propyl formate	−0.52	0.86	0.71	6.91	9.57	6.91	1.52	1.94	1.66
n-butane	0.42	0.49	0.42	4.73	8.36	5.95	0.08	1.39	0.94
isobutane	1.02	1.55	1.02	0.15	2.52	2.22	−1.80	2.67	2.01
1-butanol	0.34	3.99	3.37	−4.76	8.16	7.67	12.38	18.87	13.28
t-butanol	−5.37	6.34	5.37	−6.31	7.02	6.40	7.19	7.53	7.19
diethyl ether	0.45	0.77	0.64	5.93	9.61	6.11	1.50	2.27	2.04
diethyl sulfide	−4.16	4.39	4.16	−24.16	24.56	24.16	−40.31	40.69	40.31
diethyl amine	0.68	1.49	1.14	5.85	8.61	5.85	−8.43	10.11	8.82
n-propyl acetate	−0.92	1.18	0.92	8.73	11.81	8.73	2.25	2.46	2.25
ethyl propionate	−0.08	1.00	0.91	7.09	10.34	7.09	2.15	2.33	2.15
methyl butyrate	0.00	0.96	0.88	6.85	10.61	6.85	2.65	3.28	2.80
methyl isobutyrate	−0.47	0.95	0.81	5.85	9.40	5.85	2.67	2.86	2.67
n-pentane	0.07	0.46	0.41	3.13	5.63	4.08	−0.26	1.33	1.13
isopentane	1.28	1.93	1.28	1.10	6.12	3.88	−1.42	2.19	1.57
neopentane	−1.11	3.43	1.65	0.82	4.16	3.21	0.29	0.99	0.90
ethyl propyl ether	0.59	3.31	2.86	−2.10	6.50	5.70	54.89	78.58	56.33
bromobenzene	−0.53	0.60	0.53	2.62	2.72	2.62	2.87	2.94	2.87
chlorobenzene	0.62	0.73	0.63	2.43	2.81	2.43	0.21	0.50	0.45
fluorobenzene	0.08	0.62	0.53	6.06	8.79	6.06	0.85	1.45	1.23
iodobenzene	−0.67	0.73	0.67	1.54	1.56	1.54	2.23	2.27	2.23
benzene	0.41	1.22	0.74	4.50	8.01	4.50	−1.36	3.41	2.55
aniline	−0.36	0.72	0.61	0.57	4.75	3.61	1.08	1.28	1.11
cyclohexane	−0.10	0.50	0.41	3.85	7.24	4.97	−0.35	1.74	1.45
n-hexane	0.32	1.06	0.88	2.41	4.31	2.80	−0.03	2.18	1.79
toluene	−2.20	3.00	2.21	4.81	7.29	4.81	−3.16	3.47	3.16
n-heptane	−0.16	1.01	0.92	2.09	6.15	3.57	0.14	1.94	1.62
n-octane	0.53	2.29	1.47	2.32	4.66	3.36	−0.06	2.39	1.79
isooctane	0.32	1.11	0.74	−0.06	5.18	4.06	−7.74	8.80	7.74
m-xylene	−1.18	1.46	1.28	3.51	4.99	3.52	1.19	1.39	1.19
o-xylene	−0.80	1.39	1.19	2.78	5.33	3.25	0.71	1.11	0.89
p-xylene	−0.63	1.02	0.91	6.38	8.98	6.38	0.75	1.31	1.17
ethyl benzene	−2.92	3.18	2.92	5.27	9.27	5.49	1.12	2.11	1.53
naphthalene	−2.97	3.41	2.97	4.91	5.16	4.91	−3.74	8.39	7.37
n-decane	−0.84	2.06	1.47	4.98	7.03	4.98	1.37	1.79	1.55
diphenyl ether	2.59	3.06	2.71	−0.05	0.87	0.75	12.29	14.14	12.31

Table A.6: Overall deviations in P^s, v_l^s and v_v^s for the translated Peng-Robinson equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.25	0.47	0.39	0.51	4.63	3.44	0.32	1.59	1.39
chlorine	1.39	3.19	1.66	1.43	4.50	2.56	−0.64	3.10	2.02
fluorine	−1.26	1.43	1.31	−0.03	3.33	2.83	2.24	4.62	3.74
helium	−4.07	9.09	6.01	−8.90	12.08	10.85	6.03	13.03	8.75
hydrogen chloride	−0.43	1.77	1.44	11.53	13.64	11.53	4.03	6.37	5.25
hydrogen	1.20	5.04	4.18	−2.09	7.97	7.10	−2.77	7.13	6.31
water	−4.46	7.81	5.37	21.77	22.84	21.77	7.48	9.87	7.48
hydrogen sulfide	4.03	5.71	4.03	3.87	7.31	3.88	−7.34	7.94	7.34
ammonia	1.27	1.53	1.29	17.17	17.58	17.17	4.48	5.89	4.67
krypton	−0.41	0.74	0.61	1.59	5.01	3.29	−0.49	2.15	1.90
nitrogen	0.25	0.79	0.45	0.20	4.88	3.55	−0.98	1.59	1.17
neon	3.30	3.61	3.31	−6.31	8.18	7.57	−3.40	4.09	3.40
oxygen	0.89	1.86	1.14	−0.24	4.33	3.12	−1.21	2.27	1.72
sulfur dioxide	0.82	0.98	0.88	7.89	13.78	7.89	0.77	3.80	1.28
sulfur trioxide	−7.72	9.42	7.77	0.81	6.64	4.68	7.56	12.50	8.31
xenon	−0.05	0.44	0.39	2.89	5.77	3.47	−0.59	1.43	1.26
phosgene	−0.40	0.56	0.45	0.04	6.21	4.74	−5.99	9.78	8.72
carbon tetrachloride	−1.22	1.36	1.22	5.82	8.40	5.82	0.70	3.77	2.35
carbon tetrafluoride	2.76	5.54	2.84	−1.15	4.76	3.75	−3.41	5.34	3.41
carbon monoxide	−2.55	3.18	2.82	−1.84	3.75	3.46	5.24	6.61	5.87
carbon dioxide	−1.68	2.10	1.69	4.16	7.79	5.08	2.46	3.27	2.65
chloroform	−3.35	3.62	3.35	2.25	4.63	2.84	1.72	3.84	3.39
freon-13	−4.50	5.43	4.51	0.02	4.80	3.71	5.21	6.73	5.56
freon-12	−5.20	5.90	5.20	−1.05	4.03	3.07	6.02	6.72	6.02
freon-11	1.33	2.78	1.77	−1.48	1.71	1.62	−1.19	2.62	1.74
freon-22	0.49	2.08	0.91	6.59	8.81	6.59	0.37	2.23	1.52
freon-21	0.79	2.71	1.68	3.06	5.81	3.10	0.45	3.20	2.68
methyl chloride	2.33	2.55	2.33	4.89	4.92	4.89	−0.77	1.82	1.34
methane	1.42	1.46	1.42	1.54	5.50	3.41	−1.85	2.08	1.85
methanol	3.23	3.33	3.23	17.52	20.81	17.52	2.57	2.86	2.57
methyl mercaptan	−0.74	1.17	0.97	5.29	7.32	5.29	−27.50	32.45	27.50
freon-114	1.94	3.63	2.88	−2.09	2.16	2.09	−1.62	3.13	2.49
freon-113	1.99	3.11	2.15	−2.76	2.79	2.76	−1.76	2.83	1.90
acetylene	−0.02	1.27	1.04	5.19	8.10	5.24	1.44	2.02	1.84
acetonitrile	2.28	5.77	5.07	66.55	67.40	66.55	11.01	13.08	11.01
ethylene	0.18	1.02	0.70	3.95	7.98	4.44	0.65	1.98	1.68
ethylene oxide	−1.95	2.83	2.13	11.86	12.75	11.86	1.11	1.39	1.17
acetic acid	0.48	7.51	5.95	27.19	28.40	27.19	59.72	68.33	59.72
methyl formate	−0.49	0.80	0.71	10.61	12.27	10.61	2.09	2.72	2.46
ethyl chloride	0.33	0.42	0.35	7.39	9.07	7.39	−1.87	4.01	3.20
ethane	0.32	1.59	0.99	3.73	7.86	4.69	−0.36	2.01	1.63
dimethyl ether	0.20	1.58	1.20	6.82	9.76	6.82	0.75	2.26	1.88
ethanol	−0.80	1.02	0.85	3.98	13.48	8.55	0.19	4.23	2.31
ethyl mercaptan	−0.49	0.75	0.57	5.41	8.05	5.41	−13.35	14.77	13.46
dimethyl sulfide	−0.66	2.41	2.03	6.83	9.10	6.83	−16.07	19.76	17.01
propyne	0.30	0.37	0.30	12.17	13.66	12.17	3.83	6.08	4.03
propylene	2.81	6.28	3.24	1.13	2.94	1.80	−2.30	5.44	3.13
acetone	−0.07	0.89	0.74	17.98	18.86	17.98	−8.53	12.30	11.28

Table A.6: Overall deviations in P^s, v_l^s and v_v^s for the translated Peng-Robinson equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−1.07	2.53	2.23	14.52	15.99	14.52	1.70	1.83	1.70
ethyl formate	−0.57	0.82	0.70	9.44	11.60	9.44	1.70	2.07	1.90
methyl acetate	−0.16	0.33	0.27	9.31	11.54	9.31	1.12	1.44	1.25
cyclopropane	−0.69	0.72	0.69	9.40	10.87	9.40	0.80	1.51	1.32
propane	0.82	1.38	0.88	2.11	5.73	4.44	−0.93	2.00	1.70
1-propanol	−1.61	2.90	2.53	−2.35	9.11	7.67	5.37	6.68	6.13
2-propanol	−4.94	6.51	5.69	−0.88	9.61	7.43	10.82	16.02	14.27
methyl ethyl ether	−2.48	3.01	2.69	4.26	8.51	4.95	11.23	20.89	15.95
perfluorocyclobutane	0.02	1.01	0.76	−4.46	7.46	7.16	0.03	1.56	1.38
1,2-butadiene	−1.62	5.13	3.39	1.97	2.89	2.25	0.95	1.28	1.16
1,3-butadiene	1.91	3.97	1.91	5.52	8.07	5.52	−1.60	2.91	1.74
1-butene	0.20	0.39	0.32	2.76	5.38	3.20	−0.78	2.20	1.77
ethyl acetate	0.18	0.27	0.20	8.98	11.47	8.98	1.76	1.94	1.76
methyl propionate	0.39	0.98	0.47	8.54	11.63	8.54	1.48	1.83	1.51
n-propyl formate	0.04	0.45	0.40	7.40	9.91	7.40	0.91	1.36	1.16
n-butane	0.14	0.30	0.24	4.57	7.79	5.44	0.18	1.40	1.08
isobutane	1.03	2.06	1.03	0.27	1.77	1.49	−1.94	3.02	2.23
1-butanol	1.77	4.21	3.47	−4.63	9.38	8.59	11.21	18.55	12.78
t-butanol	−3.78	5.09	3.85	−6.73	8.04	7.25	5.57	6.07	5.57
diethyl ether	0.82	0.90	0.82	6.26	9.67	6.26	1.04	1.80	1.67
diethyl sulfide	−3.74	3.92	3.74	-23.87	24.26	23.87	−40.61	40.99	40.61
diethyl amine	1.13	1.98	1.41	6.25	8.79	6.25	−8.89	10.52	9.15
n-propyl acetate	−0.06	0.33	0.29	9.41	12.59	9.41	1.45	1.86	1.45
ethyl propionate	0.81	0.99	0.81	7.76	11.09	7.76	1.33	1.57	1.33
methyl butyrate	0.81	0.99	0.82	7.51	11.30	7.51	1.88	2.36	2.03
methyl isobutyrate	0.28	0.51	0.43	6.46	9.97	6.46	1.93	2.05	1.93
n-pentane	0.30	0.39	0.31	3.36	5.51	3.90	−0.61	1.31	0.95
isopentane	2.23	3.29	2.23	1.61	5.76	3.24	−2.40	3.18	2.40
neopentane	−1.44	3.55	1.72	0.69	3.66	2.78	0.48	1.16	1.07
ethyl propyl ether	1.23	3.15	2.78	−1.60	6.43	5.55	53.62	76.90	55.10
bromobenzene	−0.10	0.23	0.18	3.14	3.19	3.14	2.36	2.41	2.36
chlorobenzene	0.94	0.98	0.94	2.85	3.10	2.85	−0.18	0.46	0.37
fluorobenzene	0.25	0.62	0.49	6.23	8.65	6.23	0.54	1.43	1.20
iodobenzene	−0.12	0.44	0.34	2.13	2.14	2.13	1.61	1.65	1.61
benzene	0.62	1.46	0.87	4.63	7.66	4.63	−1.70	3.88	2.81
aniline	0.59	0.63	0.59	1.13	5.18	3.78	0.14	0.32	0.28
cyclohexane	−0.17	0.57	0.47	3.70	6.77	4.52	−0.48	1.94	1.56
n-hexane	1.18	1.71	1.22	2.88	4.54	3.08	−0.93	2.30	1.78
toluene	−1.86	2.95	2.10	5.12	7.30	5.12	−3.58	3.83	3.58
n-heptane	1.02	1.40	1.03	2.51	6.49	3.64	−1.04	2.05	1.46
n-octane	1.96	3.27	1.96	2.56	4.98	3.53	−1.43	2.92	1.91
isooctane	1.23	2.09	1.23	0.66	5.86	4.08	−7.75	7.91	7.75
m-xylene	−0.55	0.89	0.78	4.02	5.38	4.02	0.52	0.97	0.85
o-xylene	−0.19	0.97	0.81	3.26	5.56	3.34	0.04	0.92	0.78
p-xylene	−0.03	1.00	0.89	6.88	9.35	6.88	0.11	1.21	0.99
ethyl benzene	−2.45	2.74	2.51	5.70	9.45	5.70	0.58	1.95	1.29
naphthalene	−2.15	2.85	2.35	5.45	5.67	5.45	−4.60	8.73	7.88
n-decane	0.45	1.62	1.43	5.53	8.03	5.53	0.19	0.58	0.46
diphenyl ether	4.18	4.44	4.18	−0.02	1.11	0.96	10.53	12.58	10.78

Table A.7: Overall deviations in P^s, v_l^s and v_v^s for the Toghiani-Viswanath equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	0.43	0.51	0.44	−5.14	7.78	7.13	−0.73	1.69	1.27
chlorine	−0.29	0.94	0.82	0.93	5.41	3.55	1.25	1.60	1.43
fluorine	−0.62	1.33	1.18	−5.71	7.05	6.38	−0.57	11.93	4.70
helium	−19.78	27.05	19.91	6.39	12.81	9.80	42.01	58.47	42.01
hydrogen chloride	1.15	1.26	1.15	−4.01	8.97	7.70	0.62	5.33	3.88
hydrogen	−1.64	8.31	5.68	−2.36	10.12	9.00	1.65	11.06	7.77
water	0.85	1.84	1.37	0.62	5.93	3.73	0.23	2.43	2.10
hydrogen sulfide	1.75	2.62	2.36	38.48	39.11	38.48	−0.92	2.18	1.81
ammonia	0.81	1.53	1.06	6.12	7.30	6.12	4.01	5.14	4.27
krypton	−0.06	0.62	0.57	−2.70	6.60	5.86	−0.97	2.39	2.02
nitrogen	0.91	1.36	0.92	−5.57	8.05	7.50	−2.29	3.91	2.29
neon	6.44	6.60	6.44	−19.35	20.33	19.35	−8.12	8.40	8.12
oxygen	0.39	0.64	0.54	−4.71	7.37	6.81	−0.78	1.80	1.24
sulfur dioxide	0.31	0.45	0.37	3.71	11.57	6.71	0.54	1.80	0.93
sulfur trioxide	−9.61	11.25	9.61	−5.98	8.29	7.75	9.14	14.50	9.91
xenon	0.62	0.66	0.62	−2.89	6.85	6.09	−1.63	2.06	1.63
phosgene	−0.77	0.88	0.78	−0.72	6.78	5.48	−5.48	9.86	8.69
carbon tetrachloride	−1.26	1.45	1.26	4.55	8.04	5.08	0.80	3.84	2.45
carbon tetrafluoride	3.85	7.32	3.91	−7.11	8.74	8.34	−4.55	6.78	4.55
carbon monoxide	−4.76	6.77	5.16	5.74	7.33	5.74	9.26	11.14	9.42
carbon dioxide	−1.50	2.09	1.56	10.56	12.57	10.56	3.60	4.06	3.60
chloroform	−3.65	3.68	3.65	10.22	11.26	10.22	2.87	4.27	4.14
freon-13	−4.29	5.00	4.29	−6.61	8.44	7.90	4.41	6.08	5.20
freon-12	−5.94	6.93	5.95	−1.36	4.58	3.61	7.08	8.06	7.08
freon-11	2.48	4.22	2.76	−8.55	8.61	8.55	−2.35	3.88	2.56
freon-22	0.11	1.90	0.99	2.48	6.80	4.81	0.41	2.19	1.64
freon-21	−1.41	2.08	1.71	11.51	12.81	11.51	3.56	3.64	3.56
methyl chloride	6.23	7.45	6.23	−10.58	10.59	10.58	−4.68	6.19	4.68
methane	3.33	3.86	3.33	−7.32	9.81	9.11	−4.36	4.57	4.36
methanol	2.94	3.15	2.94	6.80	11.30	7.03	1.31	2.19	1.93
methyl mercaptan	−0.61	1.08	0.89	1.05	5.89	4.37	−27.78	32.62	27.78
freon-114	1.91	4.24	3.37	−10.62	10.63	10.62	−1.69	3.67	2.92
freon-113	1.59	3.16	2.24	−8.40	8.40	8.40	−1.39	2.88	2.04
acetylene	0.03	1.09	0.89	−1.11	6.80	5.61	0.81	2.03	1.90
acetonitrile	7.10	8.70	7.10	12.17	15.93	12.17	0.37	7.64	5.38
ethylene	−0.10	0.56	0.50	2.23	8.38	5.71	1.08	1.96	1.58
ethylene oxide	−2.25	2.99	2.26	6.77	8.40	6.77	1.21	1.57	1.34
acetic acid	3.43	3.78	3.62	3.21	6.93	3.49	50.98	55.14	50.98
methyl formate	−0.93	1.03	0.93	13.01	14.55	13.01	2.98	3.33	2.98
ethyl chloride	0.39	0.44	0.39	0.70	5.80	4.35	−2.48	4.47	3.46
ethane	0.84	2.04	1.06	−1.76	8.13	7.11	−1.18	2.48	1.85
dimethyl ether	−0.01	1.60	1.30	1.34	7.69	6.02	0.39	2.00	1.60
ethanol	−2.44	2.67	2.44	3.67	11.45	6.60	1.52	5.48	3.97
ethyl mercaptan	−0.54	0.84	0.59	2.89	7.14	4.46	−13.38	14.77	13.52
dimethyl sulfide	−0.72	2.56	2.14	4.24	7.81	4.75	−16.09	19.75	17.07
propyne	0.64	0.78	0.64	21.41	22.20	21.41	7.46	10.18	7.46
propylene	2.96	6.29	3.24	−3.66	4.94	4.67	−2.58	5.46	3.14
acetone	−1.04	1.49	1.24	4.53	7.20	4.53	−8.90	12.37	11.04

Table A.7: Overall deviations in P^s, v_l^s and v_v^s for the Toghiani-Viswanath equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−1.76	2.99	2.71	7.75	10.10	8.68	2.01	2.37	2.15
ethyl formate	−0.49	0.77	0.61	20.96	22.10	20.96	3.13	3.54	3.13
methyl acetate	−1.02	1.18	1.02	6.11	9.10	6.11	1.75	1.83	1.75
cyclopropane	−0.51	0.73	0.68	−10.20	11.82	10.86	−2.64	3.86	2.65
propane	1.06	1.67	1.06	−2.64	6.66	6.20	−1.47	2.46	1.99
1-propanol	−3.00	3.88	3.43	3.30	7.89	4.64	7.17	8.18	7.59
2-propanol	−7.49	8.49	7.49	−0.03	7.74	5.48	13.84	18.78	16.50
methyl ethyl ether	−1.43	1.64	1.43	32.29	33.31	32.29	13.35	21.36	15.57
perfluorocyclobutane	−1.19	1.53	1.31	−6.73	8.84	8.59	1.11	2.39	2.17
1,2-butadiene	−1.81	5.47	3.96	−18.20	18.29	18.20	−0.16	1.94	1.56
1,3-butadiene	2.94	6.95	2.94	−5.06	8.06	7.45	−3.63	5.42	3.63
1-butene	0.17	0.38	0.30	−1.23	5.23	4.58	−1.04	2.48	1.99
ethyl acetate	−0.36	0.60	0.48	12.09	13.94	12.09	2.70	2.80	2.70
methyl propionate	−0.35	1.12	0.83	8.14	11.21	8.14	2.24	2.53	2.26
n-propyl formate	0.75	1.13	0.95	24.17	25.10	24.17	2.09	2.73	2.09
n-butane	0.10	0.30	0.26	−0.12	6.70	5.63	−0.17	1.48	1.16
isobutane	1.82	3.53	1.83	−7.18	7.57	7.18	−3.20	4.41	3.38
1-butanol	1.21	4.10	3.46	2.01	6.97	4.85	12.42	19.59	13.34
t-butanol	−4.81	5.83	4.81	0.04	3.26	2.70	7.05	7.39	7.05
diethyl ether	0.33	0.78	0.67	6.06	9.69	6.19	1.66	2.43	2.16
diethyl sulfide	−4.51	4.74	4.52	−28.68	29.02	28.68	−40.57	40.92	40.57
diethyl amine	1.41	1.66	1.41	18.82	19.86	18.82	−7.69	9.95	8.20
n-propyl acetate	−0.53	0.88	0.68	13.25	15.45	13.25	2.43	2.81	2.43
ethyl propionate	0.21	1.02	0.94	10.57	12.98	10.57	2.29	2.42	2.29
methyl butyrate	0.23	1.00	0.92	9.78	12.70	9.78	2.81	3.29	2.81
methyl isobutyrate	−0.13	0.85	0.76	10.37	12.72	10.37	2.89	3.03	2.89
n-pentane	−0.28	0.48	0.40	−4.28	6.18	5.55	−0.68	2.03	1.49
isopentane	3.38	5.53	3.38	−8.05	9.85	9.43	−3.91	5.26	3.91
neopentane	−1.47	3.53	1.85	−7.25	8.21	7.51	−0.17	1.35	1.16
ethyl propyl ether	−0.08	2.89	2.36	−12.77	14.05	13.20	54.24	78.40	56.92
bromobenzene	−0.69	0.77	0.69	−5.82	5.85	5.82	2.73	2.77	2.73
chlorobenzene	0.27	0.38	0.33	−3.35	3.58	3.35	0.30	0.50	0.41
fluorobenzene	−0.20	0.68	0.60	3.29	7.12	4.57	0.83	1.54	1.28
iodobenzene	−1.13	1.16	1.13	6.05	6.06	6.05	2.83	2.91	2.83
benzene	0.09	1.18	0.66	2.76	6.97	4.05	−1.31	3.71	2.81
aniline	−0.52	0.80	0.68	−1.16	4.82	4.14	1.08	1.36	1.16
cyclohexane	−0.31	0.67	0.60	5.08	7.98	5.39	0.07	1.65	1.51
n-hexane	0.39	1.53	1.14	−2.43	4.19	3.88	−0.47	2.77	2.24
toluene	−2.27	2.94	2.27	8.20	9.90	8.20	−2.74	3.00	2.74
n-heptane	−0.16	1.13	0.99	−1.25	5.80	4.86	−0.06	2.03	1.69
n-octane	0.49	2.14	1.42	2.98	5.06	3.94	0.02	2.28	1.72
isooctane	0.42	1.79	1.03	−3.72	6.94	6.37	−7.33	7.48	7.33
m-xylene	−0.59	1.09	0.88	12.43	12.95	12.43	1.55	1.93	1.55
o-xylene	−0.98	1.51	1.30	1.26	4.67	3.24	0.76	1.23	1.03
p-xylene	−0.98	1.35	1.16	1.04	6.31	4.51	0.52	1.49	1.32
ethyl benzene	−3.40	3.83	3.49	−8.44	11.29	10.54	−0.31	2.11	1.83
naphthalene	−3.18	3.63	3.18	2.64	3.04	2.64	−3.57	8.33	7.32
n-decane	−0.88	2.09	1.50	4.80	6.90	4.80	1.40	1.84	1.59
diphenyl ether	2.00	2.44	2.14	−6.49	6.54	6.49	12.74	14.58	12.74

Table A.8: Overall deviations in P^s, v_l^s and v_v^s for the Trebble-Bishnoi equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−1.84	2.04	1.84	0.32	3.66	2.62	1.90	2.96	2.69
chlorine	0.17	1.70	1.26	1.62	3.39	1.86	0.16	1.95	1.63
fluorine	−0.87	1.57	1.46	−0.97	2.76	2.45	1.22	4.49	3.11
helium	4.52	7.98	7.29	−7.45	11.49	10.07	−4.74	9.47	8.66
hydrogen chloride	−7.22	8.55	7.25	−8.36	10.21	10.01	9.94	15.24	13.09
hydrogen	4.92	5.71	5.21	0.26	7.40	6.26	−6.64	7.31	6.97
water	3.37	4.82	3.85	−2.09	4.84	3.94	−2.80	4.35	3.65
hydrogen sulfide	3.21	5.27	3.28	2.47	5.61	2.57	−7.10	8.00	7.10
ammonia	−1.59	2.24	1.95	−3.61	4.11	3.95	5.03	5.69	5.15
krypton	−3.76	4.29	3.76	0.32	3.60	2.47	3.00	5.05	4.46
nitrogen	0.02	1.49	1.10	0.95	3.88	2.25	−0.96	1.98	1.53
neon	12.60	13.89	12.60	1.77	5.35	3.78	−11.16	12.06	11.16
oxygen	0.52	3.21	2.24	−1.19	3.66	2.98	−0.97	3.42	2.71
sulfur dioxide	1.84	2.87	1.92	3.28	9.56	4.09	−2.11	3.74	3.02
sulfur trioxide	−5.49	8.17	7.06	−3.04	5.02	4.49	2.86	10.07	7.07
xenon	−4.46	5.13	4.47	1.56	3.94	2.14	4.12	5.76	4.87
phosgene	3.03	4.26	3.12	3.71	5.54	3.71	−9.95	11.49	10.50
carbon tetrachloride	−3.18	3.41	3.18	2.16	4.32	2.25	1.61	5.84	4.40
carbon tetrafluoride	−0.01	1.72	1.34	−2.95	4.32	4.07	−1.40	3.27	2.33
carbon monoxide	1.55	2.72	1.65	2.38	3.24	2.38	0.70	3.85	3.04
carbon dioxide	−0.26	0.61	0.50	1.13	4.91	3.44	−0.93	2.00	1.44
chloroform	3.90	6.95	5.39	11.99	12.28	11.99	−5.93	7.15	5.93
freon-13	−3.49	3.97	3.49	0.06	2.86	2.03	3.19	4.89	4.22
freon-12	−3.61	3.95	3.61	0.95	2.45	1.01	3.62	4.27	3.81
freon-11	1.42	1.86	1.60	0.80	0.92	0.80	−1.44	1.77	1.47
freon-22	−1.38	1.63	1.43	0.87	3.61	2.40	0.69	2.54	2.21
freon-21	−1.41	1.81	1.51	−0.03	2.89	1.83	1.79	3.23	2.68
methyl chloride	−2.91	3.05	2.91	−0.40	0.79	0.70	4.52	4.58	4.52
methane	−2.22	2.66	2.33	0.84	4.09	2.35	1.80	3.42	3.13
methanol	1.55	2.72	1.96	−4.45	6.78	6.36	0.52	3.99	3.31
methyl mercaptan	−4.52	4.92	4.52	−2.09	3.74	3.39	−25.62	30.63	25.62
freon-114	3.58	5.11	4.13	0.26	0.36	0.26	−3.36	4.49	3.53
freon-113	3.14	3.44	3.14	−0.13	0.41	0.35	−2.97	3.19	2.97
acetylene	−0.80	1.32	1.17	−0.55	4.39	3.43	0.91	2.92	2.66
acetonitrile	4.71	7.47	5.38	−1.78	6.36	4.76	0.07	9.63	7.50
ethylene	−2.85	3.23	2.86	1.12	5.38	3.25	3.15	4.52	3.70
ethylene oxide	−6.43	6.58	6.43	0.71	2.85	1.92	5.00	5.80	5.36
acetic acid	1.87	3.33	2.68	−11.10	11.45	11.13	51.20	55.17	51.20
methyl formate	−3.99	4.19	3.99	−1.16	3.77	3.10	3.90	4.90	4.54
ethyl chloride	−0.69	0.77	0.72	4.66	5.60	4.66	−1.83	4.65	3.85
ethane	−0.88	1.12	0.93	4.21	6.66	4.21	0.40	2.26	1.75
dimethyl ether	3.95	6.15	4.10	11.24	12.13	11.24	−3.55	5.43	3.89
ethanol	−0.53	3.10	2.68	−2.84	8.57	6.72	−2.13	5.83	3.55
ethyl mercaptan	−1.57	1.68	1.57	2.76	4.73	2.76	−13.30	14.65	13.51
dimethyl sulfide	−4.08	5.30	4.20	−0.23	3.73	2.69	−14.14	17.94	15.69
propyne	0.04	0.11	0.09	7.43	8.70	7.43	0.95	3.72	2.78
propylene	−4.83	5.63	4.83	−2.10	2.52	2.37	4.99	6.36	5.34
acetone	−6.06	6.29	6.06	−6.23	6.72	6.45	−5.61	11.73	8.58

Table A.8: Overall deviations in P^s, v_l^s and v_v^s for the Trebble-Bishnoi equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−8.33	9.18	8.33	−11.36	12.39	11.36	7.71	9.46	8.71
ethyl formate	−3.25	3.49	3.25	−0.17	3.72	2.85	2.48	4.03	3.72
methyl acetate	−2.44	2.61	2.44	−0.39	3.76	2.71	1.48	2.84	2.57
cyclopropane	−3.16	3.39	3.16	3.45	5.18	3.45	2.11	4.17	3.70
propane	0.27	0.89	0.57	2.22	3.89	2.63	−1.08	2.43	1.84
1-propanol	1.20	5.43	3.95	−1.77	4.45	3.78	0.78	6.17	5.37
2-propanol	−3.72	7.21	6.39	−2.26	5.36	4.75	7.64	15.22	13.55
methyl ethyl ether	−3.95	4.43	3.95	−0.57	4.87	3.67	11.63	22.23	17.47
perfluorocyclobutane	8.27	10.02	8.27	2.53	3.96	2.53	−8.21	8.99	8.21
1,2-butadiene	−2.84	5.63	4.40	−1.48	1.56	1.48	1.47	1.85	1.60
1,3-butadiene	−1.23	1.99	1.61	0.56	3.35	2.65	0.20	4.08	3.56
1-butene	−0.28	0.57	0.48	1.82	3.26	1.94	−1.23	2.84	2.11
ethyl acetate	−2.05	2.24	2.05	−0.69	3.70	2.98	1.84	3.33	3.03
methyl propionate	−1.14	1.58	1.34	0.53	4.35	3.07	0.74	3.15	2.82
n-propyl formate	−1.81	1.99	1.81	0.27	3.64	2.35	1.02	3.15	2.83
n-butane	−0.98	1.08	0.98	2.23	4.64	3.13	0.25	2.11	1.85
isobutane	2.42	3.09	2.42	3.09	3.21	3.11	−3.85	4.28	3.99
1-butanol	4.71	6.45	5.41	−2.63	4.49	4.20	6.06	15.85	11.57
t-butanol	−0.48	5.52	4.37	−2.57	2.76	2.57	0.78	4.71	4.14
diethyl ether	−1.12	1.48	1.38	−0.49	4.40	3.58	1.14	4.27	3.88
diethyl sulfide	−2.92	3.22	2.93	−24.13	24.24	24.13	−41.93	42.26	41.03
diethyl amine	1.75	3.35	2.35	5.23	6.23	5.23	−10.68	12.02	10.68
n-propyl acetate	−1.98	2.15	1.98	0.45	4.74	3.08	0.90	2.78	2.54
ethyl propionate	−0.24	0.67	0.58	1.26	4.38	2.50	0.14	2.48	2.04
methyl butyrate	−0.23	0.59	0.51	1.06	4.92	3.09	0.60	3.30	2.97
methyl isobutyrate	−0.68	0.97	0.84	0.78	4.28	2.61	0.82	2.47	2.18
n-pentane	−2.58	2.78	2.58	−3.05	3.62	3.25	1.07	3.64	3.28
isopentane	−1.04	1.25	1.07	0.10	3.17	2.00	0.23	3.12	2.30
neopentane	−4.39	5.55	4.39	−3.92	4.27	3.98	2.72	3.71	3.30
ethyl propyl ether	4.02	4.07	4.02	1.09	3.68	2.18	46.62	68.20	49.45
bromobenzene	−3.67	3.68	3.67	−1.15	1.19	1.15	5.92	5.98	5.92
chlorobenzene	−1.90	1.91	1.90	−1.03	1.05	1.03	2.28	2.34	2.28
fluorobenzene	−2.61	2.85	2.61	−0.89	3.54	2.92	2.01	3.57	3.24
iodobenzene	−3.28	3.30	3.28	−0.52	0.60	0.52	4.84	4.86	4.84
benzene	−1.40	1.78	1.43	1.37	3.44	1.72	−1.26	6.64	3.93
aniline	−1.69	1.86	1.69	−7.95	8.20	7.95	0.64	2.21	1.96
cyclohexane	−1.58	1.78	1.58	0.89	3.55	2.34	−0.25	3.06	2.60
n-hexane	−0.35	0.96	0.86	−0.39	2.27	1.33	−0.45	3.19	2.18
toluene	−4.38	4.79	4.38	−0.88	2.76	2.34	−2.30	4.05	2.60
n-heptane	1.41	2.08	1.49	1.15	2.98	1.57	−2.33	2.92	2.33
n-octane	1.84	3.16	2.07	0.83	4.53	3.01	−2.32	3.22	2.54
isooctane	0.00	0.87	0.77	−1.31	3.56	2.90	−7.51	7.61	7.51
m-xylene	−2.42	2.65	2.42	−2.17	2.33	2.17	0.75	2.35	2.04
o-xylene	−1.76	2.04	1.76	−1.35	2.31	2.14	0.39	1.88	1.62
p-xylene	−1.80	2.19	1.90	0.83	3.36	1.89	0.24	2.36	2.08
ethyl benzene	−4.07	4.41	4.07	−0.03	4.45	3.13	0.39	2.28	2.00
naphthalene	−1.30	2.76	2.65	6.81	6.87	6.81	−5.74	9.28	8.59
n-decane	−1.42	2.07	1.59	−1.00	2.30	1.99	0.12	2.23	1.81
diphenyl ether	2.51	2.62	2.51	−3.55	3.57	3.55	11.75	13.75	11.75

Table A.9: Overall deviations in P^s, v_l^s and v_v^s for the Sugie-Iwahori-Lu equation of state.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.71	0.74	0.71	0.66	2.00	1.42	−0.67	2.79	2.21
chlorine	2.83	3.43	2.84	−1.22	3.26	2.86	−3.60	3.74	3.60
fluorine	−1.35	1.79	1.61	−0.43	1.12	0.98	1.50	1.77	1.54
helium	0.80	0.86	0.80	0.57	0.96	0.58	−2.92	4.20	2.95
hydrogen chloride	0.71	0.76	0.71	1.77	5.15	2.63	0.26	5.96	4.52
hydrogen	3.29	3.38	3.29	1.96	2.89	1.99	−7.51	8.42	7.51
water	0.07	0.12	0.10	2.02	3.26	2.33	−0.11	1.67	1.06
hydrogen sulfide	0.65	1.34	0.80	3.25	5.11	3.25	−5.61	7.63	5.78
ammonia	1.00	1.26	1.07	0.12	1.99	1.52	1.72	2.37	1.87
krypton	0.01	0.17	0.15	0.64	2.16	1.55	−2.68	4.04	2.95
nitrogen	−0.62	0.65	0.62	1.60	2.98	2.11	−1.25	2.77	1.98
neon	3.80	3.80	3.80	−3.09	3.68	3.49	−5.00	5.50	5.00
oxygen	0.45	0.68	0.49	2.10	3.59	2.69	−1.88	3.11	1.95
sulfur dioxide	0.37	0.64	0.50	3.24	9.05	3.83	−0.94	2.98	1.95
sulfur trioxide	−2.74	3.54	2.74	−5.75	6.95	6.39	−2.12	8.16	7.29
xenon	0.04	0.13	0.11	1.31	2.64	1.58	−2.36	3.33	2.49
phosgene	1.34	1.55	1.34	−1.03	3.45	2.70	−9.56	12.82	11.69
carbon tetrachloride	−1.34	1.35	1.34	2.39	4.27	2.39	−0.61	2.97	2.23
carbon tetrafluoride	−0.35	0.69	0.58	−0.74	3.40	3.06	−1.43	3.35	2.06
carbon monoxide	2.12	2.21	2.12	0.85	1.83	1.43	−1.38	3.62	2.77
carbon dioxide	−0.10	0.12	0.10	1.82	4.49	2.65	−1.48	2.56	1.98
chloroform	−1.17	2.00	1.53	0.00	1.78	1.24	−2.46	4.55	2.46
freon-13	−0.44	0.53	0.46	0.97	2.32	1.69	−0.91	2.77	2.04
freon-12	−0.71	0.92	0.74	0.84	2.19	1.51	0.01	0.77	0.43
freon-11	0.13	0.53	0.38	2.10	2.95	2.37	−0.31	0.50	0.32
freon-22	−0.25	0.31	0.30	1.46	3.27	2.39	−1.32	2.72	1.98
freon-21	−0.38	1.72	1.05	1.49	3.03	2.27	−0.05	3.06	2.28
methyl chloride	1.42	1.54	1.42	0.92	2.11	1.67	−0.30	1.10	0.93
methane	1.26	1.38	1.26	1.34	2.88	1.97	−3.18	3.88	3.18
methanol	1.40	1.49	1.40	3.27	6.31	3.45	0.96	3.75	3.37
methyl mercaptan	−0.69	0.89	0.77	4.17	4.61	4.17	−28.66	33.20	28.66
freon-114	−1.53	2.10	1.65	1.49	2.00	1.49	1.63	1.95	1.63
freon-113	0.25	0.51	0.44	2.04	2.63	2.10	−0.22	0.46	0.41
acetylene	0.22	0.73	0.58	1.10	3.37	1.82	−0.37	2.01	1.45
acetonitrile	−0.93	2.14	1.65	3.69	6.86	4.14	10.05	11.78	10.05
ethylene	0.32	0.53	0.43	2.33	4.47	2.62	−1.24	2.43	1.87
ethylene oxide	−1.52	2.23	1.66	0.32	2.60	2.21	−1.74	3.42	2.33
acetic acid	4.68	5.13	4.68	1.97	4.29	2.89	47.60	51.27	47.60
methyl formate	−0.09	0.28	0.24	3.57	4.72	3.57	−0.95	1.77	1.16
ethyl chloride	−0.20	0.53	0.46	−1.80	2.92	2.62	−3.52	5.67	4.32
ethane	−0.25	0.55	0.37	2.91	4.81	3.39	−1.34	3.14	1.82
dimethyl ether	0.53	2.46	1.94	1.35	3.62	2.21	−1.93	2.83	2.47
ethanol	−0.15	0.56	0.50	4.22	10.12	4.69	−2.14	4.96	2.97
ethyl mercaptan	−0.41	1.07	0.96	0.71	3.05	1.85	−15.20	16.33	15.30
dimethyl sulfide	−0.60	2.22	1.71	1.55	3.31	1.80	−17.85	20.94	18.79
propyne	−0.03	0.15	0.11	5.66	7.11	5.86	−5.88	6.93	5.92
propylene	−0.37	0.50	0.37	2.12	3.73	2.73	−0.20	1.21	0.76
acetone	−0.91	1.24	0.98	1.34	4.10	2.25	−9.78	12.76	11.85

Table A.9: Overall deviations in P^s, v_l^s and v_v^s for the Sugie-Iwahori-Lu equation (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	0.12	1.83	1.46	−1.45	5.72	3.19	−2.54	3.84	2.54
ethyl formate	0.57	0.78	0.62	2.98	4.47	2.98	−2.27	2.72	2.27
methyl acetate	−0.86	1.25	1.07	1.61	3.89	2.03	−0.05	1.24	1.01
cyclopropane	−4.52	4.65	4.52	2.73	4.05	2.73	4.65	5.04	4.75
propane	0.42	0.67	0.42	0.14	1.59	1.40	−2.35	3.79	2.46
1-propanol	0.95	1.20	0.95	1.02	3.94	2.06	−0.21	3.46	2.53
2-propanol	−2.53	4.17	3.10	3.11	6.85	3.38	5.75	11.80	10.11
methyl ethyl ether	−1.96	2.46	2.08	0.89	4.06	2.25	8.78	19.59	15.34
perfluorocyclobutane	−0.41	0.98	0.86	−3.34	4.48	4.28	−0.27	2.07	1.47
1,2-butadiene	0.03	5.40	3.28	−0.55	0.84	0.73	−1.99	2.61	1.99
1,3-butadiene	0.87	1.73	0.88	1.71	3.18	2.40	−2.31	3.06	2.31
1-butene	0.12	0.56	0.44	0.15	2.10	1.61	−2.37	3.66	2.86
ethyl acetate	0.32	0.44	0.37	1.60	4.04	2.24	−0.95	1.94	1.29
methyl propionate	−0.46	1.28	1.11	2.65	5.05	2.84	0.62	1.79	1.56
n-propyl formate	1.47	1.64	1.49	1.91	3.88	2.07	−2.98	3.41	2.98
n-butane	0.17	0.31	0.22	1.66	3.44	2.10	−1.80	2.81	1.88
isobutane	0.85	1.46	1.25	0.11	2.60	2.04	−2.88	3.82	3.05
1-butanol	5.54	7.21	5.73	−1.73	3.94	3.56	3.65	13.26	9.24
t-butanol	−0.79	3.29	2.75	0.78	1.90	1.12	0.85	0.93	0.85
diethyl ether	0.79	0.83	0.79	1.20	3.97	2.39	−1.45	3.80	2.74
diethyl sulfide	−3.99	4.12	3.99	−25.46	25.58	25.46	−41.11	41.48	41.11
diethyl amine	0.33	0.68	0.56	0.82	3.14	1.82	−10.33	11.75	11.07
n-propyl acetate	0.09	0.21	0.20	3.26	5.91	3.26	−1.23	1.89	1.40
ethyl propionate	−0.35	0.51	0.42	2.52	5.05	2.72	0.98	1.69	1.42
methyl butyrate	0.70	0.84	0.73	2.11	5.44	3.00	−0.41	3.08	2.62
methyl isobutyrate	0.54	0.58	0.54	1.46	4.54	2.51	−0.68	2.09	1.70
n-pentane	−0.45	0.51	0.45	0.25	1.58	1.09	−1.40	2.69	1.76
isopentane	0.12	0.61	0.52	2.86	3.93	2.92	−1.14	2.68	1.21
neopentane	−3.05	4.38	3.05	−0.12	1.26	1.05	1.17	2.08	1.79
ethyl propyl ether	−0.21	2.31	1.73	−3.52	4.88	4.64	54.42	77.51	56.12
bromobenzene	−0.75	0.87	0.75	−0.24	0.82	0.73	2.45	2.51	2.45
chlorobenzene	0.17	0.46	0.39	−0.32	0.77	0.70	−0.21	0.52	0.42
fluorobenzene	−0.36	0.75	0.60	0.41	3.00	1.91	−1.08	2.60	1.89
iodobenzene	0.39	0.54	0.52	0.99	1.20	0.99	0.64	1.11	0.76
benzene	−0.47	1.04	0.53	1.48	3.75	2.14	−2.06	3.78	2.84
aniline	1.12	1.24	1.14	0.39	2.35	1.67	−2.10	2.72	2.20
cyclohexane	−0.24	0.58	0.48	0.67	2.76	1.78	−2.45	3.56	2.46
n-hexane	−0.22	0.45	0.41	0.45	3.08	1.95	−0.81	3.23	2.04
toluene	−0.54	2.48	2.23	0.35	2.41	1.72	−7.23	7.82	7.23
n-heptane	−0.21	0.36	0.35	1.41	3.02	1.91	−0.73	2.24	1.40
n-octane	0.80	0.92	0.80	1.53	4.90	3.69	−1.49	2.35	1.53
isooctane	−0.27	0.37	0.27	1.91	3.83	2.43	−7.06	7.15	7.06
m-xylene	5.72	6.83	5.72	−1.98	2.24	1.98	−8.76	8.89	8.76
o-xylene	0.98	1.56	1.23	−0.45	1.99	1.54	−2.74	2.98	2.74
p-xylene	0.42	1.91	1.55	0.83	3.48	2.06	−2.33	2.83	2.33
ethyl benzene	−5.97	6.30	5.97	0.22	4.45	2.93	3.11	3.95	3.46
naphthalene	−0.11	2.77	2.62	−0.57	0.72	0.65	−7.21	10.12	9.42
n-decane	−2.08	2.69	2.17	3.21	4.26	3.21	1.94	2.53	2.31
diphenyl ether	3.03	3.35	3.03	−2.20	2.24	2.20	11.20	13.18	11.42

Table A.10: Overall deviations in P^s, v_l^s and v_v^s for equation I.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.06	0.51	0.45	−0.90	2.84	2.39	−1.19	3.00	2.43
chlorine	1.10	1.76	1.10	1.43	3.34	2.51	−1.49	2.11	1.50
fluorine	−0.78	1.09	0.96	−2.01	2.57	2.43	0.00	4.49	1.94
helium	−4.11	7.27	5.04	−11.72	13.46	12.23	4.74	10.26	7.88
hydrogen chloride	1.22	1.41	1.22	−4.12	6.50	5.93	−1.00	6.53	4.54
hydrogen	0.42	4.66	3.76	−3.45	6.78	6.17	−2.94	7.75	6.84
water	−1.48	2.89	1.72	7.55	7.92	7.55	1.90	3.32	2.40
hydrogen sulfide	4.52	6.10	4.52	1.75	4.67	2.28	−9.21	9.82	9.21
ammonia	1.45	2.67	1.86	1.38	2.46	1.79	1.27	3.02	2.40
krypton	−0.12	0.62	0.54	−0.75	2.92	2.35	−2.13	3.91	3.07
nitrogen	0.35	0.42	0.36	−0.21	2.91	2.06	−2.24	3.21	2.24
neon	2.97	4.00	3.66	−2.11	3.97	3.67	−3.46	4.93	4.21
oxygen	0.53	0.77	0.62	−0.62	2.78	2.20	−1.83	3.19	2.07
sulfur dioxide	0.93	1.19	1.01	3.72	9.01	3.95	−1.79	3.34	2.53
sulfur trioxide	−7.90	9.43	8.02	−1.59	4.38	3.95	5.57	11.93	8.33
xenon	0.29	0.46	0.41	0.16	3.03	2.03	−2.41	3.42	2.64
phosgene	0.15	0.65	0.56	1.50	3.77	2.07	−7.67	11.41	10.39
carbon tetrachloride	−0.74	0.78	0.74	1.43	3.61	1.98	−1.87	5.24	2.98
carbon tetrafluoride	1.78	2.68	1.79	−1.09	3.45	3.07	−3.53	4.45	3.53
carbon monoxide	−2.60	3.64	2.92	0.36	1.54	1.19	4.43	6.69	5.95
carbon dioxide	−1.43	1.69	1.43	0.66	3.91	2.67	−0.24	3.29	2.84
chloroform	−2.36	2.67	2.36	7.97	8.22	7.97	−0.11	3.48	2.22
freon-13	−4.04	5.06	4.04	−0.56	2.40	1.94	3.31	6.27	5.24
freon-12	−5.03	5.97	5.04	0.13	2.16	1.56	4.89	6.64	5.48
freon-11	1.17	1.56	1.17	1.42	2.34	1.85	−1.34	1.62	1.34
freon-22	0.43	1.65	0.77	1.47	3.40	2.44	−1.88	2.99	2.19
freon-21	0.72	1.98	1.23	0.71	2.90	2.17	−0.92	2.91	2.35
methyl chloride	3.66	3.87	3.66	1.82	2.62	1.94	−2.52	3.00	2.52
methane	1.60	1.63	1.60	−0.11	3.23	2.12	−3.24	3.93	3.24
methanol	1.59	1.82	1.59	−0.12	4.54	3.39	0.41	3.39	2.68
methyl mercaptan	−0.12	1.10	0.87	−1.20	2.73	2.32	−29.58	33.70	29.58
freon-114	2.16	3.21	2.61	0.31	1.30	1.07	−2.20	2.80	2.20
freon-113	1.20	1.45	1.20	0.99	1.94	1.56	−1.18	1.35	1.18
acetylene	0.46	0.91	0.77	0.19	3.50	2.26	−1.10	2.93	1.93
acetonitrile	15.09	20.72	15.09	3.30	7.30	5.00	−8.85	13.77	11.42
ethylene	0.66	1.11	0.66	0.78	4.50	2.74	−1.58	2.84	2.40
ethylene oxide	−1.58	3.18	2.59	2.91	3.90	3.09	−1.03	1.92	1.36
acetic acid	6.50	7.59	6.50	−6.05	7.02	6.36	43.92	47.25	43.92
methyl formate	−0.56	1.31	1.11	0.62	3.22	1.99	−0.49	2.06	1.72
ethyl chloride	0.87	0.93	0.87	4.06	4.82	4.06	−4.13	5.93	4.41
ethane	0.20	0.57	0.41	3.35	5.50	3.66	−1.52	2.96	1.80
dimethyl ether	0.77	1.69	1.20	8.41	9.19	8.41	−1.27	2.08	1.79
ethanol	−1.34	2.00	1.76	−0.31	7.64	4.67	−1.38	5.42	2.82
ethyl mercaptan	0.05	0.87	0.79	2.15	3.96	2.18	−15.40	16.52	15.41
dimethyl sulfide	−0.18	1.72	1.45	0.34	3.27	1.96	−18.26	21.21	19.03
propyne	0.31	0.38	0.31	5.56	6.94	5.60	−0.76	3.55	3.07
propylene	3.01	5.48	3.01	−0.66	2.95	2.60	−3.55	5.16	3.55
acetone	−0.33	2.28	2.01	−2.92	3.81	3.53	−11.87	14.59	13.48

Table A.10: Overall deviations in P^s, v_l^s and v_v^s for equation I (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−0.59	2.09	1.78	−7.63	9.27	7.63	−1.92	3.14	2.08
ethyl formate	−0.75	1.17	1.04	0.88	3.45	2.19	−0.83	2.44	1.87
methyl acetate	−0.48	0.73	0.65	0.92	3.54	2.02	−1.08	2.08	1.32
cyclopropane	−0.41	0.45	0.41	2.71	4.35	2.71	−2.23	3.33	2.37
propane	1.09	1.26	1.09	1.15	2.48	1.85	−2.67	3.66	2.67
1-propanol	−1.07	3.18	2.76	−0.66	3.74	2.66	2.91	5.63	4.92
2-propanol	−4.78	6.84	6.01	−0.81	4.67	3.43	8.64	15.36	13.70
methyl ethyl ether	−2.34	2.94	2.66	−0.51	4.36	3.14	9.01	20.59	16.57
perfluorocyclobutane	0.94	1.14	0.95	1.00	2.75	1.76	−1.76	2.51	1.76
1,2-butadiene	−1.40	5.24	3.32	−1.23	1.36	1.23	−0.51	1.06	0.79
1,3-butadiene	2.19	3.59	2.19	0.77	3.04	2.48	−4.05	4.92	4.05
1-butene	0.80	0.96	0.80	0.47	2.40	1.68	−3.07	4.15	3.25
ethyl acetate	−0.29	0.66	0.59	0.44	3.42	2.22	−0.49	2.22	1.57
methyl propionate	0.09	0.89	0.56	1.25	4.17	2.61	−1.03	2.86	2.11
n-propyl formate	−0.15	0.43	0.36	0.77	3.43	2.01	−1.27	2.85	2.04
n-butane	0.68	0.79	0.68	1.30	3.68	2.49	−2.24	2.98	2.24
isobutane	1.06	1.19	1.06	1.82	2.81	2.28	−3.05	4.26	3.14
1-butanol	2.48	4.46	3.70	−2.58	4.25	3.84	8.12	15.80	11.45
t-butanol	−2.86	4.84	3.55	−2.45	2.62	2.45	3.16	4.15	3.75
diethyl ether	0.75	0.83	0.75	−0.28	3.99	3.10	−1.47	3.80	2.65
diethyl sulfide	−3.43	3.58	3.44	−24.99	25.07	24.99	−41.92	42.26	41.92
diethyl amine	1.41	2.36	1.71	4.21	5.17	4.21	−10.87	12.11	11.06
n-propyl acetate	−0.57	0.65	0.59	1.28	4.67	2.61	−1.02	2.39	1.70
ethyl propionate	0.50	0.53	0.50	1.71	4.30	2.48	−1.03	2.49	1.75
methyl butyrate	0.53	0.55	0.53	1.40	4.73	2.77	−0.61	3.35	2.74
methyl isobutyrate	0.08	0.20	0.17	0.95	4.05	2.36	−0.42	2.37	1.94
n-pentane	0.32	0.46	0.33	−2.82	3.25	2.90	−2.69	3.71	2.69
isopentane	1.78	2.17	1.78	0.93	3.03	2.20	−2.98	3.91	2.98
neopentane	−1.01	3.27	1.70	−4.27	4.51	4.27	−1.79	2.44	1.79
ethyl propyl ether	1.81	3.14	2.87	−0.66	3.19	2.51	50.71	74.87	53.93
bromobenzene	0.31	0.47	0.45	−0.48	0.94	0.82	1.22	1.37	1.22
chlorobenzene	1.25	1.32	1.25	−0.76	1.02	0.91	−1.45	1.52	1.45
fluorobenzene	0.27	0.70	0.40	−0.59	3.13	2.43	−1.79	2.78	2.06
iodobenzene	0.42	0.61	0.53	0.13	0.71	0.60	0.61	0.75	0.62
benzene	0.82	1.46	1.04	1.36	3.58	2.12	−3.69	5.43	3.90
aniline	−0.02	0.42	0.35	−6.66	6.96	6.66	−1.52	2.35	1.52
cyclohexane	0.07	0.57	0.46	−0.26	3.09	2.40	−2.82	3.93	2.82
n-hexane	1.00	1.24	1.00	0.15	3.00	1.97	−2.24	3.82	2.37
toluene	−1.83	3.24	2.34	−0.64	2.49	1.93	−5.53	6.13	5.53
n-heptane	0.93	1.02	0.93	1.69	3.03	2.02	−2.14	3.09	2.14
n-octane	1.26	1.83	1.26	1.97	5.38	4.25	−2.05	2.85	2.06
isooctane	0.89	1.20	0.92	−1.06	3.51	2.87	−8.74	8.82	8.74
m-xylene	−0.72	1.13	0.96	−1.85	2.15	1.91	−1.56	2.37	1.69
o-xylene	−0.24	0.90	0.81	−1.24	2.16	1.89	−1.70	2.31	1.76
p-xylene	−0.16	1.26	1.10	1.03	3.23	2.00	−2.00	2.77	2.05
ethyl benzene	−2.49	2.82	2.63	−0.04	4.15	2.87	−1.89	2.67	1.91
naphthalene	−1.55	2.39	2.13	6.49	6.50	6.49	−5.66	9.27	8.45
n-decane	−0.23	1.35	0.84	−0.34	2.12	1.65	−1.44	2.50	1.62
diphenyl ether	3.99	4.15	3.99	−2.63	2.70	2.63	9.89	12.04	10.26

Table A.11: Overall deviations in P^s, v_l^s and v_v^s for equation II.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.71	0.74	0.71	0.64	2.06	0.84	−0.13	2.32	1.87
chlorine	2.83	3.43	2.84	−2.59	3.31	3.20	−3.45	3.63	3.45
fluorine	−1.35	1.79	1.61	0.04	0.91	0.66	1.98	2.21	2.02
helium	0.80	0.86	0.80	1.00	2.01	1.00	0.22	1.38	1.15
hydrogen chloride	0.71	0.76	0.71	1.63	5.03	1.72	0.36	5.91	4.48
hydrogen	3.29	3.38	3.29	1.83	3.54	1.94	−5.58	6.09	5.58
water	0.07	0.12	0.10	0.90	2.55	1.02	−0.13	1.72	1.08
hydrogen sulfide	0.65	1.34	0.80	3.29	5.15	3.29	−5.18	7.12	5.35
ammonia	1.00	1.26	1.07	0.15	1.48	0.74	1.44	2.19	1.62
krypton	0.01	0.17	0.15	0.58	2.21	1.00	−2.14	3.38	2.47
nitrogen	−0.62	0.65	0.62	1.11	2.66	1.13	−0.83	2.27	1.63
neon	3.80	3.80	3.80	−2.99	3.81	3.69	−4.31	4.72	4.31
oxygen	0.45	0.68	0.49	0.18	2.09	0.96	−1.53	2.62	1.62
sulfur dioxide	0.37	0.64	0.50	3.16	8.78	3.17	−1.11	3.04	2.05
sulfur trioxide	−2.74	3.54	2.74	−5.42	6.32	5.98	−2.28	8.30	7.42
xenon	0.04	0.13	0.11	1.25	2.75	1.29	−1.92	2.78	2.08
phosgene	1.34	1.55	1.34	−0.85	3.41	2.66	−9.37	12.62	11.50
carbon tetrachloride	−1.34	1.35	1.34	2.76	4.46	2.76	−0.40	2.81	2.13
carbon tetrafluoride	−0.35	0.69	0.58	−2.93	3.73	3.64	−1.35	3.24	1.98
carbon monoxide	2.12	2.21	2.12	0.30	0.90	0.48	−1.01	3.44	2.63
carbon dioxide	−0.10	0.12	0.10	2.29	4.23	2.29	−1.66	2.78	2.14
chloroform	−1.17	2.00	1.53	0.30	1.71	1.05	−2.25	4.38	2.25
freon-13	−0.44	0.53	0.46	0.74	1.97	0.75	−0.71	2.60	1.89
freon-12	−0.71	0.92	0.74	0.47	1.58	0.49	0.09	0.74	0.45
freon-11	0.13	0.53	0.38	0.04	0.09	0.08	−0.28	0.48	0.30
freon-22	−0.25	0.31	0.30	1.22	2.85	1.37	−1.17	2.58	1.89
freon-21	−0.38	1.72	1.05	0.62	2.06	0.74	0.12	2.91	2.18
methyl chloride	1.42	1.54	1.42	−0.36	0.39	0.36	−0.29	1.10	0.93
methane	1.26	1.38	1.26	0.73	2.69	0.96	−2.67	3.21	2.67
methanol	1.40	1.49	1.40	3.52	6.00	3.52	0.77	3.92	3.49
methyl mercaptan	−0.69	0.89	0.77	4.22	4.67	4.22	−28.49	33.09	28.49
freon-114	−1.53	2.10	1.65	0.75	0.79	0.75	1.65	1.98	1.65
freon-113	0.25	0.51	0.44	−0.12	0.15	0.13	−0.23	0.47	0.41
acetylene	0.22	0.73	0.58	1.28	3.33	1.53	−0.33	2.04	1.48
acetonitrile	−0.93	2.14	1.65	2.06	4.24	2.12	8.50	10.61	8.50
ethylene	0.32	0.53	0.43	1.92	4.49	1.93	−0.95	2.11	1.64
ethylene oxide	−1.52	2.23	1.66	0.37	2.08	1.31	−1.56	3.23	2.18
acetic acid	4.68	5.13	4.68	0.96	3.18	1.05	47.40	51.17	47.40
methyl formate	−0.09	0.28	0.24	3.88	4.83	3.88	−0.85	1.69	1.12
ethyl chloride	−0.20	0.53	0.46	−1.58	2.63	2.45	−3.41	5.56	4.23
ethane	−0.25	0.55	0.37	1.86	4.24	2.25	−1.05	2.79	1.60
dimethyl ether	0.53	2.46	1.94	1.55	3.67	1.89	−1.78	2.75	2.39
ethanol	−0.15	0.56	0.50	4.56	9.33	4.77	−2.60	5.58	3.36
ethyl mercaptan	−0.41	1.07	0.96	0.94	3.04	1.25	−15.02	16.19	15.13
dimethyl sulfide	−0.60	2.22	1.71	1.73	3.37	1.73	−17.70	20.84	18.64
propyne	−0.03	0.15	0.11	13.03	13.48	13.03	2.63	4.84	3.34
propylene	−0.37	0.50	0.37	0.22	0.79	0.37	−0.14	1.14	0.71
acetone	−0.91	1.24	0.98	1.59	3.67	1.59	−10.02	12.91	12.08

Table A.11: Overall deviations in P^s, v_l^s and v_v^s for equation II (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	0.12	1.83	1.46	−1.14	5.65	2.52	−2.45	3.76	2.45
ethyl formate	0.57	0.78	0.62	3.33	4.54	3.33	−2.22	2.69	2.22
methyl acetate	−0.86	1.25	1.07	1.85	3.59	1.85	−0.25	1.39	1.06
cyclopropane	−4.52	4.65	4.52	3.07	3.92	3.07	4.29	4.79	4.47
propane	0.42	0.67	0.42	−0.34	1.86	1.61	−2.02	3.39	2.17
1-propanol	0.95	1.20	0.95	1.58	4.05	1.74	−0.04	3.36	2.49
2-propanol	−2.53	4.17	3.10	3.64	6.30	3.64	5.32	11.81	9.96
methyl ethyl ether	−1.96	2.46	2.08	1.11	3.97	1.92	8.81	19.59	15.35
perfluorocyclobutane	−0.41	0.98	0.86	−3.51	4.36	4.23	−0.47	2.34	1.56
1,2-butadiene	0.03	5.40	3.28	−0.13	0.61	0.47	−1.93	2.58	1.93
1,3-butadiene	0.87	1.73	0.88	1.30	2.58	1.40	−2.22	2.97	2.22
1-butene	0.12	0.56	0.44	0.58	1.91	1.13	−2.20	3.49	2.71
ethyl acetate	0.32	0.44	0.37	2.00	3.79	2.00	−1.09	2.16	1.42
methyl propionate	−0.46	1.28	1.11	2.77	4.58	2.77	0.27	1.95	1.69
n-propyl formate	1.47	1.64	1.49	2.31	3.83	2.31	−3.01	3.47	3.01
n-butane	0.17	0.31	0.22	2.02	3.72	2.62	−1.56	2.55	1.65
isobutane	0.85	1.46	1.25	−0.68	1.66	0.93	−2.78	3.71	2.96
1-butanol	5.54	7.21	5.73	−1.16	3.53	3.09	3.79	13.37	9.26
t-butanol	−0.79	3.29	2.75	1.57	1.90	1.57	0.56	0.65	0.57
diethyl ether	0.79	0.83	0.79	1.65	4.00	1.94	−1.32	3.69	2.70
diethyl sulfide	−3.99	4.12	3.99	−25.15	25.26	25.15	−41.11	41.47	41.11
diethyl amine	0.33	0.68	0.56	1.27	3.06	1.30	−10.28	11.71	11.01
n-propyl acetate	0.09	0.21	0.20	3.64	5.63	3.64	−1.49	2.24	1.62
ethyl propionate	−0.35	0.51	0.42	2.68	4.49	2.68	0.54	1.74	1.44
methyl butyrate	0.70	0.84	0.73	2.43	5.02	2.43	−0.67	3.36	2.82
methyl isobutyrate	0.54	0.58	0.54	1.84	4.20	1.85	−0.87	2.34	1.85
n-pentane	−0.45	0.51	0.45	0.63	1.62	1.15	−1.31	2.63	1.70
isopentane	0.12	0.61	0.52	1.25	2.68	1.27	−1.04	2.53	1.12
neopentane	−3.05	4.38	3.05	0.32	1.00	0.54	1.29	2.13	1.85
ethyl propyl ether	−0.21	2.31	1.73	−3.25	4.32	4.16	54.06	77.39	56.11
bromobenzene	−0.75	0.87	0.75	0.11	0.13	0.11	2.45	2.51	2.45
chlorobenzene	0.17	0.46	0.39	0.27	0.28	0.27	−0.17	0.49	0.40
fluorobenzene	−0.36	0.75	0.60	0.85	2.91	1.43	−0.97	2.53	1.86
iodobenzene	0.39	0.54	0.52	0.87	0.87	0.87	0.65	1.11	0.76
benzene	−0.47	1.04	0.53	1.24	3.48	1.26	−2.03	3.78	2.84
aniline	1.12	1.24	1.14	0.87	2.00	0.91	−2.18	2.85	2.28
cyclohexane	−0.24	0.58	0.48	1.19	2.81	1.25	−2.20	3.34	2.23
n-hexane	−0.22	0.45	0.41	−0.04	2.19	0.76	−0.79	3.24	2.05
toluene	−0.54	2.48	2.23	0.71	2.28	1.07	−7.07	7.63	7.07
n-heptane	−0.21	0.36	0.35	0.87	2.64	1.43	−0.83	2.38	1.46
n-octane	0.80	0.92	0.80	0.62	4.74	3.05	−1.58	2.51	1.62
isooctane	−0.27	0.37	0.27	1.22	3.16	1.25	−7.13	7.22	7.13
m-xylene	5.72	6.83	5.72	−1.56	1.64	1.56	−8.66	8.81	8.66
o-xylene	0.98	1.56	1.23	−0.15	1.53	1.10	−2.88	3.13	2.88
p-xylene	0.42	1.91	1.55	1.09	3.09	1.40	−2.54	3.06	2.54
ethyl benzene	−5.97	6.30	5.97	0.42	3.94	2.43	2.84	3.91	3.42
naphthalene	−0.11	2.77	2.62	−0.20	1.11	0.98	−7.26	10.15	9.45
n-decane	−2.08	2.69	2.17	3.71	4.16	3.71	1.42	2.50	2.34
diphenyl ether	3.03	3.35	3.03	−1.22	1.28	1.22	11.08	13.08	11.33

Table A.12: Overall deviations in P^s, v_l^s and v_v^s for equation III.

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
argon	−0.50	0.67	0.52	1.58	3.05	1.70	−0.27	2.42	2.01
chlorine	2.01	2.86	2.50	−1.04	3.14	2.71	−2.76	3.40	3.25
fluorine	−0.92	1.29	1.18	0.41	1.62	1.10	0.65	4.39	2.48
helium	1.45	1.81	1.45	0.78	6.64	5.22	0.05	1.13	0.86
hydrogen chloride	0.77	0.81	0.77	1.96	5.35	2.66	0.25	5.98	4.60
hydrogen	2.53	2.83	2.65	3.60	6.74	4.64	−4.00	4.58	4.14
water	−3.38	5.90	3.45	1.86	3.12	2.34	3.85	7.06	4.58
hydrogen sulfide	0.56	1.38	0.82	4.02	5.91	4.02	−4.91	6.74	5.10
ammonia	0.[illegible]	1.39	1.15	−0.82	2.17	1.91	2.17	2.98	2.37
krypton	0.10	0.27	0.25	1.52	3.15	1.73	−2.10	3.34	2.49
nitrogen	−0.61	0.83	0.61	2.19	3.58	2.22	−0.84	2.52	1.93
neon	4.08	4.09	4.08	−1.94	3.76	3.46	−4.47	4.79	4.47
oxygen	−1.73	4.86	2.28	2.17	3.42	2.28	0.99	6.38	3.89
sulfur dioxide	0.38	0.64	0.49	2.80	8.65	3.68	−1.29	3.17	2.15
sulfur trioxide	−2.01	3.42	2.71	−6.03	7.22	6.61	−3.47	9.43	8.51
xenon	0.13	0.23	0.20	2.06	3.62	2.06	−1.92	2.79	2.13
phosgene	0.78	1.37	1.10	−0.85	3.58	2.72	−8.63	11.64	10.66
carbon tetrachloride	−1.01	1.07	1.01	2.75	4.30	2.75	−1.36	5.07	2.99
carbon tetrafluoride	−2.64	5.61	2.89	−0.73	3.33	2.91	1.27	7.29	4.85
carbon monoxide	1.72	1.80	1.72	1.25	1.91	1.39	−0.47	3.45	2.56
carbon dioxide	0.00	0.19	0.17	1.34	4.34	2.62	−2.08	3.32	2.50
chloroform	−1.58	2.50	2.03	0.28	1.94	1.13	−1.68	3.97	1.96
freon-13	−0.58	0.66	0.60	1.29	2.63	1.73	−0.51	2.57	1.88
freon-12	−0.10	0.30	0.21	1.09	2.37	1.47	−0.75	1.47	1.02
freon-11	−0.18	0.37	0.23	1.96	2.71	2.15	0.02	0.40	0.21
freon-22	−0.68	1.04	0.68	1.69	3.49	2.45	−0.68	2.71	2.12
freon-21	−1.09	3.29	1.52	1.72	3.26	2.25	0.96	4.36	2.86
methyl chloride	1.36	1.45	1.36	0.93	2.12	1.68	−0.24	0.99	0.86
methane	1.18	1.22	1.18	1.98	3.73	2.05	−2.48	3.12	2.49
methanol	−0.01	1.08	0.97	2.05	4.92	2.73	2.72	4.70	4.15
methyl mercaptan	−0.51	0.78	0.62	4.68	5.26	4.68	−28.68	33.20	28.68
freon-114	−1.56	2.15	1.67	1.48	1.98	1.48	1.68	2.02	1.68
freon-113	0.48	0.60	0.53	2.05	2.64	2.10	−0.45	0.48	0.45
acetylene	1.00	1.11	1.00	1.45	3.77	1.98	−1.52	2.73	1.68
acetonitrile	−0.18	2.47	1.86	1.48	6.75	4.93	5.31	10.80	8.41
ethylene	0.39	0.51	0.46	2.89	5.26	2.96	−1.05	2.34	1.86
ethylene oxide	−2.23	3.17	2.37	0.39	2.58	2.14	−0.54	2.01	1.37
acetic acid	3.92	4.57	3.93	1.45	3.95	3.00	48.62	52.59	48.62
methyl formate	−0.52	0.75	0.60	3.59	4.78	3.59	−0.26	1.49	1.21
ethyl chloride	0.13	0.28	0.25	−1.46	2.99	2.63	−3.90	6.23	4.69
ethane	−0.92	2.01	0.96	3.31	5.45	3.63	−0.29	3.57	2.44
dimethyl ether	0.78	2.36	1.72	1.79	4.18	2.48	−2.21	3.06	2.71
ethanol	−2.35	2.76	2.37	1.76	7.85	3.54	0.08	5.40	3.39
ethyl mercaptan	−0.33	0.95	0.84	1.14	3.51	1.95	−15.13	16.27	15.23
dimethyl sulfide	−0.53	2.23	1.76	1.91	3.79	2.00	−17.79	20.88	18.73
propyne	0.44	0.57	0.44	24.43	24.63	24.43	6.89	9.64	6.89
propylene	−2.14	4.76	2.15	2.15	3.57	2.62	1.82	5.71	3.08
acetone	−1.45	1.93	1.54	0.05	2.44	1.81	−10.40	13.70	12.42

Table A.12: Overall deviations in P^s, v_l^s and v_v^s for equation III (continued).

	P^s			v_l^s			v_v^s		
	%bias	%RMS	%AAD	%bias	%RMS	%AAD	%bias	%RMS	%AAD
propylene oxide	−0.60	1.66	1.48	−1.56	5.76	3.19	−1.49	2.64	1.52
ethyl formate	0.28	0.76	0.60	2.94	4.47	2.94	−1.87	2.49	1.87
methyl acetate	−0.37	0.65	0.59	1.23	3.63	2.04	−1.17	2.07	1.33
cyclopropane	−1.69	1.74	1.69	2.95	4.47	2.95	−0.42	3.00	2.52
propane	0.28	0.94	0.65	0.75	2.28	1.79	−1.81	3.49	2.43
1-propanol	−1.17	2.12	1.87	0.87	3.83	1.99	2.97	4.87	4.27
2-propanol	−5.18	6.46	5.54	0.74	4.76	2.69	9.02	15.00	13.27
methyl ethyl ether	−1.07	1.35	1.18	1.32	4.63	2.52	7.45	20.01	16.12
perfluorocyclobutane	−0.28	0.86	0.75	−3.71	4.51	4.23	−0.78	2.82	1.74
1,2-butadiene	−0.28	5.51	3.49	−0.58	0.87	0.76	−1.57	2.52	1.64
1,3-butadiene	1.28	1.62	1.28	2.11	3.60	2.64	−2.89	3.84	2.89
1-butene	0.29	0.51	0.36	0.56	2.40	1.68	−2.45	3.80	2.95
ethyl acetate	−0.07	0.43	0.38	1.00	3.55	2.13	−0.72	2.18	1.47
methyl propionate	0.27	0.94	0.55	1.99	4.44	2.64	−1.14	2.75	1.99
n-propyl formate	1.32	1.43	1.32	1.73	3.80	2.03	−2.95	3.57	2.95
n-butane	0.18	0.32	0.24	2.18	4.07	2.48	−1.52	2.54	1.59
isobutane	1.12	1.32	1.13	0.36	2.18	1.64	−3.20	4.25	3.31
1-butanol	3.46	5.30	3.78	−2.03	3.99	3.61	6.68	14.68	9.91
t-butanol	−3.16	4.62	3.24	−0.98	1.35	1.15	3.51	3.88	3.51
diethyl ether	0.61	0.67	0.61	1.43	4.22	2.47	−1.07	3.58	2.68
diethyl sulfide	−4.21	4.40	4.22	−25.73	25.81	25.73	−41.42	41.76	41.42
diethyl amine	−0.07	0.84	0.71	0.77	3.17	1.85	−9.84	11.31	10.54
n-propyl acetate	−0.20	0.30	0.28	2.21	4.59	2.51	−1.73	3.53	2.02
ethyl propionate	0.40	0.48	0.41	1.58	4.26	2.48	−0.95	2.54	1.77
methyl butyrate	0.38	0.48	0.42	1.20	4.68	2.81	−0.47	3.52	2.92
methyl isobutyrate	0.22	0.25	0.22	0.76	4.02	2.42	−0.64	2.44	1.93
n-pentane	−0.28	0.37	0.33	0.45	1.72	1.18	−1.59	2.96	1.95
isopentane	0.32	0.39	0.32	3.01	4.16	3.02	−1.33	2.99	1.48
neopentane	−2.69	4.25	2.69	0.16	1.44	1.09	0.75	2.16	1.84
ethyl propyl ether	0.31	2.65	2.20	−4.22	5.22	4.99	52.97	77.20	56.01
bromobenzene	−0.64	0.71	0.64	−0.26	0.87	0.77	2.29	2.37	2.29
chlorobenzene	0.29	0.43	0.39	−0.33	0.78	0.71	−0.37	0.66	0.54
fluorobenzene	−0.66	0.88	0.73	0.52	3.12	1.94	−0.58	2.38	1.85
iodobenzene	0.39	0.52	0.47	0.98	1.19	0.98	0.66	1.00	0.72
benzene	−0.17	1.02	0.47	1.58	3.66	2.16	−2.65	4.59	3.33
aniline	0.12	0.25	0.22	−0.27	2.03	1.66	−0.97	1.61	1.01
cyclohexane	−0.04	0.47	0.38	1.32	3.35	1.98	−2.46	3.59	2.49
n-hexane	−0.14	0.61	0.53	0.49	3.07	1.97	−0.97	3.56	2.31
toluene	−1.25	3.08	2.56	0.43	2.46	1.70	−6.09	6.54	6.09
n-heptane	−0.13	0.49	0.45	1.23	2.77	1.90	−1.03	2.77	1.69
n-octane	0.27	0.84	0.68	1.28	5.13	3.69	−1.11	2.57	1.74
isooctane	−0.15	0.43	0.26	1.80	3.76	2.50	−7.43	7.56	7.43
m-xylene	5.06	6.49	5.06	−2.01	2.26	2.01	−7.82	8.12	7.82
o-xylene	0.94	1.55	1.20	−0.90	1.98	1.68	−2.96	3.28	2.96
p-xylene	0.44	1.91	1.52	0.21	3.07	2.09	−2.75	3.35	2.75
ethyl benzene	−5.40	5.76	5.40	−0.26	4.15	2.97	1.73	3.79	3.47
naphthalene	0.14	2.49	2.31	−0.66	0.73	0.66	−7.55	10.41	9.63
n-decane	−1.68	2.49	1.86	1.47	2.55	1.69	0.52	2.66	2.39
diphenyl ether	2.52	2.75	2.52	−2.70	2.78	2.70	11.63	13.59	11.72

Appendix B

Computer Programs

Important computer programs used in this work are presented here. These are in the form of subroutines which perform specific calculations or tasks.

All programs are in FORTRAN, ANSI-1977 standard. Comments are included to clarify the programs, but they are not intended to be comprehensive.

Numerical Methods

Subroutines implementing important numerical methods used in this work are shown here. The secant method, Brent's algorithm, and the Nelder-Mead simplex method are mentioned in §3.2.

```
************************************************************************
*                              RTSEC
* Uses the secant method to find the root of a function FUNC,
* thought to lie near X1 and X2, to an accuracy XACC.
* Taken from "Numerical Recipes".
************************************************************************
      FUNCTION RTSEC(FUNC,X1,X2,XACC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (MAXIT=30)
      FL=FUNC(X1)
      F=FUNC(X2)
C-----Pick bound with lowest function value as most recent guess.
      IF (ABS(FL).LT.ABS(F)) THEN
         RTSEC=X1
         XL=X2
```

```
            SWAP=FL
            FL=F
            F=SWAP
         ELSE
            XL=X1
            RTSEC=X2
         ENDIF
C-----Secant method.
         DO 11 J=1,MAXIT
            DX=(XL-RTSEC)*F/(F-FL)
            XL=RTSEC
            FL=F
            RTSEC=RTSEC+DX
            F=FUNC(RTSEC)
            IF (ABS(DX).LT.XACC.OR.F.EQ.0D0) RETURN
   11 CONTINUE
      WRITE (6,*) '*** MAXIT EXCEEDED IN RTSEC'
      RETURN
      END

************************************************************************
*                                ZBRAC
*
* Given a function FUNC(X) and an initial range for X from X1 to X2,
* this routine expands the range until it contains a root. If
* successful, the LOGICAL variable SUCCESS is set to .TRUE., if not,
* it is set to .FALSE. . From "Numerical Recipes".
* Usually used to bracket a root prior to the use of ZBRENT.
************************************************************************
      SUBROUTINE ZBRAC(FUNC,X1,X2,SUCCES)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (FACTOR=1.6,NTRY=50)
      LOGICAL SUCCES
      IF (X1.EQ.X2) THEN
         WRITE (6,*) '*** MUST GUESS INITIAL RANGE FOR ZBRAC ***'
         SUCCES=.FALSE.
         RETURN
      ENDIF
      F1=FUNC(X1)
      F2=FUNC(X2)
      SUCCES=.TRUE.
      DO 11 J=1,NTRY
         IF (F1*F2.LT.0D0) RETURN
         IF (ABS(F1).LT.ABS(F2)) THEN
            X1=X1+FACTOR*(X1-X2)
```

```
            F1=FUNC(X1)
         ELSE
            X2=X2+FACTOR*(X2-X1)
            F2=FUNC(X2)
         ENDIF
   11 CONTINUE
      SUCCES=.FALSE.
      RETURN
      END

************************************************************************
*                             ZBRENT
*
* Uses Brent's method to find the root of function FUNC known to lie
* between X1 and X2. The root ZBRENT will have accuracy TOL.
* Taken from "Numerical Recipes".
************************************************************************
      FUNCTION ZBRENT(FUNC,X1,X2,TOL)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (ITMAX=100,EPS=1D-16)
C-----Initialize and check input.
      A=X1
      B=X2
      FA=FUNC(A)
      FB=FUNC(B)
      IF (FB*FA.GT.0D0) THEN
         WRITE (6,*) '*** ROOT MUST BE BRACKETED FOR ZBRENT ***'
         RETURN
      ENDIF
      FC=FB
C-----Main program loop.
      DO 11 ITER=1,ITMAX
         IF (FB*FC.GT.0D0) THEN
C-----------Rename A,B,C and adjust bounding interval D.
            C=A
            FC=FA
            D=B-A
            E=D
         ENDIF
         IF (ABS(FC).LT.ABS(FB)) THEN
            A=B
            B=C
            C=A
            FA=FB
            FB=FC
```

```
            FC=FA
         ENDIF
C--------Convergence check.
         TOL1=2D0*EPS*ABS(B)+0.5*TOL
         XM=0.5D0*(C-B)
         IF (ABS(XM).LE.TOL1.OR.FB.EQ.0D0) THEN
            ZBRENT=B
            RETURN
         ENDIF
         IF (ABS(E).GE.TOL1.AND.ABS(FA).GT.ABS(FB)) THEN
C-----------Attempt inverse quadratic interpolation.
            S=FB/FA
            IF (A.EQ.C) THEN
               P=2D0*XM*S
               Q=1D0-S
            ELSE
               Q=FA/FC
               R=FB/FC
               P=S*(2D0*XM*Q*(Q-R)-(B-A)*(R-1))
               Q=(Q-1D0)*(R-1D0)*(S-1D0)
            ENDIF
C-----------Check whether in bounds.
            IF (P.GT.0D0) Q=-Q
            P=ABS(P)
            IF (2D0*P.LT.MIN(3D0*XM*Q-ABS(TOL1*Q),ABS(E*Q))) THEN
C--------------Accept interpolation.
               E=D
               D=P/Q
            ELSE
C--------------Interpolation failed, use bissection.
               D=XM
               E=D
            ENDIF
         ELSE
C-----------Bounds decreasing too slowly, use bissection.
            D=XM
            E=D
         ENDIF
C--------Move last best guess to A.
         A=B
         FA=FB
C--------Evaluate new trial root.
         IF (ABS(D).GT.TOL1) THEN
            B=B+D
```

```
         ELSE
            B=B+SIGN(TOL1,XM)
         ENDIF
         FB=FUNC(B)
   11 CONTINUE
      WRITE (6,*) '*** ZBRENT HAS EXCEEDED MAXIMUM ITERATIONS ***'
      ZBRENT=B
      RETURN
      END

************************************************************************
*                             AMOEBA
*
* Mutidimensional minimization by downhill simplex (Nelder and Mead).
* Finds minimum F at NDIM-dimensional point PP of function FUNK(PP) to
* a specified fractional tolerance FTOL in ITER iterations.
* Must input an initial point PP and
* a vector of scale factors SCALE (to generate starting simplex).
* On output, SCALE is adjusted to the standard deviation of each
* simplex coordinate.
* Modified from algorithm in "Numerical Recipes".
*
************************************************************************
      SUBROUTINE AMOEBA(PP,SCALE,NDIM,F,FTOL,FUNK,ITER)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=20,ALPHA=1D0,BETA=5D-1,GAMMA=2D0,ITMAX=200)
      DIMENSION P(NMAX+1,NMAX),Y(NMAX+1),PR(NMAX),PRR(NMAX),PBAR(NMAX),
     &          SCALE(NDIM),PP(NDIM)
      MPTS=NDIM+1
C-----Generate starting simplex.
      Y(MPTS)=FUNK(PP,NDIM)
      DO 1000 I=1,NDIM
         P(MPTS,I)=PP(I)
         PP(I)=PP(I)+SCALE(I)
         DO 1001 J=1,NDIM
            P(I,J)=PP(J)
1001     CONTINUE
         Y(I)=FUNK(PP,NDIM)
         PP(I)=PP(I)-SCALE(I)
1000  CONTINUE
C-----Main program loop.
      ITER=0
C-----Determine ranking of points in simplex.
    1 ILO=1
      IF (Y(1).GT.Y(2)) THEN
```

```
         IHI=1
         INHI=2
      ELSE
         IHI=2
         INHI=1
      ENDIF
      DO 11 I=1,MPTS
         IF (Y(I).LT.Y(ILO)) ILO=I
         IF (Y(I).GT.Y(IHI)) THEN
            INHI=IHI
            IHI=I
         ELSE IF (Y(I).GT.Y(INHI)) THEN
            IF (I.NE.IHI) INHI=I
         ENDIF
   11 CONTINUE
C-----Check for termination criteria.
      RTOL=2D0*ABS(Y(IHI)-Y(ILO))/(ABS(Y(IHI))+ABS(Y(ILO)))
      IF (RTOL.LT.FTOL) THEN
         DO 1002 I=1,NDIM
            PP(I)=P(ILO,I)
            SCALE(I)=SQRT((3D0*(P(1,I)**2+P(2,I)**2+P(3,I)**2)
     &         -(P(1,I)+P(2,I)+P(3,I))**2)/6D0)
 1002    CONTINUE
         F=Y(ILO)
         RETURN
      ENDIF
      IF (ITER.EQ.ITMAX) THEN
         WRITE (6,*) '*** AMOEBA HAS EXCEEDED MAXIMUM ITERATIONS ***'
         DO 1003 I=1,NDIM
            PP(I)=P(ILO,I)
            SCALE(I)=SQRT((3D0*(P(1,I)**2+P(2,I)**2+P(3,I)**2)
     &         -(P(1,I)+P(2,I)+P(3,I))**2)/6D0)
 1003    CONTINUE
         F=Y(ILO)
         RETURN
      ENDIF
C-----New iteration begins here.
      ITER=ITER+1
C-----Find center of face across from high point (for reflection).
      DO 12 J=1,NDIM
         PBAR(J)=0D0
   12 CONTINUE
      DO 14 I=1,MPTS
         IF (I.NE.IHI) THEN
```

```
            DO 13 J=1,NDIM
               PBAR(J)=PBAR(J)+P(I,J)
   13       CONTINUE
         ENDIF
   14 CONTINUE
C-----Reflect the simplex from the high point (by a factor ALPHA).
      DO 15 J=1,NDIM
         PBAR(J)=PBAR(J)/NDIM
         PR(J)=(1D0+ALPHA)*PBAR(J)-ALPHA*P(IHI,J)
   15 CONTINUE
      YPR=FUNK(PR,NDIM)
C-----Check out the reflection.
      IF (YPR.LE.Y(ILO)) THEN
C--------Better than the lowest point, so try more extrapolation.
         DO 16 J=1,NDIM
            PRR(J)=GAMMA*PR(J)+(1D0-GAMMA)*PBAR(J)
   16    CONTINUE
         YPRR=FUNK(PRR,NDIM)
C--------See if the additional extrapolation worked.
         IF (YPRR.LT.Y(ILO)) THEN
            DO 17 J=1,NDIM
               P(IHI,J)=PRR(J)
   17       CONTINUE
            Y(IHI)=YPRR
         ELSE
            DO 18 J=1,NDIM
               P(IHI,J)=PR(J)
   18       CONTINUE
            Y(IHI)=YPR
         ENDIF
      ELSE IF (YPR.GE.Y(INHI)) THEN
C--------The reflected point is worse than the second-highest point.
         IF (YPR.LT.Y(IHI)) THEN
C-----------If its better than the highest, replace the highest.
            DO 19 J=1,NDIM
               P(IHI,J)=PR(J)
   19       CONTINUE
            Y(IHI)=YPR
         ENDIF
C--------Try to contract in 1D away from high point.
         DO 21 J=1,NDIM
            PRR(J)=BETA*P(IHI,J)+(1D0-BETA)*PBAR(J)
   21    CONTINUE
         YPRR=FUNK(PRR,NDIM)
```

```
        IF (YPRR.LT.Y(IHI)) THEN
C-----------Contraction gives an improvement, so accept it.
           DO 22 J=1,NDIM
              P(IHI,J)=PRR(J)
   22      CONTINUE
           Y(IHI)=YPRR
        ELSE
C-----------Contract in all dimensions towards low point.
           DO 24 I=1,MPTS
              IF (I.NE.ILO) THEN
                 DO 23 J=1,NDIM
                   PR(J)=0.5D0*(P(I,J)+P(ILO,J))
                   P(I,J)=PR(J)
   23            CONTINUE
                 Y(I)=FUNK(PR,NDIM)
              ENDIF
   24      CONTINUE
        ENDIF
      ELSE
C---------Refection produced a middling point. Replace high point.
        DO 25 J=1,NDIM
           P(IHI,J)=PR(J)
   25   CONTINUE
        Y(IHI)=YPR
      ENDIF
C-----Go for doneness test and next iteration.
      GOTO 1
      END

************************************************************************
*                              HESS
*
* This subroutine returns the Hessian H of function FUNC at
* N-dimensional point P. The Hessian is in symmetric storage mode (see
* IMSL manual for definition).
* Finite difference is used; DP contains the increments.
* The SCALE vector returned by AMOEBA is a good choice for DP.
************************************************************************
      SUBROUTINE HESS(FUNC,P,DP,H,N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION P(N),DP(N),H(N*(N+1)/2)
      F0=FUNC(P,N)
      DO 1000 I=1,N
         P(I)=P(I)+DP(I)
         F1=FUNC(P,N)
```

```
        P(I)=P(I)-2D0*DP(I)
        F2=FUNC(P,N)
        P(I)=P(I)+DP(I)
        H(I*(I+1)/2)=(F2-2D0*F0+F1)/DP(I)**2
        DO 1001 J=1,I-1
           P(I)=P(I)+DP(I)
           P(J)=P(J)+DP(J)
           F1=FUNC(P,N)
           P(I)=P(I)-2D0*DP(I)
           F2=FUNC(P,N)
           P(I)=P(I)+2D0*DP(I)
           P(J)=P(J)-2D0*DP(J)
           F3=FUNC(P,N)
           P(I)=P(I)-2D0*DP(I)
           F4=FUNC(P,N)
           P(I)=P(I)+DP(I)
           P(J)=P(J)+DP(J)
           H(I*(I-1)/2+J)=(F1-F2-F3+F4)/4D0/DP(I)/DP(J)
 1001   CONTINUE
 1000 CONTINUE
      F0=FUNC(P,N)
      RETURN
      END

*************************************************************************
*                        RTCUB
*
* This subroutine finds the NROOT real roots X of the cubic equation
* X**3+B*X**2+C*X+D=0. It sorts the roots and returns the number of
* negative roots NNEG. Requires the subroutine SORT.
* CAUTION: Roundoff error possible for certain coefficients,
*   eg. EOS roots for unusually low TR.
*************************************************************************
      SUBROUTINE RTCUB(B,C,D,X,NROOT,NNEG)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION X(3)
C-----Initialize important quantities.
      NNEG=0
      P=(3D0*C-B**2)/3D0
      Q=(27D0*D-9D0*B*C+2D0*B**3)/27D0
      R=(P/3D0)**3+(Q/2D0)**2
C-----Calculate roots, NROOT, NNEG.
      IF (R.GE.0D0) THEN
         NROOT=1
         AU=DSIGN(DABS(-Q/2D0+DSQRT(R))**(1D0/3D0),-Q/2D0+DSQRT(R))
```

```
         BU=DSIGN(DABS(-Q/2D0-DSQRT(R))**(1D0/3D0),-Q/2D0-DSQRT(R))
         X(1)=AU+BU-B/3D0
         IF (X(1).LT.0D0) NNEG=1
      ELSE
         NROOT=3
         P1=DACOS(DSQRT(-Q**2/P**3*27D0/4D0))/3D0
         P2=DACOS(-1D0)*2D0/3D0
         DO 1000 I=1,3
            X(I)=-DSIGN(2D0,Q)*DSQRT(-P/3D0)*DCOS(P1+P2*DFLOAT(I))-B/3D0
            IF (X(I).LT.0D0) NNEG=NNEG+1
 1000    CONTINUE
         CALL SORT(X,3)
      END IF
      RETURN
      END

************************************************************************
*                            SORT
*
* Sorts an array into ascending numerical order using the heapsort
* algorithm. From "Numerical Recipes".
************************************************************************
      SUBROUTINE SORT(RA,N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION RA(N)
      L=N/2+1
      IR=N
   10 CONTINUE
         IF (L.GT.1) THEN
            L=L-1
            RRA=RA(L)
         ELSE
            RRA=RA(IR)
            RA(IR)=RA(1)
            IR=IR-1
            IF (IR.EQ.1) THEN
               RA(1)=RRA
               RETURN
            ENDIF
         ENDIF
         I=L
         J=L+L
   20    IF (J.LE.IR) THEN
            IF (J.LT.IR) THEN
               IF (RA(J).LT.RA(J+1)) J=J+1
```

```
          ENDIF
          IF (RRA.LT.RA(J)) THEN
             RA(I)=RA(J)
             I=J
             J=J+J
          ELSE
             J=IR+1
          ENDIF
       GOTO 20
       ENDIF
       RA(I)=RRA
    GOTO 10
    END
```

Equation of State Routines

Subroutines to calculate the dimensionless parameters A, B, C and D for all equations of state considered in this work are given here. The equations are described in §4.2 and §5.2.

```
************************************************************************
* These subroutines calculate EOS parameters for the generic cubic
* EOS given temperature, pressure and required parameters.
* The user must ensure unit consistency of input if required.
*
* Input:
*   T: absolute temperature.
*   P: absolute pressure.
*   PARAM(N): Parameter vector. Its size and contents depend on the
*             particular routine. See notes for each routine.
* Output:
*   A,B,C,D: Dimensionless EOS constants.
************************************************************************

************************************************************************
*                 ESSRK(T,P,PARAM,A,B,C,D)
*
* PARAM is length 3, contains TC (units of T), PC (units of P),
* and acentric factor.
************************************************************************
      SUBROUTINE ESSRK(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION PARAM(3)
```

```
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
      OMEGAC=0.42747D0
      OMEGBC=0.08664D0
      OMEGCC=-OMEGBC
C-----Calculate ALPHA.
      SM=.480D0+1.574D0*AC-.176D0*AC**2
      ALPHA=(1D0+SM*(1D0-DSQRT(TR)))**2
C-----Calculate dimensionless constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=0D0
      RETURN
      END

************************************************************************
*                    ESPR   Peng-Robinson
*
* PARAM is length 3, contains TC (units of T), PC (units of P),
* and acentric factor.
************************************************************************
      SUBROUTINE ESPR(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION PARAM(3)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
C-----Calculate critical point constants.
      OMEGAC=0.45724D0
      OMEGBC=0.07780D0
      OMEGCC=-OMEGBC*(1D0+DSQRT(2D0))
      OMEGDC=-OMEGBC*(1D0-DSQRT(2D0))
C-----Calculate ALPHA.
      IF (AC.LT..2D0) THEN
         SM=.37464D0+1.54226D0*AC-.26992D0*AC**2
      ELSE
         SM=.37964D0+1.48503D0*AC-.16442D0*AC**2+.01667D0*AC**3
      ENDIF
      ALPHA=(1D0+SM*(1D0-DSQRT(TR)))**2
C-----Calculate dimensionless constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
```

```
      D=OMEGDC*PR/TR
      RETURN
      END
************************************************************************
*                  ESSW   Schmidt-Wenzel (improved, see FPE 9,225)
*
* PARAM is length 3, contains TC (units of T), PC (units of P),
* and acentric factor. Requires RTCUB and SORT subroutines.
************************************************************************
      SUBROUTINE ESSW(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION ROOT(3),PARAM(3)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
C-----Calculate critical point constants.
      CALL RTCUB(3D0/(6D0*AC+1D0),3D0/(6D0*AC+1D0),-1D0/(6D0*AC+1D0),
     1           ROOT,NROOT,NNEG)
      BETAC=ROOT(NNEG+1)
      ZETAC=1D0/3D0/(1+BETAC*AC)
      OMEGAC=(1D0-ZETAC*(1-BETAC))**3
      OMEGBC=BETAC*ZETAC
      W=-3D0*AC
      OMEGCC=-OMEGBC*(1D0-W+DSQRT(1D0-6D0*W+W**2))/2D0
      OMEGDC=-OMEGBC*(1D0-W-DSQRT(1D0-6D0*W+W**2))/2D0
C-----Calculate ALPHA.
      IF (TR.GT.1D0) THEN
         ALPHA=1D0-(0.4774D0+1.328D0*AC)*DLOG(TR)
      ELSE
         IF (AC.LE.0.3671) THEN
            F0=0.465D0+1.347D0*AC-0.528D0*AC**2
         ELSE
            F0=0.5361D0+0.9593D0*AC
         ENDIF
         F1=F0+1D0/70D0*(5D0*TR-3D0*F0-1D0)**2
         F2=F0+0.71D0*(TR-0.779D0)**2
         IF (AC.LE.0.4D0) THEN
            F=F1
         ELSE IF (AC.GT.0.4D0.AND.AC.LT.0.55D0) THEN
            F=(AC-0.4D0)/0.15D0*F2+(0.55D0-AC)/0.15D0*F1
         ELSE IF (AC.GE.0.55) THEN
            F=F2
         ENDIF
         ALPHA=(1D0+F*(1D0-DSQRT(TR)))**2
```

```
      ENDIF
C-----Calculate dimensionless constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END

************************************************************************
*                    ESPT  Patel-Teja
*
* PARAM is length 3, contains TC (units of T), PC (units of P),
* and acentric factor. Requires RTCUB and SORT subroutines.
************************************************************************
      SUBROUTINE ESPT(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION ROOT(3),PARAM(3)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
C-----Calculate critical point parameters.
      ZC=.329032D0-.0767992D0*AC+.0211947*AC**2
      CALL RTCUB(2D0-3D0*ZC,3D0*ZC**2,-ZC**3,ROOT,NROOT,NNEG)
      OMEGBC=ROOT(NNEG+1)
      OMEGAC=3D0*ZC**2+3D0*(1D0-2D0*ZC)*OMEGBC+OMEGBC**2+1D0-3D0*ZC
      COVERB=(1D0-3D0*ZC)/OMEGBC
      OMEGCC=-OMEGBC*(1D0+COVERB-DSQRT(1D0+6D0*COVERB+COVERB**2))/2D0
      OMEGDC=-OMEGBC*(1D0+COVERB+DSQRT(1D0+6D0*COVERB+COVERB**2))/2D0
C-----Calculate ALPHA.
      F=.452413D0+1.30982D0*AC-.295937*AC**2
      ALPHA=(1D0+F*(1D0-DSQRT(TR)))**2
C-----Calculate dimensionless constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END

************************************************************************
*                    ESTPR  Yu translated PR, corrected.
*
* PARAM is length 3, contains TC (units of T), PC (units of P),
* and acentric factor.
```

```
************************************************************************
      SUBROUTINE ESTPR(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION PARAM(3)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
C-----Calculate critical point values.
      OMEGAC=0.45724D0
      U=1.5251D0+1.1146D0*AC+1.1538D0*AC**2
      W=2D0*((2D0-U)/4D0)**2-1D0
      OMEGBC=.3112D0/(2D0+U)
      OMEGCC=-OMEGBC*(U+DSQRT(U**2-4D0*W))/2D0
      OMEGDC=-OMEGBC*(U-DSQRT(U**2-4D0*W))/2D0
C-----Calculate ALPHA.
      IF (AC.LT..2D0) THEN
         SM=.37464D0+1.54226D0*AC-.26992D0*AC**2
      ELSE
         SM=.37964D0+1.48503D0*AC-.16442D0*AC**2+.01667D0*AC**3
      ENDIF
      ALPHA=(1D0+SM*(1D0-DSQRT(TR)))**2
C-----Calculate dimensionless parameters.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END

************************************************************************
*                    ESTB   Trebble-Bishnoi
*
* NOTE: T must be in K and P must be in kPa.
* PARAM is length 4, contains TC (K), PC (bar),
* acentric factor and ZC. Requires RTCUB and SORT subroutines.
* Slightly different
* from other routines, because of temperature dependent B.
************************************************************************
      SUBROUTINE ESTB(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION ROOT(3),PARAM(4)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AF=PARAM(3)
      ZC=PARAM(4)
```

```
C-----Calculate critical point values.
      ZETAC=1.075D0*ZC
      DC=.341D0*ZC-.005D0*PARAM(2)*1D2/PARAM(1)/8.314D0
      CALL RTCUB(2D0-3D0*ZETAC,3D0*ZETAC**2,-DC**2-ZETAC**3,
     1           ROOT,NROOT,NNEG)
      BC=ROOT(NNEG+1)
      CC=1D0-3D0*ZETAC
      AC=3D0*ZETAC**2+2D0*BC*CC+BC+CC+BC**2+DC**2
C-----Calculate ALPHA and BETA.
      IF (AF.LT.-.35D0.AND.TR.LE.1D0) THEN
         Q1=-.31913D0
      ELSE IF (AF.LT.-.1D0) THEN
         Q1=.66208D0+4.63961D0*AF+7.45183D0*AF**2
      ELSE IF (AF.GE.-.1D0.AND.AF.LE..4D0) THEN
         Q1=.35D0+.7924D0*AF+.1875D0*AF**2-28.93D0*(.3D0-ZC)**2
      ELSE IF (AF.GT..4D0) THEN
         Q1=.32D0+.9424D0*AF-28.93D0*(.3D0-ZC)**2
      ENDIF
      ALPHA=DEXP(Q1*(1D0-TR))
      IF (TR.GT.1D0) THEN
         BETA=1D0
      ELSE
         IF (AF.LT.-.0423D0) THEN
            Q2=0D0
         ELSE IF (AF.GE.-.0423D0.AND.AF.LE..3D0) THEN
            Q2=.05246D0+1.15058D0*AF-1.99348D0*AF**2+1.59490D0*AF**3
     1         -1.39267*AF**4
         ELSE IF (AF.GT..3D0) THEN
            Q2=.17959D0+.23471D0*AF
         ENDIF
         BETA=1D0+Q2*(1D0-TR+DLOG(TR))
      ENDIF
C-----Calculate dimensionless parameters.
      A=ALPHA*AC*PR/TR**2
      B=BETA*BC*PR/TR
      CT=CC*PR/TR
      DT=DC*PR/TR
      C=-B*(1D0+CT/B+DSQRT(1D0+6D0*CT/B+(CT/B)**2+
     1                          4D0*(DT/B)**2))/2D0
      D=-B*(1D0+CT/B-DSQRT(1D0+6D0*CT/B+(CT/B)**2+
     1                          4D0*(DT/B)**2))/2D0
      RETURN
      END

*********************************************************************
```

```
*                  ESTV   Toghiani-Viswanath
*
* PARAM is length 4, contains TC (units of T), PC (units of P), acentric
* factor, and polar factor. Requires RTCUB and SORT subroutines.
************************************************************************
      SUBROUTINE ESTV(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION ROOT(3),PARAM(4)
      DATA A1,A2,A3,A4,A5,A6,A7,A8,B1,B2,B3,B4,B5,B6,B7,B8
     &   /.441926073D0,1.342755128D0,-.328431972D0,-15.020572758D0,
     &   -2.226936391D0,21.112706213D0,.015079204D0,234.965900518D0,
     &   .324020789D0,-.056675895D0,-.001268996D0,-3.259131762,
     &   1.399475880D0,4.769592801D0,.003431898D0,59.450596850D0/
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AF=PARAM(3)
      HS=PARAM(4)
C-----Calculate critical point constants.
      ZETAC=B1+B2*AF+B3*AF**2+B4*HS+B5*HS**2+B6*AF*HS+B7*AF**3+B8*HS**3
      CALL RTCUB(2D0/ZETAC-3D0,3D0,-1D0,ROOT,NROOT,NNEG)
      ETAC=ROOT(NNEG+1)
      CC=(1D0-3D0*ZETAC)/ZETAC/ETAC
      OMEGAC=(1D0-ZETAC*(1-ETAC))**3
      OMEGBC=ETAC*ZETAC
      OMEGCC=-OMEGBC*(1D0+CC+DSQRT(1D0+6D0*CC+CC**2))/2D0
      OMEGDC=-OMEGBC*(1D0+CC-DSQRT(1D0+6D0*CC+CC**2))/2D0
C-----Calculate ALPHA.
      SM=A1+A2*AF+A3*AF**2+A4*HS+A5*HS**2+A6*AF*HS+A7*AF**3+A8*HS**3
      ALPHA=(1D0+SM*(1D0-SQRT(TR)))**2
C-----Calculate dimensionless constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END

************************************************************************
*                  ESSIL  Sugie-Iwahori-Lu equation.
*
* PARAM is length 2, contains TC (units of T), PC (units of P).
* Must also pass function names PRSAT(TR) and ZLSAT(TR) which must
* return PR and ZL on the saturation curve at TR.
* Requires the subroutines ZBRAC, ZBRENT, ALPTR, RTCUB and SORT.
************************************************************************
```

```
      SUBROUTINE ESSIL(T,P,PARAM,PRSAT,ZLSAT,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (TOL=1D-10)
      DIMENSION PARAM(2)
      EXTERNAL FSIL
      COMMON /SILBLK/ PRTR1,PRTR2,ZL1,ZL2,OMEGBC,ATR2
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      OAC1=0.421875D0
      OAC2=0.70D0
C-----Calculate critical point values (from data at TR=.7 and TR=.9).
      PRS=PRSAT(0.7D0)
      PRTR1=PRS/0.7D0
      ZL1=ZLSAT(0.7D0,PRS)
      PRS=PRSAT(0.9D0)
      PRTR2=PRS/0.9D0
      ZL2=ZLSAT(0.9D0,PRS)
      OMEGAC=ZBRENT(FSIL,OAC1,OAC2,TOL)
      DUMMY1=1.5D0*OMEGAC**(1D0/3D0)
      DUMMY2=SQRT(4D0*OMEGAC-3D0*OMEGAC**(2D0/3D0))/2D0
      OMEGCC=1D0-DUMMY1-DUMMY2+OMEGBC
      OMEGDC=1D0-DUMMY1+DUMMY2+OMEGBC
C-----Calculate ALPHA.
      IF (TR.LT.1D0) THEN
         PRTR=PRSAT(TR)/TR
         ALPHA=ALPTR(OMEGAC,PRTR,TOL,ZLB,ZVB)*TR
      ELSE
         COEF=(SQRT(ATR2*.9D0)-1D0)/(1D0-SQRT(0.9D0))
         ALPHA=(1D0+COEF*(1D0-SQRT(TR)))**2
      ENDIF
C-----Calculate dimensionless parameters.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END
C-----This function is used by ESSIL to converge on a value of OMEGAC.
      FUNCTION FSIL(OMEGAC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (TOL=1D-10)
      COMMON /SILBLK/ PRTR1,PRTR2,ZL1,ZL2,OMEGBC,ATR2
      ATR1=ALPTR(OMEGAC,PRTR1,TOL,ZLB1,ZVB1)
      ATR2=ALPTR(OMEGAC,PRTR2,TOL,ZLB2,ZVB2)
```

```
      OMEGBC=(ZL1-ZLB1)/PRTR1
      FSIL=OMEGBC-(ZL2-ZLB2)/PRTR2
      RETURN
      END

************************************************************************
*                  ESI    Equation I
*
* PARAM is length 4, contains TC (in units of T), PC (in units of P),
* acentric factor, and ZC. Requires RTCUB and SORT subroutines.
************************************************************************
      SUBROUTINE ESI(T,P,PARAM,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION ROOT(3),PARAM(4)
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      AC=PARAM(3)
      ZC=PARAM(4)
C-----Determine critical point values.
      U=-1.95D0+1D0/3D0/ZC**2
      CALL RTCUB(0D0,3D0/U,-1D0/U,ROOT,NROOT,NNEG)
      BETAC=ROOT(NNEG+1)
      ZETAC=(1D0-2D0*BETAC)/((2D0+U*BETAC)*(1D0-BETAC)**2)
      OMEGAC=ZETAC*(1D0+U*BETAC-U*BETAC**2)**2/
     1       ((2D0+U*BETAC)*(1D0-BETAC)**2)
      OMEGBC=BETAC*ZETAC
      OMEGCC=OMEGBC*(-U-DSQRT(U**2+4D0*U))/2D0
      OMEGDC=OMEGBC*(-U+DSQRT(U**2+4D0*U))/2D0
C-----Calculate ALPHA.
      F=-.25D0*AC**2+1.31D0*AC-.209D0/ZC+.5275D0
      ALPHA=(1D0+F*(1D0-DSQRT(TR)))**2
      IF (TR.GE.0.7D0) THEN
         ALPHA=ALPHA/TR**0.4D0
      ELSE
         ALPHA=ALPHA/(.57667D0*TR**.8D0+.43352D0)
      ENDIF
C-----Calculate dimensionless EOS constants.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END

************************************************************************
```

```
*                  ESII   Equation II
*
* PARAM is length 2, contains TC (units of T), PC (units of P).
* Must also pass function names PRSAT(TR) and ZCVR(TR) which must
* return PR and ZL on the saturation curve at TR.
* Requires the subroutines ZBRAC, ZBRENT, ALPTR, RTCUB and SORT.
************************************************************************
      SUBROUTINE ESII(T,P,PARAM,PRSAT,ZLSAT,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (TOL=1D-10)
      DIMENSION PARAM(2)
      EXTERNAL FII
      COMMON /IIBLK/ PRTR,ZL,ATR,OMEGBC
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      OAC1=0.421875D0
      OAC2=0.70D0
C-----Calculate critical point values. If TR>.9, evaluate them at TR=.9.
      IF (TR.LE.0.9D0) THEN
         PRS=PRSAT(TR)
         PRTR=PRS/TR
         ZL=ZLSAT(TR,PRS)
      ELSE
         PRS=PRSAT(0.9D0)
         PRTR=PRS/0.9D0
         ZL=ZLSAT(0.9D0,PRS)
      ENDIF
      OMEGAC=ZBRENT(FIII,OAC1,OAC2,TOL)
      DUMMY1=1.5D0*OMEGAC**(1D0/3D0)
      DUMMY2=SQRT(4D0*OMEGAC-3D0*OMEGAC**(2D0/3D0))/2D0
      OMEGCC=1D0-DUMMY1-DUMMY2+OMEGBC
      OMEGDC=1D0-DUMMY1+DUMMY2+OMEGBC
C-----Calculate ALPHA.
      IF (TR.LE.0.9D0) THEN
         ALPHA=ATR*TR
      ELSE IF (TR.LT.1D0) THEN
         PRTR=PRSAT(TR)/TR
         ALPHA=ALPTR(OMEGAC,PRTR,TOL,ZLB,ZVB)*TR
      ELSE
         COEF=(SQRT(ATR*0.9D0)-1D0)/(1D0-SQRT(0.9D0))
         ALPHA=(1D0+COEF*(1D0-SQRT(TR)))**2
      ENDIF
C-----Calculate dimensionless parameters.
      A=ALPHA*OMEGAC*PR/TR**2
```

```
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END
C-----This function is used by ESII to converge on a value of OMEGAC.
      FUNCTION FII(OMEGAC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /IIBLK/ PRTR,ZL,ATR,OMEGBC
      ATR=ALPTR(OMEGAC,PRTR,1D-10,ZLB,ZVB)
      OMEGBC=(1D0-OMEGAC**(1D0/3D0))**1.5D0
      FII=ZL-PRTR*OMEGBC-ZLB
      RETURN
      END

************************************************************************
*                  ESIII  Equation III
*
* PARAM is length 2, contains TC (units of T), PC (units of P).
* Also requires PRSAT(ZL) and ZLSAT(TR,PR).
* Requires the subroutines ZBRENT, ALPTR, RTCUB and SORT.
************************************************************************
      SUBROUTINE ESIII(T,P,PARAM,PRSAT,ZLSAT,A,B,C,D)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (TOL=1D-10)
      DIMENSION PARAM(2)
      EXTERNAL FIII
      COMMON /FIIIB/ PRTR70,ZL70,ATR70,OMEGBC
      TR=T/PARAM(1)
      PR=P/PARAM(2)
      PR70=PRSAT(0.70D0)
      ZL70=ZLSAT(0.70D0,PR70)
      PRTR70=PR70/0.70D0
      PRTR60=PRSAT(0.60D0)/0.60D0
C-----Calculate critical point values.
      OAC1=0.421875D0
      OAC2=0.70D0
      OMEGAC=ZBRENT(FIII,OAC1,OAC2,TOL)
      DUMMY1=1.5D0*OMEGAC**(1D0/3D0)
      DUMMY2=SQRT(4D0*OMEGAC-3D0*OMEGAC**(2D0/3D0))/2D0
      OMEGCC=1D0-DUMMY1-DUMMY2+OMEGBC
      OMEGDC=1D0-DUMMY1+DUMMY2+OMEGBC
C------Calculate ALPHA.
      AR=LOG(ATR70*.70D0)/LOG(ALPTR(OMEGAC,PRTR60,TOL,ZLB,ZVB)*.60D0)
      AL60=LOG(.60D0)
```

```
      AL70=LOG(.70D0)
      ALT=LOG(TR)
      AN=(1D0-AR*AL60/AL70)/(AR*AL60/AL70*AL60-AL70)
      AM=LOG(ATR70*.70D0)/AL70/(1D0+AN*AL70)
      ALPHA=EXP(AM*ALT*(1D0+AN*ALT))
C-----Calculate dimensionless parameters.
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      C=OMEGCC*PR/TR
      D=OMEGDC*PR/TR
      RETURN
      END
C-----This function is used by ESIII to converge on a value of OMEGAC.
      FUNCTION FIII(OMEGAC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /FIIIB/ PRTR,ZL,ATR,OMEGBC
      ATR=ALPTR(OMEGAC,PRTR,1D-10,ZLB,ZVB)
      OMEGBC=(1D0-OMEGAC**(1D0/3D0))**1.5D0
      FIII=ZL-PRTR*OMEGBC-ZLB
      RETURN
      END
```

Mixing Rules

The subroutines required to calculate mixture parameters and their derivatives, as described in §3.1.6, are given here.

```
************************************************************************
*                     MIXAR
*
* This calculates a mixture parameter and its partial derivatives
* using the conventional arithmetic average mixing rule.
*
* Input:
*   A(NCOMP): Pure component parameters.
*   X(NCOMP): Pure component mole fractions.
*   NCOMP: Number of components.
* Output:
*   AMIX: Mixture parameter.
*   AI(NCOMP): The partial derivatives d(n*amix)/dni for each component.
************************************************************************
      SUBROUTINE MIXAR(A,X,NCOMP,AMIX,AI)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION A(NCOMP),X(NCOMP),AI(NCOMP)
```

```
      AMIX=0D0
      DO 1001 I=1,NCOMP
         AI(I)=A(I)
         AMIX=AMIX+X(I)*A(I)
 1001 CONTINUE
      RETURN
      END

**********************************************************************
*                             MIXRK
*
* This calculates a mixture parameter and its partial derivatives
* using the mixing rule of Swartzentrubber etal.(1989).
* This reduces to the Adachi-Sugie mixing rule if AM=0.5, and to the
* conventional VDW mixing rule if AL=0.
*
* Input:
*   A(NCOMP): Pure component parameters.
*   X(NCOMP): Pure component mole fractions.
*   AKJI(NCOMP*(NCOMP-1)/2): Binary interaction parameters.
*     Parameter lji (j>i) is located at j(j-3)/2+i+1. For example, for
*     a 4-component mixture, the elements of AKJI are (in order)
*     k21, k31, k32, k41, k42 and k43. kji=kij.
*   ALJI(NCOMP*(NCOMP-1)/2): Binary interaction parameters lji.
*     See AKIJ above for setup. lji=-lij.
*   AMJI(NCOMP*(NCOMP-1)/2): Binary interaction parameters mji.
*     See AKIJ above for setup. mji=1-mij.
*   NCOMP: Number of components.
* Output:
*   AMIX: Mixture parameter.
*   AI(NCOMP): The partial derivatives d(n*amix)/dni for each component.
**********************************************************************
      SUBROUTINE MIXRK(A,X,AKJI,ALJI,AMJI,NCOMP,AMIX,AI)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=20,NMAX2=400)
      DIMENSION A(NCOMP),X(NCOMP),AKJI(NCOMP*(NCOMP-1)/2)
     &   ,ALJI(NCOMP*(NCOMP-1)/2),AMJI(NCOMP*(NCOMP-1)/2),AI(NCOMP)
     &   ,AK(NMAX,NMAX),AL(NMAX,NMAX),AM(NMAX,NMAX)
      DATA AK/NMAX2*0D0/,AL/NMAX2*0D0/,AM/NMAX2*0D0/
C-----Transfer binary parameters to square matrices.
      DO 1000 J=2,NCOMP
         DO 1001 I=1,J-1
            AK(J,I)=AKJI(J*(J-3)/2+I+1)
            AL(J,I)=ALJI(J*(J-3)/2+I+1)
            AM(J,I)=AMJI(J*(J-3)/2+I+1)
```

```
            AK(I,J)=AK(J,I)
            AL(I,J)=-AL(J,I)
            AM(I,J)=1D0-AM(J,I)
 1001    CONTINUE
 1000 CONTINUE
C-----Calculate AMIX and part of AI's.
      SUM1=0D0
      SUM2=0D0
      DO 1002 I=1,NCOMP
         SUM3=0D0
         SUM4=0D0
         DO 1003 J=1,NCOMP
            C1=1D0-AK(I,J)
            C2=AM(I,J)*X(I)-AM(J,I)*X(J)
            C3=AM(I,J)*X(I)+AM(J,I)*X(J)
            IF (I.EQ.J) C3=1D0
            C4=X(I)+X(J)
            AIAJ=SQRT(A(I)*A(J))
            SUM1=SUM1+X(I)*X(J)*AIAJ*C1
            SUM2=SUM2+X(I)*X(J)*AIAJ*AL(I,J)*C2/C3*C4
            SUM3=SUM3+X(J)*AIAJ*(C1-AL(I,J)*C2/C3*C4)
            SUM4=SUM4+X(I)*X(J)*AIAJ*AL(I,J)*(C2/C3
     &         +C4/C3**2*2D0*AM(I,J)*AM(J,I)*X(J))
 1003    CONTINUE
         AI(I)=2D0*(SUM3-SUM4)
 1002 CONTINUE
      AMIX=SUM1-SUM2
C-----Complete calculation of AI's.
      DO 1004 I=1,NCOMP
         AI(I)=AI(I)-2D0*AMIX+SUM1
 1004 CONTINUE
      RETURN
      END

***********************************************************************
*                                MIXHV
*
* This calculates the mixture parameter A and its partial derivatives
* using the mixing rule of Huron and Vidal (1979).
*
* Input:
*   X(NCOMP): Pure component mole fractions.
*   AI(NCOMP),BI(NCOMP),CI(NCOMP),DI(NCOMP): Pure component parameters.
*   BMIX,CMIX,DMIX: The other mixture parameters.
*   DB(NCOMP),DC(NCOMP),DD(NCOMP): Derivatives of the other mixture
```

```
*      parameters.
*   CJI(NCOMP*(NCOMP-1)/2): Binary interaction parameters.
*     Parameter cji (j>i) is located at j(j-3)/2+i+1. For example, for
*     a 4-component mixture, the elements of CJI are (in order)
*     C21, C31, C32, C41, C42 and C43. NOTE: CIJ.NE.CJI in general.
*   CIJ(NCOMP*(NCOMP-1)/2): Counterparts of CIJ above.
*     See CIJ above for setup. NOTE: CIJ.NE.CIJ in general.
*   AIJ(NCOMP*(NCOMP-1)/2): Binary interaction parameters ALPHAij.
*     See CIJ above for setup. Aji=Aij.
*   NCOMP: Number of components.
* Output:
*   AMIX: Mixture parameter.
*   DA(NCOMP): The partial derivatives d(n*amix)/dni for each component.
*
* NOTES: The Cij here is dimensionless, equal to HV's Cij/RT.
*        The other mixture parameters and their derivatives must
*        be previously evaluated using the approriate mixing rule.
***********************************************************************
      SUBROUTINE MIXHV(X,AI,BI,CI,DI,AMIX,BMIX,CMIX,DMIX,DA,DB,DC,DD
     &   ,CIJ,CJI,AIJ,NCOMP)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=20,NMAX2=400)
      DIMENSION DA(NCOMP),DB(NCOMP),DC(NCOMP),DD(NCOMP),X(NCOMP)
     &   ,AI(NCOMP),BI(NCOMP),CI(NCOMP),DI(NCOMP)
     &   ,CIJ(NCOMP*(NCOMP-1)/2),CJI(NCOMP*(NCOMP-1)/2)
     &   ,AIJ(NCOMP*(NCOMP-1)/2)
     &   ,S1(NMAX),S2(NMAX),ALAM(NMAX),C(NMAX,NMAX),E(NMAX,NMAX)
      DATA C/NMAX2*0D0/,E/NMAX2*1D0/
C-----Transfer interaction parameters to matrices C,E.
      DO 1000 J=2,NCOMP
         DO 1001 I=1,J-1
            IPOS=J*(J-3)/2+I+1
            C(J,I)=CJI(IPOS)
            C(I,J)=CIJ(IPOS)
            E(I,J)=EXP(-AIJ(IPOS)*C(I,J))
            E(J,I)=EXP(-AIJ(IPOS)*C(J,I))
 1001    CONTINUE
 1000 CONTINUE
C-----Calculate A. Save S1, S2, ALAM and ALAMB for use below.
      AMIX=0D0
      DO 1003 I=1,NCOMP
         S1(I)=0D0
         S2(I)=0D0
         DO 1004 J=1,NCOMP
```

```
           S1(I)=S1(I)+X(J)*BI(J)*E(J,I)*C(J,I)
           S2(I)=S2(I)+X(J)*BI(J)*E(J,I)
 1004    CONTINUE
         ALAM(I)=LOG((BI(I)-DI(I))/(BI(I)-CI(I)))/(CI(I)-DI(I))
         AMIX=AMIX+X(I)*(AI(I)*ALAM(I)-S1(I)/S2(I))
 1003 CONTINUE
      ALAMB=LOG((BMIX-DMIX)/(BMIX-CMIX))/(CMIX-DMIX)
      AMIX=AMIX/ALAMB
C-----Calculate DA values.
      DO 1005 I=1,NCOMP
         SUM=0D0
         DO 1006 J=1,NCOMP
            SUM=SUM+X(J)*E(I,J)*(C(I,J)*S2(J)-S1(J))/S2(J)**2
 1006    CONTINUE
         DA(I)=AMIX*(-1D0+(DC(I)-DD(I)
     &      -(((DB(I)-DD(I))/(BMIX-DMIX)-(DB(I)-DC(I))/(BMIX-CMIX)))
     &      /ALAMB)/(CMIX-DMIX))
     &      +(AI(I)*ALAM(I)-S1(I)/S2(I)-BI(I)*SUM)/ALAMB
 1005 CONTINUE
      RETURN
      END
```

General Calculations

These are subroutines that implement some of the calculations and methods described in §3 and §6.

```
************************************************************************
*                        ZGEOS
*
* Calculates compressibility factors from the generic EOS.
* Accounts for vapor and liquid, and returns maxima and minima if any.
* Requires the subroutine RTCUB and SORT.
*
* Input:
*   A,B,C,D: dimensionless EOS parameters.
* Output:
*   Z(2): Compressibility factors.
*   ZLIMIT(2): Location of minimum (ZLIMIT(1)) and maximum (ZLIMIT(2)).
*              Set equal to Z if they don't exist (ie. supercritical).
*   ISTATE: If ISTATE=1, Z(1)=Z(2).
*           If ISTATE=2, Z(1) corresponds to liquid and Z(2) to vapor.
************************************************************************
      SUBROUTINE ZGEOS(A,B,C,D,Z,ZLIMIT,ISTATE)
```

```
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      EXTERNAL FCUB
      COMMON /FCUBBK/ BB,CC,DD
      DIMENSION ROOT(3),Z(2),ZLIMIT(2)
C-----Calculate roots.
      BB=-1D0-B-C-D
      CC=A+C+D+B*C+B*D+C*D
      DD=-A*B-C*D-B*C*D
      CALL RTCUB(BB,CC,DD,ROOT,NROOT,NNEG)
C-----Select appropriate roots. Watch out for negative roots!
      IF (NROOT.EQ.1) THEN
         ISTATE=1
         Z(1)=ROOT(1)
         Z(2)=ROOT(1)
      ELSE IF (NNEG.NE.0) THEN
         ISTATE=1
         Z(1)=ROOT(3)
         Z(2)=ROOT(3)
      ELSE
         ISTATE=2
         Z(1)=ROOT(1)
         Z(2)=ROOT(3)
      ENDIF
C-----Calculate minimum and maximum, if subcritical.
      SUBCRI=4D0*BB**2-12D0*CC
      IF (SUBCRI.GT.0D0) THEN
         ZLIMIT(1)=(-2D0*BB-SQRT(SUBCRI))/6D0
         ZLIMIT(2)=(-2D0*BB+SQRT(SUBCRI))/6D0
      ELSE
         ZLIMIT(1)=ROOT(1)
         ZLIMIT(2)=ROOT(1)
      ENDIF
      RETURN
      END

***********************************************************************
*                          FGCOEF
*
* Returns the fugacity coefficient FGCOEF of a component in a mixture,
* calculated from the general EOS.
* Accounts for special case when C=D to within less than 1D-10.
*
* Input:
*   A,B,C,D: dimensionless EOS parameters of the mixture.
*   AI,BI,CI,DI: the partial derivatives d(n*parameter)/dni evaluated
```

```
*                for the component of interest.
*   Z: Compressibility factor of the mixture.
* Output:
*   FGCOEF: the fugacity coefficient of the component.
************************************************************************
      FUNCTION FGCOEF(A,B,C,D,AI,BI,CI,DI,Z)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      FGCOEF=BI/(Z-B)-LOG(Z-B)
      IF (ABS(C-D).LT.1D-10) THEN
         FGCOEF=FGCOEF-(A+AI)/(Z-C)-A*CI/(Z-C)**2
      ELSE
         FGCOEF=FGCOEF+
     1   ((CI-DI)/(C-D)-1D0-AI/A)*A/(C-D)*LOG((Z-D)/(Z-C))-
     2   A/(C-D)*(CI/(Z-C)-DI/(Z-D))
      ENDIF
      FGCOEF=EXP(FGCOEF)
      RETURN
      END

************************************************************************
*                             ALPTR
*
* Function subroutine to calculate ALPHA/TR to within TOL for any
* cubic EOS given OMEGAC (A at the critical point) and the ratio
* PRTR (Pr/Tr on the saturation curve at the Tr of interest).
* Implements method of Sugie et al., but modified by providing
* for the case where C=D (i.e., OAC=0.421875).
* Also returns ZLB and ZVB (ZL-B and ZV-B) on the saturation curve.
* NOTE: Does not work for OMEGAC<.421875!
* Uses the subroutines RTCUB and SORT.
************************************************************************
      FUNCTION ALPTR(OMEGAC,PRTR,TOL,ZLB,ZVB)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (MAXIT=15)
      DIMENSION ROOT(3)
C-----Initialize quantities.
      DUMMY1=OMEGAC**(1D0/3D0)
      DUMMY2=SQRT(4D0*OMEGAC-3D0*OMEGAC**(2D0/3D0))
      F=1D0-DUMMY1
      G=(DUMMY1+DUMMY2)/2D0
      H=(DUMMY1-DUMMY2)/2D0
      ALPTR=(1D0-F/(1D0-F)*LOG(PRTR))
C-----Successive substitution to find alpha/Tr.
      DO 1020 IT=1,MAXIT
         ALPTRN=ALPTR
```

```
C--------Find ZV-B and ZL-B by solving a cubic.
         CALL RTCUB(PRTR*(1D0-3D0*F)-1D0,
     &      PRTR**2*F**3-PRTR*(1D0-3D0*F-OMEGAC*ALPTRN),
     &      -PRTR**2*F**3,ROOT,NROOT,NNEG)
         ZLB=ROOT(1)
         ZVB=ROOT(3)
         IF (OMEGAC.EQ.0.421875D0) THEN
C-----------Use this if OMEGAC=27/64 (ie. C=D, eg. VDW eos).
            ALPTR=(ZLB-ZVB+LOG(ZVB/ZLB))/OMEGAC/PRTR/(ZVB-ZLB)*
     &         (ZLB+PRTR*(G-F))*(ZVB+PRTR*(G-F))
         ELSE
C-----------Use this if OMEGAC<>27/64 (most equations of state).
            ALPTR=(H-G)*(ZLB-ZVB+LOG(ZVB/ZLB))/OMEGAC/
     &         LOG((ZVB+PRTR*(G-F))*(ZLB+PRTR*(H-F))/
     &         (ZVB+PRTR*(H-F))/(ZLB+PRTR*(G-F)))
         ENDIF
C--------Check if converged.
         IF (DABS(ALPTRN-ALPTR).LT.TOL) RETURN
 1020 CONTINUE
      WRITE (6,*) '*** MAXIT EXCEEDED IN ALPTR'
      RETURN
      END

*************************************************************************
*                        BUBP
*
* Calculates bubble-point pressure P and corresponding vapor
* compositions Y for NCOMP components, given temperature T, liquid
* compositions X for NCOMP components, and initial values of P and Y.
* The user must supply routine KCALC(X,Y,T,P,EQCON,NCOMP), where EQCON
* outputs the equilibrium constants for each component.
* Also requires RTSEC subroutine.
*************************************************************************
      SUBROUTINE BUBP(X,Y,T,P,NCOMP)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      EXTERNAL FBUBP
      LOGICAL SUCCES
      PARAMETER (NMAX=20,TOL=1D-6)
      DIMENSION X(NCOMP),Y(NCOMP)
      COMMON /FBPBLK/ XCOM(NMAX),YCOM(NMAX),TCOM,NCOM
C-----Set up common block to communicate with FBUBP.
      NCOM=NCOMP
      TCOM=T
      DO 1000 I=1,NCOMP
         XCOM(I)=X(I)
```

```
         YCOM(I)=Y(I)
 1000 CONTINUE
C-----Solve, using secant method. DO NOT use root bracketing,
C-----because it causes problems near the critical point.
      P1=P
      P2=P*.98D0
      P=RTSEC(FBUBP,P1,P2,TOL)
C-----Return values of Y.
      DO 1001 I=1,NCOMP
         Y(I)=YCOM(I)
 1001 CONTINUE
      RETURN
      END
C-----Function used by BUBP.
      FUNCTION FBUBP(P)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=20,ITMAX=10,TOL=1D-6)
      LOGICAL FLAG
      DIMENSION EQCON(NMAX),YTEMP(NMAX)
      COMMON /FBPBLK/ X(NMAX),Y(NMAX),T,NCOMP
C-----Successive substitution routine to find Y'S.
      ITER=0
 1001 CONTINUE
         CALL KCALC(X,Y,T,P,EQCON,NCOMP)
         YSUM=0D0
         DO 1000 I=1,NCOMP
            YTEMP(I)=X(I)*EQCON(I)
            YSUM=YSUM+YTEMP(I)
 1000    CONTINUE
         FLAG=.TRUE.
         DO 1004 I=1,NCOMP
            YTEMP(I)=YTEMP(I)/YSUM
            FLAG=FLAG.AND.ABS(YTEMP(I)-Y(I)).LT.TOL
            Y(I)=YTEMP(I)
 1004    CONTINUE
         ITER=ITER+1
         IF (ITER.GE.ITMAX) FLAG=.TRUE.
      IF (.NOT.FLAG) GO TO 1001
C-----Calculate objective function.
      FBUBP=1D0
      DO 1015 I=1,NCOMP
         FBUBP=FBUBP-X(I)*EQCON(I)
 1015 CONTINUE
      RETURN
```

```
      END
*********************************************************************
*                              KCALC
*
* Calculates K-values for VLE for use by BUBP.
* See BUBP for parameter list description.
* Common block KCBLK1 supplies the binary interaction coefficients,
* and returns the liquid and vapor mole fractions ZL and ZV.
* It also identifies the data point IDATA for which the K values are
* required. Common block KCBLK2 supplies the EOS parameters at
* unit pressure for the M data points, for each of the components.
*********************************************************************
      SUBROUTINE KCALC(X,Y,T,P,EQC,NCOMP)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=200,M=20)
      DIMENSION X(M),Y(M),EQC(M),Z(M),ZLIM(M),A(M),B(M),C(M),D(M),
     &   AIL(M),BIL(M),CIL(M),DIL(M),AIV(M),BIV(M),CIV(M),DIV(M)
      COMMON /KCBLK1/ AK(M*(M-1)/2),AL(M*(M-1)/2),AM(M*(M-1)/2)
     &   ,ZL,ZV,IDATA
      COMMON /KCBLK2/ AR(M,NMAX),BR(M,NMAX),CR(M,NMAX),DR(M,NMAX)
C-----Adjust pure component parameters to new pressure.
      DO 1001 I=1,NCOMP
         A(I)=AR(I,IDATA)*P
         B(I)=BR(I,IDATA)*P
         C(I)=CR(I,IDATA)*P
         D(I)=DR(I,IDATA)*P
 1001 CONTINUE
C-----Calculate mixture parameters. User must select appropriate mixing
C-----rule for A.
      CALL MIXAR(B,X,NCOMP,BML,BIL)
      CALL MIXAR(C,X,NCOMP,CML,CIL)
      CALL MIXAR(D,X,NCOMP,DML,DIL)
      CALL MIXRK(A,X,AK,AL,AM,NCOMP,AML,AIL)
C     CALL MIXHV(X,A,B,C,D,AML,BML,CML,DML,AIL,BIL,CIL,DIL
C    &   ,AK,AL,AM,NCOMP)
      CALL MIXAR(B,Y,NCOMP,BMV,BIV)
      CALL MIXAR(C,Y,NCOMP,CMV,CIV)
      CALL MIXAR(D,Y,NCOMP,DMV,DIV)
      CALL MIXRK(A,Y,AK,AL,AM,NCOMP,AMV,AIV)
C     CALL MIXHV(Y,A,B,C,D,AMV,BMV,CMV,DMV,AIV,BIV,CIV,DIV
C    &   ,AK,AL,AM,NCOMP)
C-----This selects appropriate Zs.
      CALL ZGEOS(AML,BML,CML,DML,Z,ZLIM,ISTATE)
      ZL=Z(1)
```

```
      CALL ZGEOS(AMV,BMV,CMV,DMV,Z,ZLIM,ISTATE)
      ZV=Z(2)
C-----Calculate the equilibrium constant.
      DO 1000 I=1,NCOMP
         EQC(I)=FGCOEF(AML,BML,CML,DML,AIL(I),BIL(I),CIL(I),DIL(I),ZL)/
     &         FGCOEF(AMV,BMV,CMV,DMV,AIV(I),BIV(I),CIV(I),DIV(I),ZV)
 1000 CONTINUE
      RETURN
      END

************************************************************************
*                         FSAT
*
* This function returns the difference between saturated liquid and
* vapor fugacities at a pressure P. Used as objective function for pure
* substance saturation calculations. Input is PP=LOG(1-P/PC),
* meant to prevent root-finding routine from searching PR>1.
* The common block FSBLK passes any required pure fluid properties
* through PROP, as well as the temperature T. It returns the
* compressibility factors ZL and ZV.
************************************************************************
      FUNCTION FSAT(PP)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION Z(2),ZLIM(2)
      COMMON /FSBLK/ PROP(9),T,ZL,ZV
C-----Calculate the Zs.
      P=PROP(3)*(1D0-EXP(PP))
C-----The user must put the proper call to an equation of state here.
      CALL ES...
      CALL ZGEOS(A,B,C,D,Z,ZLIM,ISTATE)
C-----This selects appropriate Zs, protecting against the case where
C-----a single root is found---this provision makes searches stable
C-----near the critical point.
      IF (Z(1).GT.ZLIM(1)) THEN
         ZL=ZLIM(1)
      ELSE
         ZL=Z(1)
      ENDIF
      IF (Z(2).LT.ZLIM(2)) THEN
         ZV=ZLIM(2)
      ELSE
         ZV=Z(2)
      ENDIF
C-----Calculate the difference.
      FSAT=FGCOEF(A,B,C,D,A,B,C,D,ZL)-FGCOEF(A,B,C,D,A,B,C,D,ZV)
```

```
      RETURN
      END

************************************************************************
*                               FBIN
*
* Calculates an objective function for binary VLE given interaction
* parameters PAR(NPAR).
* Communicates with main program and KCALC via common blocks.
* User must initialize PP and YP to an initial estimate.
* Data is passed through common block DATA, and results are returned
* through common block RESULT. Common block KCBLK1 communicates
* with KCALC. See KCALC for description of contents.
************************************************************************
      FUNCTION FBIN(PAR,NPAR)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      LOGICAL YFLAG
      PARAMETER (NMAX=200,M=20)
      DIMENSION PAR(NPAR),WORK(2),XI(2),YI(2)
      COMMON /DATA/ T(NMAX),P(NMAX),X(NMAX),Y(NMAX),NDATA,YFLAG
      COMMON /RESULT/ PP(NMAX),YP(NMAX),ZLP(NMAX),ZVP(NMAX)
      COMMON /KCBLK1/ AK(M*(M-1)/2),AL(M*(M-1)/2),AM(M*(M-1)/2)
     &    ,ZLPRED,ZVPRED,I
C-----Initialize.
      AK=PAR(1)
      IF (NPAR.EQ.1) THEN
         AL=0D0
      ELSE
         AL=-PAR(2)
      ENDIF
      IF (NPAR.EQ.2) THEN
         AM=0.5D0
      ELSE
         AM=1D0-PAR(3)
      ENDIF
C-----Remove comment statements on these if HV mixing rule is used.
C     AL=PAR(2)
C     AM=PAR(3)
      FBIN1=0D0
      FBIN2=0D0
      FBIN3=0D0
C-----Calculate bubble point pressure at each data point.
      DO 1001 I=1,NDATA
         XI(1)=X(I)
         XI(2)=1D0-X(I)
```

```
         YI(1)=Y(I)
         YI(2)=1D0-Y(I)
         PP(I)=P(I)
         CALL BUBP(XI,YI,T(I),PP(I),2)
         YP(I)=YI(1)
         ZLP(I)=ZLPRED
         ZVP(I)=ZVPRED
         FBIN1=FBIN1+((PP(I)-P(I)))**2
         FBIN2=FBIN2+((YP(I)-Y(I)))**2
         FBIN3=FBIN3+(PP(I)-P(I))*(YP(I)-Y(I))
 1001 CONTINUE
C-----Evaluate objective function based on Box-Draper method.
      IF (YFLAG) THEN
         FBIN=FBIN1*FBIN2-FBIN3**2
      ELSE
         FBIN=FBIN1
      ENDIF
      RETURN
      END

************************************************************************
*                             FUW
* Calculates an objective function from volumes given U and W values.
* Communicates with main program through common block FUWBLK.
************************************************************************
      FUNCTION FUW(PARAM)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NMAX=300,R=8.31439D1)
      COMMON /FUWBLK/ TR(NMAX),PR(NMAX),VL(NMAX),ZV(NMAX),VLP(NMAX),
     &   ZVP(NMAX),ALPHA(NMAX),TC,PC,OAC,OBC,ND
      DIMENSION ROOT(3),PARAM(2)
C-----Critical point parameters.
      U=PARAM(1)
      W=PARAM(2)
      X1=U**2-4D0*W
      X2=U**2+4D0*U+4D0
      CALL RTCUB(-3D0*(U**2+U-3D0*W+1D0)/X2,3D0*X1/X2,-X1/X2,
     &   ROOT,NROOT,NNEG)
      OAC=ROOT(NNEG+1)**3
      OBC=SQRT((4D0*OAC-3D0*OAC**(2D0/3D0))/X1)
C-----Calculate objective function, by calculating at each data point.
      FUW1=0D0
      FUW2=0D0
      FUW3=0D0
      DO 1000 I=1,ND
```

```
C--------Find exact alpha, and predicted VL and ZV.
         PRTR=PR(I)/TR(I)
         ALPHA(I)=ALPTR(OAC,PRTR,1D-10,ZLB,ZVB)*TR(I)
         VLP(I)=(ZLB/PRTR+OBC)*R*TC/PC
         ZVP(I)=ZVB+OBC*PRTR
C--------Update objective function.
         FUW1=FUW1+((VLP(I)-VL(I)))**2
         FUW2=FUW2+((ZVP(I)-ZV(I)))**2
         FUW3=FUW3+(ZVP(I)-ZV(I))*(VLP(I)-VL(I))
 1000 CONTINUE
C-----User must select appropriate objective function.
      FUW=FUW1*FUW2-FUW3**2
C     FUW=FUW1
C     FUW=FUW2
      WRITE (7,*) U,W,FUW
      RETURN
      END
```