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EQUATIONS OF STATE FOR NONELECTROLYTE AND ELECTROLYTE SOLUTIONS

by

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A

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Abstract

A modification of the Adachi-Sugie-Lu (ALS) (1983) equation of state for better simultaneous representation of vapor-liquid equilibria, saturated liquid and vapor volumes, and vaporization enthalpies was presented. The Wong-Sandler mixing rule (1992) was extended for a general cubic equation of state, and its application was further extended to electrolyte solutions.

A critical review of equations of state was made in order to identify important consideration in equation of state design. Mixing rules were briefly reviewed for the purpose of selecting a suitable mixing rule for the modified ALS equation. The models for electrolyte solutions were briefly reviewed for selecting a suitable model for calculating thermodynamic properties of electrolyte solutions by using the modified ALS equation. Monte Carlo computer simulation methods were reviewed as well since they were used in this work for the determination of equation parameters for ionic species.

The modification of the ALS equation was based on an analysis of the Clapeyron equation, which describes the relationship between the vaporization volume change ΔV_{vap} and enthalpy change ΔH_{vap}. A new characteristic parameter, $T_r(\Delta Z=0.5)$, was introduced for improving the performance of the equation on the simultaneous representation of volumetric and energy properties. Analysis of pure component data for 86 polar and non-polar fluids shows that a balanced and better representation of saturated vapor and liquid volumes is achieved.

A new exponential form for $\alpha(T)$ was proposed. The first derivative of this new $\alpha(T)$

function is zero at the critical point, making the extension of α to the super-critical region easier and in a smooth manner.

An extended Wong-Sandler mixing rule was proposed for its application to the modified ALS equation, which can represent most of cubic equations of state. The extended Wong-Sandler mixing rule with the modified ALS equation was evaluated using vapor-liquid equilibrium, volumetric and excess enthalpy data. Comparisons of several cubic equations of state with several mixing rules were made. This work gives better results for the simultaneous representation of vapor-liquid equilibrium and volumetric properties. For the simultaneous representation of VLE and excess enthalpy data, the results from this work are comparable with those obtained by using the PRSV equation (Stryjek and Vera, 1986) with the original Wang-Sandler mixing rule and better than those obtained by using other equations and mixing rules.

The application of the extended Wong-Sandler mixing rule was further extended to electrolyte solutions by combining an activity coefficient model proposed by Chen et al (1982, 1986). The results obtained from the new approach for the calculated osmotic coefficients of aqueous electrolyte solutions are comparable with the original Chen's model (1986) but better than those reported by Zuo and Guo (1991), who obtained the values by means of a different cubic equation of state. The new approach was also applied to represent VLE values of ethanol-water-salt systems. The results show that the extension work is successful.

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Nomenclature

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a	cohesion parameter in equations of state	$Pa \cdot m^6/mol^2$
A	dimensionless parameter in equations of state	
A^E	excess Helmholtz free energy	J/mol
A_ϕ	Debye-Hückel parameter	
b	covolume parameter in equations of state	m^3/mol
$\mathbf{b_1}$, $\mathbf{b_2}$, $\mathbf{b_3}$	parameters in the ALS equation	m^3/mol
B_1, B_2, B_3	dimensionless parameters in equations of state	
B	second virial coefficient	
C	parameter in the Wong-Sandler mixing rule	
D	dielectric constant	
e	charge of an electron	4.802×10^{-10} esu
E	configurational internal energy	J/mol
f, g, h	quantities defined by Eqn. (3.27)	
f_i	fugacity of component i	Pa
g_{ij}	binary interaction coefficients in the NRTL model	J/mol

G^E	excess Gibbs energy	J/mol
H^E	excess enthalpy	J/mol
I_x	ionic strength on a mole basis	
k	Boltzmann constant 1.3805×10^{-16} erg/K	
k_{ij}, l_{ij}, m_{ij}	binary interaction coefficients in mixing rules	
L_{max}	maximum extent of the particle movement in Monte Carlo simulation	
M_s	molar mass of solvent	g/mol
N	the number of particles	
N_a	Avogadro constant 6.023×10^{23} mol^{-1}	
$\mathcal{P}$	probability	
P	pressure	Pa, KPa, MPa, (mmHg)
q_1, q_2	binary interaction coefficients in the Van Laar model	
r	distance between two molecules	m
r_c	cut off distance	m
R	universal Gas constant	8.314 J/mol·K
T	temperature	K
u	parameter in the SW equation	
u(r)	potential function	J/mol
V	molar volume	m^3/mol

w	parameter in the SW equation
$w(r)$	intermolecular pair virial function
x_i	mole fraction of component i
X_i	effective local mole fraction
y	b/4V
y_i	mole fraction of component i in the vapor phase
z_i	valence of charged ion i
Z_i	absolute charge number of ion i
Z	compressibility factor
Z_c^*	calculated compressibility factor at the critical point

Greek Letters

α	parameter in equations of state
α^I	polarizability of ionic species ml
α_a, α_n, α_m	parameters in the new α function, Eqn. (4.24)
α_{ij}	nonrandomness factor in the NRTL model
β	1/kT
β_c, β_d, β_e	parameters in new equation. Eqn. (4.14)

γ_i	activity coefficient of component i	
ϵ	energy parameter in potential functions	J/mol
ϵ_{H2O}	permitivity of water	
ϕ	osmotic coefficient	
ϕ_i	fugacity coefficient of component i	
σ	diameter of molecule or ion	m
θ	closest approach parameter in the Pitzer-Debye-Hückel equation	
λ	quantity (=Z-B)	
ρ	number density	$1/m^3$
τ_{ij}	binary interaction coefficient in the NRTL model	
ω	acentric factor	
Ω	dimensionless parameter in equations of state	

Subscripts

∞	infinite pressure
att	attraction
c	critical properties
i, j	component i and j, respectively
ij	binary interaction term or coefficients of component i and j

L	liquid phase
LRC	long range correction
m	mixture
r	reduced properties
rep	repulsion
vap	vaporization
V	vapor phase

Superscripts

*	dimensionless properties
0	ideal gas properties
∞	infinite pressure
E	excess properties
ELE	electrolyte part
EOS	equation of state part
HS	hard sphere term
IG	ideal gas
INT	internal term
ION	ionic term

L	liquid phase
LC	local composition term
PDH	Pitzer-Debye-Hückel term
R	residual properties
s, sat	saturated properties
SR	short range term
V	vapor phase

Abbreviations

AAD	average absolute deviation
AAPD	average absolute percentage deviation
ALS	Adachi-Lu-Sugie equation
CCOR	cubic chain of rotator
DH	Debye-Hückel theory
EOS	equation of state
HCLJ	hard core Lennard-Jones fluid
HK	Harmens-Knapp equation
ICL	Ishikawa-Chung-Lu equation
LJ	Lennard-Jones fluid

LLE	liquid-liquid equilibrium
LLS	Lee-Lambardo-Sandler equation
MSA	mean spherical approximation
MSRK	modified Soave-Redilich-Kwong equation by Mathlas
MVDW	modified van der Waals equation by Adachi and Lu
NRTL	nonrandom-two-liquid model
NPT	constant number-pressure-temperature
NVT	constant number-volume-temperature
PDH	Pitzer-Debye-Hückel theory
PHCT	perturbed-hard-chain theory
PR	Peng-Robinson equation
PRSV	modified PR equation by Stryjek and Vera
PT	Patel-Teja equation
RDF	radial distribution function
SGR	Schwartzentruber, Galiver-Solastriouk and Renon mixing rule
SRK	Soave-Redlich-Kwong equation
SS	Sowers-Sandler equation
SW	Schmidt-Wenzel equation
SW	square well fluid

SWLE	square-well-linear-extension potential function
TPR	volume-translated PR equation
VDW	van der Waals equation
VLE	vapor-liquid equilibrium
YL	Yu-Lu equation
μVT	constant chemical potential-volume-temperature

Chapter 1

Introduction

The calculation and prediction of thermodynamic properties of pure substances and their mixtures are frequently required in the chemical process design and simulation. Equations of state (EOS) are effective tools for this purpose. The equations of state considered in this work are of the form

$$P = f(V, T, \text{composition}) \tag{1.1}$$

where P is pressure, V is molar volume, and T is temperature.

Since van der Waals (VDW) (1873) proposed his famous equation over a hundred years ago, numerous equations have been proposed. The most popular equations in use

today are the van der Waals type cubic equations, which have the form of

$$P=\frac{RT}{V-b}-\frac{a}{g(V)} \tag{1.2}$$

where R is the universal gas constant, **a** and **b** are the equation parameters, and g(V) is a quadratic function of volume.

All of this kind of cubic equations can be expressed by

$$V^3+\zeta V^2+\theta V+\xi=0 \tag{1.3}$$

where ζ, θ and ξ are functions of temperature, pressure and compositions. Engineers prefer to use this kind of equations because the roots Eqn. (1.3) for both liquid and vapor phases can be obtained analytically.

There are three kinds of properties that are often calculated by using equations of state:

(1). Vapor-liquid equilibrium (VLE) behavior, such as boiling point temperature, vapor pressure, and saturated liquid and vapor phase concentrations at equilibrium for mixtures.

(2). Volumetric properties, which include liquid and vapor volumes.

(3). Energy properties, such as enthalpy and entropies.

In spite of the fact that cubic equations have been widely used to calculate the above three kinds of properties in the design, simulation, analysis and optimization of chemical

processes, further development is still needed.

For the VLE calculation for pure components (vapor pressure calculation), the current popular equations, such as the Redlich-Kwong equation modified by Soave (SRK) (1972), the Peng-Robinson equation (PR) (Peng and Robinson, 1976), the PR equation modified by Stryjek and Vera (PRSV) (1986) and the Patel-Teja (PT) (Patel and Teja, 1982) equation, can be used with satisfactory accuracy. However, for the calculation of volumetric and energy properties, additional modification is still required.

For the calculation of thermodynamic properties of mixtures, mixing rules are essential. In general, the parameters in mixing rules (binary interaction coefficients) are obtained by fitting VLE data. These parameters are not necessarily suitable for the calculation of volumetric and energy properties of mixtures, and also different mixing rules may yield different results for simultaneous representations of all of these properties. The selection and development of suitable mixing rules are very important for mixture property calculations. The recently proposed mixing rules (e.g. Huron and Vidal, 1979; Heidemann and Kokal, 1990; Michelsen, 1990; Wong and Sandler, 1992), which coupled cubic equations and excess Gibbs energy (G^E) models, have stronger theoretical bases and have the capability to represent VLE data as accurately as G^E models. Among them, the Wong-Sandler mixing rule has been proved to be capable for simultaneously representing the VLE and excess enthalpy (H^E) data (Wang et al., 1993). However, the

original Wong-Sandler mixing rule is limited to two-parameter cubic equations and predicts unreliable excess volumes (Satyro and Sim, 1994). Since the two-parameter cubic equations are not good enough for the simultaneous representation of the three kinds of properties mentioned above, there is a need to have a mixing rule for the multi-parameter cubic equations of state that can be used to represent VLE and excess properties simultaneously.

Electrolyte solutions are important in chemical processes involving chemical absorption, azeotropic distillation and industrial waste treatment. The relative importance of the studies of electrolyte solutions is increasing because treatment of industrial waste is becoming more and more important for the purpose of saving the environment. The design and simulation of these processes require thermodynamic properties for electrolyte solutions. Although activity coefficient and solubility models are available for electrolyte solutions, they can be used only to calculate some specific properties. From the thermodynamic point of view, EOS is a more effective tool than other models for the representation and prediction of thermodynamic properties of solutions. Several equations have been proposed for electrolyte solutions in recent years, but generally are in complicated forms.

Objectives and Scope of the Research Work

The above analysis shows the need for further development of EOS from an engineering point of view. To meet these needs, the following objectives were made in this work

(1). To modify a suitably selected equation of state to improve its performance in the simultaneous representation of vapor-liquid equilibrium behavior, volumetric properties and energy properties for pure substances.

(2). To select or modify a mixing rule suitable for the modified equation.

(3). To apply this modified equation to electrolyte solutions.

In order to meet the first objective, a number of EOS have been considered. The Adachi-Lu-Sugie (ALS) (Adachi et al., 1983) equation was selected and modified to improve its performance in the representation of thermodynamic properties of pure substances. A comparison of the results obtained from this work with those from several other equations was made to evaluate the new approach.

To meet the second objective, the Wong-Sandler mixing rule was extended for application to the modified ALS equation, which is referred to as the extended Wong-Sandler mixing rule in this work. The extended Wong-Sandler mixing rule can be used

not only with the modified ALS equation but also with other van der Waals type cubic equations with two to four parameters. The generalized expressions for the calculation of fugacity coefficients and enthalpy departures were also derived, which would be beneficial for practical uses of this extended Wong-Sandler mixing rule with other equations.

To meet the third objective, namely, to apply the modified equation to electrolyte solutions, values of the co-volume parameter b_i in the modified ALS equation for ionic species were determined by using molecular simulation results. For this purpose, the hard core Lennard-Jones fluid was selected to be simulated in both single-phase and two-phase VLE regions by using Monte Carlo simulation methods. Subsequently, the application of the extended Wong-Sandler mixing rule was further extended to electrolyte solutions. Osmotic coefficients for a number of electrolytes in aqueous solutions were represented to evaluate the new approach.

The effect of salts on phase equilibrium has been utilized in many separation processes in chemical industry. Because of the existence of an azeotropic point in the phase equilibrium of the ethanol-water system, the salting-out effect has often been used for producing high purity ethanol. In this work, the modified equation was applied to represent the vapor liquid equilibria of such systems.

Chapter 2

Literature Review

In order to select a suitable equation to be modified for better representation of thermodynamic properties of pure substances, a brief review of equations of state for non-electrolyte solutions was carried out and is presented in this chapter.

Some available mixing rules were reviewed for the purpose of selecting a suitable mixing rule for the modified equation.

For the purpose of applying the modified equation to electrolyte solutions, a review of the theories and methodologies for estimating thermodynamic properties of electrolyte solutions is also included in this chapter.

To determine the equation parameters for ionic species, more simulation data for the

hard core Lennard-Jones fluid are needed. Therefore, Monte Carlo simulation methods and their previous applications were also briefly reviewed.

2.1 Equations of State for Non-electrolyte Solutions

Equations of state may be divided into two groups: empirical and semi-empirical, and theoretical. True theoretical equations are very rare. Usually, equations derived from molecular thermodynamics are considered theoretical but the parameters are frequently obtained by fitting with the experimental or simulation data.

2.1.1 Empirical and Semi-empirical Equations of State

The most popular empirical equations are of the cubic form in terms of volume. The oldest, simplest and best known cubic equation is the van der Waals equation (VDW) (van der Waals, 1873):

$$P=\frac{RT}{V-b}-\frac{a}{V^2} \qquad (2.1)$$

This equation contains only two parameters, the cohesion parameter **a** and the co-volume parameter **b**, which were treated originally as constants. Nearly all of the current popular cubic equations are extensions of the VDW equation. The SRK (Soave,

1972) and the PR (Peng and Robinson, 1976) equations also contain two parameters, but the parameter a was treated as temperature dependent. The parameters of both equations were generalized in terms of the critical temperature T_c, the critical pressure P_c, and the acentric factor ω of pure substances. The critical compressibility factor Z_c predicted by these equations is constant for all pure components. By means of these equations, vapor pressures and saturated vapor volumes of pure non-polar substances could be reasonably predicted, but the absolute average percentage deviation (AAPD) of the predicted saturated liquid volumes could be up to 20 - 30%, especially for polar fluids (Margerum, 1989).

Many efforts have been further made for improving the performance of cubic equations. For improving the representation of vapor pressures for polar substances, component dependent constants were introduced to the parameter a without changing equation forms, such as the PR equation modified by Stryjek and Vera (1982) and the SRK equation modified by Mathias (1983). By introducing these component dependent constants, the accuracy of calculated vapor pressures for polar substances are much improved. However, the improvement of the calculation of volumetric properties was not considered in their work. It has been demonstrated by Adachi and Lu (1984) that the complexity of EOS form contributes little towards the representation of VLE values. For example, the modified van der Waals (MVDW) (Adachi and Lu, 1984) equation, with

its parameter a considered temperature dependent and determined from vapour pressures, is capable of achieving practically the same satisfactory VLE results for pure substances as those obtained from the SRK equation, the PR equation and the four-parameter equation proposed by Adachi et al. (1983). Furthermore, the MVDW, the Clausius (1880) and the Martin (1979) equations can yield identical VLE values for mixtures at the same specified temperature and pressure.

However, for the volumetric property representations, improvements have been generally made by increasing the number of parameters in EOS.

A third parameter was introduced by several researchers. In order to introduce a substance dependent critical compressibility factor, Schmidt-Wenzel (1980) proposed a general van der Waals type equation (SW) in the following form

$$P=\frac{RT}{V-b}-\frac{a}{V^2+ubV+wb^2} \qquad (2.2)$$

Most van der Waals type cubic equations can be obtained by specifying u and w. For examples, for the SRK equation

$$u=1\ ,\quad \text{and}\quad w=0 \qquad (2.3)$$

and for the Peng-Robinson equation

$$u=2\ ,\quad \text{and}\quad w=-1 \tag{2.4}$$

All of the parameters of the SW equation are generalized and the representations of liquid volumes for pure non-polar substances are improved by the modification, but the deviations of the calculated liquid volumes for polar fluids are still high (Margerum, 1989). The Patel-Teja (PT) (1982) equation containing two substance-dependent constants was proposed especially for polar substances. The representation of saturated liquid volumes for polar fluids at reduced temperatures (T_r) lower than 0.8 has been improved. A volume-translation technique has been adopted to improve the volumetric calculation while leaving the predicted VLE conditions unchanged. Such a translation technique has been applied to the SRK equation by Peneloux (1982), and to the PR equation by Yu and Lu (TPR) (1986). Better agreement between the calculated saturated liquid volumes and experimental data has been obtained but with some loss of accuray in the calculated saturated vapor volumes.

Adachi et al. (1983) proposed another general van der Waals type cubic equation

$$P=\frac{RT}{V-b_1}-\frac{a}{(V-b_2)(V-b_3)} \tag{2.5}$$

where

$$a=\frac{\Omega_a R^2 T_C^2}{P_C}, \qquad \Omega_a=\Omega_{ac}\alpha \tag{2.6}$$

where α is a temperature function.

Different EOS may be obtained by specifying b_2 and b_3. A comparison of Eqns. (2.2) and (2.5) yields the following relationships between the parameters

$$\begin{aligned} b_2 &= b(-u-\sqrt{u^2-4w})/2 \\ b_3 &= b(-u+\sqrt{u^2-4w})/2 \\ u &= -(b_2+b_3)/b_1 \\ w &= b_2 b_3/b_1^2 \end{aligned} \tag{2.7}$$

All the parameters of the ALS equation are generalized. The overall deviations of the calculated values of P^{sat}, V_V^{sat} and V_L^{sat} for 19 normal fluids are smaller than those obtained from the SRK, the PR, the HK (Harmens and Knapp, 1980), and the ICL (Ishikawa et al., 1980) equations. However, the overall AAPD for the calculated V_L^{sat} is still large (4.26%). Sugie et al. (1989) adopted the form of the ALS equation and proposed an analytical method to calculate the parameter α from vapor pressures of pure fluids, and the other parameters were determined by fitting saturated liquid volumes at two temperatures. The results obtained for the representation of saturated liquid volumes are improved (AAPD=1.86%) for the 16 normal fluids tested, but the deviations for the

representation of saturated vapor volumes are equal to or higher than those obtained from the SRK and the PR equations (Sugie et al., 1989).

There are also five parameter cubic equations proposed in the literature for improving the accuracies of the calculated volumetric properties (Kumar and Starling, 1982; Adachi et al., 1986). The representations of volumetric properties are much improved; however, these equations have not been used for the VLE calculations for mixtures.

Much less information is available in the literature for the prediction of energy properties. The PT equation (Patel and Teja, 1982) yields an AAPD of about 2% in the predicted enthalpy departures of saturated liquids for eight non-polar substances. No results have been reported by these authors for polar fluids. Trebble and Bishnoi (1986) found that the enthalpy and heat capacity predictions produced by the PR equation were quite accurate and always physically meaningful and also found that for some equations, in which the parameter **b** was treated as temperature dependent, negative heat capacities were predicted. However, no comparison was made in their work.

In summary, the current popular cubic equations can be used to represent VLE behavior with satisfactory accuracies, but for the calculation of volumetric and energy properties, improvements are still needed.

2.1.2 Theoretical Equations of State

Theoretical equations can be developed based on molecular thermodynamics. The perturbation theory has been widely used for the development of theoretical equations. A good introduction to the theory has been given by Prausnitz et al. (1986). Generally, a theoretical equation based on the perturbation theory can be expressed by

$$P = \sum_i P_i \tag{2.8}$$

in which, each term P_i represents a contribution from a particular source. The basic or reference term usually represents the repulsive effects of the molecular core and other terms represent perturbations. The repulsion term introduced by van der Waals in 1873 is of the form

$$P_{rep} = \frac{RT}{V-b} \tag{2.9}$$

Although this term is considered inaccurate from a theoretical point of view (Kim et al, 1986), it has been widely used in the empirical cubic equations. The expression of Carnahan and Starling (1969), Eqn. (2.10), yields accurate representation of the pressure of a hard sphere fluid

$$P_{rep} = \frac{RT}{V}\left[\frac{1+y+y^2-y^3}{(1-y)^3}\right] \qquad (2.10)$$

where y=b/4V. This expression has been widely used in the development of theoretical equations.

To apply the perturbation theory to cubic equations, a simplified repulsion term was proposed by Lin et at. (1983)

$$P_{rep} = \frac{RT(1+0.77b/V)}{V-0.42b} \qquad (2.11)$$

This term is in good agreement with the Carnahan-Starling expression when $y<0.45$.

The perturbation terms in theoretical equations can be developed based on model fluids. A perturbation term to represent the square well fluid (SW) (Alder et al., 1972) was developed by Lee et al. (LLS) (1985) from the generalized van der Waals partition function with the coordination number model. Sowers and Sandler (SS) (1991a) extended the LLS square well term to the hard core Lennard-Jones fluid (HCLJ) (Stell and Weis, 1980) by adding two correction terms. In their work, another perturbation term for representing the square-well fluid was also proposed. The two equations proposed by Sowers and Sandler were further extended to the Lennard-Jones fluid (LJ) by treating the hard core diameter as temperature dependent (Sowers and Sandler, 1991b). A pseudo

potential function, the so-called square well linear extension potential function (SWLE), was proposed by Shen and Lu (1993a). Based on this pseudo potential function, an equation was proposed and applied to represent the SW fluid, the HCLJ fluid (Shen and Lu, 1993a) and several soft core fluids (Shen and Lu, 1993b).

Some equations derived from molecular theories can be used to represent thermodynamic properties of real fluids, such as the PHCT equation (Beret and Prausnitz, 1975), which was developed based on the perturbed hard-chain theory; and the CCOR equation (Lin et al., 1983) equation, which was developed based on a chain of rotators model and simplified to a cubic equation.

Most of the theoretical equations are more complex in their expressions than those of the empirical cubic equations, thus presenting a barrier to their acceptance in practical applications. However, research is ongoing and appears to bear some promise for the future.

2.2 Mixing Rules

Mixing rules are required for the calculation of thermodynamic properties of mixtures by using equations of state. Some of the frequently used mixing rules and the most recently proposed mixing rules, which coupled cubic equations and G^E models, were

briefly reviewed.

2.2.1 The Conventional Mixing Rules

The mixing rules of the van der Waals one-fluid model are referred to in this work as the conventional mixing rules

$$a=\sum_i \sum_j x_i x_j a_{ij} \tag{2.12}$$

$$b=\sum_i \sum_j x_i x_j b_{ij} \tag{2.13}$$

Generally, a geometric mean is used to calculate a_{ij}, and an arithmetic mean to calculate b_{ij}:

$$a_{ij}=(a_i a_j)^{1/2} \tag{2.14}$$

$$b_{ij}=(b_i+b_j)/2 \tag{2.15}$$

where a_i, b_i and a_j, b_j are the parameters for pure components, i and j, respectively.

The conventional mixing rules can be improved considerably by adding a binary

interaction coefficient to the mixing rule of parameter a

$$a_{ij}=(a_i a_j)^{1/2}(1-k_{ij}) \tag{2.16}$$

where k_{ij} ($=k_{ji}$) is the binary interaction coefficient between components i and j. k_{ij} is determined normally by fitting binary vapor liquid equilibrium data, and is usually found to be weakly dependent on temperature.

The conventional mixing rules work quite well for non-polar or slightly polar fluids. However, they often fail badly for highly asymmetric mixtures (i.e., mixtures of dissimilar molecules, such as polar + non-polar mixtures) (Adachi and Sugie, 1986). Therefore, many attempts have been made to improve them. Most of the modifications have been done on the mixing rule of parameter a.

2.2.2 The Adachi-Sugie Mixing Rule (Adachi and Sugie, 1985,1986)

Adachi and Sugie proposed their Redlich-Kister (1948) type mixing rule in 1985. The mixing rule was further simplified (Adachi and Sugie, 1986) to

$$a_{ij}=(a_i a_j)^{1/2}[1-k_{ij}-l_{ij}(x_i-x_j)] \tag{2.17}$$

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

This mixing rule was successfully used for some non-polar and polar systems (Adachi

and Sugie, 1985, 1986).

2.2.3 The S-G-R Mixing Rule (Schwartzentruber et al., 1987)

Schwartzentruber et al. proposed a mixing rule for a_{ij} to overcome the false liquid phase splitting problem which often happens in the VLE calculation of alcohol-hydrocarbon mixtures. This mixing rule has three binary interaction coefficients.

$$a_{ij}=(a_j a_j)^{1/2}\left[1-k_{ij}-l_{ij}\frac{m_{ij}x_i-m_{ji}x_j}{m_{ij}x_i+m_{ji}x_j}(x_i+x_j)\right] \qquad (2.18)$$

where $k_{ij} = k_{ji}$, $l_{ij} = -l_{ji}$, and $m_{ij} = 1-m_{ji}$.

This mixing rule for a_{ij} improves significantly the description of some highly asymmetric mixtures and also prevents false liquid-phase splitting for such systems (Schwartzentruber et al., 1987; Margerum and Lu, 1990).

2.2.4 The Mixing Rules Coupling Cubic EOS and Excess Gibbs Energy, G^E, Models

Huron and Vidal (1979) first coupled cubic EOS with a G^E model. They matched G^E values predicted by activity models with those predicted by a cubic equation. Although

the resulting mixing rule cannot take advantage of the correlated interaction parameters for activity coefficient models in the DECHEMA chemistry data series, their method provides a very flexible framework for the correlation of VLE and LLE data. By forcing a match of the predicted G^E values from the activity model with those predicted by a cubic equation at zero pressure, Heidemann and Kokal (1990) made the use of previously correlated parameters possible, but the resulting mixing rule is in an implicit form for the calculation of the parameter **a** for mixtures. Based on the Heidemann and Kokal mixing rule, Michelsen (1990) developed an explicit expression for the parameter **a** for mixtures by using a linear approximation. As indicated by Wong and Sandler (1992), the mixing rules based on Huron and Vidal's work do not satisfy the requirement that the second virial coefficient be a quadratic function of composition, and therefore are inconsistent with statistical mechanic theory.

Wong and Sandler proposed their mixing rule in 1992 and considered it as a theoretically correct mixing rule. This mixing rule is based on two conditions:

(1). The excess Helmholtz free energy, A^E, at infinite high pressure was assumed equal to the excess Gibbs free energy at low pressures.

$$G^E(T, x, P = \text{low}) = A^E(T, x, P = \text{low}) = A^E(T, x, P = \infty) \qquad \textbf{(2.19)}$$

This assumption makes the excess Gibbs free energy models or the activity coefficient

models applicable to equations of state. A^E is a weak function of pressure, so that the mixing rule can be used at high pressures.

(2). The composition dependence of the second virial coefficient is quadratic.

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \tag{2.20}$$

This condition satisfies the theoretical requirement.

To satisfy these two conditions, the following mixing rule was proposed by Wong and Sandler (1992)

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 + \frac{A_\infty^E(x)}{RT} - \sum_i x_i \left(\frac{a_i}{b_i RT}\right)} \tag{2.21}$$

and

$$a_m = b_m \left[\sum_i x_i \frac{a_i}{b_i} - \frac{A_\infty^E(x)}{C}\right] \tag{2.22}$$

where

$$\left(b-\frac{a}{RT}\right)_{ij}=\frac{\left(b_i-\frac{a_i}{RT}\right)+\left(b_j-\frac{a_j}{RT}\right)}{2}(1-k_{ij}) \tag{2.23}$$

The value of the quantity C depends on the equation of state used. For the Peng-Robinson equation (Wong and Sandler, 1992),

$$C=\ln(2^{1/2}-1)/2^{1/2} \tag{2.24}$$

This mixing rule can be used together with different activity coefficient models. In their paper (Wong et al., 1992), two activity coefficient models were considered

(1). NRTL model (Renon and Prausnitz, 1968):

$$\frac{A_\infty^E}{RT}=\sum_i x_i\left(\frac{\sum_j x_j\tau_{ji}g_{ji}}{\sum_k x_k g_{ki}}\right) \tag{2.25}$$

where

$$g_{ij}=\exp(-\alpha_{ij}\tau_{ij}) \ , \qquad (\alpha_{ij}=\alpha_{ji}) \tag{2.26}$$

(2). Van Laar model (1929). For binary systems:

$$\frac{G^E}{RT}=\frac{2\alpha_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2} \tag{2.27}$$

Five mixtures representing five general classes of mixtures were selected by Wong et al. (1992) for testing their mixing rule. They reported the following two observations:

(1). The results obtained directly from the activity coefficient model and those obtained from the EOS, which incorporates with the same activity coefficient model and its parameters, are comparable. In both cases, the deviations from the experimental data are quite small.

(2). The value of k_{ij}, the binary interaction coefficient of the second virial coefficient, is approximately a constant for each binary mixture, and is reasonably independent of both temperature and the activity coefficient model used.

The Wong-Sandler mixing rule has been tested by several authors. By comparing the results obtained from different mixing rules with different equations, Wang et al. (1993) obtained the following conclusions:

(1). Mixing rules have a stronger effect on simultaneous representation of VLE and H^E values than EOS themselves.

(2). A better representation of vapor pressure at a given temperature by means of EOS can not guarantee a better fitting of H^E, because the variation of the equation parameters with temperature contributes a more important factor in the calculation of H^E.

(3). The Wong-Sandler mixing rule could be used for simultaneous representation of VLE and H^E even for systems containing strong polar components.

Recently, Satyro and Sim (1994) studied 15 binary systems by using the Wong-Sandler mixing rule, and the results indicate that the Wong-Sandler mixing rule produces unreliable excess volumes.

2.3 Electrolyte Solutions

In addition to theoretical studies, numerous efforts have been made on the development of new approaches for representing and/or predicting properties of electrolyte solutions.

2.3.1 Theoretical Development

Aqueous solutions of electrolytes are of particular importance in chemical industries. Any discussion of physical property correlations for these solutions must begin with an examination of the pioneering work of Debye and Hückel (DH) (1923). Their work laid the foundation for all subsequent theoretical developments. The DH theory provides the limiting law at infinite dilution. In this theory, the ions are point charges and the solvent molecules are replaced by a dielectric continuum with the permittivity of water, ϵ_{H2O}. For charged hard spheres, the potential function between ion 1 and ion 2 is given by the Coulomb interaction subject to the hard core repulsion:

$$u(r)=\begin{cases}\infty & r\le\sigma \\ \dfrac{z_1 z_2 e^2}{\epsilon_{H_2O} r} & r>\sigma\end{cases} \qquad (2.28)$$

where σ is the diameter of ions, z_j (j=1,2) is the valence of the charged ion j, and e is the charge of an electron. In the DH theory, σ is taken to be zero.

Many Debye and Hückel type electrostatic excess Gibbs energy expressions have been proposed in the literature to represent the long-range contribution. The most widely applied model was that proposed by Pitzer (1973, 1977). Based on the DH theory, Pitzer recovered a similar result to that of Debye and Hückel with higher order terms and extended it to electrolyte solutions of higher concentrations. Pitzer's equation is a "virial" development of excess Gibbs free energy, G^E, in terms of molalities of ions. It has been applied successfully to represent activity coefficients and osmotic coefficients within experimental errors from dilute solutions to solutions with a molality up to 6M for both aqueous single strong electrolyte systems (Pitzer and Mayorga, 1973) and aqueous mixed strong electrolyte systems (Pitzer and Kim, 1974).

Chen and coworkers extended the Pitzer model to molecular solutes in water (Chen et al., 1979). To obtain an extended form of the Pitzer equation, which can be applied for electrolyte systems with molecular solutes, the coefficients in the basic Pitzer equation for molecule-ion and molecule-molecule interactions were considered in their

work. An electrolyte local composition model was developed (Chen et al., 1982) for the excess Gibbs free energy by combining with the nonrandom two-liquid (NRTL) model. In this excess Gibbs free energy model, two contributions were summed up: one resulting from the long range electrostatic forces between ions and the other from the short range forces between all the species. The Pitzer-Debye-Hückel formula was also normalized to mole fractions in their work (Chen et al., 1982). This electrolyte NRTL model was further extended to mixed electrolyte solutions (Chen et al., 1986).

Excellent correlations and predictions have been achieved by using the principle of the mean spherical approximation model (MSA) (Planche and Renon, 1981; Ball et al., 1985). Because of their complex forms and volume dependence, these approaches are not adopted in this work.

2.3.2 Equations of State

Historically, phase equilibrium behaviors of mixtures containing electrolytes have been described by activity coefficient models. However, recent investigations have shown that such mixtures can also be adequately described by equations of state, which can provide a unified description of thermodynamic properties (e.g. enthalpy, entropy and density) as well as phase equilibrium.

One of the first attempts to develop an equation of state for electrolyte solutions was

that of Planche and Renon (1981). The resulting Helmholtz free energy A contains four terms

$$A = A^{HS} + A^{SR} + A^{ION} + A^{INT} \tag{2.29}$$

Because the internal term A^{INT} is only temperature dependent, three terms are left out after partial differentiation at constant temperature:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = P^{HS} + P^{SR} + P^{ION} \tag{2.30}$$

The Percus-Yevick expression (1958) was used for the hard-sphere term A^{HS}. The short range term A^{SR} was used for the interactions between all types of compounds. The ionic term A^{ION} was derived from the mean spherical approximation (MSA) with a non-primitive model. Subsequently, the model was modified by Ball et al. (1985) and applied to a large number of strong electrolyte solutions. Recently, Fürst and Renon (1993) proposed a new equation containing a nonelectrolyte part and an ionic part. The nonelectrolyte part was taken from the equation of state of Schwartzentruber et al. (1989). The ionic part consisted of a MSA term to account for interactions between ions and a short-range term for interactions between molecules and ions.

The above equations are of more complicated forms than cubic equations, thus limited their practical applications. Two cubic equations were found in the literature for

electrolyte solutions. One was proposed by Zuo and Guo in 1991:

$$\ln\phi_i = \ln\phi_i^{EOS} + \ln\phi_i^{ELE} \tag{2.31}$$

The Patel and Teja (PT) (1982) equation was adopted for the EOS part, and the Li and Pitzer model (1986) was used for the electrolyte (ELE) part. Conventional mixing rules were used for the nonelectrolyte part. Hence, there is only one binary interaction coefficient for each electrolyte. The expression of the parameter **a** adopted in their work was proposed by Hu et al. (1984, 1985)

$$a = 2.57012\pi\epsilon N_a^2\sigma^3 f \tag{2.32}$$

where ϵ is the ionic energy parameter and f is an empirical constant. Value of f was empirically set to be 6 by Zuo and Guo. Another expression proposed by Hu et al. (1984) is given by

$$a = (\epsilon_{ij}/k)\sigma^3 N_a\{0.48(\alpha\epsilon_{ij}/kT)^{-1}[\exp(0.98\alpha\epsilon_{ij}/kT) - 1] + 0.18\} \quad \text{bar/mol K} \tag{2.33}$$

where δ is a density dependent parameter. For keeping the equation in a cubic form, Eqn. (2.33) is not considered in this work. Osmotic coefficients for 27 electrolytes were represented by Zuo and Guo (1991) with an average absolute percentage deviation (AAPD) of 3.53%. This deviation is higher than those obtained by the activity coefficient

model proposed by Chen et al. The root mean square deviation (RMSD) reported by Chen et al. (1986) is around 2% for these electrolyte solutions.

The other equation of state proposed by Aasberg-Petersen et al. (1991) is identical to Eqn. (2.31). The ALS (Adachi et al., 1983) equation was adopted for the EOS part and an expression based on the Debye-Hückel activity coefficient expression developed by Macedo et al. (1990) was used for the electrolyte part. Because a volume dependent mixing rule was used in their work, this equation became non-cubic for electrolyte solutions.

Both equations were proposed only for the representation of vapor-liquid equilibrium of electrolyte solutions and were aiming at expressing the influence of electrolytes on the fugacity of molecular compounds. Long range interactions were not considered in the volumetric property calculations.

2.4 Computer Simulation of Fluid Properties

Computer simulated properties of a model fluid are useful for the evaluation and development of theoretical models. Monte Carlo method is an effective computer simulation technique, which can be used to simulate the properties of model fluids at both single phase region (Metropolis et al, 1953) and two phase VLE region (Panagiotopoulos

et al., 1987, 1988).

The canonical (NVT) ensemble Monte Carlo technique was introduced by Metropolis et al. (1953). When a model of fluid is given in the form of particles obeying classical statistical mechanics and interacting with a pairwise-additive potential, the technique permits the calculation of pressures and energies over a wide range of densities and temperatures. This technique has been used in the computer simulations of thermodynamic properties for a number of model fluids, such as the square-well fluid (Alder et al., 1972), the hard-core Lennard-Jones fluid (Sowers et al., 1991a), and the Lennard-Jones fluid (Nicolas et al., 1979; Sowers and Sandler, 1991b). This technique has also been used to simulate the properties of real fluids, such as water (Jorgensen, 1981).

Extensions of Metropolis's technique to the constant pressure (NPT) ensemble (Wood, 1968; McDonald, 1972) and the grand canonical (μVT) ensemble (Adams, 1976, 1979) have significantly broadened the scope of the basic methodology. The μVT ensemble allows the specification of chemical potential and thus can be used to study the phase coexistence properties of fluids. Gibbs ensemble Monte Carlo simulation was introduced by Panagiotopoulos (1987). This technique was specifically developed to facilitate the calculation of coexistence phase properties of fluids. The simulation is performed in both the liquid and the vapor phases and is a combination of the NVT, NPT

and μVT techniques. Three types of perturbations (displacements of molecules within each region, volume changes and particle transfers between the regions) are performed in such a way which ensures that the criteria of phase coexistence are satisfied in a statistical sense. Recently, the Gibbs ensemble technique has been applied to the calculation of phase equilibria for a number of model fluids, such as the Lennard-Jones fluid (Panagiotopoulos et al., 1987, 1988) and the square-well fluid (Vega et al., 1992). A method for the prediction of the critical properties from saturation properties was proposed by Vega et al. (1992) and used for predicting the critical properties of the square-well fluids with different well width.

2.5 Concluding Remarks

Through the above literature review, the following concluding remarks are reached:

(1). Further development of cubic equations is needed for the simultaneous representation of VLE, volumetric and energy properties of pure substances.

(2). For the calculation of thermodynamic properties of mixtures, the Wong-Sandler mixing rule gives better results than other mixing rules. But it is limited to two parameter cubic equations, so that an extension of this mixing rule is needed for applying to more than two parameter cubic equations.

(3). Equations of state can be used to represent thermodynamic properties of electrolyte solutions. There is a need to develop a simple equation of state, (e.g. a cubic equation), which can represent the thermodynamic properties with relatively high precision.

Chapter 3

Theories and Methodologies

In this chapter, the theories and methodologies applied in this research work are presented.

The methods for the calculation of VLE behaviors and enthalpies and for the direct determination of the parameter α from vapor pressure data for the general van der Waals type cubic equation used in this work are given in Section 3.1. For the calculation of the thermodynamic properties of electrolyte solutions, the electrolyte nonrandom two liquid (NRTL) model proposed by Chen et al. (1982, 1986) was adopted in this work. The expressions for their model are briefly presented in Section 3.2. The theories and schemes of the Monte Carlo simulations in the canonical (NVT) and Gibbs ensembles

adopted in this work for the simulation of the hard core Lennard-Jones fluid are presented in Section 3.3.

3.1 Methods for Calculating Thermodynamic Properties by Using a General van der Waals Type Cubic Equation of State

The general form proposed by Adachi et al. (1983), Eqn. (2.5), can be rearranged to give

$$1=\frac{1}{Z-B_1}-\frac{A}{(Z-B_2)(Z-B_3)} \tag{3.1}$$

where Z is the compressibility factor

$$Z=\frac{PV}{RT} \tag{3.2}$$

and the parameters, A, B_1, B_2 and B_3, are given by

$$A=\frac{aP}{(RT)^2}=\frac{a_c\alpha P}{(RT)^2}=\frac{\Omega_{ac}\alpha P_r}{T_r^2} \tag{3.3}$$

and

$$B_k = \frac{b_k P}{RT} = \frac{\Omega_{bk} P_r}{T_r}, \qquad k=1,2,3 \tag{3.4}$$

Other general forms have been proposed. For example, Van Ness and Abbott (Van Ness and Abbott, 1982) proposed a five-parameter general cubic equation. However, most of the van der Waals type cubic equations of state can be represented by Eqn. (3.1). All the derivations of expressions presented in this section are based on Eqn. (3.1).

3.1.1 Direct Solution of Cubic Equations

The advantage of the cubic equations of state is that an analytical method can be used to solve the cubic equations to obtained the roots of the volumes (Margerum, 1989; Press et al., 1986).

Eqn. (3.1) can be rearranged to give

$$Z^3 + pZ^2 + qZ + r = 0 \tag{3.5}$$

where

$$
\begin{aligned}
p &= -1 - B_1 - B_2 - B_3 \\
q &= A + B_2 + B_3 + B_1B_2 + B_1B_3 + B_2B_3 \\
r &= -AB_1 - B_2B_3 - B_1B_2B_3
\end{aligned}
\tag{3.6}
$$

Let

$$
\begin{aligned}
Q &= (p^2 - 3q)/9 \\
R &= (2p^3 - 9pq + 27r)/54 \\
S &= (\sqrt{R^2 - Q^3} + |R|)^{1/3}
\end{aligned}
\tag{3.7}
$$

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

$$
Z_i = -2\sqrt{Q}\cos\left[\frac{\theta + 2\pi(i-1)}{3}\right] - \frac{p}{3} \tag{3.8}
$$

where $\theta = \arccos(R/Q^{3/2})$. The largest root is for the vapor phase, and the smallest root is for the liquid phase.

Otherwise, there is only one real root

$$
Z = -\mathrm{sgn}(R)(S + Q/S) - p/3 \tag{3.9}
$$

where

$$
\mathrm{sgn}(R) = \begin{cases} -1 & R < 0 \\ 0 & R = 0 \\ 1 & R > 0 \end{cases}
$$

3.1.2 Vapor-liquid Equilibrium (VLE) Calculation

VLE calculations are very important in the design and simulation of chemical processes. The criterion of the phase equilibrium can be expressed by using fugacities

$$f_i^{\alpha} = f_i^{\beta} \tag{3.10}$$

where f_i^{α} and f_i^{β} are the fugacities for the component i in the α and β phases, respectively.

The fugacity of component i in a mixture can be expressed by

$$f_i = x_i \phi_i P \tag{3.11}$$

where ϕ_i is the fugacity coefficient of component i.

For VLE calculations, the following criterion must be satisfied

$$x_i \phi_i^L = y_i \phi_i^V \tag{3.12}$$

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively.

For a pure component, $x_i = y_i = 1$, so that

$$\phi^L = \phi^V \tag{3.13}$$

From Eqn. (3.12), the calculation of the fugacity coefficient ϕ_i for both the liquid and the vapor phases is the main point in VLE calculations by means of equations of state.

The expression of ϕ_i obtained from Eqn. (3.1) is given by (Margerum, 1989)

$$\ln\phi_i = \frac{\hat{B}_{1i}}{Z-B_1} - \ln(Z-B_1) + \left(\frac{\hat{B}_{2i}-\hat{B}_{3i}}{B_2-B_3} - 1 - \frac{\hat{A}_i}{A}\right)\frac{A}{B_2-B_3}\ln\frac{Z-B_3}{Z-B_2} - \frac{A}{B_2-B_3}\left(\frac{\hat{B}_{2i}}{Z-B_2} - \frac{\hat{B}_{3i}}{Z-B_3}\right) \tag{3.14}$$

where

$$\hat{A}_i = \left[\frac{\partial(nA)}{\partial n_i}\right]_{T,V,n_j(j\neq i)} \tag{3.15}$$

and

$$\hat{B}_{ki} = \left[\frac{\partial(nB_k)}{\partial n_i}\right]_{T,V,n_j(j\neq i)}, \qquad k=1,2,3 \tag{3.16}$$

The expressions for the derivatives of the parameters vary with the mixing rule used.

For pure fluids, Eqn. (3.14) can be used directly with the derivatives of mixture parameters set equal to the pure component parameters (e.g. $\hat{A}_i = A_i$). After some simplifications, the resulting expression is obtained as

$$\ln\phi = Z-1-\ln(Z-B_1)+\frac{A}{B_2-B_3}\ln\frac{Z-B_2}{Z-B_3} \tag{3.17}$$

There are several kinds of VLE calculations, such as bubble-point, dew-point and flash calculations. In this research work, the bubble-point pressure calculation was used. In this calculation, vapor pressure and vapor phase compositions are obtained from known temperature and liquid phase compositions. The FORTRAN programs used in the calculation are given in Appendix D.

3.1.3 Enthalpy Calculation

In the simulation and analysis of chemical processes, an enthalpy calculation is needed. For using equations of state to calculate enthalpies of fluids, ideal gas is usually selected as the reference state. So the enthalpy can be calculated by

$$H = H^0 + H^R \tag{3.18}$$

where H^0 is the ideal gas enthalpy and H^R is the residual enthalpy.

The ideal gas enthalpy can be calculated by

$$H^0 = \sum_i x_i C^0_{Pa,i} + \sum_i x_i C^0_{Pb,i} T + \sum_i x_i C^0_{Pc,i} T^2 + \sum_i x_i C^0_{Pd,i} T^3 \tag{3.19}$$

where $C^0_{Pa,i}$, $C^0_{Pb,i}$, $C^0_{Pc,i}$, and $C^0_{Pc,i}$ are constants for a given component i.

The relationship between the residual enthalpy and PVT properties is expressed as

$$H^R = H - H^0 = \int_{V_0}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV + PV - RT \tag{3.20}$$

where V_0 is the molar volume of ideal gas.

From Eqn. (3.20), the following expression was obtained in this work

$$\frac{H - H^0}{RT} = -\frac{B_1'}{Z - B_1} + \frac{A}{B_2 - B_3}\left(\frac{B_2'}{Z - B_2} - \frac{B_3'}{Z - B_3}\right) + \frac{\ln\dfrac{Z - B_2}{Z - B_3}}{B_2 - B_3} \times \left[(A - A') + \frac{A(B_2' - B_3')}{B_2 - B_3} \right] + (Z - 1) \tag{3.21}$$

where

$$A' = \left(\frac{\partial A}{\partial T}\right)_{V,n} \tag{3.22}$$

and

$$B_k' = \left(\frac{\partial B_k}{\partial T} \right)_{V,n} \qquad k=1,2,3 \tag{3.23}$$

Again, the derivatives of the parameters are different for different equations of state and mixing rules.

3.1.4 Analytical Determination of α from Vapor Pressures

The temperature dependency of the parameter α is usually determined from vapor pressures of pure components. The method given by Sugie et al. (1989) for direct calculation of α from vapor pressure data is presented as follows.

The quantity λ is defined as

$$\lambda = Z - B_1 \tag{3.24}$$

then

$$(Z - B_2) = \lambda + (B_1 - B_2) \tag{3.25}$$

and

$$(Z - B_3) = \lambda + (B_1 - B_3) \tag{3.26}$$

The quantities f, g and h, are defined as

$$\begin{aligned} f &= Z_c^* - \Omega_{b1} \\ g &= Z_c^* - \Omega_{b2} \\ h &= Z_c^* - \Omega_{b3} \end{aligned} \tag{3.27}$$

where Z_C^* is the calculated compressibility factor from EOS at the critical point. Furthermore, from Eqns. (3.4) and (3.27)

$$\begin{aligned} (B_1 - B_2) &= \frac{P_r}{T_r}(\Omega_{b1} - \Omega_{b2}) = \frac{P_r}{T_r}(g - f) \\ (B_1 - B_3) &= \frac{P_r}{T_r}(\Omega_{b2} - \Omega_{b3}) = \frac{P_r}{T_r}(h - f) \end{aligned} \tag{3.28}$$

Substituting Eqns. (3.25), (3.26), (3.27), and (3.28) into Eqn. (3.1) yields

$$\lambda^3 + S_2\lambda^2 + S_1\lambda - S_0 = 0 \tag{3.29}$$

where

$$\begin{aligned} S_2 &= \frac{P_r}{T_r}(1 - 3f) - 1 \\ S_1 &= \left(\frac{P_r}{T_r}\right)^2 f^3 - \frac{P_r}{T_r}\left(1 - 3f - \Omega_{ac}\frac{\alpha}{T_r}\right) \\ S_0 &= \left(\frac{P_r}{T_r}\right)^2 f^3 \end{aligned} \tag{3.30}$$

The largest and the smallest roots of Eqn. (3.29) are the vapor phase λ_V (= Z_V - B_l) and the liquid phase λ_L (=Z_L - B_l), respectively. Their values can be easily obtained by solving Eqn. (3.29) analytically.

At the condition of VLE, the fugacities of the liquid and vapor phases are equal. Applying the fugacity coefficient expression for pure fluids, Eqn. (3.17), and introducing λ through Eqns. (3.24) to (3.26) yield the following expression for the determination of parameter α

$$\frac{\alpha}{T_r} = \frac{(h-g)[(\lambda_L-\lambda_V)+\ln(\lambda_V/\lambda_L)]}{\Omega_{ac}\ln\dfrac{[\lambda_V+(P_r/T_r)(g-h)][\lambda_L+(P_r/T_r)(h-f)]}{[\lambda_V+(P_r/T_r)(h-f)][\lambda_L+(P_r/T_r)(g-f)]}} \qquad (3.31)$$

From Eqn. (3.31), the parameter α can be obtained for each temperature from known vapor pressure values.

3.2 Local Composition Model for Aqueous Electrolyte Solutions (Chen et al., 1982, 1986)

Chen et al. (1982, 1986) extended the NRTL activity coefficient model for the calculation of VLE properties of electrolyte solutions. The expression for the excess Gibbs energy obtained is given by

$$\frac{G^{ex}}{RT}=\frac{G^{ex,PDH}}{RT}+\frac{G^{ex,lc}}{RT} \tag{3.32}$$

where the Pitzer-Debye-Hückel (PDH) term is used to describe the long range interactions between ions and the local composition (lc) term is used to account for the short range interactions between all species.

(1). The Pitzer-Debye-Hückel term is represented by

$$\frac{G^{ex,PDH}}{RT}=-\left(\sum_k x_k\right)\left(\frac{1,000}{M_s}\right)^{1/2}(4A_\phi I_x/\theta)\ln(1+\theta I_x^{1/2}) \tag{3.33}$$

where k is for all species, M_s is the molar mass of the solvent and θ which was set to be 14.9 is the closest approach parameter of the Pitzer-Debye-Hückel equation.

The usual Debye-Hückel parameter, A_ϕ, is given by

$$A_\phi=(1/3)(2\pi N_a\sigma/1,1000)^{1/2}(e^2/DkT)^{3/2} \tag{3.34}$$

and the ionic strength on a mole fraction basis, I_x, is

$$I_x=(1/2)\sum_i Z_i^2 x_i \tag{3.35}$$

where Z_i is the charge number of ion i. Chen et al. (1982) proposed a temperature function of A_ϕ for aqueous solutions

$$
\begin{aligned}
A_\phi = & -61.44534\exp[(T-273.15)/273.15] \\
& +2.864468\{\exp[(T-273.15)/273.15]\}^2 \\
& +183.5379\ln(T/273.15)-0.6820223(T-273.15) \\
& +0.0007875695(T^2-273.15^2)+58.95788(273.15/T)
\end{aligned}
\tag{3.36}
$$

Eqn. (3.36) was adopted in this work for the calculation of aqueous solutions.

(2). The local composition term (Chen et al., 1982,1986)

Using the local composition model, Chen and coworkers derived an electrolyte NRTL model for electrolyte solutions. The derivation is based on two assumptions. The first is the like-ion repulsion assumption, suggesting that the local composition of cations (anions) around cations (anions) is zero, which is equivalent to assuming that the repulsive forces between like charged ions are extremely large. The second is the assumption of local electroneutrality, suggesting that the distribution of cations and anions around a central solvent molecule results in that the net local ionic charge is zero. The resulting excess Gibbs free energy for multi-component electrolyte systems is given by Chen et al. (1986) as follows:

$$
\begin{aligned}
G^{E,lc} = & \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'} \sum_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_{a''} X_{a''} \sum_k X_k G_{kc,a'c}} \\
& + \sum_a X_a \sum_{c'} \frac{X_{c'} \sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_{c''} \sum_k X_k G_{ka,c'a}}
\end{aligned}
\tag{3.37}
$$

where X is the effective local mole fraction, and m, c, and a denote molecule, cation and anion, respectively. Furthermore,

$$X_i = x_i K_i \tag{3.38}$$

For ions, $K_i = Z_i$ and for molecules, $K_i = 1$.

In Eqn. (3.37) G and τ are the parameters in the NRTL model

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \tau_{ij} = (g_{ij} - g_{jj})/RT \tag{3.39}$$

where α_{ij} is the nonrandomness factor, and g_{ij} and g_{jj} are energies of interactions between i - j and j - j species, respectively. The quantities $G_{ji,ki}$ and $\tau_{ji,ki}$ are defined as

$$G_{ji,ki} = \exp(-\alpha_{ji,ki}\tau_{ji,ki}) \qquad \tau_{ji,ki} = (g_{ji} - g_{ki})/RT \tag{3.40}$$

The value of α was set to be 0.2 for all cases in Chen's work (Chen et al., 1982).

This model was successfully applied to the calculation of osmotic coefficients and activity coefficients for aqueous solutions with single electrolyte (Chen et al., 1982) and multi-electrolytes (Chen et al., 1986).

3.3 Theories and Methods of the Monte Carlo Simulations

The Monte Carlo simulation method was adopted in this work to simulate the properties of the hard core Lennard-Jones fluid in order to determine the parameters for ionic species.

3.3.1 Monte Carlo Simulation in the Canonical (NVT) Ensembles

The Monte Carlo simulation method in canonical ensembles was introduced by Metropolis et al. (1953). Because in a canonical ensemble, the number of particles, N, the volume, V, and the temperature, T, are kept constant, this ensemble is also called the NVT ensemble. In general, when a model of a fluid is given in the form of particles obeying classical statistical mechanics and interacting with a pairwise-additive potential, the technique permits the calculation of pressures and energies over a wide range of densities and temperatures. The method used in this work is briefly described here. More details can be found in the book written by Allen and Tildesly (1987).

A cubic box with unit volume is set up for the simulation purpose, in which $-0.5 < x < 0.5$, $-0.5 < y < 0.5$ and $-0.5 < z < 0.5$, where x, y, and z are the three dimention of the box. N particles can be initially put into the cubic box randomly or as

a close-packed lattice.

For a model fluid with a potential function u(r), the configurational internal energy, E, is calculated by

$$E=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u(r_{ij})+E_{LRC} \tag{3.41}$$

where r_{ij} is the distance between the particles i and j, and E_{LRC} is the long range correction term for the configurational internal energy, which is calculated by

$$E_{LRC}=2\pi N\rho\int_{r_c}^{\infty} r^2 u(r)dr \tag{3.42}$$

where ρ is the number density and r_c is the cut-off distance, which is usually set to be one half of the box length.

The calculation of $u(r_{ij})$ is in the range of zero to the cut-off distance, r_c, and the centre image is used in the calculation, which means that the cubic box as a centre box is surrounded by cubic boxes with the same configurations as the centre box.

A new configuration is created by moving a particle, selected randomly or in turn, randomly within the range of $|\Delta x| \leq L_{max}$, $|\Delta y| \leq L_{max}$, and $|\Delta z| \leq L_{max}$, where L_{max} is the maximum extent of the particle movement.

The probability $\wp$ of the acceptance of new configurations is

$$\rho=\exp(-\beta\Delta E) \tag{3.43}$$

where β is equal to $(kT)^{-1}$, and ΔE is the change of the configurational internal energy caused by the movement. The acceptance ratio is usually adjusted to about 50% by varying the maximum extent of the particle movement, L_{max}.

By creating a large number of configurations, the configurational energy E at equilibrium is calculated by

$$E=\left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) \right\rangle + E_{LRC} \tag{3.44}$$

where $< >$ denotes an ensemble average.

The calculation of the compressibility factor, Z, varies with the potential function. For a model fluid with a continuous potential function, such as the Lennard-Jones fluid, Z is calculated by

$$Z=1-\left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r_{ij}\frac{du(r_{ij})}{dr_{ij}} \right\rangle / 3NkT + Z_{LRC} \tag{3.45}$$

where Z_{LRC} is the long range correction of the compressibility factor, which is calculated by

$$Z_{LRC}=-\frac{2}{3}\pi N\rho kT\int_{r_c}^{\infty} r^2 w(r)dr \tag{3.46}$$

where w(r) is the intermolecular pair virial function

$$w(r) = r\frac{du(r)}{dr} \tag{3.47}$$

3.3.2 Monte Carlo Simulation in the Gibbs Ensembles

The Gibbs ensemble technique was proposed by Panagiotopoulos(1987, 1988). In the simulation, two separated boxes were set up denoting the coexisting vapor and liquid phases without the presence of an interface. The simulation is simultaneously processed in both the vapor and liquid phases as separated subsystems.

The simulation begins with the particles placed in both boxes randomly or as closed-packing lattices. As mentioned above, three perturbations are performed in the simulation.

(1) Particle displacement in each phase

This perturbation is to ensure that an equilibrium is reached in each phase, and is the same as in the NVT ensembles. The probability of the acceptance is the same as given by Eqn. (3.43).

(2) Volume rearrangement between the two phases

This perturbation is to ensure that the same pressure is reached in both phases. The

volume changes of the two phases were coupled, with the overall volume V remaining constant. The acceptance probability for the volume change is given by

$$\wp=\exp[-\beta(\Delta E^{I}+\Delta E^{II}-N^{I}kT\ln\frac{V^{I}+\Delta V}{V^{I}}-N^{II}kT\ln\frac{V^{II}-\Delta V}{V^{II}})] \qquad (3.48)$$

The maximum allowable volume displacement is usually adjusted to yield an approximately 50% acceptance ratio for the volume change.

(3) Particles interchange between the two phases

This perturbation is to ensure that there exists a phase equilibrium. This is achieved by creating a particle at a random position in one subsystem and taking out a randomly chosen particle in the other subsystem. This move is corresponding to the grand canonical (μVT) ensemble and the probability is given by

$$\wp=\exp\left(-\beta\left[\Delta E^{I}+\Delta E^{II}+kT\ln\frac{V^{II}(N^{I}+1)}{V^{I}N^{II}}\right]\right) \qquad (3.49)$$

The number of interchange movements attempted is adjusted so that about 1% to 5% of the total number of particles are interchanged in each cycle.

The calculations of the configurational internal energy and compressibility factor are the same as those in the NVT ensembles.

Chapter 4

Better Representation of Pure Component Properties

The ALS (Adachi et al., 1983) equation of state

$$P=\frac{RT}{V-b_1}-\frac{a}{(V-b_2)(V-b_3)} \qquad (2.5)$$

has the following advantages

(1). This equation is a general van der Waals type cubic equation of state. It can be easily reduced to a two-parameter equation and all the expressions for the general equation, presented in Chapter 3, can be used directly for this equation.

(2). The modified version of this equation (Sugie et al., 1989) has the capability of representing the liquid densities with satisfactory accuracies.

(3). It is simpler than the five parameter cubic equations for practical applications.

In order to improve the calculated densities for pure liquids at saturated conditions, Sugie et al. (1989) determined two of the equation parameters by exactly fitting two saturated liquid densities at reduced temperatures T_r=0.7 and T_r=0.9. As mentioned in Chapter 2, the calculation of the saturated liquid volumes was improved, but the calculated deviations for the saturated vapor volumes of normal fluids were generally between or higher than those obtained from the SRK and PR equations of state (Sugie et al., 1989).

In this work, a further modification of the ALS equation was made for the purpose of improving the simultaneous representation of VLE behavior, volumetric properties, and energy properties for pure substances.

4.1 Development of a Characteristic Parameter

In order to maintain the dome-shaped saturation curve on a T_r-Z diagram of pure components so that proper V_L^{sat} and V_V^{sat} values could be well represented simultaneously by means of a cubic equation of state, it is necessary to have the saturation curve fixed

at certain location(s). To improve the calculation of energy properties at the same time, the accuracy of the calculated vaporization enthalpies must be considered.

The Clapeyron equation describes the relationship between the volume change of vaporization ΔV_{vap} and latent heat of vaporization ΔH_{vap}

$$\frac{dP^{sat}}{dT} = \frac{\Delta H_{vap}}{T\Delta V_{vap}} \tag{4.1}$$

where

$$\Delta V_{vap} = V_V^{sat} - V_L^{sat} \tag{4.2}$$

$$\Delta H_{vap} = H_V^{sat} - H_L^{sat} \tag{4.3}$$

From Eqn. (4.1), two calculated properties, dP^{sat}/dT and ΔV_{vap}, will affect the accuracy of the predicted ΔH_{vap} values. The accuracy of the calculated dP^{sat}/dT can be easily improved by selecting a desirable α function as mentioned in Chapter 2, so the accuracy of the predicted ΔH_{vap} values is mainly dependent on the accuracy of the calculated ΔV_{vap} values. For the purpose of improving the calculation of the latent heat of vaporization, instead of improving the calculated saturated liquid and vapor volumes

separately, an improvement of the calculation of ΔV_{vap} was considered in this work.

The change of the compressibility factor of the vaporization is

$$\Delta Z = Z_V^{sat} - Z_L^{sat} \tag{4.4}$$

For pure substances

$$\Delta Z = \frac{P^{sat}}{RT} \Delta V_{vap} \tag{4.5}$$

It is impossible to fix all the calculated ΔZ values to experimental data with limited parameters. It was observed that if ΔZ was fixed too close to the critical point, such as $T_r > 0.95$, the results of the calculated volumes at low temperatures would be very poor and if ΔZ was fixed far from the critical point, the results of the calculated volumes near the critical point would be much off. Therefore, it is desirable to fix a ΔZ value in the vicinity of $T_r = 0.95$.

For the determination of a suitable ΔZ value, the T_r vs. ΔZ curves for nitrogen and water were calculated and shown in Figure 4.1 and 4.2, respectively.

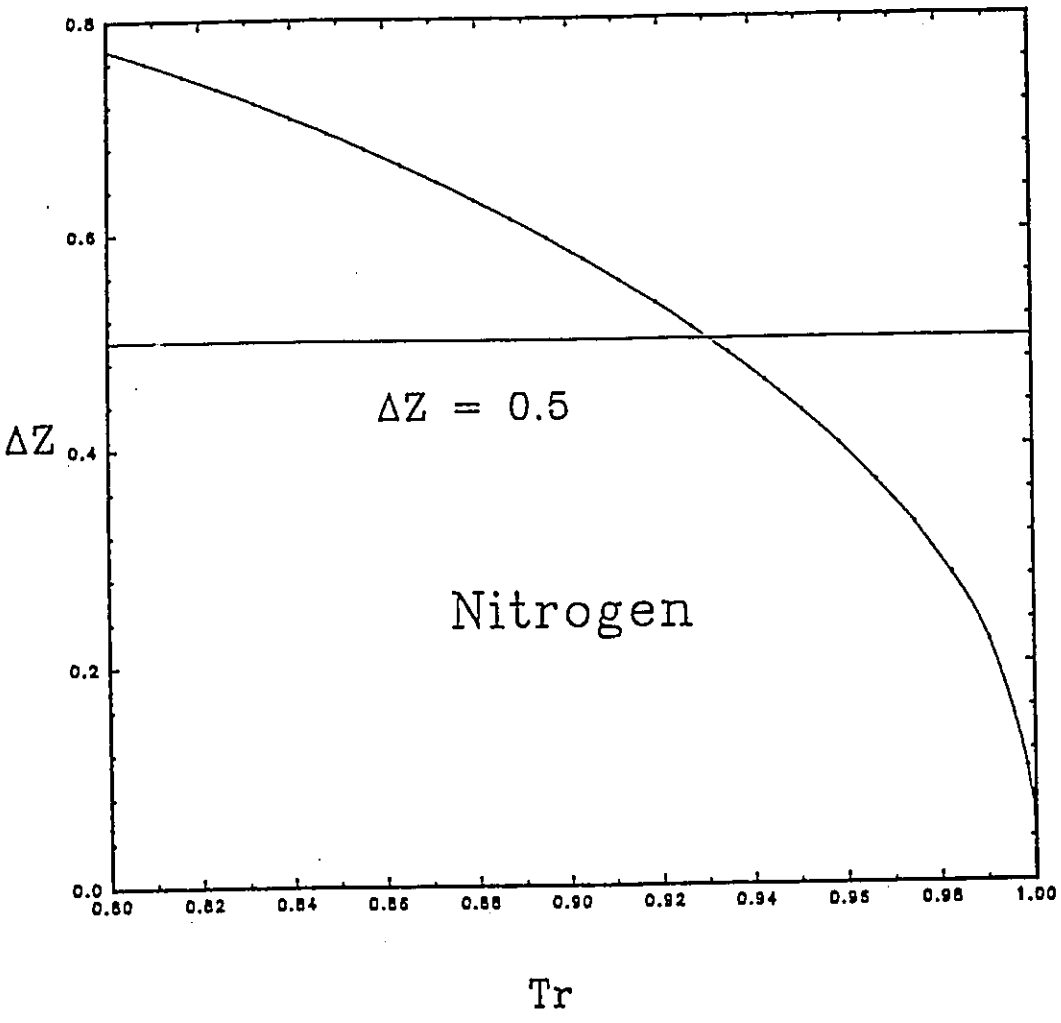


Figure 4.1 A diagram of reduced temperature T_r vs. compressibility factor change of vaporization, ΔZ, for nitrogen

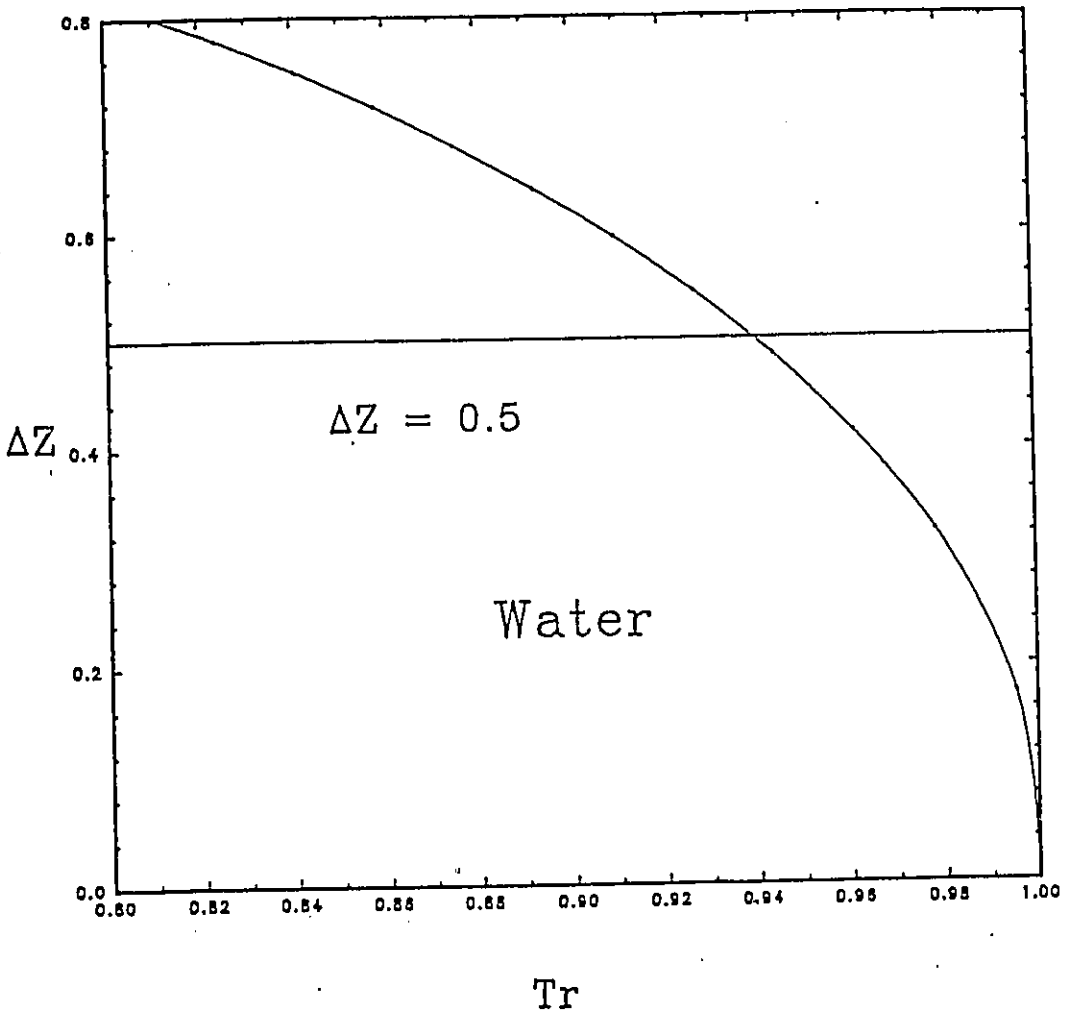


Figure 4.2 A diagram of reduced temperature T_r vs. compressibility factor change of vaporization, ΔZ, for water

The curves shown in Figures 4.1 and 4.2 indicate that when the value of ΔZ was taken to be 0.5, the reduced temperature T_r was found to be around 0.93-0.94. This observation was found to be true for most of the pure substances investigated. Therefore, the T_r value at $\Delta Z=0.5$ for a given substance is considered as a characteristic parameter of that substance and applied to the determination of the equation parameters in the next section. The T_r values of this new characteristic parameter were determined by interpolating available experimental Z_L^{sat} and Z_V^{sat} values with a cubic spline method in this work. Table 4.1 lists the T_r values, at $\Delta Z = 0.5$, for 21 pure substances. The critical properties and the acentric factors for these substances are also listed in Table 4.1. The values for all the 86 substances investigated in this work are listed in Appendix A. The results listed in Table A.2 indicate that the modified ALS equation gives better results than other equations of state tested.

Table 4.1 The critical properties, acentric factors and characteristic parameter values (T_r at $\Delta Z=0.5$) for 21 pure substances.

Substance	T_C (K)	P_C(bar)	ω	$T_r(\Delta Z=0.5)$
Methane	190.4	46.0	0.011	0.93487
Ethane	305.4	48.8	0.099	0.93414
Propane	369.8	42.5	0.153	0.93658
n-Butane	425.2	38.0	0.199	0.93880
n-Pentane	469.7	33.7	0.251	0.94025
n-Hexane	507.5	30.1	0.299	0.93962
i-Butane	408.2	36.5	0.183	0.93895
Ethylene	282.4	50.4	0.089	0.92324
Propylene	364.9	46.0	0.144	0.93754
1-Butene	419.6	40.2	0.191	0.94222
Acetylene	308.3	41.4	0.190	0.93551
Benzene	562.2	48.9	0.212	0.94061
CO	132.9	35.0	0.066	0.93029
CO_2	304.1	73.8	0.239	0.93868
Nitrogen	126.2	33.9	0.039	0.93196
Oxygen	154.6	50.4	0.025	0.94043
Methanol	512.6	80.9	0.556	0.94521
Ethanol	513.9	61.4	0.644	0.95216
Propanol	536.8	51.7	0.623	0.94327
Ammonia	405.5	113.5	0.250	0.92861
Water	647.3	221.2	0.344	0.93929

4.2 Balanced and Better Representation of Saturated Liquid and Vapor Volumes

As presented in Chapter 3, the ALS equation, Eqn. (2.5), can be expressed in terms of the compressibility factor Z as follows

$$1=\frac{1}{Z-B_1}-\frac{A}{(Z-B_2)(Z-B_3)} \tag{3.1}$$

where

$$A=\frac{aP}{(RT)^2}=\frac{\Omega_a P_r}{T_r^2}=\frac{\Omega_{ac}\alpha P_r}{T_r^2} \tag{3.3}$$

and

$$B_k=\frac{b_k P}{RT}=\frac{\Omega_{bk} P_r}{T_r}, \qquad k=1,2,3 \tag{3.4}$$

At the critical point, α equals 1 and Ω_a equals Ω_{ac}.

Using the two derivative conditions at the critical point, $(\partial P/\partial V)_T=0$ and $(\partial^2 P/\partial V^2)_T=0$, together with Eqn. (3.1), the following expressions can be obtained:

$$\Omega_{b1}+\Omega_{b2}+\Omega_{b3}+1=3Z_c^* \tag{4.6}$$

$$\Omega_{b1}\Omega_{b2}+\Omega_{b2}\Omega_{b3}+\Omega_{b3}\Omega_{b1}+\Omega_{b2}+\Omega_{b3}+\Omega_{ac}=3(Z_c^*)^2 \tag{4.7}$$

$$\Omega_{b1}\Omega_{b2}\Omega_{b3}+\Omega_{b2}\Omega_{b3}+\Omega_{b1}\Omega_{ac}=(Z_c^*)^3 \tag{4.8}$$

In these expressions, Z_c^* is the calculated compressibility factor from Eqn. (3.1) at the critical point. From the definitions of f, g and h, Eqn. (3.27)

$$\begin{aligned} f&=Z_c^*-\Omega_{b1} \\ g&=Z_c^*-\Omega_{b2} \\ h&=Z_c^*-\Omega_{b3} \end{aligned} \tag{3.27}$$

the following relationships are obtained after rearrangement

$$f+g+h=1 \tag{4.9}$$

$$fg+gh+fh-(g+h)+\Omega_{ac}=0 \tag{4.10}$$

$$fgh-gh+f\Omega_{ac}=0 \tag{4.11}$$

In the work of Sugie et al. (1989), **f**, **g** and **h** were all considered constants for a

given pure substance. Rearranging Eqns. (4.9) to (4.11) yields an expression for **h** in terms of **f** as follows

$$h=(1-f)(1-\sqrt{1-4f})/2 \tag{4.12}$$

In the present work, the relationships as expressed in Eqns. (4.9) to (4.11) were maintained at the critical point as required in the derivations. However, at temperatures other than the critical point, both **h** and **g** were treated as temperature dependent. In an effort to introduce a temperature function for **h**, Eqn. (4.12) was modified as follows

$$h=(1-f)(\beta-\sqrt{\beta-4f})/2 \tag{4.13}$$

The temperature function of the quantity β was selected empirically as

$$\beta=4f+(1-4f)\exp\left[\beta_c T_r^{\beta_d}(1-T_r^{\beta_e})\right] \tag{4.14}$$

where β_c , β_d , β_e are constants for a given substance. When $T_r = 1$, $\beta = 1$, the conditions required by Eqns. (4.9) to (4.11) are still satisfied at the critical point.

The quantity Ω_{b1} and **f** were treated as constants for a given substance and **g** was obtained from Eqn. (4.9).

In summary, the modified ALS equation of state has 5 substance dependent constants for a pure substance (Ω_{b1}, f, β_c, β_d, and β_e) with the parameter α determined from the

vapor pressure of pure substances by using the method presented in Chapter 3.

The parameter f was selected to fit the T_r value at $\Delta Z=0.5$, and other parameters were used to fit liquid densities. This technique was referced to "a balanced and better representation of saturated liquid and vapor volumes", in this work.

For the convenience of the calculation, two parameters were fixed and one parameter was generalized for the nonpolar and slightly polar substances in the following manner:

$$\beta_d=12.0\ , \qquad \text{and} \qquad \beta_c=34.0 \tag{4.15}$$

and

$$f=0.225372-0.06176\omega \tag{4.16}$$

Therefore, for these fluids, there are only two substance dependent parameters, Ω_{b1} and β_c, with the substance dependent parameter α determined from vapor pressure of pure substances.

The calculated results of saturation curves for nitrogen and water are shown in Figures 4.3 and 4.4, respectively, indicating that the calculated saturated liquid and vapor volumes are very close to the literature data. The AAPDs of the calculated liquid volumes and vapor volumes for nitrogen is 0.62% and 2.13% respectively and for water, 1.13% and 0.34% respectively.

The saturation data of 16 pure substances compiled by Canjar and Manning (1967) were used in the evaluation of the proposed technique and a comparison of the results with those of the original ALS equation and Sugie et al.'s work is listed in Table 4.2. For all of the 16 substances, Eqns. (4.15) and (4.16) were applied in this work with the parameter α individually determined from vapor pressures of pure substances. The values of the paramters, Ω_{b1} and f, are listed in Table 4.3.

It is seen from Table 4.2 that the results for both saturated liquid volumes and vapor volumes from this new approach are much better than those obtained from the original approach of Adachi et al. (1983) and Sugie et al. (1989). It may be considered that the modification is successful and a balanced and better representation of saturated liquid and vapor volumes was achieved.

The computer programs in the FORTRAN language for the determination of parameters for pure substances are presented in Appendix.

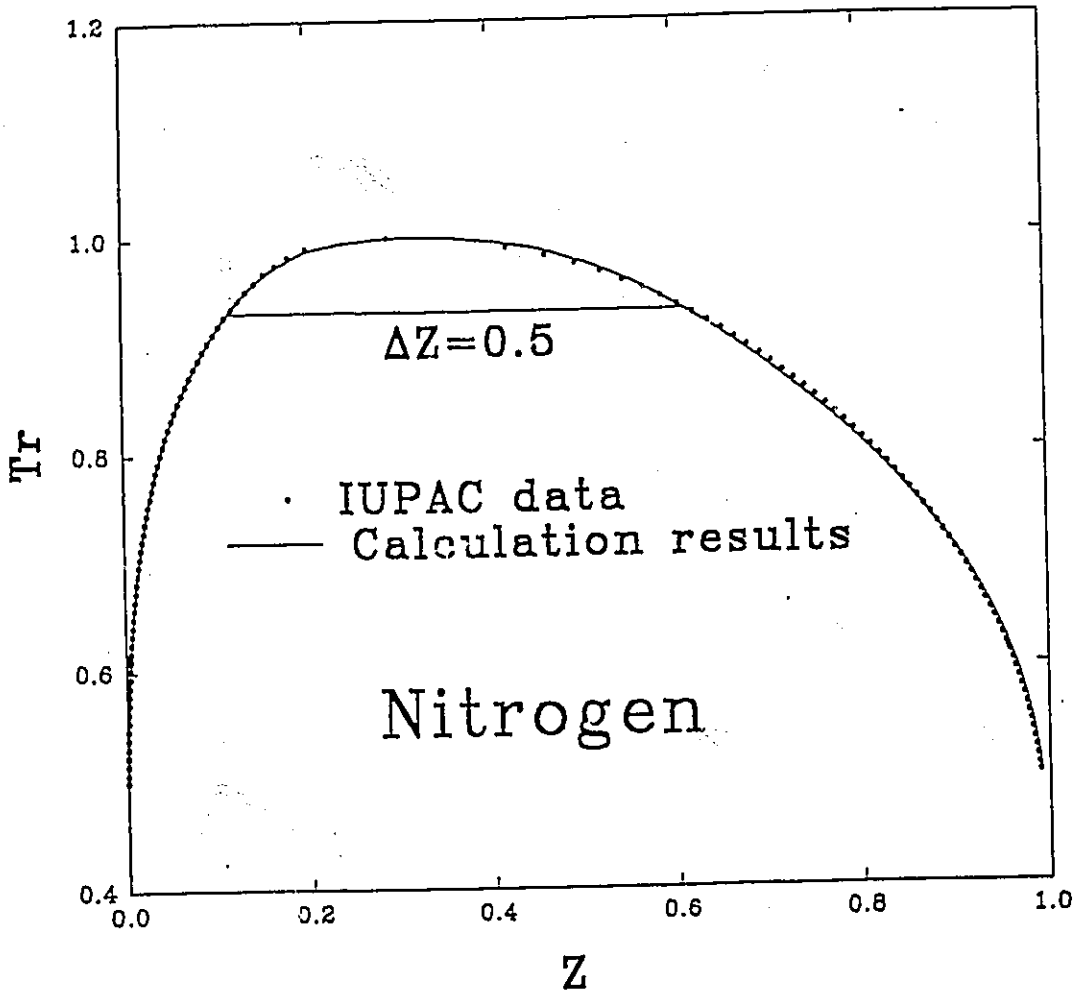


Figure 4.3 Comparison of the calculated results with the literature values on the saturation curve for nitrogen

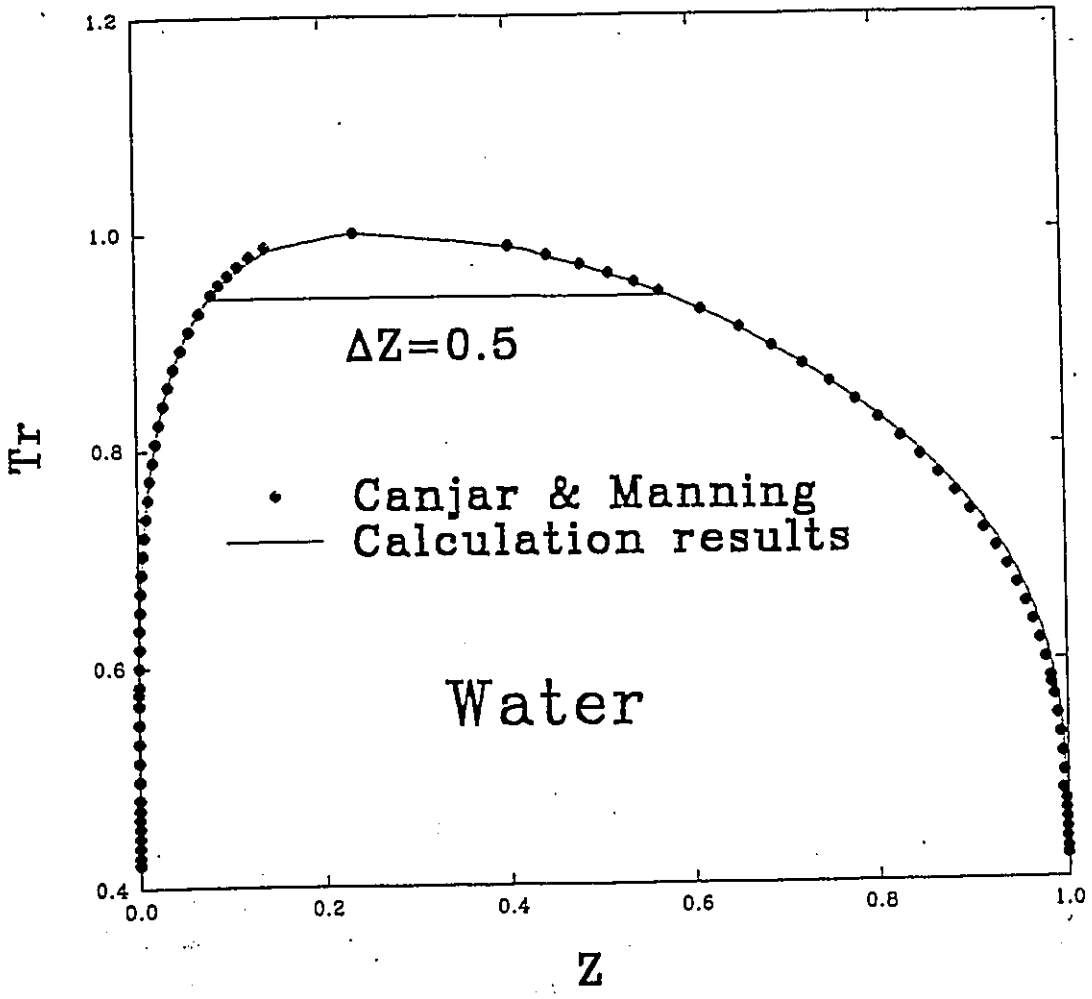


Figure 4.4 Comparison of the calculated results with the literature values on the saturation curve for water

Table 4.2 Comparison of the results obtained by the modified ALS equation with those obtained by the Adachi et al. (1983) and Sugie et al. (1989) for saturated liquid volumes* and vapor volumes* by using the α values individually determined from vapor pressures*

Substance	V_L^{sat} (AAPD)			V_V^{sat} (AAPD)		
	ALS	Sugie et al.	This work	ALS	Sugie et al.	This work
Methane	4.94	1.53	0.70	2.18	3.34	0.84
Ethane	8.46	3.10	1.49	1.40	3.15	1.25
Propane	6.62	1.85	1.10	1.78	3.27	0.54
n-Butane	4.75	1.42	0.53	1.46	1.92	1.02
n-Pentane	4.45	1.95	0.77	0.95	1.95	1.05
n-Hexane	5.72	2.10	1.33	0.97	0.84	1.15
i-Butane	--	1.44	0.50	--	2.28	0.74
Ethylene	3.31	1.65	0.39	1.79	1.89	2.23
Propylene	3.61	1.44	0.87	1.43	1.17	0.93
1-Butene	3.86	1.63	1.24	1.81	3.13	1.49
Acetylene	4.54	1.83	0.84	0.77	1.22	1.75
Benzene	--	1.98	1.33	--	3.32	2.15
CO	2.41	1.44	0.56	1.11	3.24	3.60
CO_2	4.69	2.19	0.95	3.04	2.47	1.18
Nitrogen	4.20	1.75	0.62	3.36	4.03	2.13
Oxygen	2.79	1.41	0.53	3.61	4.34	2.87
Overall average	4.60	1.82	0.86	1.83	2.60	1.56

* Canjar and Manning (1967)

Table 4.3 The parameters of the modified ALS equation for 16 substances

Substance	Ω_{b1}	β_c
Methane	0.089980	0.9469
Ethane	0.090410	2.1654
Propane	0.089970	1.8372
n-Butane	0.087430	0.6949
n-Pentane	0.086490	1.0134
n-Hexane	0.084770	0.8571
i-Butane	0.087564	0.0441
Ethylene	0.088940	0.7538
Propylene	0.088720	0.6804
1-Butene	0.089218	1.5223
Acetylene	0.085880	0.8158
Benzene	0.085450	0.7751
CO	0.093150	0.5298
CO_2	0.088960	1.3713
Nitrogen	0.092760	0.7120
Oxygen	0.091790	0.7632

4.3 Development of a New α Function

The functional form of the parameter α is usually determined from vapor pressure. Sugie et al. (1989) proposed an analytical method for the calculation of α values from vapor pressure, P^{sat}, as mentioned in Chapter 3. It is efficient and is applicable to any van der Waals type cubic equations of state with the form of Eqn. (3.1).

For the calculation of energy properties, such as enthalpy calculations, the derivative of the parameter **a** with respect to temperature is necessary. It is difficult to obtain this derivative numerically from Sugie's technique, so an expression for the temperature dependency of the parameter **a** is needed.

The parameter **a** can be expressed by

$$a=\Omega_a(RT_C)^2/P_C \tag{4.17}$$

where Ω_a is a function of temperature.

Usually, Ω_a is expressed by

$$\Omega_a=\Omega_{ac}\alpha \tag{4.18}$$

By manipulating the critical conditions, Eqns. (4.9) to (4.11), it can be shown that the value of Ω_{ac} is related to **f** as follows

$$\Omega_{ac}=(1-f)^3 \tag{4.19}$$

From Eqn. (4.11), another relation can be obtained

$$\Omega_{ac}=(1-f)g_c h_c/f \tag{4.20}$$

where g_c and h_c are the values of g and h at the critical point, respectively. It should be mentioned that Eqn. (4.19) and (4.20) are identical.

The most common α function used in the literature was that proposed by Soave (1972)

$$\alpha^{0.5}=1+m(1-T_r^{0.5}) \tag{4.21}$$

where m is a substance dependent constant. In Soave's work, m was generalized with the acentric factor ω.

Eqn. (4.21) was modified by Stryjek and Vera (1986) for polar substances as

$$\alpha^{0.5}=1+k(1-T_r^{0.5}) \tag{4.22}$$

with

$$k=k_0+k_1(1+T_r^{0.5})(0.7-T_r) \tag{4.23}$$

The quantity k_0 was generalized with the acentric factor ω, and k_1 is a substance dependent constant.

Theoretically, the temperature function of the parameter α could be expressed in an exponential form (Lee et al., 1985; Sandler, 1990; Shen and Lu, 1992). Therefore, an exponential form of the expression for parameter α was proposed in this work

$$\alpha = \exp(\alpha_a(1-T_r^{\alpha_n})^{2\alpha_m+1}) \tag{4.24}$$

where α_a, α_n, and α_m are constants for a given substance. Because the first derivative of α with respect to temperature

$$\frac{d\alpha}{dT} = \exp(\alpha_a(1-T_r^{\alpha_n})^{2\alpha_m+1})2\alpha_m\alpha_a(1-T_r^{\alpha_n})^{2\alpha_m}(-T_r^{\alpha_n-1})/T_C \tag{4.25}$$

is equal to zero at the critical point, the α vs T_r curve can be kept smooth at the critical point when the parameters are different in the subcritical region($T_r < 1$) and the supercritical ($T_r > 1$) region. This condition makes the proposed α function more flexible.

For evaluating the new α function and choosing a suitable Ω_a expression, four different methods for representing the temperature dependency of the parameter a were compared in this work.

(1). The Ω_{ac} values were calculated by means of Eqn. (4.19) and the α values were

calculated by using the expression proposed by Stryjek and Vera, Eqn. (4.22).

(2). The Ω_{ac} values were agai calculated by Eqn. (4.19) and the α values were calculated by the new α function, Eqn. (4.24).

(3). The following expression was used for the calculation of Ω_a

$$\Omega_a = \frac{(1-f)gh}{f}\alpha \qquad (4.26)$$

with α values calculated by Eqn. (4.22).

(4). Eqn. (4.26) was used to calculate the Ω_a values, in which α values were calculated by Eqn. (4.24).

A comparison of the overall results for the calculated vapor pressures, saturated liquid and vapor volumes, and latent heat of vaporization for 21 substances are listed in Table 4.4. The data sources for those 21 substances is shown in Table 4.5.

Table 4.4 A comparison of the results obtained by using four different Ω_a functions for

21 substances (in AAPD).

methods	$\Delta P^{sat}\%$	$\Delta V_L^{sat}\%$	$\Delta V_V^{sat}\%$	$\Delta H_{vap}\%$
(1)	2.015	0.914	3.314	7.498
(2)	0.860	0.819	1.973	3.492
(3)	0.620	0.828	1.670	4.069
(4)	0.542	0.994	1.562	1.832

The results presented in Table 4.4 indicate that the calculated vaporization enthalpies

vary with the Ω_a function used. Method (4), in which the Ω_a values were calculated by Eqn. (4.26) and α values were calculated by Eqn. (4.24), yielded the best results and therefore was adopted all through this work.

The detailed results obtained from Method (4) for the 21 substances are presented in Tables 4.6 to 4.9. These results are also compared in these tables with the results obtained from the SRK, the PR, the SW and the PT equations of state. The parameters obtained for these 21 substances are listed in Table 4.10.

It is seen from Tables 4.6 to 4.9 that the accuracies of the calculated vapor volumes do not have much difference among those obtained from different equations of state for non-polar substances. However, the results obtained from this work for polar substances are generally better than those from other equations of state tested. For the calculation of saturated liquid volumes, the results obtained from this work are much better than those from the other equations of state tested. For the calculation of vapor pressure, the results from this work are comparable with those from other equations of state tested, and the AAPDs are generally less than 1%. For the prediction of latent heat of vaporization, ΔH_{vap}, the results obtained from this work are also better than those from other equations of state tested, as expected.

Table 4.5 Data sources of 21 pure substances

substances	N	T_r Range	Data Sources
Methane	29	0.586-0.990	Canjar and Manning (1967)
Ethane	27	0.604-0.991	Canjar and Manning (1967)
Propane	31	0.625-0.991	Canjar and Manning (1967)
n-Butane	28	0.641-0.993	Canjar and Manning (1967)
n-Pentane	30	0.658-0.993	Canjar and Manning (1967)
n-Hexane	43	0.538-0.995	Canjar and Manning (1967)
i-Butane	29	0.626-0.993	Canjar and Manning (1967)
Ethylene	21	0.600-0.983	Canjar and Manning (1967)
Propylene	26	0.618-0.989	Canjar and Manning (1967)
1-Butene	26	0.651-0.979	Canjar and Manning (1967)
Acetylene	22	0.624-0.991	Canjar and Manning (1967)
Benzene	46	0.553-0.988	Canjar and Manning (1967)
CO	24	0.513-0.981	Canjar and Manning (1967)
CO_2	32	0.712-0.995	Canjar and Manning (1967)
Nitrogen	18	0.613-0.989	Canjar and Manning (1967)
Oxygen	24	0.583-0.987	Canjar and Manning (1967)
Methanol	20	0.659-0.991	Washburn (1928)
Ethanol	17	0.648-0.979	Washburn (1928)
1-Propanol	19	0.656-0.993	Washburn (1928)
Ammonia	21	0.493-0.986	Din (1956)
Water	41	0.442-0.991	Canjar and Manning (1967)

N: number of data points

Table 4.6 A comparison of calculated vapor pressures in terms of average absolute percentage deviations (AAPD)

	P^{sat}, AAPD				
Substance	SRK	PR	SW	PT	This work
Methane	1.25	0.45	0.72	0.83	0.65
Ethane	0.82	0.18	0.59	0.34	0.80
Propane	0.99	0.36	0.20	0.58	0.56
n-Butane	0.89	0.25	0.25	0.24	0.63
n-Pentane	0.96	0.31	0.19	0.28	0.33
n-Hexane	1.65	0.82	0.47	0.86	0.43
i-Butane	1.08	0.29	0.10	0.51	0.28
Ethylene	1.58	1.00	0.74	1.17	1.00
Propylene	0.77	0.29	0.54	0.50	0.18
1-Butene	1.03	0.31	0.29	0.46	0.53
Acetylene	1.68	1.04	0.96	0.95	0.42
Benzene	0.98	0.56	0.34	0.62	0.27
CO	3.87	2.82	3.49	0.68	0.69
CO_2	1.17	1.96	2.15	0.26	0.41
Nitrogen	0.60	0.44	0.60	0.92	0.42
Oxygen	1.20	0.32	0.75	0.79	0.19
Methanol	4.02	4.00	4.87	1.52	0.83
Ethanol	0.19	1.04	2.50	1.23	0.61
1-Propanol	1.64	2.38	3.00	3.87	0.73
Ammonia	2.22	0.58	0.96	2.27	0.87
Water	9.43	5.43	8.07	1.37	0.55
Overall	1.81	1.18	1.51	0.96	0.54

SRK (Soave, 1972); PR (Peng and Robinson, 1976); SW (Schmidt and Wenzel, 1980); PT (Patel and Teja, 1982).

Table 4.7 A comparison of calculated saturated liquid volumes in terms of average absolute percentage deviation (AAPD)

	V_L^s, AAPD				
Substance	SRK	PR	SW	PT	This work
Methane	7.89	7.33	7.06	5.28	0.71
Ethane	13.4	6.68	8.90	6.38	1.63
Propane	13.8	5.85	7.19	7.04	1.22
n-Butane	13.1	4.69	4.90	4.53	0.52
n-Pentane	15.0	4.44	7.72	4.41	0.98
n-Hexane	15.7	3.46	3.55	3.65	1.46
i-Butane	11.0	4.83	3.92	3.92	2.14
Ethylene	9.35	6.03	5.39	4.37	0.49
Propylene	11.0	5.05	4.81	6.34	0.94
1-Butene	12.2	4.44	4.10	3.72	1.27
Acetylene	14.6	4.79	6.50	4.64	0.92
Benzene	13.9	3.84	5.01	3.59	0.94
CO	3.66	8.83	3.28	3.47	0.45
CO_2	13.7	4.24	4.27	4.11	1.07
Nitrogen	6.02	8.03	4.70	4.96	0.61
Oxygen	5.11	7.77	3.91	3.97	0.51
Methanol	42.7	26.4	17.7	6.48	1.52
Ethanol	27.8	13.1	4.62	8.80	0.57
1-Propanol	21.6	7.75	5.98	5.16	0.92
Ammonia	29.7	14.9	18.0	2.88	0.70
Water	37.9	22.2	21.7	3.10	1.31
Overall	16.2	8.32	7.15	4.80	0.99

Table 4.8 A comparison of calculated saturation vapor volumes in terms of average absolute percentage deviation (AAPD)

	V_V^s , AAPD				
Substance	SRK	PR	SW	PT	This work
Methane	2.48	2.75	2.02	2.36	0.95
Ethane	1.00	1.96	1.55	1.33	1.32
Propane	0.66	1.69	1.12	1.38	1.12
n-Butane	1.23	1.46	1.38	1.46	1.01
n-Pentane	1.34	1.10	0.76	1.06	0.99
n-Hexane	2.08	1.42	1.40	1.56	1.36
i-Butane	0.63	1.15	0.63	1.11	1.67
Ethylene	2.37	1.79	2.88	1.97	1.43
Propylene	1.74	1.13	1.96	1.34	0.99
1-Butene	1.39	1.97	1.20	1.80	1.29
Acetylene	2.19	1.93	2.21	1.37	1.56
Benzene	1.66	2.80	2.44	2.60	1.91
CO	7.61	5.74	6.98	3.29	2.73
CO_2	2.59	1.93	2.65	0.94	1.00
Nitrogen	2.06	3.14	1.78	2.41	2.17
Oxygen	3.80	4.20	3.82	3.47	2.73
Methanol	3.98	2.51	2.10	2.91	2.70
Ethanol	1.76	1.39	2.50	1.89	1.80
1-Propanol	6.69	5.64	5.07	8.24	2.26
Ammonia	5.90	3.50	5.05	3.97	0.80
Water	12.6	7.16	11.2	2.01	1.02
Overall	3.13	2.68	2.89	2.31	1.56

Table 4.9 A comparison of calculated latent heat of vaporization in terms of average absolute percentage deviations (AAPD)

	ΔH_{vap}, AAPD				
Substance	SRK	PR	SW	PT	This work
Methane	3.57	2.60	16.80	3.12	0.85
Ethane	3.62	2.85	15.28	3.10	3.00
Propane	3.46	2.85	14.58	3.04	2.55
n-Butane	2.44	1.72	10.01	1.77	0.48
n-Pentane	2.02	1.32	8.82	1.44	1.19
n-Hexane	2.66	2.17	5.93	2.20	1.22
i-Butane	2.53	1.89	8.16	2.18	2.07
Ethylene	2.54	1.63	12.77	1.98	1.47
Propylene	2.54	1.73	11.88	2.19	1.04
1-Butene	2.62	1.99	11.65	2.18	1.45
Acetylene	3.70	3.27	8.34	3.21	1.83
Benzene	2.75	2.55	8.34	2.55	0.73
CO	3.12	2.44	10.14	2.16	2.27
CO_2	2.97	2.46	9.72	1.77	1.45
Nitrogen	3.18	3.02	18.22	3.08	2.09
Oxygen	4.06	2.95	15.94	3.38	1.34
Methanol	6.28	5.27	6.41	5.47	4.26
Ethanol	1.39	0.57	2.40	0.87	0.94
1-Propanol	4.08	4.25	2.57	4.91	3.55
Ammonia	3.55	2.65	6.15	2.13	0.98
Water	4.70	3.24	9.22	1.36	1.61
Overall	3.29	2.61	9.48	2.63	1.83

Table 4.10 The parameters of the modified ALS equation for 21 substances

Substance	Ω_{b1}	f	β_c	β_d	β_e	α_a	α_n	α_m
Methane	0.089980	correlation	0.9469	constant	constant	0.5329	0.7336	0.0195
Ethane	0.090410	correlation	2.1654	constant	constant	0.6969	0.7948	0.0731
Propane	0.089970	correlation	1.8372	constant	constant	1.0852	0.4974	0.0290
n-Butane	0.087430	correlation	0.6949	constant	constant	1.1227	0.5105	0.0219
n-Pentane	0.086490	correlation	1.0134	constant	constant	1.2143	0.5219	0.0264
n-Hexane	0.084770	correlation	0.8571	constant	constant	1.6353	0.3707	0.0020
i-Butane	0.087564	correlation	0.0441	constant	constant	1.1166	0.4681	0.0020
Ethylene	0.088940	correlation	0.7538	constant	constant	0.9059	0.5133	0.0242
Propylene	0.088720	correlation	0.6804	constant	constant	0.9465	0.5678	0.0290
1-Butene	0.089218	correlation	1.5223	constant	constant	1.0411	0.5989	0.0465
Acetylene	0.085880	correlation	0.8158	constant	constant	1.2106	0.4281	0.0020
Benzene	0.085450	correlation	0.7751	constant	constant	1.1372	0.5135	0.0190
CO	0.093150	correlation	0.5298	constant	constant	1.3607	0.2733	0.0020
CO_2	0.088960	correlation	1.3713	constant	constant	1.5697	0.3994	0.0396
Nitrogen	0.092760	correlation	0.7120	constant	constant	0.6236	0.7096	0.0393
Oxygen	0.091790	correlation	0.7632	constant	constant	0.6455	0.6189	0.0226
Methanol	0.056350	0.19360	0.6943	-1.1353	11.9344	2.4383	0.5061	0.0423
Ethanol	0.064560	0.21211	1.0080	-1.1000	19.6600	1.7595	0.9309	0.0869
1-Propanol	0.073130	0.19564	0.6534	-0.9677	14.7539	2.9124	0.5143	0.0884
Ammonia	0.069010	0.18991	0.9479	0.6010	5.0876	0.6548	1.3130	0.1310
Water	0.057430	0.20092	0.7257	-0.9437	11.9525	1.5619	0.6615	0.0801

The literature data for 86 substances were used to evaluate the results calculated from the proposed procedure and those from some other selected equations of state. The parameter values and the calculated results are listed in Appendix A. The results obtained from the SRK, the PR, the SW, and the PT equations are also listed in Appendix A for comparison. The new approach produces better results in the calculated saturated vapor and liquid volumes than those obtained by the other four equations.

4.4 Concluding Remarks

In this work, a new characteristic parameter, T_r at $\Delta Z = 0.5$, was introduced for improving the performance of the ALS equation for the simultaneous calculation of saturated liquid and vapor volumes, and the latent heat of vaporization of pure substances. A balanced and better representation of saturated liquid and vapor volumes was achieved.

A new exponential temperature function of the parameter α was proposed and found to be more suitable for the modified ALS equation than the α function proposed by Stryjek and Vera (1986).

Chapter 5

Application of the Modified ALS Equation of State to Mixtures

Mixing rules are required for the calculation of thermodynamic properties of mixtures by using equations of state. Wang et al. (1993) demonstrated that the Wong-Sandler mixing rule is capable of simultaneously representing VLE and H^E values more accurately than the conventional, the Adachi-Sugie and the SGR mixing rules. Therefore, the application of the Wong-Sandler mixing rule was extended to the modified ALS equation in this work. Since the ALS equation is a general van der Waals type cubic equation, the expressions developed in this chapter can be used by many cubic equations.

For validating the extended Wong-Sandler mixing rule, the VLE data of 14 binary systems were represented and the results were compared with those obtained from the conventional, the Adachi-Sugie, and the SGR mixing rules by using the modified ALS equation. The results were also compared with those obtained by using the SRK, the PR, the PT and the PRSV equations with the extended Wong-Sandler mixing rule. In addition, the VLE data of six ternary systems with their 18 constituent binary systems were represented and the results were compared with those obtained from different mixing rules for testing the capability of these mixing rules on the prediction of multi-component VLE values from binary data. The VLE, saturated and compressed liquid volume data for three binary systems were also represented and compared by using different mixing rules and different equations of state. The sources of VLE, volume and excess enthalpy data used in this chapter are listed in Appendix C.

5.1 Extension of the Wong-Sandler Mixing Rule to the Modified ALS Equation of State

The Wong-Sandler mixing rule is a theoretically correct mixing rule for cubic equations. Up to now, this mixing rule has only been used for two parameter cubic equations, such as the PR and the PRSV equations. Two parameter cubic equations can represent the

VLE data very well, but are not necessarily good enough for simultaneous representation of volumetric and energy data, especially for polar fluids as mentioned in Chapter 2.

In the extension, the following three criteria must be satisfied:

(1). The extended mixing rule must be consistent for mixtures and pure components so that the expressions for mixture parameters can be reduced to those for pure components.

(2). The extended mixing rule should be reducible to the original mixing rule for the two parameter cubic equations.

(3). All the parameters for mixtures should have explicit forms for the convenience of calculation.

As mentioned in Chapter 3, the Wong-Sandler mixing rule was developed based on the following two conditions:

(1). The excess Helmholtz free energy at high pressure was assumed equal to the excess Gibbs free energy at low pressure.

(2). The composition dependence of the second virial coefficient should be quadratic.

With these two conditions, two expressions can be established to determine two of the equation parameters.

The modified ALS equation has the form

$$P=\frac{RT}{V-b_1}-\frac{a}{(V-b_2)(V-b_3)} \qquad (2.5)$$

Since this equation contains four parameters, a, b_1, b_2 and b_3, two more other expressions are needed.

For pure component i, the Helmholtz free energy departure function is given by

$$\begin{aligned} A(T,P)-A^{IG} &= \left(-\int_{V=\infty}^{V} PdV\right)-\left(-\int_{V=\infty}^{V=\frac{RT}{P}} PdV\right) \\ &= -RT\ln\frac{P(V-b_{1i})}{RT}+\frac{a_i}{b_{1i}}C_i \end{aligned} \tag{5.1}$$

where

$$C_i=\frac{b_{1i}}{b_{2i}-b_{3i}}\ln\frac{V-b_{2i}}{V-b_{3i}} \tag{5.2}$$

For mixtures, the excess Helmholtz free energy is given by

$$\begin{aligned} A^{E} &= A_m(T,P,x)-A_m^{ID}(T,P,x) \\ &= A_m(T,P,x)-\sum x_i A_i(T,P)-RT\sum x_i \ln x_i \\ &= -RT\ln\frac{P(V_m-b_{1m})}{RT}+RT\sum x_i\ln\frac{P(V_i-b_{1i})}{RT} \\ &\quad +\frac{a_m}{b_{1m}}C_m-\sum x_i\frac{a_i}{b_{1i}}C_i \end{aligned} \tag{5.3}$$

where

$$C_m=\frac{b_{1m}}{b_{2m}-b_{3m}}\ln\frac{V-b_{2m}}{V-b_{3m}} \tag{5.4}$$

For the modified ALS equation, the second virial coefficient B can be expressed as

$$B = b_1 - \frac{a}{RT} \tag{5.5}$$

Based on the second condition, the composition dependence of the second virial coefficient should be quadratic

$$B_m = \sum_i \sum_j x_i x_j B_{ij} \tag{5.6}$$

so that

$$b_{1m} - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left(b_1 - \frac{a}{RT} \right)_{ij} \tag{5.7}$$

where

$$\left(b_1 - \frac{a}{RT}\right)_{ij} = \frac{\left(b_{1i} - \frac{a_i}{RT}\right) + \left(b_{1j} - \frac{a_j}{RT}\right)}{2} (1 - k_{ij}) \tag{5.8}$$

in which, k_{ij} is the binary interaction coefficient.

Let $P \Rightarrow \infty$, then $V_i \Rightarrow b_{1i}$ and $V_m \Rightarrow b_{1m}$, Eqns (5.2) and (5.4) become

$$C_i^{\infty} = \frac{b_{1i}}{b_{2i} - b_{3i}} \ln \frac{b_{1i} - b_{2i}}{b_{1i} - b_{3i}} \tag{5.9}$$

and

$$C_m^{\infty} = \frac{b_{1m}}{b_{2m}-b_{3m}} \ln \frac{b_{1m}-b_{2m}}{b_{1m}-b_{3m}} \tag{5.10}$$

respectively.

For a two-parameter cubic equation

$$C_i^{\infty} = C_m^{\infty} = \text{constant} \tag{5.11}$$

For example, for the Peng-Robinson equation

$$C_i^{\infty} = C_m^{\infty} = \frac{\ln(\sqrt{2}-1)}{\sqrt{2}} \tag{5.12}$$

Howerer, for EOS with more than two parameters, C_i^{∞} is not necessarily equal to C_m^{∞}. Therefore, a mixing rule is needed for the calculation of C_m^{∞}.

First, let

$$C_{2i} = \frac{b_{2i}}{b_{1i}}, \quad \text{and} \quad C_{3i} = \frac{b_{3i}}{b_{1i}} \tag{5.13}$$

and

$$C_{2m} = \frac{b_{2m}}{b_{1m}}, \quad \text{and} \quad C_{3m} = \frac{b_{3m}}{b_{1m}} \tag{5.14}$$

Then, Eqns. (5.9) and (5.10) can be rewritten in the following manner

$$C_i^{\infty} = \frac{1}{C_{2i} - C_{3i}} \ln \frac{1 - C_{2i}}{1 - C_{3i}} \tag{5.15}$$

and

$$C_m^{\infty} = \frac{1}{C_{2m} - C_{3m}} \ln \frac{1 - C_{2m}}{1 - C_{3m}} \tag{5.16}$$

Following the conventional mixing rules

$$C_{2m} = \sum_i \sum_j x_i x_j C_{2ij} \tag{5.17}$$

and

$$C_{3m} = \sum_i \sum_j x_i x_j C_{3ij} \tag{5.18}$$

where

$$C_{2ij} = \frac{1}{2}(C_{2i} + C_{2j})$$
$$C_{3ij} = \frac{1}{2}(C_{3i} + C_{3j}) \tag{5.19}$$

leads to

$$b_{1m}=\frac{\sum_i\sum_j x_i x_j(b_1-\frac{a}{RT})_{ij}}{1-\frac{1}{C_m^{\infty}RT}(\sum_i \frac{a_i}{b_{1i}}C_i^{\infty}+A_{\infty}^{E})} \tag{5.20}$$

and

$$a_m=\frac{b_{1m}}{C_m^{\infty}}(\sum_i x_i\frac{a_i}{b_{1i}}C_i^{\infty}+A_{\infty}^{E}) \tag{5.21}$$

Eqns. (5.20) and (5.21) together with Eqns. (5.16) to (5.18) are referred here as the extended Wong-Sandler (E-W-S) mixing rule.

The logrithm of the fugacity coefficient for component i is given by Eqn. (3.14)

$$\ln\phi_i=\frac{\hat{B}_{1i}}{Z-B_1}-\ln(Z-B_1)+\left(\frac{\hat{B}_{2i}-\hat{B}_{3i}}{B_2-B_3}-1-\frac{\hat{A}_i}{A}\right)\frac{A}{B_2-B_3}\ln\frac{Z-B_3}{Z-B_2} -\frac{A}{B_2-b_3}\left(\frac{\hat{B}_{2i}}{Z-B_2}-\frac{\hat{B}_{3i}}{Z-B_3}\right) \tag{3.14}$$

where

$$A=\frac{a_m P}{R^2T^2}\ ,\quad \hat{A}_i=\frac{\partial nA}{\partial n_i} \tag{5.22}$$

and

$$B_k = \frac{b_{km} P}{RT} , \quad \hat{B}_{ki} = \frac{\partial n B_k}{\partial n_i} , \quad k = 1,2,3 \tag{5.23}$$

Let

$$Q = \sum_i \sum_j x_i x_j (b_1 - \frac{a}{RT})_{ij} \tag{5.24}$$

and

$$G = \sum_i x_i \frac{a_i}{b_{1i}} C_i^{\infty} + A_{\infty}^{E} \tag{5.25}$$

Differentiation of Eqns. (5.24) and (5.25) yields

$$\frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} = 2 \sum_j x_j (b_1 - \frac{a}{RT})_{ij} \tag{5.26}$$

and

$$\frac{\partial n G}{\partial n_i} = \frac{a_i}{b_{1i}} C_i^{\infty} + \frac{\partial n A_{\infty}^{E}}{\partial n_i} \tag{5.27}$$

and leads to the following two expressions

$$\frac{\partial n b_{1m}}{\partial n_i} = \frac{1}{n}\frac{\partial n^2 Q}{\partial n_i}\frac{1}{(1.0 - G/C_m^{\infty} RT)} - \frac{Q}{(1 - G/C_m^{\infty} RT)^2}\left[1 - \frac{1}{C_m^{\infty} RT}\left(\frac{\partial nG}{\partial n_i} - \frac{G}{C_m^{\infty}} n \frac{\partial C_m^{\infty}}{\partial n_i}\right)\right] \tag{5.28}$$

and

$$\frac{\partial n a_m}{\partial n_i} = \left(\frac{\partial n b_{1m}}{\partial n_i} - b_{1m} - \frac{b_{1m}}{C_m^{\infty}} n \frac{\partial C_m^{\infty}}{\partial n_i}\right)\frac{G}{C_m^{\infty}} + \frac{b_{1m}}{C_m^{\infty}}\frac{\partial nG}{\partial n_i} \tag{5.29}$$

where

$$n\frac{\partial C_m^{\infty}}{\partial n_i} = -\ln\left(\frac{1 - C_{2m}}{1 - C_{3m}}\right)\frac{\hat{C}_{2m} - \hat{C}_{3m}}{(C_{2m} - C_{3m})^2} - \frac{1}{C_{2m} - C_{3m}}\left(\frac{\hat{C}_{2m}}{1 - C_{2m}} - \frac{\hat{C}_{3m}}{1 - C_{3m}}\right) \tag{5.30}$$

In Eqn. (5.30),

$$\hat{C}_{2m} = n\frac{\partial C_{2m}}{\partial n_i} = 2\sum_j x_j C_{2ij} - 2C_{2m}$$
$$\hat{C}_{3m} = n\frac{\partial C_{3m}}{\partial n_i} = 2\sum_j x_j C_{3ij} - 2C_{3m} \tag{5.31}$$

The above expressions are useful for many van der Waals type cubic equations, such

as the SRK, the PR, the PRSV and the PT equations.

As mentioned in Chapter 3, the Wong-Sandler mixing rule with the NRTL model (Renon and Prausnitz, 1968) gives better results than with the Van Laar model for the simultaneous representation of VLE and H^E values (Wang et al., 1993). Therefore, the NRTL model was adopted in this work to calculate excess Helmholtz energy.

5.2 Vapor Liquid Equilibrium Calculations for Binary and Ternary Mixtures

5.2.1 Binary Systems

For testing the extended Wong-Sandler mixing rule, the VLE behaviors for fourteen binary systems, including polar + polar systems (e.g. methanol + water) and polar + non-polar systems (e.g. alcohol + normal alkane), were represented and the results were compared with those obtained from the conventional, the Adachi-Sugie, and the SGR mixing rules. The results were also compared with those obtained by using different equations, such as the SRK, the PR, the PT and the PRSV equations, with the extended Wong-Sandler mixing rule. A comparison of the results obtained by means of different mixing rules and different EOS are listed in Tables 5.1 and 5.2, respectively, and the

binary interaction coefficients obtained in these calculations are listed in Tables 5.3 and 5.4.

The results shown in Table 5.1 indicate that the extended Wong-Sandler mixing rule gives better results than other mixing rules. In some cases, false liquid phase splitting occurred in the calculation. For example, for the methanol + n-hexane system at 323.15 and 333.15 K, false liquid phase splitting occurred in the calculations by using the conventional and the Adachi-Sugie mixing rules but did not occur by using the SGR mixing rule and the extended Wong-Sandler mixing rule with the NRTL activity coefficient model. The results for this system at 333.15 K are shown in Figure 5.1.

The results shown in Table 5.2 indicate that the modified ALS and the PRSV equation give better results than other equations. This difference is mostly caused by the accuracy of the calculated vapor pressure of the pure components as shown in Figure 5.2 for 1-butanol + toluene system at 333.31 K.

Table 5.1 A comparison of the calculated VLE results for fourteen binary systems by using the modified ALS equation of state with four different mixing rules in terms of AAPD for P^s and AAD×100 for y

Systems (Temperature)	Conventional		Adachi-Sugie		SGR		E-W-S	
	P^s	y	P^s	y	P^s	y	P^s	y
Methanol+Water (523.13K)	1.75	1.35	0.43	0.64	0.59	0.54	0.44	0.60
Methanol+n-Hexane (323.15K)	14.87 *	10.38 *	6.97 *	4.98 *	1.22	1.02	0.99	1.05
Methanol+n-Hexane (333.15K)	14.09 *	9.95 *	6.26 *	4.52 *	0.77	0.70	0.60	0.77
Ethanol+n-Hexane (323.15K)	8.65 *	5.92 *	1.82	1.27	0.26	0.38	0.40	0.36
Ethanol+n-Heptane (343.15K)	6.18 *	3.70 *	2.39	1.33	0.75	1.06	0.71	1.09
Ethanol+n-Octane (328.15K)	12.58	7.69	3.84	2.00	1.50	1.01	0.93	.65

* False liquid phase splitting occurred

Table 5.1 (continued)

Systems (Temperature)	Conventional		Adachi-Sugie		SGR		E-W-S	
	P^s	y	P^s	y	P^s	y	P^s	y
n-Propanol+n-Heptane (348.15K)	5.76	4.31	1.95	2.21	2.14	1.64	1.67	1.33
n-Propanol+n-Octane (313.15K)	7.30 *	-	2.02	-	0.82	-	0.89	-
1-Butanol-n-Pentane (303.15K)	8.42	0.44	2.80	0.09	0.63	0.11	0.49	0.08
1-Butanol+n-Hexane (298.15K)	8.08	0.57	3.99	0.61	0.85	0.34	0.74	0.33
1-Butanol+n-Heptane (323.15K)	4.82	2.30	1.84	0.95	1.14	0.79	1.14	0.79
1-Butanol+n-Octane (313.15K)	4.98	-	1.85	-	1.23	-	1.21	-
1-Butanol+n-Decane (373.15K)	7.10	2.19	1.76	1.73	1.21	1.57	1.09	1.58
1-Butanol + Toluene (333.31K)	5.48	3.08	0.48	0.46	0.46	0.47	0.30	0.40
Average	8.01	4.34	2.48	1.85	0.97	0.80	0.83	0.75

Table 5.2 A comparison of the calculated VLE results for fourteen binary systems by using the extended Wong-Sandler mixing rule with five different equations of state in terms of AAPD for P^s and AAD×100 for y

Systems (Temperature)	SRK		PR		PT		PRSV		This work	
	P^s	y	P^s	y	P^s	y	P^s	y	P^s	y
Methanol+Water (523.15K)	0.73	0.23	0.73	0.29	0.76	0.52	0.72	0.42	0.44	0.60
Methanol+n-Hexane (323.15K)	1.54 *	1.37 *	0.91	0.71	0.94	0.77	1.07	0.83	0.99	1.05
Methanol+n-Hexane (333.15K)	0.96	0.93	0.64	0.48	0.66	0.58	0.74	0.55	0.60	0.77
Ethanol+n-Hexane (323.15K)	0.65	0.65	0.62	0.68	0.35	0.27	0.40	0.29	0.40	0.36
Ethanol+n-Heptane (343.15K)	0.74	1.11	1.17	1.07	0.66	1.13	0.68	1.05	0.71	1.09
Ethanol+n-Octane (328.15K)	1.30	0.86	1.66	1.05	0.92	0.63	0.96	0.61	0.93	0.65

Table 5.2 (continued)

Systems (Temperature)	SRK		PR		PT		PRSV		This work	
	P^s	y	P^s	y	P^s	y	P^s	y	P^s	y
n-Propanol+n-Heptane (348.15K)	2.12	1.49	2.11	1.82	2.24	1.66	2.32	1.68	1.67	1.33
n-Propanol+n-Octane (313.15K)	0.91	-	2.34	-	0.74	-	0.73	-	0.89	-
1-Butanol+n-Pentane (303.15K)	2.89	1.24	4.49	1.96	3.33	1.42	0.59	0.29	0.49	0.08
1-Butanol+n-Hexane (298.15K)	4.56	1.48	6.57	2.16	5.08	1.67	0.51	0.37	0.74	0.33
1-Butanol+n-Heptane (323.15K)	1.21	1.80	1.26	3.10	1.21	2.32	1.61	0.87	1.14	0.79
1-Butanol+n-Octane (313.15K)	2.58	-	4.05	-	2.80	-	1.65	-	1.21	-
1-Butanol+n-Decane (373.15K)	2.19	1.01	3.24	1.59	1.53	1.04	0.88	0.96	1.09	1.58
1-Butanol+Toluene (333.31K)	2.39	2.56	3.85	3.53	-	-	0.74	0.88	0.30	0.40
Average	1.77	1.21	2.40	1.52	1.63	1.09	0.97	0.73	0.83	0.75

Table 5.3 Values of binary interaction coefficients of the modified ALS equation obtained by using four different mixing rules for fourteen binary systems

Systems (Temperature)	Mixing rules	k_{ij}			
		k_{ij}	l_{ij}		
		k_{ij}	l_{ij}	m_{ij}	
		k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
Methanol+ Water (523.15K)	Conventional	-0.02846			
	Adachi-Sugie	-0.02229	0.034386		
	SGR	-0.01974	0.035136	0.45953	
	Ext. Wong-Sandler	0.001276	0.72755	5924.7	3734.2
Methanol+ n-Hexane (323.15K)	Conventional	0.089529			
	Adachi-Sugie	0.11879	-0.08599		
	SGR	0.17200	-0.11163	0.80930	
	Ext. Wong-Sandler	0.37814	-1.3445	2883.8	2045.3
Methanol+ n-Hexane (333.15K)	Conventional	0.10109			
	Adachi-Sugie	0.12932	-0.08988		
	SGR	0.17952	-0.11074	0.79003	
	Ext. Wong-Sandler	0.24575	0.32117	6931.9	11514.
Ethanol+ n-Hexane (323.15K)	Conventional	0.047804			
	Adachi-Sugie	0.067407	-0.05325		
	SGR	0.083815	-0.06227	0.65408	
	Ext. Wong-Sandler	-0.41369	-0.45776	5051.0	3992.8
Ethanol+ n-Heptane (343.15K)	Conventional	0.075754			
	Adachi-Sugie	0.084721	-0.06106		
	SGR	0.12820	-0.08350	0.76583	
	Ext. Wong-Sandler	0.055556	-0.80773	3811.0	3395.9

Table 5.3 (continued)

Systems (Temperature)	Mixing rules	k_{ij}			
		k_{ij}	l_{ij}		
		k_{ij}	l_{ij}	m_{ij}	
		k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
Ethanol+ n-Octane (328.15K)	Conventional	0.006134			
	Adachi-Sugie	0.040481	-0.08290		
	SGR	0.64962	-0.07927	0.69381	
	Ext. Wong-Sandler	0.35903	-0.90589	3449.6	2122.9
n-Propanol+ n-Heptane (348.15K)	Conventional	0.084210			
	Adachi-Sugie	0.089920	-0.03318		
	SGR	0.10266	-0.03839	0.68942	
	Ext. Wong-Sandler	0.48381	0.72986	2064.4	7422.1
n-Propanol+ n-Octane (313.15K)	Conventional	0.058815			
	Adachi-Sugie	0.063176	-0.03866		
	SGR	0.087589	-0.05223	0.75193	
	Ext. Wong-Sandler	-0.15006	0.28429	7430.9	8191.6
1-Butanol+ n-Pentane (303.15K)	Conventional	0.043300			
	Adachi-Sugie	0.056856	-0.02289		
	SGR	0.082087	-0.04531	0.79269	
	Ext. Wong-Sandler	-0.71876	0.22332	3654.4	15011.
1-Butanol+ n-Hexane (298.15K)	Conventional	0.050999			
	Adachi-Sugie	0.060460	-0.02657		
	SGR	0.098220	-0.05604	0.85960	
	Ext. Wong-Sandler	0.34482	0.67939	2467.0	8130.7

Table 5.3 (continued)

Systems (Temperature)	Mixing rules	k_{ij}			
		k_{ij}	l_{ij}		
		k_{ij}	l_{ij}	m_{ij}	
		k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
1-Butanol+ n-Heptane (323.15K)	Conventional	0.065898			
	Adachi-Sugie	0.061232	-0.03173		
	SGR	0.072943	-0.03324	0.66550	
	Ext. Wong-Sandler	-0.16561	0.28936	2799.1	6333.9
1-Butanol+ n-Octane (313.15K)	Conventional	0.057234			
	Adachi-Sugie	0.068186	-0.03741		
	SGR	0.084159	-0.04711	0.67159	
	Ext. Wong-Sandler	-0.06558	-0.66714	3265.0	2011.8
1-Butanol+ n-Decane (373.15K)	Conventional	0.081092			
	Adachi-Sugie	0.087819	-0.04920		
	SGR	0.11084	-0.06051	0.68860	
	Ext. Wong-Sandler	0.35586	0.37363	473.16	7572.7
1-Butanol+ Toluene (333.31)	Conventional	0.002188			
	Adachi-Sugie	0.008082	-0.03359		
	SGR	0.008681	-0.03372	0.51025	
	Ext. Wong-Sandler	0.24729	0.70705	2814.7	4881.6

Table 5.4 Values of binary interaction coefficients of four equations obtained by using the extended Wong-Sandler mixing rule for fourteen binary systems

Systems (Temperature)	Equations of state	k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
Methanol+ Water (523.15K)	SRK	-0.10263	-0.041192	9207.6	-5134.7
	PR	-0.093241	-0.36980	3364.4	834.01
	PT	-0.090161	0.13926	-2568.7	8814.9
	PRSV	-0.11122	-0.22753	5152.2	-904.48
Methanol+ n-Hexane (323.15K)	SRK	0.41327	-1.3419	2766.4	1918.8
	PR	0.42616	-1.4540	2624.6	1785.8
	PT	0.42606	-1.4780	2597.6	1792.2
	PRSV	0.44985	-1.5426	2534.2	1665.6
Methanol+ n-Hexane (333.15K)	SRK	0.34613	-1.1231	3097.6	2246.6
	PR	0.37190	-1.2220	2936.4	2061.1
	PT	0.36247	-1.2228	2935.8	2106.7
	PRSV	0.38627	-1.2596	2886.0	1984.7
Ethanol+ n-Hexane (323.15K)	SRK	-0.54649	-0.46467	4575.0	4420.4
	PR	0.029681	-0.69225	3336.4	2599.3
	PT	-0.35308	-0.50606	4148.6	3852.9
	PRSV	-0.23862	-0.53600	3974.4	3529.5
Ethanol+ n-Heptane (343.15K)	SRK	0.024451	0.30006	9972.8	9310.9
	PR	0.21584	-1.0613	3001.9	2542.7
	PT	0.070127	0.32072	9063.9	9140.9
	PRSV	0.079627	0.32117	9027.4	9185.2

Table 5.4 (continued)

Systems (Temperature)	Equations of state	k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
Ethanol+ n-Octane (328.15K)	SRK	0.34746	0.37218	5462.5	7931.9
	PR	0.49536	-0.72960	3485.5	548.91
	PT	0.41768	0.37506	3393.5	7822.5
	PRSV	0.44662	0.37449	2989.0	7904.8
n-Propanol+ n-Heptane (348.15K)	SRK	-1.4178	-0.45343	5413.7	6187.2
	PR	0.032509	0.38072	4141.2	6443.7
	PT	-0.23412	-0.60418	3492.6	3502.7
	PRSV	-0.25807	-0.60429	3568.0	3571.7
n-Propanol+ n-Octane (313.15K)	SRK	0.40030	-0.73968	3166.9	67.568
	PR	-0.39085	-0.34763	4226.4	3041.4
	PT	0.36610	-0.95242	2701.9	683.32
	PRSV	0.18579	-0.93870	2655.5	2170.4
1-Butanol+ n-Pentane (303.15K)	SRK	0.39972	0.70281	1281.7	10012.
	PR	0.42674	0.78022	1101.1	9082.0
	PT	0.39957	0.63108	1258.5	11532.
	PRSV	0.33353	0.71297	1592.9	8389.6
1-Butanol+ n-Hexane (298.15K)	SRK	0.33527	0.59075	2148.4	9979.4
	PR	0.35166	0.75078	1933.6	6625.9
	PT	0.33923	0.72245	2027.3	6869.7
	PRSV	0.30474	0.57490	2371.0	9899.5

Table 5.4 (continued)

Systems (Temperature)	Equations of state	k_{ij}	α_{ij}	Δg_{ij}	Δg_{ji}
1-Butanol+ n-Heptane (323.15K)	SRK	0.52037	0.39294	-2263.5	7639.2
	PR	0.16923	0.27685	-50.001	5048.9
	PT	0.052607	0.23654	735.20	5235.5
	PRSV	-0.36919	-0.59486	3573.7	2542.4
1-Butanol+ n-Octane (313.15K)	SRK	-0.78014	-0.35531	4662.8	3599.6
	PR	-0.95531	0.14449	5053.5	7588.2
	PT	-1.1590	-0.41272	4546.6	4239.7
	PRSV	-0.12649	-0.59484	3592.3	2335.6
1-Butanol+ n-Decane (373.15K)	SRK	0.16009	-0.49424	3979.4	1830.7
	PR	-0.26160	-0.26388	4357.1	4381.4
	PT	0.19911	-0.66032	3541.3	1836.3
	PRSV	0.13170	-0.84890	3197.1	2494.0
1-Butanol+ Toluene (333.31K)	SRK	-0.30207	0.21955	1246.3	7768.7
	PR	-0.82585	0.072986	-893.05	11740.0
	PT	-	-	-	-
	PRSV	-0.19378	0.37983	3343.3	6664.8

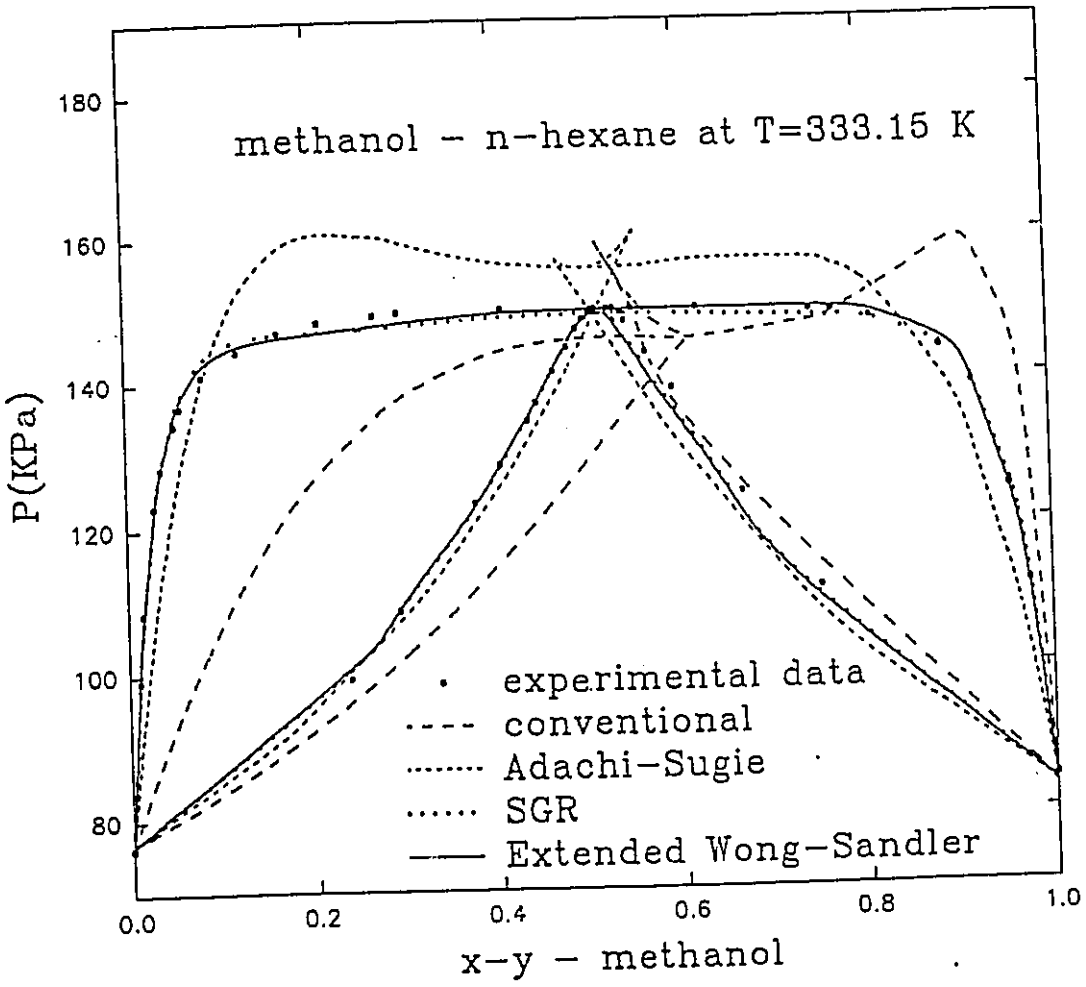


Figure 5.1 A comparison of the calculated VLE values for the methanol +n-hexane system at 333.15 K

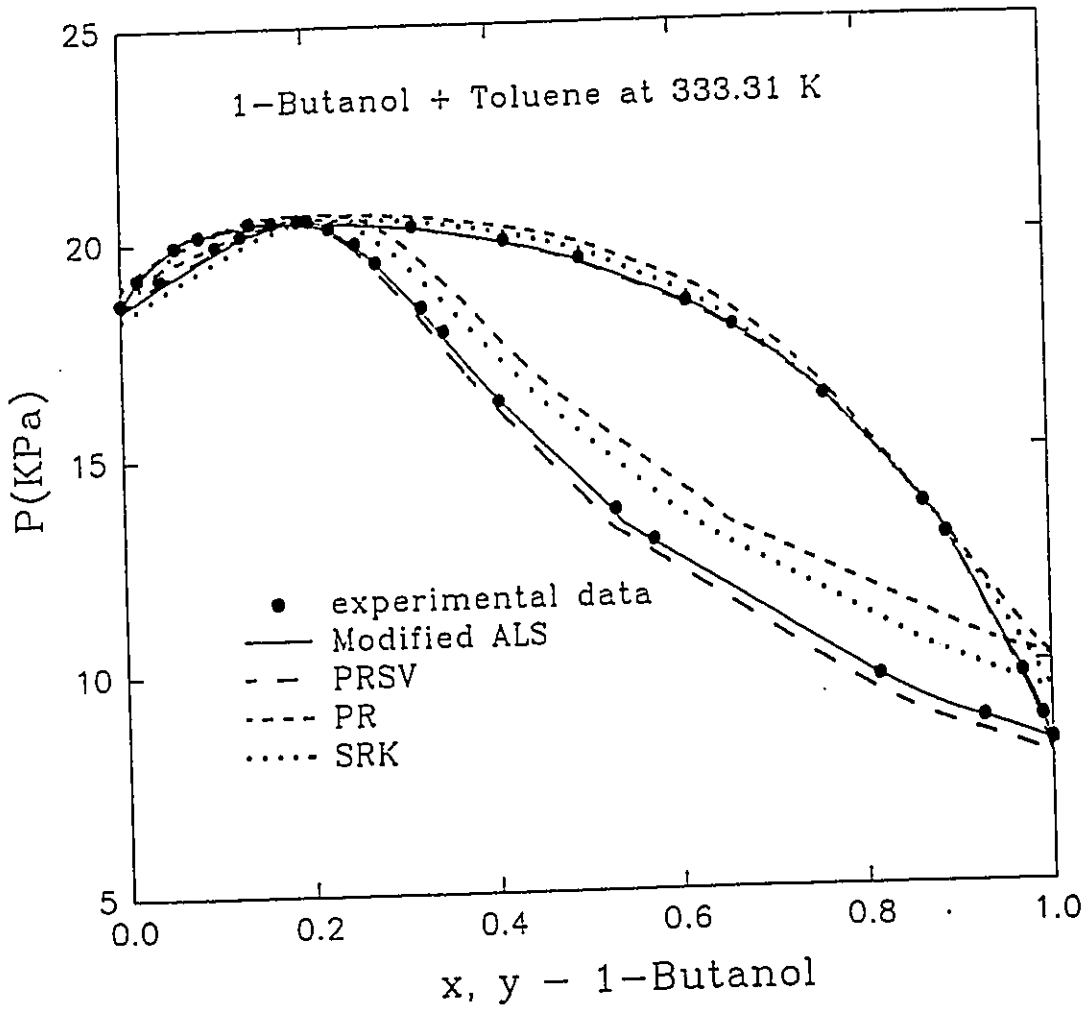


Figure 5.2 A comparison of the calculated VLE values for the 1-butanol + toluene system at 333.31 K

5.2.2 Ternary Systems

The VLE of six ternary systems were predicted in this work by using the modified ALS equation with the conventional, the Adachi-Sugie, the SGR, and the extended Wong-Sandler mixing rules.

For the multi-parameter mixing rules, such as the SGR and the extended Wong-Sandler mixing rules, there is an uncertainty in the prediction of ternary properties from binary data since multi-minimum points of the object function exist. Different sets of binary interaction coefficients can be obtained to yield almost same results for binary systems, but these binary interaction coefficients are not necessarily good for the prediction of the properties of ternary systems. It is found that for the SGR mixing rule, the parameter m_{ij} should be kept in the range of 0.15-0.85 and for the extended Wong-Sandler mixing rule, multi-sets of data for a binary system at different temperatures would be better represented simultaneously by using the same Δg_{ij} and Δg_{ji} values.

The overall calculated results for the six ternary systems and the 18 constituent binary systems are listed in Table 5.5 and 5.6, respectively. The individual results for each ternary system are listed in Tables 5.7 to 5.12. The results indicate that for the non-polar systems, all mixing rules give reasonable results for both the binary and the ternary systems tested. however, for the asymmetric systems, such as alcohol-alkane system, only the SGR and the extended Wong-Sandler mixing rules yield good results. The

extended Wong-Sandler mixing rule gives somewhat better results than the SGR mixing rule.

Table 5.5 Overall results for six ternary systems

Mixing rules	$\Delta P^s\%$	$\Delta y \times 100$
Conventional	4.99	3.15
Adachi-Sugie	2.81	1.56
SGR	2.11	1.56
Extended Wong-Sandler	1.35	1.58

Table 5.6 Overall results for the eighteen constituent binary systems

Mixing rules	$\Delta P^s\%$	$\Delta y \times 100$
Conventional	3.98	3.07
Adachi-Sugie	1.54	1.54
SGR	0.68	0.90
Extended Wong-Sandler	0.67	0.89

Table 5.7 A comparison of four mixing rules for calculating VLE values for systems containing acetone, methanol, and water at 373.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} k_{ij} k_{ij} k_{ij}	 l_{ij} l_{ij} α_{ij}	 m_{ij} Δg_{ij}	 Δg_{ji}	Deviations P^s	 y
Acetone + Methanol (373.15K)	Conventional	0.02055	-	-	-	1.24	1.15
	Adachi-Sugie	0.02056	0.00157	-	-	1.21	1.21
	SGR	0.01906	0.00261	0.78814	-	1.16	1.22
	E-W-S	-0.62242	0.37244	4581.9	5190.9	1.10	1.35
Acetone + Water (373.15K)	Conventional	-0.11214	-	-	-	8.46	4.13
	Adachi-Sugie	-0.07669	0.05479	-	-	1.85	0.70
	SGR	-0.08675	0.04900	0.59960	-	1.51	0.50
	E-W-S	0.16913	0.42203	3530.0	6150.4	1.57	0.45
Methanol + Water (373.15K)	Conventional	-0.08534	-	-	-	1.04	1.08
	Adachi-Sugie	-0.08546	-0.0003	-	-	1.03	1.09
	SGR	-0.08677	-0.0021	0.30440	-	0.99	1.12
	E-W-S	0.001952	0.27033	-2112.3	6319.8	1.00	1.02
Acetone + Methanol + Water (373.15K)	Conventional	Same as above				4.97	3.52
	Adachi-Sugie					1.54	1.73
	SGR					2.03	1.97
	E-W-S					1.30	1.93

Table 5.8 A comparison of four mixing rules for calculating VLE values for systems containing acetone, methanol, and 2-propanol at 328.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} k_{ij} k_{ij} k_{ij}	l_{ij} l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}	Deviations P^s	y
Acetone + Methanol (328.15K)	Conventional	0.025287	-	-	-	0.34	0.60
	Adachi-Sugie	0.025294	0.00004	-	-	0.34	0.60
	SGR	0.025335	0.00005	0.5281	-	0.34	0.60
	E-W-S	-0.62242	0.32831	4581.9	5190.9	0.34	0.54
Acetone + 2-Propanol (328.15K)	Conventional	0.028342	-	-	-	1.21	0.39
	Adachi-Sugie	0.027900	-0.0042	-	-	0.99	0.50
	SGR	0.022210	-0.0090	0.1680	-	0.69	0.53
	E-W-S	-0.03568	-0.1415	1513.2	1151.9	1.04	0.41
Methanol + 2-Propanol (328.15K)	Conventional	0.002408	-	-	-	0.99	0.58
	Adachi-Sugie	0.002444	0.00608	-	-	0.70	0.43
	SGR	0.004105	0.00644	0.3574	-	0.67	0.44
	E-W-S	-0.03772	0.76712	2486.5	-1002.5	0.67	0.45
Acetone + Methanol + 2-Propanol (328.15K)	Conventional	Same as above				2.98	1.55
	Adachi-Sugie					0.75	0.67
	SGR					0.59	0.68
	E-W-S					0.97	0.90

Table 5.9 A comparison of four mixing rules for calculating VLE values for systems containing n-hexane, ethanol, and benzene at 328.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} / k_{ij} / k_{ij} / k_{ij}	l_{ij} / l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}	Deviations P^s	Deviations y
n-Hexane + Ethanol (328.15K)	Conventional	0.05537	-	-	-	9.78	5.40
	Adachi-Sugie	0.07298	0.05506	-	-	1.81	3.03
	SGR	0.10021	0.07106	0.2842	-	1.11	2.26
	E-W-S	-0.41369	-0.5150	3962.3	4963.9	1.09	2.06
Benzene + n-Hexane (328.15K)	Conventional	0.00933	-	-	-	0.18	0.27
	Adachi-Sugie	0.00952	-0.0001	-	-	0.21	0.23
	SGR	0.009268	-0.0011	0.3661	-	0.21	0.22
	E-W-S	0.15163	0.20000	3191.9	-1849.3	0.20	0.18
Ethanol + Benzene (328.15K)	Conventional	0.07164	-	-	-	3.09	2.83
	Adachi-Sugie	0.07277	-0.0254	-	-	1.05	1.26
	SGR	-0.0902	-0.0331	0.7850	-	0.55	0.67
	E-W-S	0.27996	-1.5060	2303.8	1049.9	0.47	0.66
n-Hexane + Ethanol + Benzene (328.15K)	Conventional	Same as above				7.70	3.06
	Adachi-Sugie					3.87	2.16
	SGR					2.51	2.01
	E-W-S					2.73	2.06

Table 5.10 A comparison of four mixing rules for calculating VLE values for systems containing ethanol, acetonitrile and benzene at 318.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} k_{ij} l_{ij} k_{ij} l_{ij} m_{ij} k_{ij} α_{ij} Δg_{ij} Δg_{ji}	Deviations P^s y
Ethanol + Acetonitrile (293.15K)	Conventional	-0.0276 - - -	1.12 2.28
	Adachi-Sugie	-0.0274 0.00332 - -	1.04 2.26
	SGR	-0.0281 0.00396 0.6074 -	0.97 2.27
	E-W-S	0.00367 0.36147 4539.1 2754.6	0.66 2.37
Ethanol + Benzene (318.15K)	Conventional	0.05944 - - -	2.76 2.86
	Adachi-Sugie	0.06006 -0.0205 - -	1.05 1.07
	SGR	0.07349 -0.0273 0.7733 -	0.21 0.72
	E-W-S	0.28741 -1.4466 2303.8 1049.9	0.15 0.75
Acetonitrile + Benzene (318.15K)	Conventional	0.05387 - - -	0.50 0.73
	Adachi-Sugie	0.05410 0.00511 - -	0.23 0.40
	SGR	0.05580 0.00557 0.3261 -	0.20 0.37
	E-W-S	0.05305 0.49547 1848.0 1354.6	0.21 0.34
Ethanol + Acetonitrile + Benzene (328.15K)	Conventional	Same as above	5.46 1.78
	Adachi-Sugie		5.42 1.87
	SGR		4.95 1.72
	E-W-S		0.74 0.86

Table 5.11 A comparison of four mixing rules for calculating VLE values for systems containing methanol, carbon tetrachloride and benzene at 308.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} k_{ij} k_{ij} k_{ij}	 l_{ij} l_{ij} α_{ij}	 m_{ij} Δg_{ij}	 Δg_{ji}	Deviations P^s	 y
Methanol + Carbon Tetrachloride (308.15K)	Conventional	0.10711	-	-	-	9.51	9.32
	Adachi-Sugie	0.11356	-0.0673	-	-	6.34	5.16
	SGR	0.15700	-0.0751	0.8403	-	0.91	1.18
	E-W-S	0.42210	-1.8146	2205.8	1160.9	0.80	1.27
Methanol + Benzene (308.15K)	Conventional	0.10046	-	-	-	6.46	6.02
	Adachi-Sugie	0.10072	-0.0382	-	-	2.67	3.23
	SGR	0.12120	-0.0404	0.8019	-	0.70	1.57
	E-W-S	-0.09959	-0.7256	3419.5	2638.8	0.77	1.55
Carbon tetrachloride + Benzene (313.15K)	Conventional	0.00821	-	-		0.66	0.56
	Adachi-Sugie	0.00810	0.00511	-	-	0.19	0.33
	SGR	0.01137	0.00659	0.2352	-	0.16	0.26
	E-W-S	-0.12158	1.8367	1511.4	711.87	0.14	0.30
Methanol +Carbon tetrachloride + Benzene (308.15K)	Conventional	Same as above				2.97	4.01
	Adachi-Sugie					2.03	1.90
	SGR					1.73	1.83
	E-W-S					0.71	2.20

Table 5.12 A comparison of four mixing rules for calculating VLE values for systems containing methanol, carbon tetrachloride and benzene at 328.15K with the modified ALS equation of state in terms of AAPD for P^s and AAD×100 for y.

Systems	Mixing rules	k_{ij} k_{ij} k_{ij} k_{ij}	l_{ij} l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}	Deviations P^s	y
Methanol + Carbon Tetrachloride (328.15K)	Conventional	0.14517	-	-	-	15.3	10.5
	Adachi-Sugie	0.13072	-0.0736	-	-	4.86	3.81
	SGR	0.16982	-0.0726	0.8219	-	1.12	0.89
	E-W-S	0.42930	-1.8240	2205.8	1160.9	1.01	0.92
Methanol + Benzene (328.15K)	Conventional	0.11926	-	-	-	8.07	5.98
	Adachi-Sugie	0.11678	-0.0436	-	-	2.07	1.98
	SGR	0.13561	-0.0445	0.7597	-	0.35	0.88
	E-W-S	-0.0493	-0.7308	3419.5	2638.8	0.37	0.77
Carbon tetrachloride + Benzene (323.15K)	Conventional	0.00667	-	-	-	0.86	0.56
	Adachi-Sugie	0.00693	0.00553	-	-	0.33	0.45
	SGR	0.01015	0.00653	0.2356	-	0.43	0.50
	E-W-S	-0.13092	1.8367	1511.4	711.87	0.45	0.56
Methanol +Carbon tetrachloride + Benzene (328.15K)	Conventional	Same as above				5.83	5.00
	Adachi-Sugie					3.22	1.04
	SGR					0.87	1.15
	E-W-S					1.63	1.53

5.3 Simultaneous Representation of VLE and Volumes

For evaluating the capability of the extended Wong-Sandler mixing rule with the modified ALS equation, VLE and liquid volume data for three binary systems were represented by using the modified ALS equation with three additional mixing rules (conventional, Adachi-Sugie, and SGR). In addition, four other EOS (SRK, PR, PT and PRSV) were also used with the extended Wong-Sandler mixing rule for the purpose of comparison. The three binary systems include a non-polar system (hydrogen sulfide and n-pentane), an asymmetric system (ethane and methanol) and a polar system (ammonia and water). All data sources and the binary interaction coefficients obtained in this work are listed in Appendix C.

5.3.1 Representation of VLE and Liquid Volumes of the Hydrogen Sulfide + n-Pentane System

The values of VLE, saturated and compressed liquid volumes for the system reported by Sage and Lacey (1955) were calculated. The binary interaction coefficients were obtained by simultaneously fitting the VLE and saturated liquid volume values. The results are listed in Tables 5.13 to 5.15. The calculated saturated liquid volumes are also shown in Figure 5.3.

The results indicate that the modified ALS equation with the extended Wong - Sandler mixing rule gives better results. All the equations with the extended Wong-Sandler mixing rules give reasonable results. The results shown in Figure 5.3 indicate that for this system, the curve of liquid volumes is close to a straight line, so that the volumes of the mixture are close to the volumes of an ideal solution and the differences between equations are mainly due to the calculated liquid volumes of pure fluids.

Among the different mixing rules, the Wong-Sandler mixing rule gives much better results than other mixing rules. The reason is mainly due to that the simultaneous fitting of VLE and liquid volume values was used in the calculation. Other mixing rules cannot represent the VLE data as good as the extended Wong-Sandler mixing rule for this system, resulting in their poor representations of liquid volumes.

Table 5.13 A comparison of the calculated P^s and y values for the hydrogen sulphide + n-pentane system

T (K)	SRK		PR		PT		PRSV		Modified ALS							
	Extended W-S								Conventional		Adachi-Sugie		SGR		Extended W-S	
	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$	ΔP^s%	$\Delta y \times 100$
277.59	2.65	0.29	4.35	0.26	2.41	0.20	2.01	0.23	2.36	0.18	1.28	0.30	0.90	0.30	1.96	0.21
310.93	0.81	0.93	1.02	0.59	0.69	0.82	1.09	0.68	0.59	0.56	0.27	0.58	0.26	0.59	0.30	0.71
344.26	1.17	1.96	0.84	1.70	1.03	1.87	0.61	1.76	0.78	1.55	0.68	1.61	0.84	1.59	0.51	1.68
377.59	2.49	1.76	1.39	0.82	1.63	1.09	1.15	0.74	6.64	2.20	6.30	2.15	2.98	2.15	1.20	0.89
410.93	1.74	2.11	0.41	0.52	0.55	0.87	0.63	0.54	3.48	13.46	3.48	13.46	2.96	10.62	0.95	0.97
Overall	1.77	1.14	1.60	0.78	1.26	0.97	1.10	0.79	2.77	3.59	2.40	3.62	1.59	3.05	0.98	0.89

Table 5.14 A comparison of the calculated V_L^s and V_V^s values for the hydrogen sulphide + n-pentane system

T (K)	SRK		PR		PT		PRSV		Modified ALS							
	Extended W-S								conventional		Adachi-Sugie		SGR		Extended W-S	
	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$
277.59	4.99	1.66	2.20	1.18	2.04	1.31	1.96	1.16	2.07	1.46	2.05	1.44	2.05	1.43	1.42	1.52
310.93	4.60	0.98	2.02	0.96	2.22	0.82	1.78	1.00	1.65	0.80	1.64	0.82	1.63	0.80	0.84	0.79
344.26	5.47	1.54	2.56	1.57	2.81	1.51	2.18	1.66	2.40	1.61	2.36	1.72	2.33	1.72	0.36	1.04
377.59	4.41	2.72	2.14	4.65	2.28	3.68	1.79	4.66	5.08	12.38	5.13	11.99	6.95	11.63	1.79	4.54
410.93	8.00	8.07	1.48	1.52	1.28	2.66	1.65	1.46	6.21	32.26	6.21	32.26	7.43	25.31	0.75	2.18
overall	5.49	2.99	2.08	1.98	2.13	2.00	1.87	1.99	3.48	9.70	3.48	9.65	4.08	8.18	1.03	2.01

Table 5.15 A comparison of the calculated compressed liquid volumes for the hydrogen sulphide + n-pentane system

T (K)	SRK	PR	PT	PRSV	Modified ALS			
	Extended W-S				conventional	Adachi-Sugie	SGR	Extended W-S
277.59	3.19	2.13	1.95	1.68	2.98	2.95	2.93	1.52
310.93	3.22	3.22	3.09	2.97	1.83	1.83	1.82	1.01
344.26	3.36	5.21	5.09	4.99	1.46	1.45	1.43	0.63
377.59	4.12	7.13	6.30	7.04	2.50	2.58	3.22	3.09
410.93	5.17	7.48	6.85	7.75	3.82	3.82	4.52	5.20
Overall	3.81	5.04	4.66	4.89	2.52	2.53	2.79	2.29

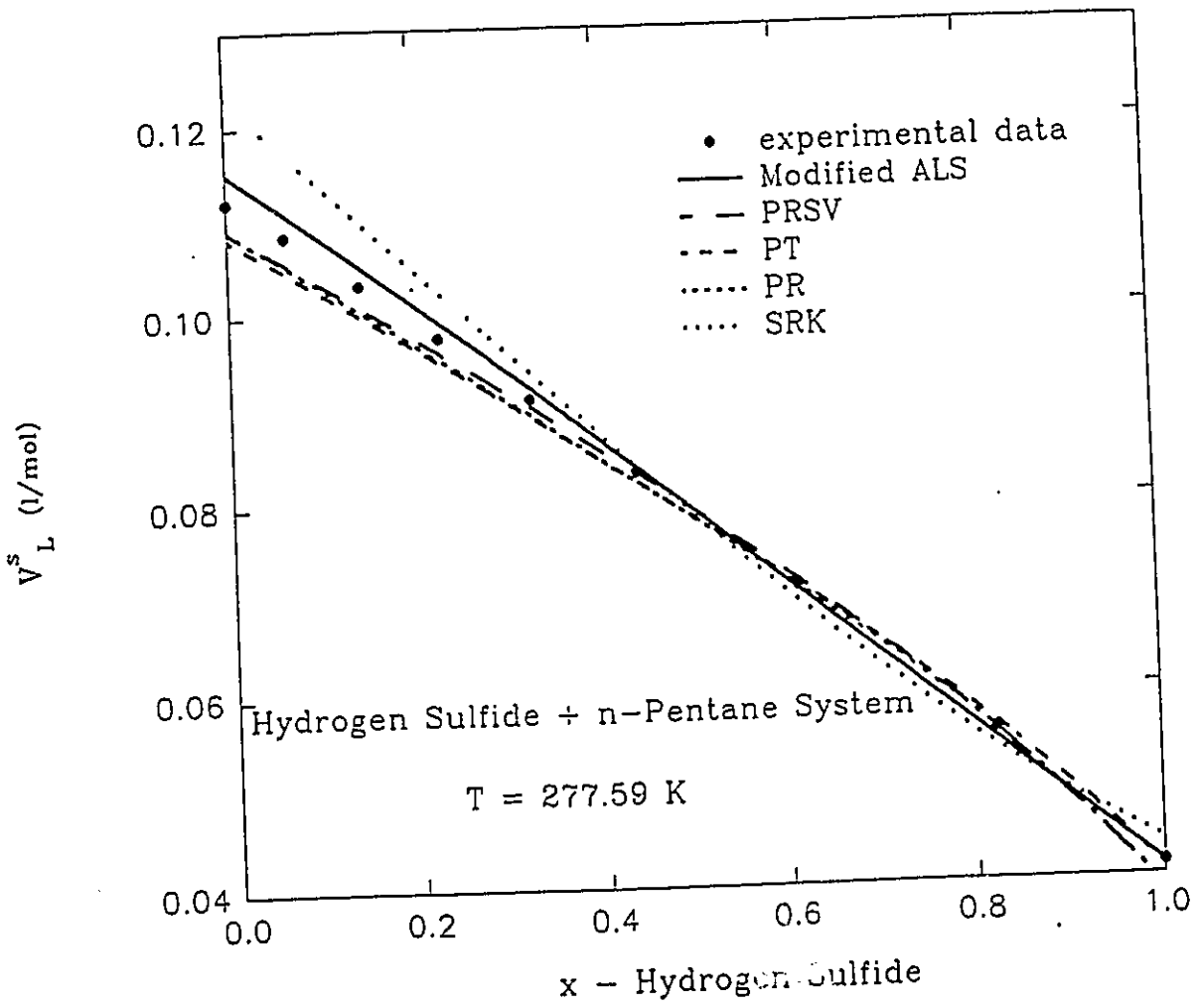


Figure 5.3 Representation of saturated liquid volumes of hydrogen sulfide - n-pentane system at 277.59 K

5.3.2 Representation of VLE, Saturated Liquid and Vapor Volumes of the Ethane + Methanol System

The VLE and saturated liquid and vapor volume values reported by Ma and Kohn (1964) were represented by using the same five equations and the four mixing rules. The results listed in Table 5.16 indicate that the modified ALS equation gives better results in the representation of saturated liquid volumes for this system. But it was found that the predictions of the saturated vapor volumes were much off, and the deviations are generally more than 10% for all the equations and mixing rules studied.

Table 5.16 A comparison of the calculated values of P^s, y and V_L^s for the ethane + methanol system

Equation	Mixing Rule	Dev.	323.15 K	348.15 K	372.15 K	overall
SRK	Extended W-S	$\Delta P^s\%$	1.29	0.99	2.39	1.56
		$\Delta y*100$	2.15	2.89	7.38	4.14
		$\Delta V_L^s\%$	17.92	19.37	22.73	20.01
PR	Extended W-S	$\Delta P^s\%$	1.21	1.23	2.08	1.51
		$\Delta y*100$	2.10	2.79	7.56	4.15
		$\Delta V_L^s\%$	7.66	7.40	8.54	7.87
PT	Extended W-S	$\Delta P^s\%$	1.32	0.79	1.44	1.18
		$\Delta y*100$	3.42	2.56	3.63	3.20
		$\Delta V_L^s\%$	8.17	2.11	1.49	3.92
PRSV	Extended W-S	$\Delta P^s\%$	1.78	1.15	1.77	1.57
		$\Delta y*100$	2.08	2.80	7.63	4.17
		$\Delta V_L^s\%$	7.71	7.39	8.46	7.85
Modified ALS	conventional	$\Delta P^s\%$	*	5.19	2.09	3.64
		$\Delta y*100$	*	5.33	4.37	4.85
		$\Delta V_L^s\%$	*	1.30	0.86	1.08
Modified ALS	Adachi-Sugie	$\Delta P^s\%$	*	6.27	2.33	4.30
		$\Delta y*100$	*	3.79	4.23	4.01
		$\Delta V_L^s\%$	*	1.27	0.84	1.06
Modified ALS	SGR	$\Delta P^s\%$	5.34	1.45	1.79	2.86
		$\Delta y*100$	2.09	2.08	3.95	2.71
		$\Delta V_L^s\%$	1.33	1.28	0.85	1.15
Modified ALS	Extended W-S	$\Delta P^s\%$	2.91	1.07	1.53	1.84
		$\Delta y*100$	3.27	2.78	4.18	3.41
		$\Delta V_L^s\%$	4.90	2.38	0.78	2.69

* no convergence in the calculation

5.3.3 Representation of VLE and Saturated Liquid Volumes of the Ammonia + Water System

Ammonia + water mixtures are important in the refrigeration process. The VLE (Scatchard et al., 1947) and saturated liquid volume (ASHRAE handbook, 1982) data for 277.59, 288.71, 299.82, 310.93, and 322.04 K were represented in this section. The results are listed in Table 5.17 and 5.18 and also shown in Figure 5.4 to 5.7. The results indicate that the modified ALS and the PT equations give better results for the representation of saturated liquid volumes, which is due to the better representation of the saturated liquid volumes of pure components. The SGR mixing rule also gives good results for the representation of VLE data for this system.

Table 5.17 A comparison of the calculated values of vapor pressures and vapor phase compositions for the ammonia + water system

T (K)	SRK		PR		PT		PRSV		Modified ALS							
	Extended W-S								conventional		Adachi-Sugie		SGR		Extended W-S	
	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100	ΔP'%	Δy*100
277.59	7.10	0.53	6.07	0.27	5.54	0.19	4.19	0.16	11.10	0.21	6.69	0.19	4.02	0.10	6.86	0.16
288.71	6.36	0.43	5.27	0.20	5.28	0.20	3.75	0.21	9.51	0.20	6.09	0.21	3.71	0.12	6.22	0.18
299.82	6.01	0.62	4.86	0.27	5.00	0.19	3.42	0.21	8.30	0.21	5.62	0.21	3.49	0.12	5.79	0.18
310.93	5.30	0.65	4.32	0.34	4.56	0.20	3.00	0.21	7.59	0.22	5.11	0.22	3.08	0.14	5.36	0.19
322.04	4.61	0.68	3.69	0.36	4.16	0.21	2.60	0.22	7.14	0.23	4.65	0.25	2.60	0.15	5.11	0.21
overall	5.88	0.58	4.84	0.29	4.91	0.20	3.39	0.20	8.73	0.21	5.63	0.22	3.38	0.13	5.87	0.18

Table 5.18 A comparison of the calculated saturated liquid volumes of the ammonia + water system in terms of AAPD

T (K)	SRK	PR	PT	PRSV	Modified ALS			
	Extended W-S				conventional	Adachi-Sugie	SGR	Extended W-S
277.59	10.72	5.61	1.43	5.64	2.34	2.42	2.49	1.45
288.71	10.91	5.76	1.37	5.79	2.12	2.19	2.25	1.28
299.82	11.12	5.89	1.34	5.91	1.75	1.82	1.89	1.21
310.93	11.32	6.02	1.25	6.05	1.48	1.49	1.52	1.12
322.04	11.46	6.10	1.20	6.72	1.23	1.19	1.18	0.54
overall	11.11	5.88	1.32	6.02	1.78	1.82	1.87	1.12

5.4 Simultaneous Representation of VLE and Excess Enthalpies

Six binary systems including symmetric and asymmetric systems were represented by using the modified ALS equations with different mixing rules. Four other equations with the extended Wong-Sandler mixing rule were also applied for the purpose of comparison. All the binary interaction coefficients are listed in Appendix C.

The results listed in Tables 5.19 and 5.20 indicate that for the non-polar systems, such as carbon tetrachloride + n-heptane, benzene + cyclohexane and benzene + n-heptane systems, every equation with every mixing rule gives reasonable results and no significant differences were found. However, for the polar systems, such as n-hexane +ethanol, ethanol + cyclohexane and 1-butanol + n-heptane systems, only the extended Wong-Sandler mixing rule gives better results. Different equations give different results for different systems, and no significant difference was found. However, the PRSV, the PR and the modified ALS equations give better overall results than the SRK and the PT equations.

Table 5.19 A comparison of the calculated values of P^s and y for six binary systems

SYSTEMS	SRK		PR		PT		PRSV		Modified ALS							
	Extended W-S								conventional		Adachi-Sugie		SGR		Extended W-S	
	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100	ΔP%	Δy*100
1	0.32	0.25	1.39	0.89	1.19	0.80	0.35	0.27	2.13	0.50	2.12	0.56	2.09	0.50	0.93	0.52
2	0.11	0.08	1.84	1.34	1.33	0.98	0.61	0.62	7.42	1.97	7.41	1.97	7.41	1.97	0.81	0.64
3	1.16	---	1.98	---	2.32	---	0.75	---	5.49	---	5.42	---	5.42	---	0.72	---
4	19.30	5.21	2.84	1.28	11.49	5.67	3.35	1.42	55.22	27.18	52.21	25.84	51.65	26.27	5.97	2.98
5	11.26	7.37	2.24	1.42	9.16	6.77	2.59	1.83	47.45	23.08	46.69	23.41	46.32	23.99	1.79	1.32
6	4.99	---	7.25	---	4.94	---	4.38	---	42.35	---	38.38	---	40.29	---	4.50	---
overall	6.19	3.23	2.92	1.23	5.07	3.56	2.01	1.04	26.68	13.18	25.37	12.95	25.53	13.18	2.45	1.37

1 - Carbon Tetrachloride - n-Heptane
2 - Benzene - Cyclohexane
3 - Benzene - n-Heptane
4 - n-Hexane - Ethanol
5 - Ethanol - Cyclohexane
6 - 1-Butanol - n-Heptane

Table 5.20 A comparison of the calculated excess enthalpies of six binary systems

SYSTEMS	SRK	PR	PT	PRSV	Modified ALS			
	Extended W-S				conventional	Adachi-Sugie	SGR	Extended W-S
	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$	$\Delta H^E\%$
1	0.23	0.22	0.93	0.22	2.28	0.66	0.21	0.22
2	0.62	0.63	0.92	0.61	1.28	1.08	1.08	0.62
3	0.25	0.21	0.33	0.17	1.16	1.16	1.16	0.17
4	16.12	1.31	9.04	1.70	47.37	5.76	2.62	1.65
5	10.81	1.13	10.45	1.40	44.40	12.04	2.73	2.16
6	3.03	7.87	3.98	7.30	45.30	28.60	5.40	7.64
OVERALL	5.18	1.90	4.28	1.90	23.63	8.22	2.20	2.08

1 - Carbon Tetrachloride - n-Heptane
2 - Benzene - Cyclohexane
3 - Benzene - n-Heptane
4 - n-Hexane - Ethanol
5 - Ethanol - Cyclohexane
6 - 1-Butanol - n-Heptane

5.5 Concluding Remarks

The Wong-Sandler mixing rule was successfully extended for the general cubic equation so that it is applicable for many cubic equations.

VLE, volume and excess enthalpy values were represented by using the extended Wong-Sandler mixing rule with five equations to establish its validity. For comparison, the same data were represented by using the modified ALS equation with three additional mixing rules (conventional, Adachi - Sugie and SGR mixing rules).

The results of the representation of VLE data of binary and ternary systems indicate that the modified ALS equation with the extended Wong-Sandler mixing rule gives better overall results than other equations and mixing rules.

The results of simultaneous representation of VLE and volume data also show that the modified ALS equation with the extended Wong-Sandler mixing rule gives better results than other equations and mixing rules.

The results for simultaneous representation of VLE and excess enthalpy data indicate that the outcomes from the modified ALS equation with the extended Wong-Sandler mixing rule are as good as those given by the PRSV equation with the same mixing rule, and better than those from other equations and mixing rules studied.

Chapter 6

Application of the Modified ALS Equation to Electrolyte Solutions

Historically, thermodynamic properties of electrolyte solutions were calculated by using activity coefficient models:

$$\ln\gamma_i = f(T, x_i) \tag{6.1}$$

In general, by using activity coefficient models, vapor-liquid equilibrium values can be represented more accurately than using equations of state. But activity coefficient models have their drawbacks:

(1). They cannot be used to simultaneously calculate the VLE, the volumetric, and the

energy properties.

(2). They are not recommended to be used at high pressure.

(3). Usually they are only used for the liquid phase, and an equation of state is needed for the vapor phase. Therefore, there is a discontinuity between the calculation of thermodynamic properties for the liquid phase and that for the vapor phase.

The modified ALS equation has the capability to represent VLE behavior for pure substances and mixtures with high precision. The purpose of this work is to apply this equation to electrolyte solutions. The focus is placed on systems with a single completely dissociated electrolyte in a single or multi-solvents.

The parameters in the modified ALS equation for non-electrolyte fluids are related to the critical properties of pure components. For ionic species, the critical properties are not available. In the literature, the equation parameters of ionic species are often related to the ionic parameters, such as the ionic diameter σ and the polarizability α (e.g. Zuo and Guo, 1991; Aasberg et al., 1991). In this work, an analysis of the parameter $\mathbf{b}_1$ was made to ensure its determination. The computer simulation results of the hard core Lennard-Jones fluid were used to determine the parameter $\mathbf{b}_1$ for ionic species.

6.1 Analysis of the Parameter b_1

A cubic equation expressed in terms of P often can be divided into a repulsion term P_{rep} and an attractive term P_{att}:

$$P = P_{rep} + P_{att} \tag{6.2}$$

The first term represents the effect of the repulsive forces between molecules on pressure and the latter the effect of the attractive forces. Three different repulsion terms were investigated:

(1). van der Waals (VDW) (1873)

$$P_{rep} = \frac{RT}{V-b} = \frac{RT}{V(1-4y)} \tag{6.3}$$

where b corresponds to b_1 of the ALS equation.

Although the repulsion term was proposed by van der Waals over a hundred years ago, it is still the most popular repulsion term used in cubic equations of state because of its simple form.

(2). Carnahan-Starling (CS)(1969):

$$P_{rep} = \frac{RT}{V}\frac{(1+y+y^2-y^3)}{(1-y)^3} \tag{6.4}$$

The CS term has a strong theoretical basis. It can well represent computer simulation results for the hard sphere fluid.

(3). CCOR (Lin et al., 1983):

$$P_{rep} = \frac{RT}{V}\frac{(1+3.08y)}{(1-1.68y)} \tag{6.5}$$

The CCOR term was developed to simplify the CS term.

In the above equations:

$$y = \frac{b}{4V} \tag{6.6}$$

and

$$b = \Omega_b RT_c/P_c \tag{6.7}$$

For the purpose of determining Ω_b values, a general van der Waals type attractive term was used:

$$P_{att} = -\frac{a}{V^2+ubV+wb^2} \tag{6.8}$$

The PVT data of argon (Ar) (Argus et al., 1971), carbon dioxide (CO_2) (Argus et al., 1973), and methane (CH_4) (Argus et al., 1976) were arbitrarily selected in the investigation. By fitting these data, AAPD of P_{att} (ΔP_{att}%) for different Ω_b values were

obtained at a given temperature as shown in Figures 6.1 to 6.3. An optimized Ω_b value can be obtained from a Ω_b vs $\Delta P_{att}\%$ plot. The curves shown in Figures 6.1 to 6.3 indicate that the optimized Ω_b values, which correspond to the minimum $\Delta P_{att}\%$ values, obtained from the Carnahan-Starling and the CCOR terms are much higher than that obtained from the VDW term.

Zuo and Guo (1991) used the following expression for the parameter **b** in the VDW repulsion term for ionic species

$$b=(2/3)\pi N_a\sigma^3 \tag{6.9}$$

Eqn. (6.9) is the same as that used in the Carnahan-Starling and the CCOR terms (Sower and Sandler, 1991a, 1991b). From the above analysis, the value of **b** in the VDW term should be smaller than and about one half of that in the Carnahan-Starling and CCOR equations. The following expression was proposed in this work for the determination of the value of parameter **b**:

$$b=\lambda(2/3)\pi N_a\sigma^3 \tag{6.10}$$

For the determination of the value of λ, the hard core Lennard-Jones fluid was simulated by using the Monte Carlo method.

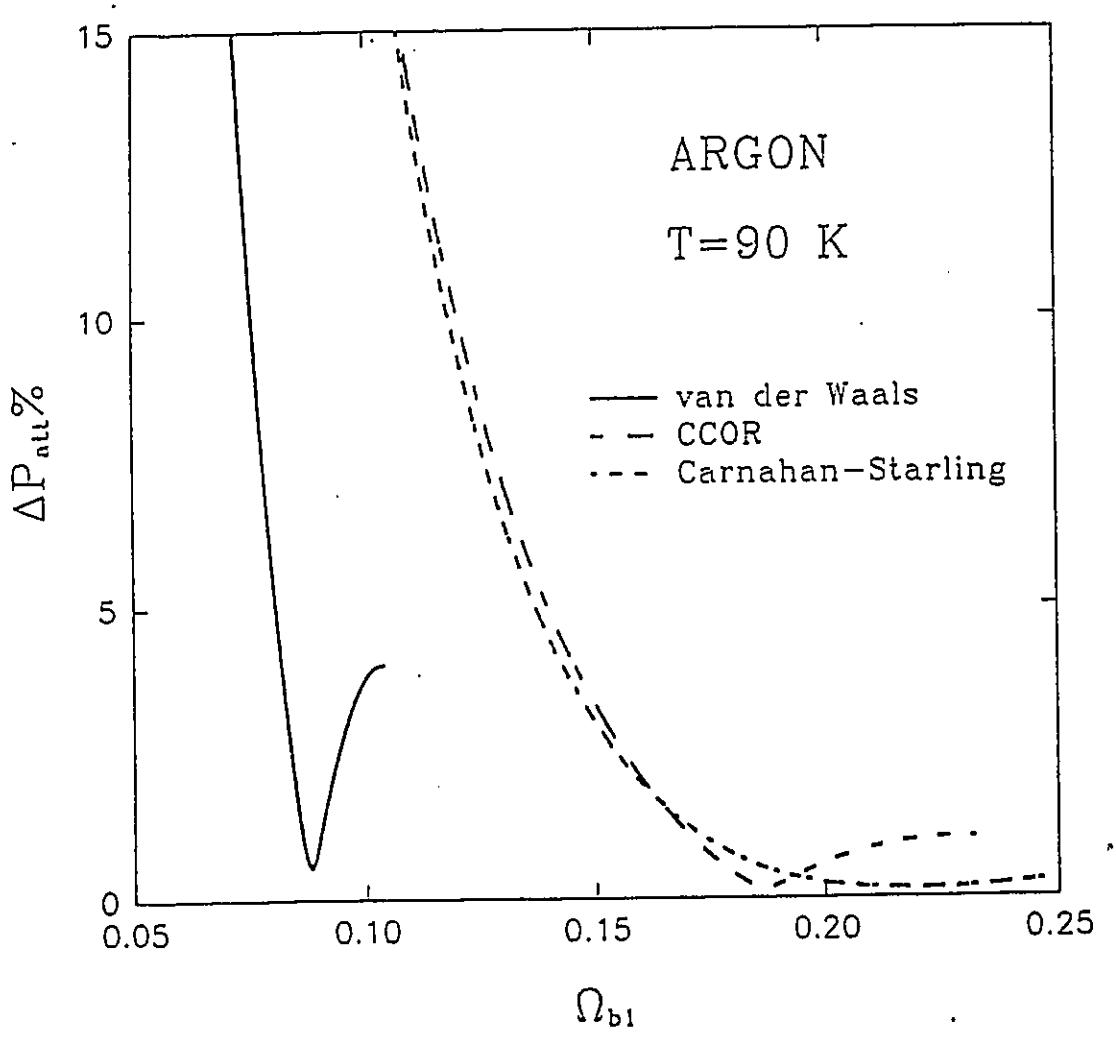


Figure 6.1 Determination of optimum Ω_{b1} values for argon

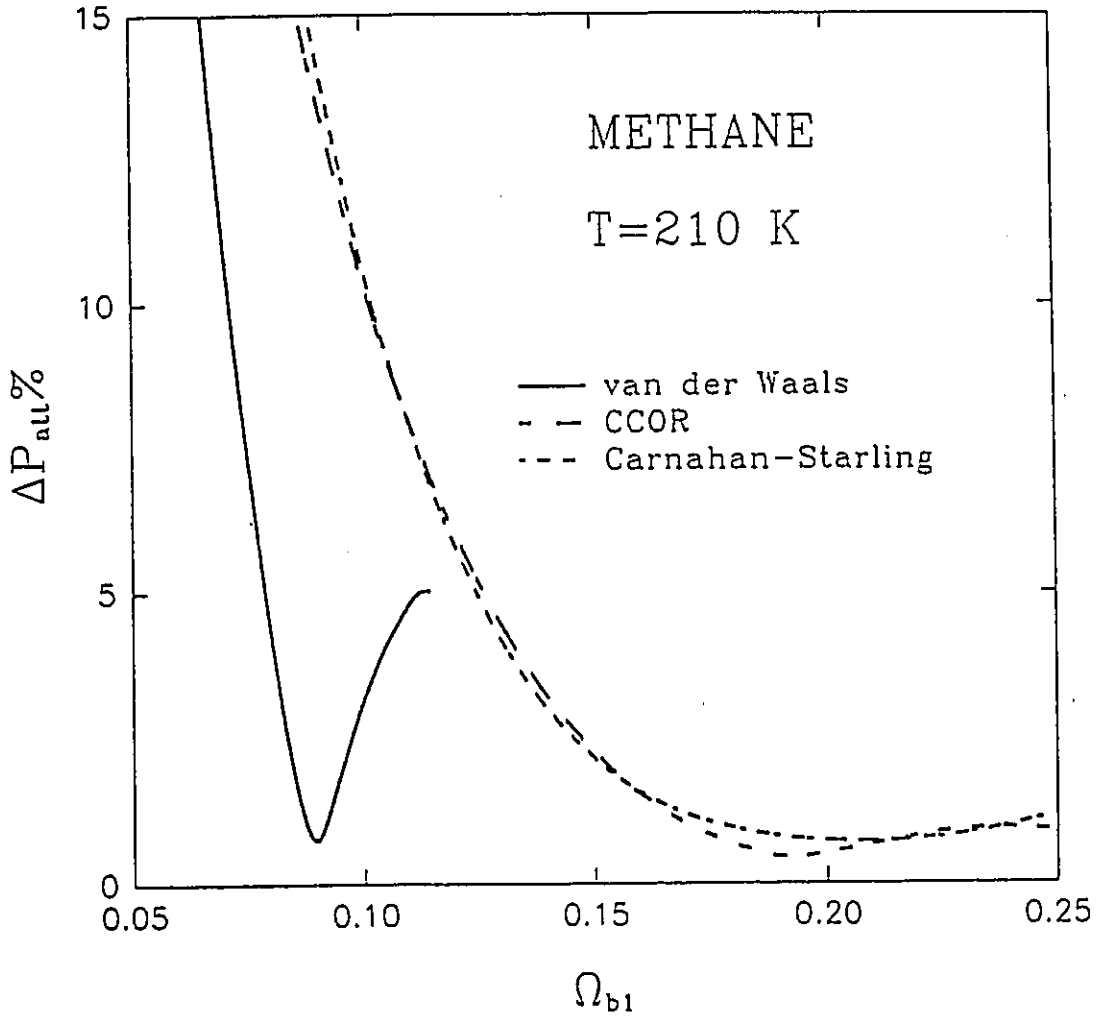


Figure 6.2 Determination of optimum Ω_{b1} values for methane

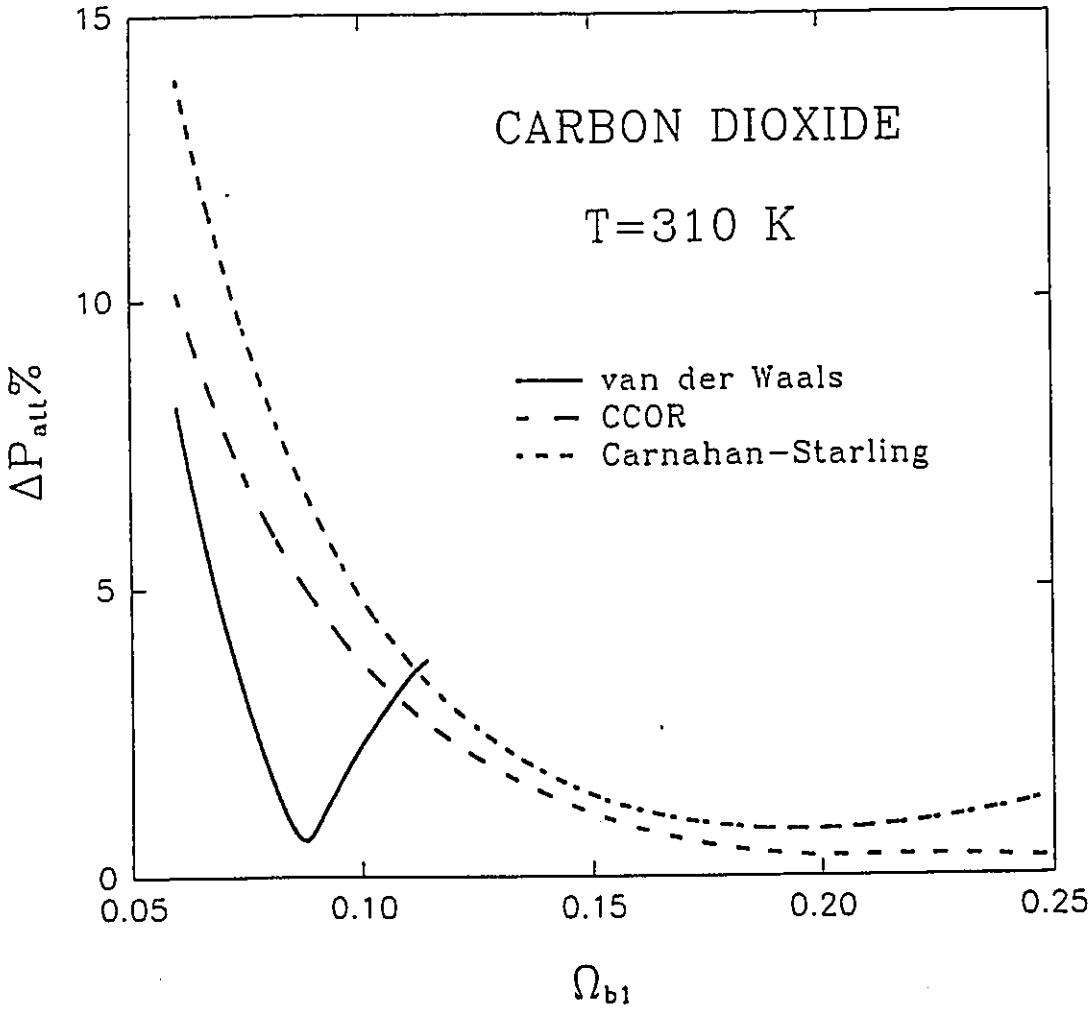


Figure 6.3 Determination of optimum Ω_{b1} values for carbon dioxide

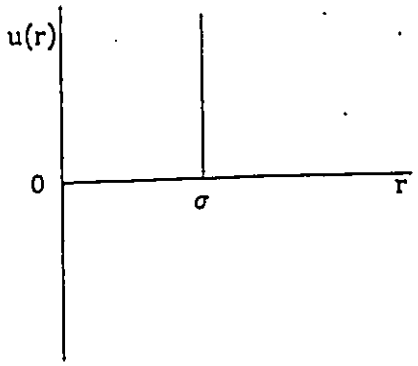
6.2 Monte Carlo Simulations of Thermodynamic Properties of the Hard Core Lennard-Jones Fluid

The potential function of the hard-core Lennard-Jones (HCLJ) (Stell and Weis, 1980) fluid is:

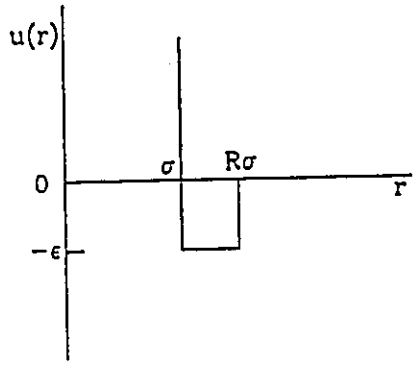
$$u(r)=\begin{cases}\infty & r < \sigma \\ -\epsilon & \sigma \le r \le 2^{1/6}\sigma \\ 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right) & r > 2^{1/6}\sigma\end{cases} \qquad (6.11)$$

where ϵ is the energy parameter, σ is the hard core diameter, and r is the distance between two molecules. The potential function of this fluid is shown in Figure 6.4 together with those of the hard sphere, the square-well, and the Lennard-Jones fluids.

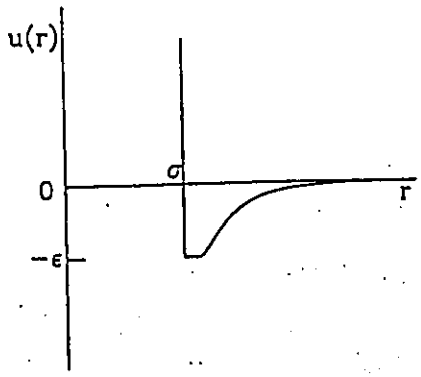
Ionic species are usually considered as hard spheres with strong interaction forces with other species. In this work, the hard core Lennard-Jones fluid was selected as a model fluid to be simulated because it contains an attraction part in addition to the hard core part. Figure 6.4 shows that the HCLJ fluid is more realistic than the square well fluid, because of the presence of the smooth tail, and simpler than the Lennard-Jones fluid since it does not have a soft repulsion part. The results of the simulation were used to determine the parameter **b** in the equation of state for ionic species.



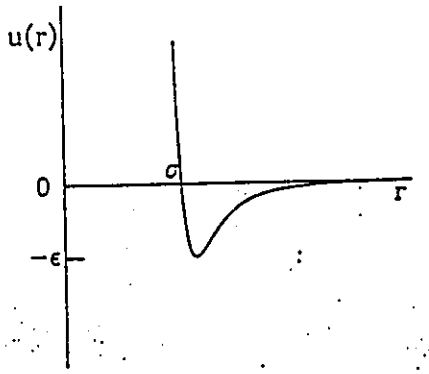
Hard Sphere Fluid



Square Well Fluid



Hard Core Lennard–Jones Fluid



Lennard–Jones Fluid

Figure 6.4 Potential functions of four different model fluids

6.2.1 Simulation of Thermodynamic Properties in the Single Phase Region

The Metropolis (1953) method was used to generate the pressure-volume-temperature (PVT) and energy properties of the HCLJ fluid in canonical (NVT) ensembles for a single phase for the purpose of validating the programs.

A unit cubic box was set up for the simulation. In the simulation, the conditions were set to be the same as those in the work of Sowers and Sandler (1991a). The number of particles N was chosen to be 112 with a random initial configuration, the first 100,000 configurations were discarded for reaching equilibrium and a total of 3×10^6 configurations were made for the dimensionless density $\rho^* \leq 0.3$ and 1.5×10^6 configurations for $\rho^* > 0.3$.

Following the work of Sowers and Sandler (1991a), the compressibility factor Z and configurational internal energy E were calculated by

$$Z=1+\frac{2}{3}\rho\sigma^3 g(\sigma^+)-\left\langle\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij}\frac{du(r_{ij})}{dr_{ij}}\right\rangle/3NkT+Z_{LRC} \qquad \textbf{(6.12)}$$

and

$$E^{CONF}=\left\langle\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u(r_{ij})\right\rangle+E_{LRC} \qquad \textbf{(6.13)}$$

respectively. In these expressions, $< >$ denotes ensemble average, r_{ij} is the distance between atoms i and j, and $g(\sigma^+)$ is the value of the radial distribution function (RDF) at contact. The value of $g(\sigma^+)$ was determined by fitting the simulated RDF values near the core to a quadratic polynomial and then extrapolating to the core by using the obtained quadratic polynomial. The cut-off distance in the simulation was one half of the box length, and the long range corrections Z_{LRC} and E_{LRC} were calculated in the usual way as mentioned in Chapter 3.

For verifying the validity of the computer program, 9 points were calculated to duplicate those reported by Sowers and Sandler(1991a). A comparison with their values indicates that the differences in the calculated values of the compressibility factor and the configurational internal energy are less than 0.05 and 0.01, respectively.

Table 6.1 A comparison of the calculated Z and E values with those reported by Sowers and Sandler (1991a)

T^*	ρ^*	Z	Z_{ss}	$\Delta Z\%$	E	E_{ss}	$\Delta E\%$
1.35	0.10	0.7173	0.716	0.18	-0.8481	-0.848	0.01
1.35	0.50	0.2867	0.299	4.10	-3.7608	-3.758	0.07
1.35	0.90	5.0302	4.996	0.68	-7.1184	-7.122	0.05
3.00	0.10	1.0208	1.022	0.12	-0.6847	-0.685	0.04
3.00	0.50	1.8913	1.883	0.44	-3.6508	-3.648	0.08
3.00	0.90	8.1824	8.193	0.13	-7.0996	-7.105	0.08
6.00	0.10	1.1095	1.133	2.07	-0.6418	-0.642	0.03
6.00	0.50	2.5272	2.576	1.89	-3.6179	-3.621	0.09
6.00	0.90	9.4105	9.392	0.20	-7.0976	-7.100	0.03
overall				1.09			0.05

ss - reported by Sowers and Sandler (1991a)

6.2.2 Simulation of VLE Values

The Gibbs ensemble technique proposed by Panagiotopoulos(1987, 1988) was adopted in this work to simulate phase equilibrium properties. The details of the simulation technique are presented in Chapter 3.

The simulation was begun with the particles placed in a face-centred lattice. Both the vapor and the liquid phases were started with 150 particles and the initial densities were selected to ensure that each phase had enough particles at equilibrium. Three perturbations were performed as follows.

In the case of particle displacement perturbation, the 300 particles were chosen in turn in each cycle and displaced randomly within the boxes following the well-established canonical (NVT) Metropolis scheme. The acceptance ratio of the movements for each subsystem was adjusted to about 50% by varying the maximum extent of particle displacements.

A random change in volume was attempted in each cycle. The volume changes of the two phases were coupled, with the overall volume V remaining constant. The acceptance probability for the volume change was essentially the same as given by Wood (1968) for simulations in the isothermal-isobaric (NPT) ensemble. The maximum allowable volume displacement was also adjusted to yield an approximately 50% acceptance ratio for the volume change.

According to Panagiotopoulos (1987, 1988), the last stage of the Gibbs ensemble method involves particle interchanges between the two subsystems. This was achieved by creating a particle at a random position in one subsystem and taking out a randomly chosen particle in the other subsystem. This move is corresponding to the grand canonical (μVT) ensemble. The number of interchange movements attempted was adjusted so that about 1% to 5% of the total number of particles were interchanged in each cycle.

For the simulation of phase equilibria at a given temperature, the first 1.0×10^6 configurations were used to reach equilibrium and averages were taken from a total of 2.0×10^6 configurations with each 150,000 configurations as a block for the purpose of estimating simulation errors. The simulation results are listed in Table 6.2.

Table 6.2 Simulated vapor pressure, vapor and liquid phase densities and configurational internal energies for the HCLJ fluid

T^*	P^*_V	ρ^*_V	E^*_V	ρ^*_L	E^*_L
0.90	0.0267	0.0322	-0.344	0.8015	-5.957
0.95	0.0287	0.0418	-0.454	0.7901	-5.825
1.00	0.0315	0.0458	-0.466	0.7547	-5.569
1.05	0.0395	0.0542	-0.523	0.7304	-5.371
1.10	0.0566	0.0779	-0.740	0.6701	-4.873
1.15	0.0667	0.0918	-0.843	0.6288	-4.579
1.20	0.0794	0.1148	-1.011	0.5791	-4.203
1.25	0.1006	0.1461	-1.244	0.4981	-3.642
1.30	0.1177	0.1987	-1.635	0.3918	-2.950

$T^* = kT/\epsilon$, $\rho^* = \rho\sigma^3$, $P^* = P\sigma^3/\epsilon$, and $E^* = E/N\epsilon$

6.2.3 Estimation of Critical Properties

An advantage of the Gibbs ensemble Monte Carlo technique over other computer simulation methods is that a closer proximity to the critical point can be achieved. The method for estimating critical properties presented by Vega et al.(1992) was adopted in this work. Two expressions were used for the calculation in Vega's method

$$\rho_{\pm}=\rho_c+C_2|t|\pm\frac{1}{2}B_o|t|^{\alpha} \tag{6.14}$$

and

$$\ln P=A+\frac{B}{T} \tag{6.15}$$

where $\rho_{\pm}$ denotes ρ_V (-) and ρ_L (+), $t=(1-T/T_c)$, T_c and ρ_c are the critical temperature and the critical density, respectively, and A, B, C_2, B_o and α are constants.

First ρ_c, T_c, C_2, B_o, and α were obtained from Eqn. (6.14) by fitting the simulated saturation density data. The critical pressure was then calculated from Eqn. (6.15), with the constants A and B just obtained, by fitting the vapor pressure values. The calculated critical properties are listed in Table 6.3.

Table 6.3 Calculated critical properties of the Hard Core Lennard-Jones fluid

$T_C^*(kT/\epsilon)$	$\rho_C^*(\rho\sigma^3)$	$P_C^*(P\sigma^3/\epsilon)$
1.3131	0.3050	0.1209

6.3 Determination of the Parameters in the Modified ALS Equation of State for Ionic Species

There are four parameters in the modified ALS equation [Eqn. (3.1)]: **a**, b_1, b_2, and b_3. In this work, for ionic species, the parameter a was determined from a theoretical equation, the parameter b_1 was determined by using the simulation results for HCLJ fluid, and the parameters b_2 and b_3 were determined in an empirical manner.

6.3.1 Determination of the Parameter b_1

In this work, the short range interactions between ionic species were assumed similar to those of the hard core Lennard-Jones fluid. The λ in the expression of the parameter b_1, Eqn (6.10), was determined with the following method.

Introducing dimensionless temperature T^* and pressure P^* to Eqn. (6.7) yields

$$b_1 = \Omega_{b1}\frac{RT_C}{P_C} = \Omega_{b1}\frac{N_a T_C^* \sigma^3}{P_C^*} \qquad (6.16)$$

Combining Eqn. (6.16) and Eqn. (6.10), the value of the λ can be obtained by

$$\lambda = \frac{3}{2\pi}\frac{\Omega_{b1} T_C^*}{P_C^*} \tag{6.17}$$

In the ALS equation (Adachi et al, 1983), the parameter Ω_{b1} was generalized in terms of the acentric factor ω

$$\Omega_{b1} = 0.08974 - 0.03452\omega + 0.00330\omega^2 \tag{6.18}$$

If ω equals zero, then

$$\Omega_{b1} = 0.08974 \tag{6.19}$$

Using this Ω_{b1} value and introducing the values of critical properties of the hard-core Lennard-Jones fluid obtained from the simulations into Eqn. (6.17) yield

$$\lambda = 0.46537 \tag{6.20}$$

This λ value is close to the analysis results (Section 6.1) for the parameter $\mathbf{b_1}$, in which, the value of λ should be around 0.5.

6.3.2 Determination of the Parameter a

In order to find a proper expression for the parameter **a**, three theoretical equations

of state were evaluated by using the simulation data of the hard core Lennard-Jones fluid:

(1). Sowers-Sandler-I (S-S I) (1991a):

$$Z=\frac{1+y+y^2-y^3}{(1-y)^3}-a\frac{\epsilon}{kT}\rho^*-c\left\{b_1\frac{\epsilon}{kT}+b_2\left[3\left(\frac{\epsilon}{kT}\right)^2+\sqrt{\frac{\epsilon}{kT}}\right]\right\}\times \qquad (6.21)$$
$$(2\rho^*-\rho_b^{*}\rho^*)\exp[-c\rho^*(\rho^*-\rho_b^*)]$$

where, $y=(\pi/6)\rho\sigma^3$, $\rho^*_b=0.9$, and a, b_1, b_2, and c are the equation parameters

(2). Sowers-Sandler-II (S-S-II) (1991a):

$$Z=\frac{1+y+y^2-y^3}{(1-y)^3}-\frac{Z_m[\exp(\frac{\epsilon}{2kT})-1]y}{\pi\sqrt{2}/6+[\exp(\frac{\epsilon}{2kT})-1]y}+2a\frac{\epsilon}{2kT}\exp\left(-\sqrt{\frac{kT}{\epsilon}}\right)\rho^{*2} \qquad (6.22)$$
$$+\left[b_1\frac{\epsilon}{kT}+b_2\left(\frac{\epsilon}{kT}\right)^2\right]\rho^*$$

where, $Z_m=18$ is the lattice coordination number for the square-well fluid (Lee et al. 1985).

(3). Shen-Lu (S-L) (1993a)

$$Z=\frac{1+y+y^2-y^3}{(1-y)^3}-\frac{\epsilon}{2kT}\left[\rho\left(\frac{\partial G}{\partial\rho}\right)+8R^3y+\frac{24\alpha F}{(3-R)}y\right] \qquad (6.23)$$

where R is the reduced well width,

$$F=27-81/4-R^3+R^4/4 \tag{6.24}$$

and

$$G=kT\left(\frac{\partial\rho}{\partial P}\right)_o=\frac{(1-y)^4}{(1+4y+4y^2-4y^3+y^4)} \tag{6.25}$$

It should be mentioned that there are several correlation parameters in Eqns. (6.18) and (6.19), but the equation of Shen and Lu, developed from a pseudo potential function, contains no correlation parameters.

A comparison was made of the calculated VLE properties with the three equations of state. The results are listed in Table 6.4 and shown in Figure 6.5.

Table 6.4 A comparison of the calculated saturation properties with simulation data

	Sowers-Sandler I			Sowers and Sandler II			Shen-Lu		
T^*	$\Delta P^*_V\%$	$\Delta\rho^*_V\%$	$\Delta\rho^*_L\%$	$\Delta P^*_V\%$	$\Delta\rho^*_V\%$	$\Delta\rho^*_L\%$	$\Delta P^*_V\%$	$\Delta\rho^*_g\%$	$\Delta\rho^*_l\%$
0.90	66.48	66.96	0.54	50.42	50.08	1.84	75.61	76.43	1.68
0.95	51.80	62.21	2.73	34.25	47.33	4.42	64.89	73.24	4.00
1.00	35.16	50.10	2.20	17.19	34.92	4.42	52.85	65.09	3.57
1.05	26.54	40.27	3.14	11.17	26.37	5.93	46.81	58.96	4.48
1.10	29.43	43.16	0.59	18.61	33.32	3.00	49.28	61.87	0.60
1.15	19.80	34.73	1.47	11.25	26.84	2.93	42.89	57.59	0.76
1.20	11.82	29.83	3.42	6.00	24.70	1.92	37.94	56.26	3.70
1.25	10.67	25.59	11.13	8.03	23.60	4.44	38.01	56.17	13.55
1.30	3.59	25.14	26.86	4.03	26.74	18.28	34.22	59.43	34.75
overall	28.36	42.00	5.79	17.88	32.66	5.24	49.17	62.78	7.46

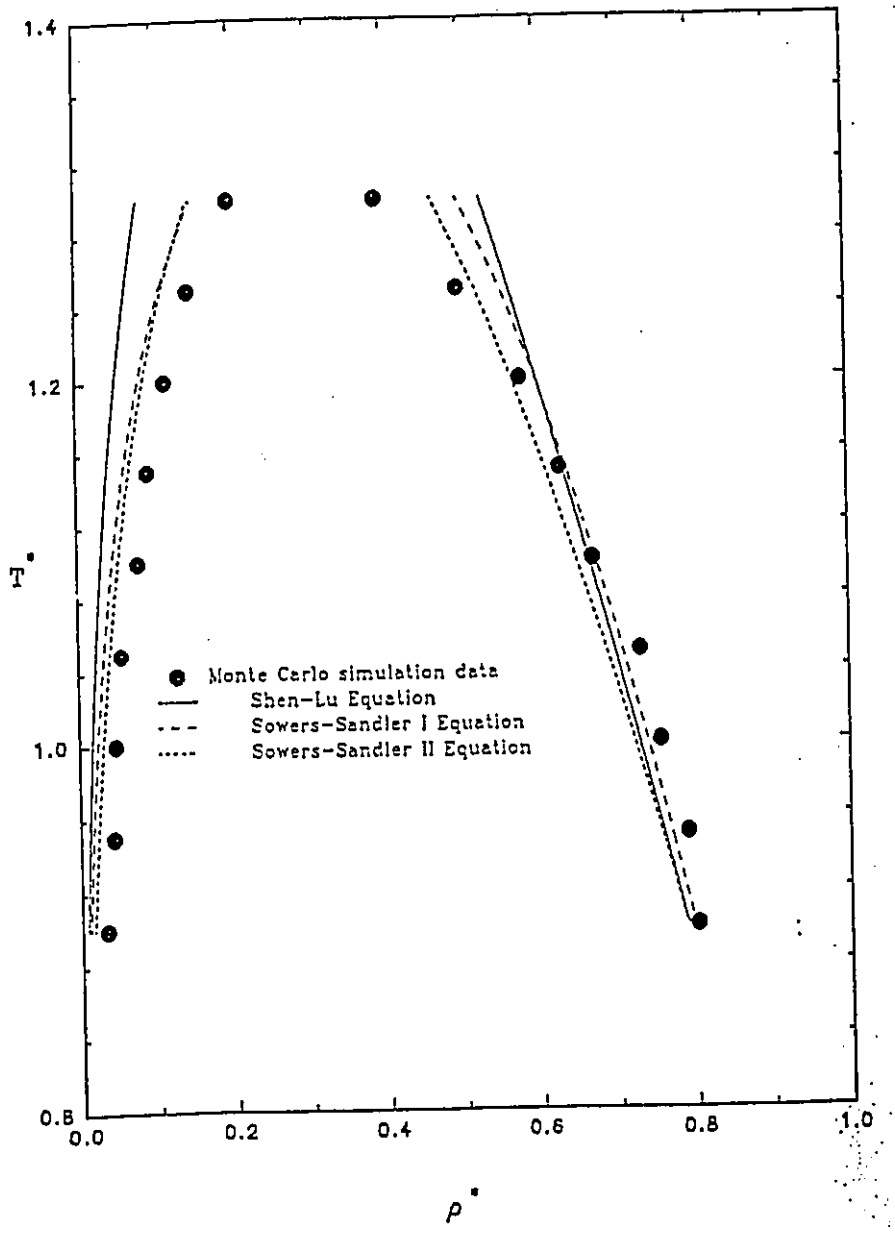


Figure 6.5 A comparison of the simulated VLE values with those obtained from three equations of state

The results indicate that the values obtained from the S-S II equation are closer to the simulation data, so the expression of the S-S II was arbitrarily selected to determine the value of parameter a. In order to keep the form of the equation cubic, only the square well part of the S-S II was considered in this work.

The square-well part of the S-S II equation was originally proposed by Lee and coworkers (Lee, et al., 1985)

$$Z=\frac{1+y+y^2-y^3}{(1-y)^3}-\frac{Z_m[\exp(\frac{\epsilon}{2kT})-1]y}{\pi\sqrt{2}/6+[\exp(\frac{\epsilon}{2kT})-1]y} \tag{6.26}$$

It can be rewritten as

$$Z=\frac{1+y+y^2-y^3}{(1-y)^3}-\frac{Z_m V_0[\exp(\frac{\epsilon}{2kT})-1]}{V+V_0[\exp(\frac{\epsilon}{2kT})-1]} \tag{6.27}$$

where

$$V_0=N_a\sigma^3/\sqrt{2} \tag{6.28}$$

By comparing Eqn. (6.27) with the general van der Waals type equation of state, Eqn. (3.4), the parameter a can be expressed by

$$a = Z_m V_0 RT[\exp(\frac{\epsilon}{2kT}) - 1] \tag{6.29}$$

Shoor and Gubbins (1969), Harvey and Prausnitz (1989), and Zuo and Guo (1991) calculated the Lennard-Jones energy parameter ϵ by using the dispersion theory of Mavroyannis and Stephen (1962)

$$\frac{\epsilon_{LJ}}{k} = 2.2789 \times 10^{-8} Z_I^{1/2} \alpha_I^{3/2} \sigma^{-6} \tag{6.30}$$

where, Z_I is the number of electrons on an ion, and α_I is the ion polarizability. The numerical value of Eqn. (6.30) has units of (K).

Because the square well term was adopted in this work, an adjustment of the energy parameter ϵ was made as follows.

The potential function for the Lennard-Jones fluid is given by

$$u(r)_{LJ} = 4\epsilon_{LJ}\left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\right] \tag{6.31}$$

and the potential function for the square-well fluid is given by

$$u(r)_{SW} = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \le r \le R\sigma \\ 0 & r > R\sigma \end{cases} \tag{6.32}$$

Let

$$\int_{\sigma}^{R\sigma} u(r)_{SW} dr = \int_{\sigma}^{\infty} u(r)_{LJ} dr \qquad (6.33)$$

The following relationship was obtained between ϵ and ϵ_{LJ} when the well width R is taken to be 1.5

$$\epsilon = 0.8727272 \epsilon_{LJ} \qquad (6.34)$$

Substituting Eqn. (6.34) into Eqn. (6.30) yields

$$\frac{\epsilon}{k} = 1.9889 \times 10^{-8} Z_I^{1/2} \alpha_I^{3/2} \sigma^{-6} \qquad (6.35)$$

Eqn. (6.35) was applied in the calculations in this work.

In the work of Zuo and Guo (1991), the expression of the parameter **a** adopted in their work was proposed by Hu et al. (1984, 1985)

$$a = 2.57012 \pi \epsilon N_a^2 \sigma^3 f \qquad (6.36)$$

where f is an empirical constant, which was empirically set to be 6 by Zuo and Guo (1991). In Section 6.4, the three different expressions, Eqns. (6.30), (6.34), and (6.36), were compared for the purpose of selecting a suitable parameter **a** expression for ionic species.

6.3.3 Determination of the Parameters b_2 and b_3

The parameters b_2 and b_3 in the original ALS equation (Adachi et al., 1983) were determined by

$$b_2=\Omega_{b2}\frac{RT_C}{P_C}, \quad \text{and} \quad b_3=\Omega_{b3}\frac{RT_C}{P_C} \tag{6.37}$$

where

$$\begin{aligned}\Omega_{b2}&=0.03686+0.00405\omega-0.01073\omega^2+0.00157\omega^3\\ \Omega_{b3}&=-0.15400-0.14122\omega+0.00272\omega^2+0.00484\omega^3\end{aligned} \tag{6.38}$$

In this work, letting $\omega=0$ and introducing Eqn. (6.16) into Eqn. (6.37) yields

$$\begin{aligned}b_2&=0.03686\frac{b_1}{\Omega_{b1}}\\ b_3&=-0.15400\frac{b_1}{\Omega_{b1}}\end{aligned} \tag{6.39}$$

where b_1 and Ω_{b1} were determined by Eqns. (6.10) and (6.19), respectively.

These values are identical to those from the work of Sugie et al. (1989), if the Ω_{ac} value in the original ALS equation is used as follows.

In the expression of Sugie et al., the quantity f is given by

$$f=Z_C^*-\Omega_{b1}=1-\Omega_{ac}^{1/3} \tag{6.40}$$

In the original ALS equation, Ω_{ac} is given by

$$\Omega_{ac}=0.44869+0.04024\omega+0.01111\omega^2-0.00576\omega^3 \tag{6.41}$$

If $\omega=0$, then

$$\Omega_{ac}=0.44869 \tag{6.42}$$

Introducing Ω_{ac}, Eqn. (6.42), and Ω_{b1}, Eqn. (6.19) values to Eqn. (6.40) yields

$$f=0.234435\ , \quad \text{and} \quad Z_C^*=0.324165 \tag{6.43}$$

By introducing these values to Eqns. (3.26), (4.9), (4.12) and (6.13), the values of the parameters b_2 and b_3 were determined to be

$$b_2=-0.15413\frac{b_1}{\Omega_{b1}}$$
$$b_3=0.036894\frac{b_1}{\Omega_{b1}} \tag{6.44}$$

Eqn. (6.39) and (6.44) are essentially identical because b_2 and b_3 are symmetric in the ALS equation, Eqn. (2.5). Eqn. (6.44) was applied in this work.

6.4 Extension of the Extended Wong-Sandler Mixing Rules to Electrolyte Solutions

The extended Wong-Sandler mixing rule has been successfully applied to the representation of thermodynamic properties of non-electrolyte solutions. In this section, this mixing rule was further extended to the representation of thermodynamic properties of electrolyte solutions.

Chen et al. (1982, 1986) extended the NRTL activity coefficient model to calculate the VLE properties of electrolyte solutions. The model of Chen et al. has been successfully applied to the calculation of the osmotic coefficients and activity coefficients for aqueous solutions with single electrolyte (Chen et al., 1982) and multi-electrolytes (Chen et al., 1986). This model was selected in this work for applying the modified ALS equation and the extended Wong-Sandler mixing rule to electrolyte solutions. There are two reasons for selecting this model:

(1). The model is already normalized to the molar basis.

Equations of state use mole fraction to represent the compositions of the components in mixtures. Therfore, compared with some other models involving the use of molality as a composition variable, Chen's model is easier to use with equations of state.

(2). The model was developed from the NRTL model and can be reduced to the NRTL

model if all the species in the mixture are molecules.

The NRTL model was already used in this work for representing thermodynamic properties of non-electrolyte solutions so there is a consistent consideration for using this model.

The details and expressions of the model proposed by Chen et al. (1982) were presented in Section 3.2. In the calculation, to reduce the number of parameters, the k_{ij} values for ionic species with molecules or other ionic species were empirically set equal to zero. The nonrandomness factor α was set to be 0.2 for all the cases, which is the same as that in the original Chen's model. The binary interaction coefficients between ionic species were all set to be zero because the forces between ions were described in the Pitzer-Debye-Hückel term, Eqn. (3.33). Therefore, there are only two binary interaction coefficients for an electrolyte in a single solvent.

6.4.1 Representation of Osmotic Coefficients in Aqueous Solutions with Single Electrolyte

Osmotic coefficients are important quantities in the VLE calculation for aqueous solutions. The definition of osmotic coefficient, ϕ, is given by (Robinson and Stokes, 1955)

$$\ln a_A = -\frac{\nu m W_A}{1000}\phi \qquad (6.45)$$

where a_A is the activity of the solvent, ν ($= \nu_- + \nu_+$) denotes the total number of moles of ions given by one mole of electrolyte, m is the molality of the solution, and W_A is the molar mass of the solvent.

For selecting a suitable expression for the parameter a, three different expressions, the original energy parameter, Eqn. (6.30) with Eqn. (6.29), the corrected energy parameter, Eqn. (6.35) with Eqn. (6.29), and the expression used by Zuo and Guo (1991), Eqn. (6.36), were compared by representing the osmotic coefficients of 38 electrolytes. The osmotic coefficient values collected by Robinson and Stokes (1959) were used in this section for determining the binary interaction coefficients of aqueous electrolyte solutions. A comparison of the results is listed in Table 6.5, indicating that the calculated values obtained by using the corrected energy parameter are somewhat better than those obtained by using the original energy parameter. The results obtained from both cases with Eqn. (6.29) are much better than those obtained by applying the expression used by Zuo and Guo, Eqn. (6.36). Therefore, this arbitrarily selected corrected energy parameter, Eqn. (6.35), with Eqn. (6.29) was applied in this work.

Table 6.5 A comparison of the calculated osmotic coefficients for 38 electrolytes in aqueous solution by using three different expressions of the parameter a

	AAPD	RMSD
Zuo and Guo's expression	6.78	7.24
This work with original ϵ_{LJ}	1.89	2.31
This work with corrected ϵ	1.87	2.29

The osmotic coefficients for the same 38 electrolytes in aqueous solutions were calculated and compared with the results obtained by Chen et al. (Chen et al., 1986). The results are listed in Table 6.6 in terms of root mean square deviation (RMSD), in order to be consistent with the work reported by Chen et al. (1986). The results indicate that the osmotic coefficients can be represented as well as those obtained from activity coefficient models by using the extended Wong Sandler mixing rule together with the modified ALS equation. The parameters obtained from this work listed in Table 6.7 are close to those obtained by Chen et al. (1986). A comparison of the results obtained from this work with those obtained by Zuo and Guo (1991) is presented in Table 6.8 in terms of AAPD, same as reported by Zuo and Guo. The new approach gives much better results.

Table 6.6 A comparison of the calculated osmotic coefficients with those reported by Chen et al. (1986) in terms of root mean square deviation (RMSD)

Salt	Max. Molality	RMSD	
		Chen et al.	This work
NaCl	6	1.2	0.71
NaBr	4	0.6	0.35
NaI	3.5	0.7	0.45
NaF	1	0.02	0.31
$NaNO_3$	6	0.2	0.80
KCl	4.8	0.2	0.41
KBr	5.5	0.3	0.45
KI	4.5	0.2	0.40
LiCl	6	2.4	1.82
$LiNO_3$	3.5	0.4	0.35
KNO_3	3.5	0.6	1.19
RbCl	5	0.2	0.70
RbBr	5	0.2	0.74
RbI	5	0.1	0.76
CsCl	6	0.4	1.10
NH_4Cl	6	0.07	0.68
NH_4NO_3	6	0.5	1.20
HCl	6	1.9	1.43
HBr	3	0.8	0.47
HI	3	1.0	0.59
HNO_3	3	0.5	0.22
LiBr	6	2.8	2.27

Table 6.6 (Continue)

Salt	Max. Molality	RMSD	
		Chen et al.	This work
LiI	3	1.5	1.03
$HClO_4$	6	3.3	2.79
NaOH	6	2.3	1.71
KOH	6	1.5	1.54
$CaCl_2$	6	9.0	8.06
$CaBr_2$	6	13.0	11.93
CaI_2	2	2.4	1.40
$MgCl_2$	5	9.0	7.64
$MgBr_2$	5	9.0	8.43
MgI_2	5	11.0	10.1
$SrCl_2$	4	5.0	3.53
$BaCl_2$	1.8	1.2	0.26
Na_2SO_4	4	2.2	1.16
$(NH_4)_2SO_4$	5.5	0.8	2.39
$MgSO_4$	3	5.0	2.67
$AlCl_3$	1.8	6.0	4.52
overall average		2.57	2.29

Table 6.7 Parameters obtained by Chen et al. (1986) and from this work

Salt	Chen et al.		This work	
	$\tau_{ac,w}$	$\tau_{w,ca}$	$\tau_{ac,w}$	$\tau_{w,ca}$
NaCl	-4.5916	9.0234	-3.9108	5.8017
NaBr	-4.6070	8.9288	-4.0429	5.8360
NaI	-4.6920	8.9820	-4.2788	6.0348
NaF	-3.7493	7.4322	-3.7774	5.9183
$NaNO_3$	-3.6151	7.2886	-2.2321	3.4738
KCl	-4.1341	8.1354	-3.2441	4.7235
KBr	-4.1707	8.1699	-3.4805	5.0324
KI	-4.1217	7.9408	-3.4734	4.6955
LiCl	-5.1737	10.1242	-4.7290	7.1011
$LiNO_3$	-4.6136	8.7565	-4.0652	5.6110
KNO_3	-3.2747	7.2728	-2.2223	4.4903
RbCl	-4.1357	8.2053	-3.5321	5.0732
RbBr	-4.0399	8.0151	-3.5330	4.8970
RbI	-4.0916	8.1419	-3.7583	5.1124
CsCl	-4.3726	8.4238	-3.6290	5.3730
NH_4Cl	-4.0121	7.8599	-2.9308	4.1373
NH_4NO_3	-3.3162	6.8739	-1.8899	3.3451
HCl	-5.2286	10.1728	-4.8037	7.1876
HBr	-5.2194	9.9746	-4.8719	7.1020
HI	-5.2039	9.7714	-4.9007	6.8836
HNO_3	-4.3663	8.7223	-4.0455	5.7275
LiBr	-5.3628	10.5393	-5.0358	7.6533

Table 6.7 (Continue)

Salt	Chen et al.		This work	
	$\tau_{ac,w}$	$\tau_{w,ca}$	$\tau_{ac,w}$	$\tau_{w,ca}$
LiI	-5.0883	9.5925	-4.8357	6.7359
$HClO_4$	-5.4365	10.7078	-5.2117	7.9144
NaOH	-4.7893	9.4200	-4.1714	6.2346
KOH	-5.0644	9.2928	-4.5587	6.7669
$CaCl_2$	-5.2549	10.5126	-4.9685	7.7161
$CaBr_2$	-5.4801	11.0038	-5.3265	8.3441
CaI_2	-5.1151	9.7214	-5.0547	7.0705
$MgCl_2$	-5.3583	10.6681	-5.1016	7.9011
$MgBr_2$	-5.5307	10.9725	-5.3909	8.2980
MgI_2	-5.7064	11.3459	-5.6749	8.7620
$SrCl_2$	-4.9537	9.7230	-4.7421	6.9331
$BaCl_2$	-4.2068	7.9145	-4.1548	5.3404
Na_2SO_4	-3.8760	7.9756	-2.8207	4.6253
$(NH_4)_2SO_4$	-3.7871	7.7870	-2.5431	4.1735
$MgSO_4$	-4.1796	8.2533	-3.7085	5.5672
$AlCl_3$	-5.2306	10.0495	-5.3201	7.4832

Table 6.8 A comparison of the calculated osmotic coefficients with those reported by Zuo and Guo (1991) in terms of absolute average percentage deviation (AAPD)

Salt	No.	Max. Molality	AAPD	
			ZUO & GUO	This work
NaCl	35	6.0	3.48	0.62
KCl	29	4.8	1.72	0.29
LiCl	23	6.0	4.91	1.48
LiBr	23	6.0	6.94	1.82
LiI	17	3.0	2.18	0.84
$LiNO_3$	23	6.0	3.24	0.31
HCi	23	6.0	4.54	1.17
HBr	10	1.0	0.37	0.15
HI	17	3.0	2.33	0.50
HNO_3	17	3.0	1.44	0.18
NaOH	23	6.0	1.94	1.44
NaBr	19	4.0	2.17	0.28
NaI	17	3.0	1.74	0.38
$NaNO_3$	19	4.0	1.05	0.64
KBr	17	3.0	1.03	0.36
KOH	23	6.0	2.50	1.02
KI	20	4.5	1.59	0.31

Table 6.8 (continue)

Salt	No.	Max. Molality	AAPD	
			ZUO & GUO	This work
KNO_3	18	3.5	1.29	1.03
K_2SO_4	7	0.7	1.18	0.97
Na_2SO_4	19	4.0	5.28	0.96
$MgCl_2$	19	4.0	7.42	4.20
$MgSO_4$	17	3.0	4.91	2.20
$MgBr_2$	17	3.0	5.90	2.51
$Mg(NO_3)_2$	17	3.0	3.88	1.40
$CaBr_2$	17	3.0	5.70	2.36
$CaCl_2$	19	4.0	7.22	3.51
$Ca(NO_3)_2$	23	6.0	5.93	1.73
overall average	528		3.53	1.21

6.4.2 Representation of VLE Data for Ethanol-Water-Salt System

A salt dissolved in a mixed solvent is capable of altering the composition of the equilibrium vapor phase. Hence salt effect on vapor-liquid equilibrium provides a potential technique of extractive distillation for difficult separations. Ethanol is a useful material to both industry and human life. Because there is an azeotropic point in the ethanol-water system, the salt effect is important for the production of pure ethanol.

In the application of Chen's model to multi-solvent electrolyte solutions, one of the difficulties is the determination of the Debye-Hückel parameter A_ϕ. In this work, for simplicity, the expression proposed by Chen et al. (1982), Eqn. (3.36), for aqueous solutions was adopted for all the calculation. This simplification could cause errors for the multi-solvent systems, but would avoid difficulties when data are not available.

Isobaric VLE of three systems, ethanol + water with sodium chloride, calcium chloride, or zinc chloride were calculated. The reason for considering isobaric VLE data is because they are more useful for practical usage. A bubble-point temperature calculation was used. In the calculation, the binary interaction coefficients of ethanol and water were obtained from the binary VLE data of the ethanol-water system, while those for salt and water were obtained by fitting the osmotic coefficients in Section 6.4.1, and for salt and ethanol were obtained by fitting the ternary VLE data. The results and interaction coefficients for the ethanol-water system are listed in Table 6.9. A comparison

of the calculated equilibrium compositions with the experenmental data is shown in Figure 6.6. The results and parameters for the three salt-containing systems are listed in Table 6.10. The results are also shown in Figure 6.7 to 6.9.

The results shown in these tables and figures indicate that the modified ALS equation with the extended Wang-Sandler mixing rule can be used to represent the VLE of these systems well. The azeotropic point of the ethanol-water system was well represented and the salt effect on this system was also well represented. For the ethanol-water-sodium chloride system, the azeotropic point still exists. For both the ethanol-water-calcium chloride and ethanol-water-zinc chloride systems, the azeotropic point disappeared and the salt effect is more evident in the case of the presence of calcium chloride.

Table 6.9 Results and binary interaction coefficients of the ethanol-water system obtained by using the modified ALS equation with the extended Wang-Sandler mixing rule

system	k_{12}	α_{12}	Δg_{12}	Δg_{21}	ΔT	$\Delta y*100$
ethanol(1) - water(2)	-0.21863	0.28819	2156.7	8661.3	1.87	0.65

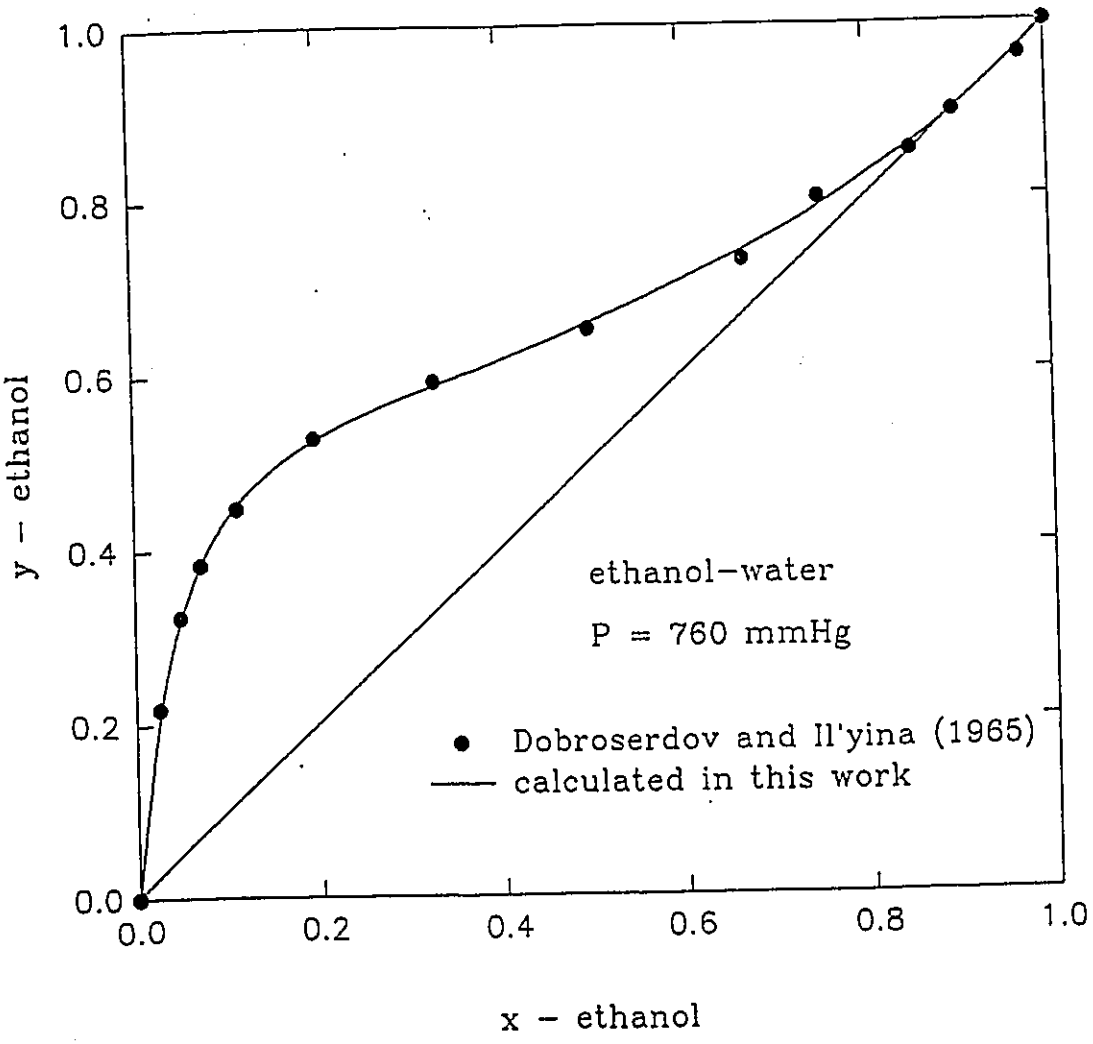


Figure 6.6 A plot of equilibrium compositions for the ethanol - water system at 760 mmHg

Table 6.10 Results and binary interaction coefficients of three salt containing ethanol-water-salt systems obtained by using the modified ALS equation with the extended Wang-Sandler mixing rule

system	$\Delta g_{e,ca}$*	$\Delta g_{ca,e}$*	ΔT(K)	Δy*100
ethanol-water-sodium chloride	85309.0	1871300.	0.85	2.08
ethanol-water-calcium chloride	7239.2	34859.	1.29	1.68
ethanol-water-zinc chloride	2932.7	35209.	0.99	1.13

* $\Delta g_{e,ca}$ and $\Delta g_{ca,e}$ are binary interaction parameters, e denotes ethanol, and ca denotes cation or anion.

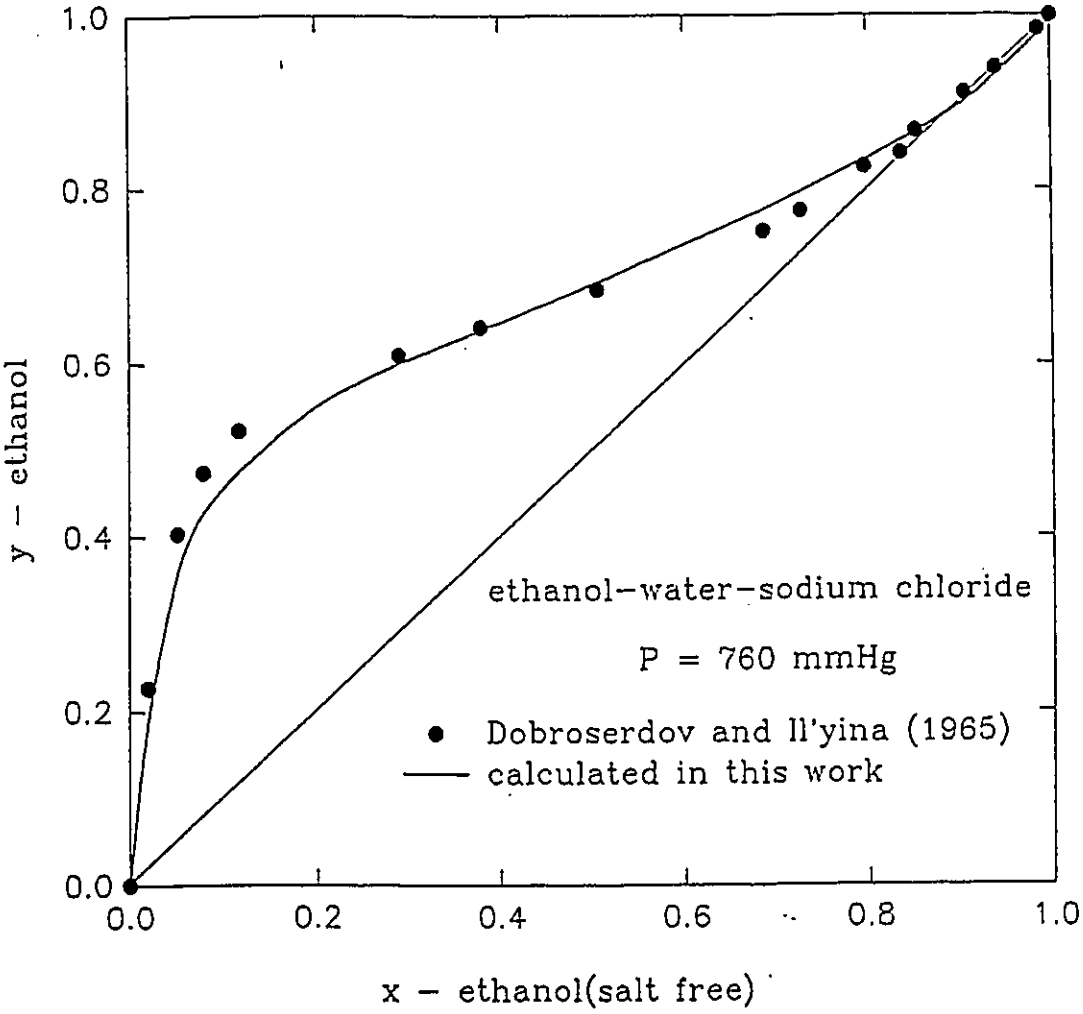


Figure 6.7 A plot of equilibrium compositions for the ethanol - water - sodium chloride system at 760 mmHg

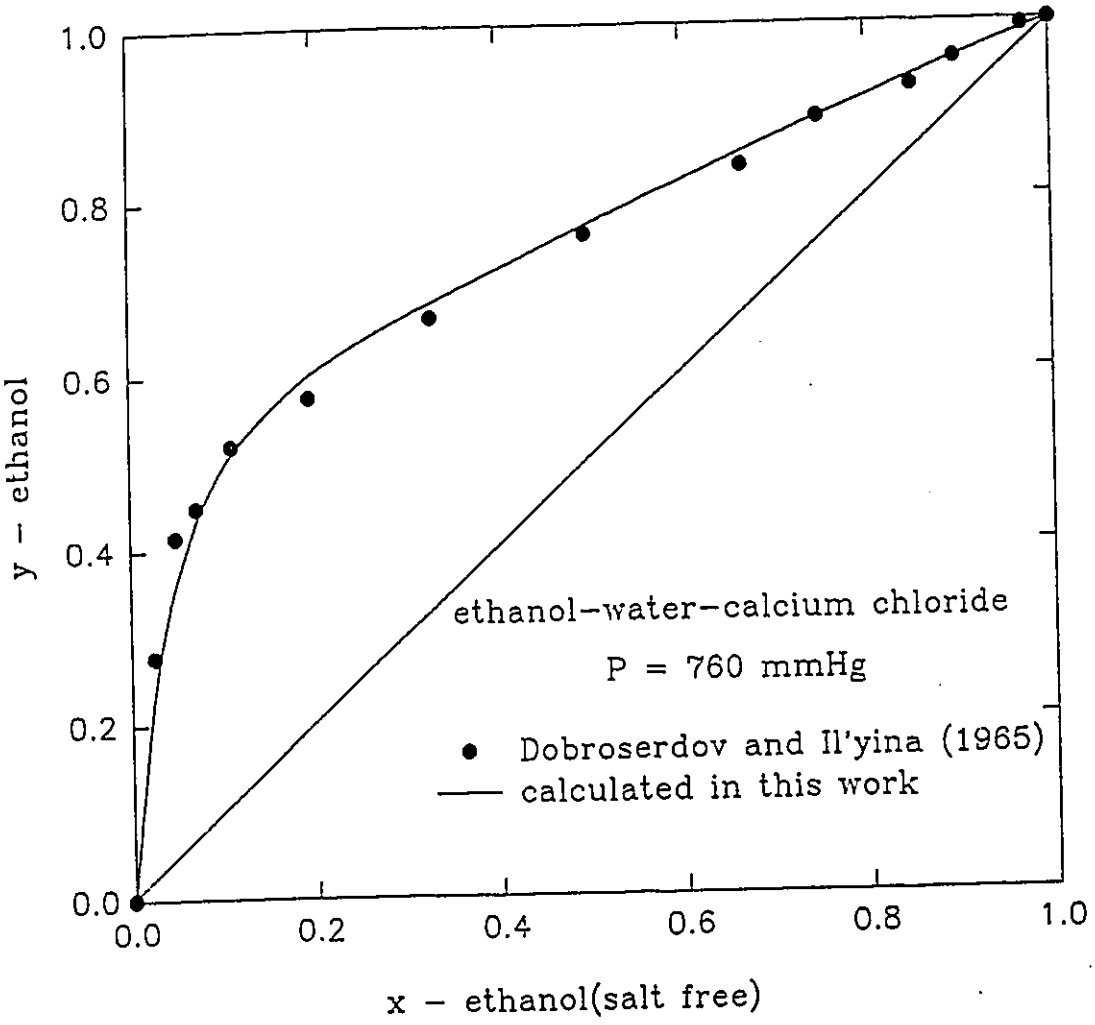


Figure 6.8 A plot of equilibrium compositions for the ethanol - water - calcium chloride system at 760 mmHg

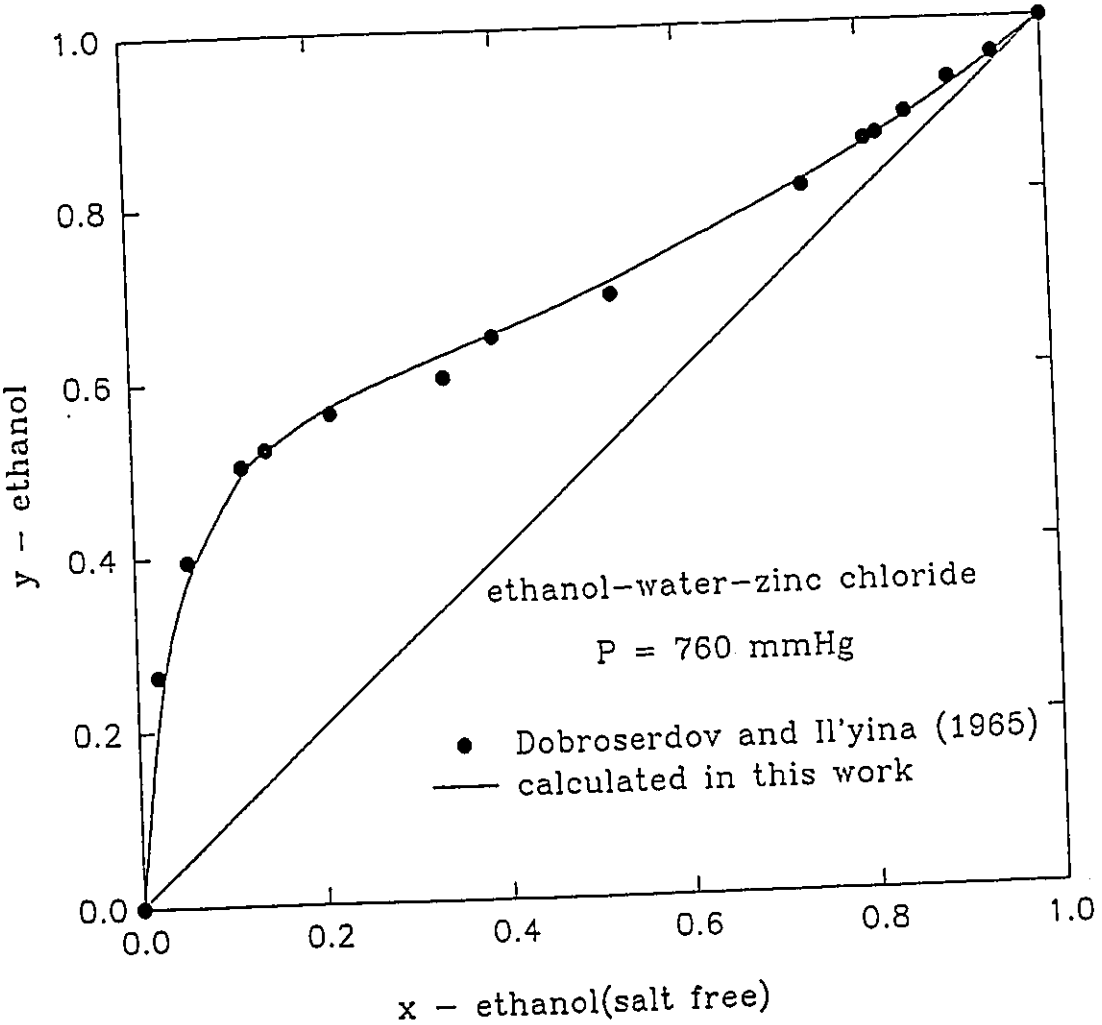


Figure 6.9 A plot of equilibrium compositions for the ethanol - water - zinc chloride system at 760 mmHg

6.5 Concluding Remarks

For determining the equation of state parameter $\mathbf{b}_i$ for ionic species, an analysis was made by investigating a wide range of PVT data for three normal fluids. It was found that the expression for the parameter $\mathbf{b}_i$ in the van der Waals repulsion term should be different from the common theoretical expression for b_i in the Carnahan-Starling and CCOR terms. This observation is considered important in the determination of the parameter $\mathbf{b}_i$ for ionic species by using van der Waals type equations.

An expression for the parameter **a** in the modified ALS equation for ionic species was arbitrarily selected from a truncated Sowers-Sandler equation II (1991a). A justification was made for the energy parameter ϵ in the expression for parameter **a**. The results indicate that this expression with the justificated energy parameter ϵ gives better results than the expression with original energy parameter ϵ_{LJ} (Shoor and Gubbins, 1969) and the expression used by Zuo and Guo (1991).

The extended Wong-Sandler mixing rule was further extended for the application to electrolyte solutions by combining with Chen's electrolyte local composition model. Extensive evaluations were made. The calculated osmotic coefficients for electrolyte aqueous solutions are comparable with those obtained from the original Chen's model without increasing the number of binary interaction coefficients. The results are much

better than those obtained by Zuo and Guo, who also used a cubic equation of state. This work shows that the osmotic coefficients for aqueous solutions can be represented by using the modified ALS equation with the extended Wang-Sandler mixing rule as precisely as by the activity coefficient models proposed by Chen et al. (1982).

The isobaric VLE data of three ethanol-water-salt systems were also represented. The deviations of the temperature and vapor phase composition are around 1 K and 1 to 2 mole%, respectively. This work shows that the VLE of electrolyte solutions can be represented by means of the modified ALS equation with acceptable accuracies.

Chapter 7

Conclusions

A modification of the ALS equation has been successfully accomplished. The modification is based on a new characteristic parameter for improving the performance of the equation in the simultaneous representation of vapor-liquid equilibrium, volumetric and energy properties for pure substances. The Wong-Sandler mixing rule has been successfully extended to a general cubic equation of state and its application has been further extended to electrolyte solutions.

It was found that by fitting the difference between the volume of saturated vapor and that of saturated liquid at a certain temperature using equation of state parameters, the accuracy of the calculated saturated liquid and vapor volumes by that equation can be improved simultaneously and the prediction of latent heat of vaporization can also be improved. This temperature was found to be that for which the corresponding T_r value

is near but not over 0.95. Based on this finding, a new characteristic parameter, T_r at $\Delta Z=0.5$, was developed and applied in the modification of the ALS equation. The new approach was evaluated by comparing the calculated fluid properties for pure polar and non-polar systems with those calculated from several other equations. The new approach performed better than the other equations tested.

The Wong-Sandler mixing rule is a theoretically correct mixing rule and can be used to represent VLE data with high precision. In this work, the Wong-Sandler mixing rule was extended to a general van der Waals type cubic equation so that it can be used with most of the available cubic equations of state, such as the SRK, the PR, the PT and the modified ALS equation.

The extended Wong-Sandler mixing rule was used with different equations for the representation of binary VLE data and the prediction of ternary VLE values. It was also compared with other mixing rules involved in this study. Overall, the extended Wong-Sandler and the SGR mixing rules give better results than other mixing rules and prevent the false liquid phase splitting from happenning in the cases tested. With the Extended Wong-Sandler mixing rule, the results from the modified ALS equation are as good as those from the PRSV equation and better than those from the SRK, the PR and the PT equations.

For validating the ability of the extended Wong-Sandler mixing rule, simultaneous

representations of VLE and volumes or VLE and excess enthalpies were made. The results indicate that the modified ALS equation with the extended Wong-Sandler mixing rule gives better overall results than other equations and mixing rules.

For determining equation parameters for ionic species, an analysis of the parameter $\mathbf{b_1}$ in the repulsive term was made by investigating a wide range of PVT data for three normal fluids. It was found that the expression for the parameter $\mathbf{b_1}$ in the van der Waals repulsive term should be different from the common theoretical expression in the Carnahan-Starling and CCOR terms. This discovery is important in the determination of the parameter $\mathbf{b_1}$ for ionic species by using van der Waals type equations.

The extended Wong-Sandler mixing rule was further extended for application to electrolyte solutions by combining with Chen's electrolyte local composition model. The calculated osmotic coefficients for aqueous electrolyte solutions have a same degree of accuracy as those obtained from the original Chen's model without increasing the number of binary interaction coefficients, and much better than those obtained by Zuo and Guo, who also used a cubic equation of state. The VLE data for three ethanol-water-salt systems were also represented. The deviations of temperature and vapor phase composition are around 1 K and 1-2 mole%, respectively. This work shows that the VLE behavior of electrolyte solutions can be represented with satisfactory accuracy by using the modified ALS equation with the extended Wang-Sandler mixing rule.

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Appendix A

Data Sources and Results for Pure Substances

The data sources for a total of 86 substances tested in this work are given in Table A.1 with the determined values of the characteristic parameter T_r (at $\Delta Z = 0.5$). For the purpose of comparison, the overall results for the 86 substances obtained by the SRK, the PR, the SW, the PT and the modified ALS equations are listed in Table A.2. The detailed results of vapor pressures, saturated liquid volumes and saturated vapor volumes for pure substances obtained by using the modified ALS equation are given in Table A.3 and the detailed results calculated by using the SRK, the PR, the SW, the PT and the SIL equations are given in Tables A.4 to A.8. The expressions of the equations other than the modified ALS equation are given in Appendix B.

Table A.1 Data sources and the character parameter T_r (at $\Delta Z=0.5$) of the total 86 substances (only the first author is listed in the data sources)

SUBSTANCES	$T_r(\Delta Z=0.5)$	NP	Tr RANGE	DATA SOURCES
ARGON	0.92498	68	0.556-0.995	Angus (1971)
CHLORINE	0.92771	51	0.413-0.995	Angus (1985)
FLUORINE	0.92224	20	0.658-0.988	Vargaftik (1975)
HELIUM	0.87362	55	0.420-0.973	Angus (1977)
HYDROGEN CHLORIDE	0.92986	14	0.579-0.964	Washburn (1928)
HYDROGEN	0.91014	22	0.422-0.985	Vargaftik (1975)
WATER	0.93980	209	0.422-0.992	ASME (1967)
HYDROGEN SULFIDE	0.94468	29	0.565-0.982	Starling (1973)
AMMONIA	0.92875	29	0.602-0.986	Canjar (1967)
KRYPTON	0.92902	47	0.553-0.993	Vargaftik (1975)
NITROGEN	0.93071	64	0.500-0.991	Angus (1977)
NEON	0.92004	20	0.563-0.991	Vargaftik (1975)
OXYGEN	0.92902	101	0.352-0.990	Vargaftik (1975)
SULFUR DIOXIDE	0.93964	36	0.593-0.994	Canjar (1967)
XENON	0.92725	65	0.557-0.994	Vargaftik (1975)
PHOSGENE	0.95050	18	0.618-0.974	Washburn (1928)
CARBON TETRACHLORIDE	0.93924	21	0.635-0.994	Washburn (1928)
CARBON TETRAFLUORIDE	0.94293	16	0.394-0.967	Lobo (1981)
CARBON MONOXIDE	0.93029	24	0.513-0.981	Canjar (1967)
CARBON DIOXIDE	0.93976	46	0.712-0.996	Angus (1973)
CHLOROFORM	0.97112	9	0.624-0.942	Schludnder (1983)
FREON-13	0.93789	69	0.540-0.991	Vargaftik (1975)
FREON-12	0.93485	77	0.528-0.982	Vargaftik (1975)
FREON-22	0.93748	73	0.469-0.994	Vargaftik (1975)
FREON-21	0.93652	119	0.472-0.995	Vargaftik (1975)
METHANE	0.92782	51	0.476-0.987	Angus (1976)
METHANOL	0.94521	20	0.659-0.991	Washburn (1928)
METHYL MERCAPTAN	0.94695	20	0.594-0.985	Washburn (1928)
ACETYLENE	0.93551	22	0.624-0.991	Canjar (1967)
ACETONITRILE	0.93341	11	0.547-0.977	Franscesconi (1975)
ETHYLENE	0.92876	75	0.507-0.996	Angus (1972)
ETHYLENE OXIDE	0.94366	9	0.605-0.938	Schludnder (1983)
ACETIC ACID	0.87562	31	0.495-0.984	Washburn (1928)
METHYL FORMATE	0.93735	19	0.626-0.992	Washburn (1928)
ETHYL CHLORIDE	0.94790	18	0.620-0.984	Washburn (1928)
ETHANE	0.93288	35	0.436-0.991	Starling (1973)
DIMETHYL ETHER	0.93475	17	0.624-0.983	Washburn (1928)
ETHANOL	0.95216	17	0.684-0.979	Washburn (1928)
ETHYL MERCAPTAN	0.95678	20	0.616-0.988	Washburn (1928)
DIMETHYL SULFIDE	0.94637	20	0.614-0.980	Washburn (1928)
PROPYNE	0.93470	12	0.803-0.994	Vohra (1962)
PROPYLENE	0.93433	45	0.370-0.959	Angus (1986)

Table A.1 (continued)

ACETONE	0.94351	19	0.648-0.990	Washburn (1928)
PROPYLENE OXIDE	0.93526	9	0.638-0.954	Schludnder (1983)
ETHYL FORMATE	0.93986	20	0.644-0.990	Washburn (1928)
METHYL ACETATE	0.94108	19	0.652-0.993	Washburn (1928)
CYCLOPROPANE	0.93519	21	0.737-0.988	Lin (1970)
PROPANE	0.93762	38	0.495-0.984	Starling (1973)
N-PROPANOL	0.94327	19	0.658-0.994	Washburn (1928)
2-PROPANOL	0.95787	9	0.700-0.980	Schludnder (1983)
METHYL ETHYL ETHER	0.94857	17	0.641-0.989	Washburn (1928)
PERFLUOROCYCLOBUTANE	0.94575	53	0.600-0.991	Vargaftik (1975)
1,2-BUTADIENE	0.92871	9	0.640-0.902	Schludnder (1983)
1,3-BUTADIENE	0.93946	47	0.407-0.977	Vargaftik (1975)
1-BUTENE	0.94222	26	0.951-0.979	Canjar (1967)
ETHYL ACETATE	0.94188	19	0.670-0.990	Washburn (1928)
METHYL PROPIONATE	0.94388	21	0.665-0.995	Washburn (1928)
N-PROPYL FORMATE	0.94336	19	0.958-0.991	Washburn (1928)
N-BUTANE	0.94040	29	0.627-0.993	Starling (1973)
ISOBUTANE	0.94176	39	0.469-0.993	Starling (1973)
1-BUTANOL	0.93822	10	0.694-0.993	Schludnder (1983)
T-BUTANOL	0.94357	9	0.703-0.948	Schludnder (1983)
DIETHYL ETHER	0.94032	18	0.659-0.992	Washburn (1928)
DIETHYL SULFIDE	0.98041	20	0.653-0.993	Washburn (1928)
DIETHYL AMINE	0.95208	18	0.662-0.993	Washburn (1928)
N-PROPYL ACETATE	0.94426	18	0.682-0.989	Washburn (1928)
ETHYL PROPIONATE	0.94215	20	0.682-0.995	Washburn (1928)
METHYL BUTYRATE	0.94409	19	0.678-0.989	Washburn (1928)
METHYL ISOBUTYRATE	0.94098	18	0.676-0.986	Washburn (1928)
N-PENTANE	0.94276	30	0.638-0.981	Starling (1973)
ISOPENTANE	0.94429	31	0.470-0.989	Starling (1973)
CHLOROBENZENE	0.92861	14	0.653-0.859	Washburn (1928)
FLUOROBENZENE	0.93892	20	0.648-0.988	Washburn (1928)
BENZENE	0.94061	46	0.553-0.988	Canjar (1967)
ANILINE	0.94347	9	0.655-0.966	Schludnder (1983)
CYCLOHEXANE	0.94116	16	0.639-0.981	Washburn (1928)
N-HEXANE	0.94471	42	0.525-0.984	Starling (1973)
TOLUENE	0.95620	9	0.649-0.972	Schludnder (1983)
N-HEPTANE	0.94877	30	0.545-0.987	Starling (1973)
N-OCTANE	0.94590	27	0.488-0.976	Starling (1973)
ISOOCTANE	0.95071	26	0.502-0.980	Vargaftik (1975)
M-XYLENE	0.94402	9	0.668-0.980	Schludnder (1983)
O-XYLENE	0.94647	9	0.663-0.960	Schludnder (1983)
P-XYLENE	0.94530	9	0.669-0.982	Schludnder (1983)
ETHYL BENZENE	0.94703	10	0.663-0.993	Schludnder (1983)
N-DECANE	0.94840	9	0.724-0.971	Schludnder (1983)

Table A.2 A comparison of the overall results of the calculated P^s, V_L^s and V_V^s for the total 86 substances from five equations in terms of AAPD

Equation of state	$\Delta P^s\%$	$\Delta V_L^s\%$	$\Delta V_V^s\%$
Soave-Redlich-Kwong	2.095	17.228	5.515
Peng-Robinson	1.729	8.323	4.993
Schmidt-Wenzel	1.773	8.064	5.251
Patel-Teja	1.873	4.349	5.216
Sugie-Iwahori-Lu	1.301	2.677	4.946
Modified ALS	0.781	1.409	3.717

Table A.3 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the modified ALS equation of state in terms of AAPD

SUBSTANCES	P^s	V_L^s	V_V^s
ARGON	.43	.86	.80
CHLORINE	.71	1.46	1.34
FLUORINE	.73	.39	2.26
HELIUM	.57	1.92	1.59
HYDROGEN CHLORIDE	1.13	.81	2.60
HYDROGEN	.60	.97	.49
WATER	.49	.71	.81
HYDROGEN SULFIDE	.82	1.97	2.56
AMMONIA	1.38	.68	1.59
KRYPTON	.46	.51	1.06
NITROGEN	.29	.55	.68
NEON	1.19	.77	1.96
OXYGEN	.24	.69	.49
SULFUR DIOXIDE	.76	1.75	1.60
XENON	.34	.62	1.14
PHOSGENE	.91	1.74	6.59
CARBON TETRACHLORIDE	.33	1.03	.86
CARBON TETRAFLUORIDE	1.02	2.02	1.62
CARBON MONOXIDE	.69	.45	2.73
CARBON DIOXIDE	.37	1.17	.74
CHLOROFORM	.67	3.41	3.51
FREON-13	.58	.96	1.10
FREON-12	.10	.87	.38
FREON-22	.50	1.26	.79
FREON-21	.67	1.25	1.16
METHANE	.33	.93	.93
METHANOL	.83	1.52	2.70
METHYL MERCAPTAN	.57	.89	27.30
ACETYLENE	.42	.92	1.56
ACETONITRILE	1.60	2.52	7.48
ETHYLENE	.37	1.10	1.79
ETHYLENE OXIDE	1.43	1.64	.83
ACETIC ACID	.73	.83	52.78
METHYL FORMATE	.50	1.14	.49
ETHYL CHLORIDE	1.02	.91	3.34
ETHANE	.85	1.76	1.20
DIMETHYL ETHER	.75	1.03	1.41
ETHANOL	.61	.57	1.80
ETHYL MERCAPTAN	.56	1.36	11.27
DIMETHYL SULFIDE	.63	1.38	16.02
PROPYNE	.32	2.13	1.16

Table A.3 (continued)

PROPYLENE	.13	1.65	.29
ACETONE	.74	2.53	10.95
PROPYLENE OXIDE	1.49	3.22	1.09
ETHYL FORMATE	.92	1.38	.97
METHYL ACETATE	.58	1.78	.74
CYCLOPROPANE	.82	.78	1.08
PROPANE	.72	.90	.95
N-PROPANOL	.73	.92	2.26
2-PROPANOL	2.57	5.20	8.54
METHYL ETHYL ETHER	.59	1.32	13.65
PERFLUOROCYCLOBUTANE	.39	1.61	.76
1,2-BUTADIENE	3.76	.49	3.81
1,3-BUTADIENE	.52	1.01	.57
1-BUTENE	.53	1.27	1.29
ETHYL ACETATE	.66	1.28	.60
METHYL PROPIONATE	.38	2.27	1.34
N-PROPYL FORMATE	.54	1.50	.95
N-BUTANE	.62	2.09	.91
ISOBUTANE	.50	.67	2.19
1-BUTANOL	3.48	1.07	10.05
T-BUTANOL	2.74	.71	1.12
DIETHYL ETHER	.57	1.17	1.76
DIETHYL SULFIDE	.38	2.81	40.09
DIETHYL AMINE	.52	1.22	7.27
N-PROPYL ACETATE	.49	1.36	.52
ETHYL PROPIONATE	.95	1.58	1.05
METHYL BUTYRATE	.54	1.20	1.50
METHYL ISOBUTYRATE	1.02	.88	.64
N-PENTANE	.33	.84	.76
ISOPENTANE	.79	1.31	.89
CHLOROBENZENE	.21	3.48	.69
FLUOROBENZENE	.42	.83	.53
BENZENE	.40	.95	1.91
ANILINE	.31	1.57	.79
CYCLOHEXANE	.59	.72	1.15
N-HEXANE	.45	1.92	1.33
TOLUENE	2.08	1.92	4.05
N-HEPTANE	.43	1.63	1.13
N-OCTANE	.54	1.25	1.81
ISOOCTANE	.13	1.82	6.91
M-XYLENE	1.38	.58	1.43
O-XYLENE	.92	1.31	.96
P-XYLENE	.55	1.84	1.39
ETHYL BENZENE	1.23	3.94	2.83
N-DECANE	1.05	1.96	1.66

Table A.4 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the SRK equation of state in terms of AAPD

SUBSTANCES	P^s	V_L^s	V_V^s
ARGON	1.47	4.73	2.16
CHLORINE	1.85	6.60	2.56
FLUORINE	1.04	5.88	4.21
HELIUM	11.82	12.98	19.37
HYDROGEN CHLORIDE	2.46	17.70	6.01
HYDROGEN	6.34	8.91	8.83
WATER	9.81	37.99	13.52
HYDROGEN SULFIDE	3.95	9.03	5.95
AMMONIA	1.51	29.73	5.55
KRYPTON	1.80	5.36	2.58
NITROGEN	1.35	4.43	1.66
NEON	3.61	6.47	2.81
OXYGEN	3.99	3.72	4.75
SULFUR DIOXIDE	1.25	17.11	1.59
XENON	1.49	6.91	1.83
PHOSGENE	.52	8.27	8.69
CARBON TETRACHLORIDE	.90	14.60	1.99
CARBON TETRAFLUORIDE	1.95	6.50	2.30
CARBON MONOXIDE	3.87	3.66	7.61
CARBON DIOXIDE	1.18	14.31	3.43
CHLOROFORM	3.03	12.28	3.53
FREON-13	4.53	9.03	6.38
FREON-12	5.84	7.64	7.57
FREON-22	.86	16.76	2.24
FREON-21	1.03	12.33	2.67
METHANE	2.12	5.09	2.25
METHANOL	4.02	42.65	3.98
METHYL MERCAPTAN	.96	13.53	26.67
ACETYLENE	1.68	14.61	2.19
ACETONITRILE	6.49	85.48	12.07
ETHYLENE	1.19	9.43	2.75
ETHYLENE OXIDE	1.96	22.19	1.90
ACETIC ACID	7.84	60.32	65.41
METHYL FORMATE	.30	22.69	3.16
ETHYL CHLORIDE	1.16	17.05	3.08
ETHANE	1.78	9.56	2.21
DIMETHYL ETHER	.58	15.63	2.39
ETHANOL	.19	27.84	1.76
ETHYL MERCAPTAN	.89	14.87	12.92
DIMETHYL SULFIDE	2.59	16.43	16.54
PROPYNE	1.16	19.78	2.84

Table A.4 (continued)

PROPYLENE	1.41	7.96	1.68
ACETONE	.93	33.01	11.30
PROPYLENE OXIDE	2.49	27.59	2.43
ETHYL FORMATE	.36	22.32	2.86
METHYL ACETATE	.70	23.67	2.18
CYCLOPROPANE	.29	17.92	1.61
PROPANE	1.23	9.95	1.18
N-PROPANOL	1.64	21.62	6.69
2-PROPANOL	4.64	24.82	13.58
METHYL ETHYL ETHER	2.11	15.24	15.46
PERFLUOROCYCLOBUTANE	.45	9.14	1.25
1,2-BUTADIENE	3.49	13.20	1.28
1,3-BUTADIENE	1.74	14.99	1.22
1-BUTENE	1.04	12.14	1.39
ETHYL ACETATE	.83	24.58	2.86
METHYL PROPIONATE	1.05	22.57	2.41
N-PROPYL FORMATE	.79	21.12	1.87
N-BUTANE	.88	14.27	1.04
ISOBUTANE	1.30	8.59	1.92
1-BUTANOL	3.65	16.92	14.23
T-BUTANOL	2.90	16.36	5.75
DIETHYL ETHER	1.37	18.60	2.22
DIETHYL SULFIDE	3.25	14.51	39.43
DIETHYL AMINE	1.68	19.00	8.39
N-PROPYL ACETATE	.85	24.85	2.13
ETHYL PROPIONATE	1.59	23.13	2.18
METHYL BUTYRATE	1.61	22.30	2.83
METHYL ISOBUTYRATE	1.10	20.58	2.72
N-PENTANE	1.00	14.58	.68
ISOPENTANE	1.42	11.23	1.76
CHLOROBENZENE	1.40	13.92	.55
FLUOROBENZENE	.92	17.49	1.69
BENZENE	1.10	13.89	1.66
ANILINE	1.45	16.66	.97
CYCLOHEXANE	.57	13.82	.89
N-HEXANE	1.69	14.55	1.65
TOLUENE	1.99	16.88	2.78
N-HEPTANE	1.39	16.92	1.70
N-OCTANE	1.58	18.99	1.41
ISOOCTANE	1.38	12.30	5.96
M-XYLENE	.73	17.73	1.48
O-XYLENE	1.07	16.48	.89
P-XYLENE	.69	20.76	1.46
ETHYL BENZENE	1.94	18.62	1.83
N-DECANE	2.05	25.73	.88

Table A.5 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the PR equation of state in terms of AAPD

SUBSTANCES	P^s	V_L^s	V_V^s
ARGON	.39	8.57	1.76
CHLORINE	1.69	6.82	1.89
FLUORINE	1.41	6.87	2.59
HELIUM	6.01	19.93	9.34
HYDROGEN CHLORIDE	1.50	4.10	4.80
HYDROGEN	4.18	13.71	7.24
WATER	5.78	22.35	7.79
HYDROGEN SULFIDE	4.17	5.49	7.41
AMMONIA	1.03	14.74	4.79
KRYPTON	.62	7.89	2.28
NITROGEN	.56	8.87	1.68
NEON	3.31	14.26	4.03
OXYGEN	1.20	9.47	1.97
SULFUR DIOXIDE	.65	4.70	.46
XENON	.40	7.11	1.70
PHOSGENE	.67	5.98	8.95
CARBON TETRACHLORIDE	1.26	4.01	1.80
CARBON TETRAFLUORIDE	2.84	7.26	3.55
CARBON MONOXIDE	2.82	8.83	5.74
CARBON DIOXIDE	1.92	4.68	2.81
CHLOROFORM	3.60	3.54	3.61
FREON-13	4.51	5.88	5.52
FREON-12	5.59	5.73	6.35
FREON-22	.88	4.68	1.50
FREON-21	1.57	4.04	2.63
METHANE	.67	8.22	1.39
METHANOL	4.00	26.44	2.51
METHYL MERCAPTAN	.97	4.46	27.74
ACETYLENE	1.04	4.79	1.93
ACETONITRILE	5.11	64.26	10.25
ETHYLENE	.72	6.74	1.62
ETHYLENE OXIDE	2.21	7.94	1.34
ACETIC ACID	5.93	32.86	59.23
METHYL FORMATE	.85	8.60	2.44
ETHYL CHLORIDE	.35	4.23	3.39
ETHANE	.92	7.58	1.84
DIMETHYL ETHER	1.21	4.97	1.54
ETHANOL	1.04	13.14	1.39
ETHYL MERCAPTAN	.57	4.54	13.67
DIMETHYL SULFIDE	2.03	4.51	17.21
PROPYNE	.37	6.60	1.04

Table A.5 (continued)

PROPYLENE	3.24	5.20	3.17
ACETONE	.71	17.70	10.60
PROPYLENE OXIDE	2.45	12.73	1.92
ETHYL FORMATE	.81	8.32	1.92
METHYL ACETATE	.37	9.47	1.37
CYCLOPROPANE	.69	5.13	1.49
PROPANE	.88	6.19	1.91
N-PROPANOL	2.38	7.75	5.64
2-PROPANOL	5.06	10.51	13.46
METHYL ETHYL ETHER	2.80	5.37	16.28
PERFLUOROCYCLOBUTANE	.76	6.31	1.40
1,2-BUTADIENE	3.57	1.97	1.28
1,3-BUTADIENE	1.91	5.38	1.98
1-BUTENE	.32	4.44	1.97
ETHYL ACETATE	.18	10.29	1.95
METHYL PROPIONATE	.47	8.49	1.55
N-PROPYL FORMATE	.44	7.18	1.29
N-BUTANE	.24	5.51	1.14
ISOBUTANE	1.03	3.88	2.40
1-BUTANOL	3.71	4.66	13.02
T-BUTANOL	3.30	2.97	5.18
DIETHYL ETHER	.63	5.72	1.90
DIETHYL SULFIDE	3.98	24.33	40.01
DIETHYL AMINE	1.29	5.34	9.05
N-PROPYL ACETATE	.31	10.45	1.37
ETHYL PROPIONATE	.80	8.94	1.38
METHYL BUTYRATE	.82	8.24	2.03
METHYL ISOBUTYRATE	.46	6.64	2.04
N-PENTANE	.31	3.83	1.17
ISOPENTANE	1.69	5.04	2.05
CHLOROBENZENE	.63	1.11	.40
FLUOROBENZENE	.51	4.69	1.19
BENZENE	.68	3.83	2.80
ANILINE	.55	3.50	.35
CYCLOHEXANE	.52	4.77	1.73
N-HEXANE	.89	2.53	1.70
TOLUENE	2.16	3.82	3.42
N-HEPTANE	.87	3.56	1.38
N-OCTANE	1.96	5.96	1.88
ISOOCTANE	.98	3.82	7.54
M-XYLENE	.89	4.14	.87
O-XYLENE	.85	3.28	.79
P-XYLENE	.88	6.85	.99
ETHYL BENZENE	2.63	5.44	1.35
N-DECANE	1.51	11.14	.39

Table A.6 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the SW equation of state in terms of AAPD

SUBSTANCES	P^s	V_L^s	V_V^s
ARGON	1.24	4.55	2.74
CHLORINE	0.49	3.23	1.81
FLUORINE	1.98	3.59	5.55
HELIUM	12.51	7.85	22.25
HYDROGEN CHLORIDE	1.31	13.47	6.04
HYDROGEN	3.23	8.38	4.39
WATER	8.32	22.23	12.16
HYDROGEN SULFIDE	3.47	6.37	5.90
AMMONIA	0.99	18.00	5.36
KRYPTON	1.36	5.21	1.83
NITROGEN	0.72	3.99	0.98
NEON	2.23	5.85	0.84
OXYGEN	1.80	3.59	2.51
SULFUR DIOXIDE	0.54	8.66	1.64
XENON	1.01	6.54	1.72
PHOSGENE	0.82	4.80	8.06
CARBON TETRACHLORIDE	1.43	7.15	2.72
CARBON TETRAFLUORIDE	1.28	3.79	1.70
CARBON MONOXIDE	3.49	3.28	6.98
CARBON DIOXIDE	2.03	5.58	3.41
CHLOROFORM	3.76	3.52	3.87
FREON-13	4.83	3.81	6.06
FREON-12	5.88	2.95	7.14
FREON-22	0.56	7.58	1.87
FREON-21	0.89	3.87	2.29
METHANE	0.39	4.91	0.42
METHANOL	3.06	17.36	2.40
METHYL MERCAPTAN	1.14	6.91	26.72
ACETYLENE	0.96	6.50	2.22
ACETONITRILE	5.26	67.06	11.72
ETHYLENE	0.71	6.22	2.43
ETHYLENE OXIDE	2.42	12.97	1.98
ACETIC ACID	7.21	27.84	62.71
METHYL FORMATE	0.94	11.38	3.03
ETHYL CHLORIDE	0.17	8.71	2.57
ETHANE	0.91	5.75	1.78
DIMETHYL ETHER	1.38	8.08	2.70
ETHANOL	1.52	6.51	2.86
ETHYL MERCAPTAN	0.80	6.70	12.78
DIMETHYL SULFIDE	1.84	8.12	16.36
PROPYNE	0.14	13.68	5.40

Table A.6 (continued)

PROPYLENE	0.75	2.19	1.21
ACETONE	0.86	18.48	11.11
PROPYLENE OXIDE	2.34	15.21	2.27
ETHYL FORMATE	0.89	10.02	2.39
METHYL ACETATE	0.35	9.67	1.56
CYCLOPROPANE	1.19	11.84	2.43
PROPANE	0.38	5.23	1.00
N-PROPANOL	3.00	6.10	6.44
2-PROPANOL	6.45	5.79	14.99
METHYL ETHYL ETHER	2.93	5.38	15.78
PERFLUOROCYCLOBUTANE	0.72	6.74	1.14
1,2-BUTADIENE	3.69	2.85	1.64
1,3-BUTADIENE	1.01	6.72	0.65
1-BUTENE	0.29	4.09	1.20
ETHYL ACETATE	0.28	9.17	1.78
METHYL PROPIONATE	0.44	8.76	1.59
N-PROPYL FORMATE	0.32	7.81	1.32
N-BUTANE	0.25	6.33	1.02
ISOBUTANE	0.20	2.04	1.08
1-BUTANOL	3.36	7.67	12.96
T-BUTANOL	4.47	6.50	5.95
DIETHYL ETHER	0.56	6.86	1.79
DIETHYL SULFIDE	3.97	23.49	40.31
DIETHYL AMINE	1.50	6.78	8.70
N-PROPYL ACETATE	0.15	9.47	1.28
ETHYL PROPIONATE	0.91	7.82	1.33
METHYL BUTYRATE	0.87	7.59	1.85
METHYL ISOBUTYRATE	0.29	6.63	1.97
N-PENTANE	0.19	4.40	0.71
ISOPENTANE	0.36	3.44	0.73
CHLOROBENZENE	0.66	3.53	0.45
FLUOROBENZENE	0.43	7.09	1.78
BENZENE	0.47	5.53	2.57
ANILINE	0.67	3.41	0.29
CYCLOHEXANE	0.66	5.18	1.65
N-HEXANE	0.50	3.49	1.19
TOLUENE	2.31	5.81	2.99
N-HEPTANE	0.76	3.41	1.07
N-OCTANE	1.17	3.96	0.94
ISOOCTANE	0.31	3.66	7.63
M-XYLENE	0.91	4.37	1.15
O-XYLENE	0.81	3.68	0.97
P-XYLENE	1.00	7.26	1.16
ETHYL BENZENE	2.68	6.16	1.26
N-DECANE	1.17	5.39	0.40

Table A.7 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the PT equation of state in terms of AAPD

SUBSTANCE	P^s	V_L^s	V_V^s
ARGON	.73	2.44	1.36
CHLORINE	1.08	1.64	1.12
FLUORINE	1.12	2.11	2.69
HELIUM	10.78	8.76	18.24
HYDROGEN CHLORIDE	1.76	7.93	4.92
HYDROGEN	6.01	8.67	7.19
WATER	1.59	2.01	2.20
HYDROGEN SULFIDE	.89	1.65	2.82
AMMONIA	1.65	2.22	4.01
KRYPTON	.90	2.41	1.92
NITROGEN	.65	2.24	1.17
NEON	3.88	5.70	3.49
OXYGEN	1.69	2.69	2.35
SULFUR DIOXIDE	.50	1.72	1.15
XENON	.79	2.92	1.40
PHOSGENE	.70	3.00	8.90
CARBON TETRACHLORIDE	1.36	2.87	1.98
CARBON TETRAFLUORIDE	2.05	3.33	2.62
CARBON MONOXIDE	.49	2.12	3.06
CARBON DIOXIDE	.59	1.75	1.37
CHLOROFORM	3.54	2.65	3.49
FREON-13	4.64	2.60	5.52
FREON-12	5.63	2.74	6.53
FREON-22	1.11	2.45	1.81
FREON-21	1.39	1.30	2.57
METHANE	1.05	2.88	1.56
METHANOL	1.42	2.28	3.81
METHYL MERCAPTAN	.87	2.94	27.79
ACETYLENE	.66	1.85	1.64
ACETONITRILE	4.50	45.07	10.99
ETHYLENE	.60	2.49	1.73
ETHYLENE OXIDE	2.31	10.25	1.49
ACETIC ACID	5.49	22.00	62.53
METHYL FORMATE	1.42	6.08	2.62
ETHYL CHLORIDE	.66	4.83	3.31
ETHANE	.78	3.72	1.38
DIMETHYL ETHER	1.32	3.65	1.75
ETHANOL	2.11	4.83	2.60
ETHYL MERCAPTAN	.94	2.75	13.75
DIMETHYL SULFIDE	1.90	4.01	17.18
PROPYNE	.71	2.77	2.40

Table A.7 (continued)

PROPYLENE	1.11	2.51	1.25
ACETONE	1.61	12.21	10.53
PROPYLENE OXIDE	2.43	11.21	2.65
ETHYL FORMATE	1.63	4.28	2.47
METHYL ACETATE	1.40	4.62	2.15
CYCLOPROPANE	.68	6.32	1.35
PROPANE	.60	3.03	1.48
N-PROPANOL	4.40	1.86	9.08
2-PROPANOL	7.38	3.75	16.20
METHYL ETHYL ETHER	3.13	2.05	16.48
PERFLUOROCYCLOBUTANE	1.35	6.44	2.17
1,2-BUTADIENE	3.60	2.07	1.38
1,3-BUTADIENE	1.50	1.46	1.64
1-BUTENE	.59	1.45	1.82
ETHYL ACETATE	1.28	3.87	2.88
METHYL PROPIONATE	1.32	2.87	2.72
N-PROPYL FORMATE	1.10	3.12	2.11
N-BUTANE	.37	3.72	1.10
ISOBUTANE	.74	2.53	2.01
1-BUTANOL	2.77	3.40	12.67
T-BUTANOL	5.76	7.66	7.57
DIETHYL ETHER	.54	1.78	2.90
DIETHYL SULFIDE	4.60	26.16	39.99
DIETHYL AMINE	1.37	2.72	9.10
N-PROPYL ACETATE	1.63	3.59	2.44
ETHYL PROPIONATE	.95	2.44	2.77
METHYL BUTYRATE	.95	1.84	3.39
METHYL ISOBUTYRATE	1.09	1.76	3.23
N-PENTANE	1.20	3.28	1.74
ISOPENTANE	1.03	2.01	1.53
CHLOROBENZENE	.63	2.42	.44
FLUOROBENZENE	.78	2.60	1.56
BENZENE	.96	1.57	2.68
ANILINE	1.05	3.11	1.36
CYCLOHEXANE	.64	1.78	1.53
N-HEXANE	.80	2.67	1.83
TOLUENE	2.69	2.09	3.15
N-HEPTANE	.84	1.74	1.23
N-OCTANE	1.86	3.85	1.86
ISOOCTANE	.97	2.75	6.92
M-XYLENE	1.69	3.00	1.46
O-XYLENE	1.50	1.43	1.04
P-XYLENE	1.39	2.70	1.43
ETHYL BENZENE	3.46	1.39	1.25
N-DECANE	1.42	2.57	1.64

Table A.8 Deviations of calculated vapor pressure, P^s, saturated liquid volume, V_L^s, and saturated vapor volume, V_V^s, obtained from the SIL equation of state in terms of AAPD

SUBSTANCES	ΔP^s%	ΔV_L^s%	ΔV_V^s%
ARGON	0.71	1.42	2.21
CHLORINE	2.84	2.86	3.60
FLUORINE	1.61	0.98	1.54
HELIUM	0.80	0.58	2.95
HYDROGEN CHLORIDE	0.71	2.63	4.52
HYDROGEN	3.29	1.99	7.51
WATER	0.10	2.33	1.06
HYDROGEN SULFIDE	0.80	3.25	5.78
AMMONIA	1.07	1.52	1.87
KRYPTON	0.15	1.55	2.95
NITROGEN	0.62	2.11	1.98
NEON	3.80	3.49	5.00
OXYGEN	0.49	2.69	1.95
SULFUR DIOXIDE	0.50	3.83	1.95
XENON	0.11	1.58	2.49
PHOSGENE	1.34	2.70	11.69
CARBON TETRACHLORIDE	1.34	2.39	2.23
CARBON TETRAFLUORIDE	0.58	3.06	2.06
CARBON MONOXIDE	2.12	1.43	2.77
CARBON DIOXIDE	0.10	2.65	1.98
CHLOROFORM	1.53	1.24	2.46
FREON-13	0.46	1.69	2.04
FREON-12	0.74	1.51	0.43
FREON-22	0.30	2.39	1.98
FREON-21	1.05	2.27	2.28
METHANE	1.26	1.97	3.18
METHANOL	1.40	3.45	3.37
METHYL MERCAPTAN	0.77	4.17	28.66
ACETYLENE	0.58	1.82	1.45
ACETONITRILE	1.65	4.14	10.05
ETHYLENE	0.43	2.62	1.87
ETHYLENE OXIDE	1.66	2.21	2.33
ACETIC ACID	4.68	2.89	47.60
METHYL FORMATE	0.24	3.57	1.16
ETHYL CHLORIDE	0.46	2.62	4.32
ETHANE	0.37	3.39	1.82
DIMETHYL ETHER	1.94	2.21	2.47
ETHANOL	0.50	4.69	2.97
ETHYL MERCAPTAN	0.96	1.85	15.30
DIMETHYL SULFIDE	1.71	1.80	18.79
PROPYNE	0.11	5.86	5.92

Table A.8 (continued)

PROPYLENE	0.37	2.73	0.76
ACETONE	0.98	2.25	11.85
PROPYLENE OXIDE	1.46	3.19	2.54
ETHYL FORMATE	0.62	2.98	2.27
METHYL ACETATE	1.07	2.03	1.01
CYCLOPROPANE	4.52	2.73	4.75
PROPANE	0.42	1.40	2.46
1-PROPANOL	0.95	2.06	2.53
2-PROPANOL	3.10	3.38	10.11
METHYL ETHYL ETHER	2.08	2.25	15.34
PERFLUOROCYCLOBUTANE	0.86	4.28	1.47
1,2-BUTADIENE	3.28	0.73	1.99
1,3-BUTADIENE	0.88	2.40	2.31
1-BUTENE	0.44	1.61	2.86
ETHYL ACETATE	0.37	2.24	1.29
METHYL PROPIONATE	1.11	2.84	1.56
N-PROPYL FORMATE	1.49	2.07	2.98
N-BUTANE	0.22	2.10	1.88
ISOBUTANE	1.25	2.04	3.05
1-BUTANOL	5.73	3.56	9.24
T-BUTANOL	2.75	1.12	0.85
DIETHYL ETHER	0.79	2.39	2.74
DIETHYL SULFIDE	3.99	25.46	41.11
DIETHYL AMINE	0.56	1.82	11.07
N-PROPYL ACETATE	0.20	3.26	1.40
ETHYL PROPIONATE	0.42	2.72	1.42
METHYL BUTYRATE	0.73	3.00	2.62
METHYL ISOBUTYRATE	0.54	2.51	1.70
N-PENTANE	0.45	1.09	1.76
ISOPENTANE	0.52	2.92	1.21
CHLOROBENZENE	0.39	0.70	0.42
FLUOROBENZENE	0.60	1.91	1.89
BENZENE	0.53	2.14	2.84
ANILINE	1.14	1.67	2.20
CYCLOHEXANE	0.48	1.78	2.46
N-HEXANE	0.41	1.95	2.04
TOLUENE	2.23	1.72	7.23
N-HEPTANE	0.35	1.91	1.40
N-OCTANE	0.80	3.69	1.53
ISOOCTANE	0.27	2.43	7.06
M-XYLENE	5.72	1.98	8.76
O-XYLENE	1.23	1.54	2.74
P-XYLENE	1.55	2.06	2.33
ETHYL BENZENE	5.97	2.93	3.46
N-DECANE	2.17	3.21	2.31

Table A.9 Parameters of the modified ALS equation for 86 pure substances

SUBSTANCES	Ω_{bl}	f	β_c	β_d	β_e	α_a	α_n	α_m
ARGON	.093170	.225310	.7443	12.0000	34.0000	.5462	.6941	.0312
CHLORINE	.090088	.219814	.6715	12.0000	34.0000	.9711	.4550	.0110
FLUORINE	.092680	.222037	.7619	12.0000	34.0000	.8385	.6252	.0848
HELIUM	.120680	.206600	.6645	4.9140	31.9510	-1.2611	.3249	.0654
HYDROGEN CHLORIDE	.078773	.203355	1.3643	.9425	5.7246	.6314	.8237	.0349
HYDROGEN	.108990	.215150	.8617	6.5054	17.2480	-.1011	-.5217	.3643
WATER	.057430	.200920	.7257	-.9437	11.9525	1.5619	.6615	.0801
HYDROGEN SULFIDE	.093828	.220369	1.7915	1.5300	5.7330	.6877	.6569	.0496
AMMONIA	.069010	.189910	.9479	.6010	5.0876	.6548	1.3130	.1310
KRYPTON	.091077	.225063	.7699	12.0000	34.0000	.5925	.6227	.0224
NITROGEN	.092760	.222960	.7120	12.0000	34.0000	.6236	.7096	.0393
NEON	.103257	.227163	.4896	12.0000	34.0000	.2401	1.6905	.0020
OXYGEN	.091790	.223830	.7632	12.0000	34.0000	.6455	.6189	.0226
SULFUR DIOXIDE	.085214	.209561	1.2781	2.1801	10.9505	1.0786	.5215	.0020
XENON	.089765	.224878	.8820	12.0000	34.0000	.5129	.7811	.0379
PHOSGENE	.094347	.233651	3.1554	1.8319	7.3000	.4115	1.8643	.1189
CARBON TETRACHLORIDE	.085809	.213391	1.3931	12.0000	34.0000	1.1260	.5627	.0562
CARBON TETRAFLUORIDE	.089934	.214440	1.2707	12.0000	34.0000	.8452	.7268	.0507
CARBON MONOXIDE	.093150	.221300	.5298	12.0000	34.0000	1.3607	.2733	.0020
CARBON DIOXIDE	.088960	.210610	1.3713	12.0000	34.0000	1.5697	.3994	.0396
CHLOROFORM	.087993	.211908	.0000	.9999	4.0549	.9464	.7779	.0963
FREON-13	.090090	.213144	.8577	12.0000	24.0000	.9591	.5937	.0363
FREON-12	.089685	.212773	.6741	12.0000	24.0000	1.4796	.3505	.0136
FREON-22	.084598	.211723	.9727	12.0000	24.0000	1.4319	.4002	.0171

Table A.9 (continued)

FREON-21	.087628	.209488	1.3157	1.6698	8.2040	1.0404	.4939	.0072
METHANE	.089980	.224690	.9469	12.0000	34.0000	.5329	.7336	.0195
METHANOL	.056350	.193600	.6943	-1.1353	11.9344	2.4383	.5061	.0423
METHYL MERCAPTAN	.082589	.230305	.9722	5.4372	20.9848	1.2646	.4972	.0377
ACETYLENE	.085880	.213640	.8158	12.0000	34.0000	1.2106	.4281	.0020
ACETONITRILE	.043368	.173413	.4482	-.4964	4.4023	1.0600	.7799	.0826
ETHYLENE	.088940	.219880	.7538	12.0000	34.0000	.9059	.5133	.0242
ETHYLENE OXIDE	.078208	.232786	2.9684	1.1400	5.8500	.3246	3.7052	.4542
ACETIC ACID	.056598	.170004	.6059	.0024	4.3842	.8820	1.2677	.1141
METHYL FORMATE	.075434	.209697	.9976	-.0703	12.1000	1.1099	.7448	.0754
ETHYL CHLORIDE	.084741	.213576	1.3338	1.3000	8.5000	1.3756	.3532	.0020
ETHANE	.090410	.219260	2.1654	12.0000	34.0000	.6969	.7948	.0731
DIMETHYL ETHER	.085263	.210094	1.1586	.6829	8.1300	.9123	.7380	.0695
ETHANOL	.064560	.212110	1.0080	-1.1000	19.6600	1.7595	.9309	.0869
ETHYL MERCAPTAN	.085428	.231265	1.8579	.3800	22.6000	.3150	3.0374	.1918
DIMETHYL SULFIDE	.081394	.223764	1.6157	.3639	15.6450	.3935	2.0641	.0797
PROPYNE	.086198	.206293	1.3062	1.6900	8.6000	1.1750	.5419	.0421
PROPYLENE	.088720	.216479	.6804	12.0000	34.0000	.9465	.5678	.0290
ACETONE	.070510	.217460	1.5736	5.0388	12.9200	1.0179	.8331	.0783
PROPYLENE OXIDE	.073545	.208759	.4934	1.3010	5.4450	1.1811	.4666	.0020
ETHYL FORMATE	.078212	.210784	.9955	.1509	12.2260	.8973	.9112	.0705
METHYL ACETATE	.078660	.205238	.7543	12.0000	34.0000	1.4090	.5240	.0393
CYCLOPROPANE	.083354	.217343	.8557	12.0000	34.0000	.8195	.7041	.0644
PROPANE	.089970	.215920	1.8372	12.0000	34.0000	1.0852	.4974	.0290
N-PROPANOL	.073130	.195640	.6534	-.9677	14.7539	2.9124	.5143	.0884
2-PROPANOL	.067292	.231351	23.2452	18.0217	1.4139	.9572	2.0317	.1855
METHYL ETHYL ETHER	.082929	.224684	1.4651	-.0530	18.3555	.7115	1.3823	.1521

Table A.9 (continued)

PERFLUOROCYCLOBUTANE	.091954	.203385	.6339	12.0000	34.0000	1.6193	.4390	.0236
1,2-BUTADIENE	.085333	.209623	.6840	12.0000	34.0000	.2941	4.7515	.5504
1,3-BUTADIENE	.086421	.213329	.7613	12.0000	34.0000	1.2533	.4220	.0020
1-BUTENE	.089218	.213576	1.5223	12.0000	34.0000	1.0411	.5989	.0465
ETHYL ACETATE	.075095	.207033	.9471	.0490	11.8000	1.0147	.9302	.0630
METHYL PROPIONATE	.080398	.203756	.6648	12.0000	34.0000	1.4637	.4852	.0217
N-PROPYL FORMATE	.081192	.205979	.7781	12.0000	34.0000	1.5013	.4654	.0312
N-BUTANE	.087430	.213080	.6949	12.0000	34.0000	1.1227	.5105	.0219
ISOBUTANE	.087564	.214070	.0441	12.0000	34.0000	1.1166	.4681	.0020
1-BUTANOL	.083428	.170375	.7063	1.2157	5.8481	1.4260	.8031	.0691
T-BUTANOL	.078090	.202976	1.5887	1.0899	5.4100	1.0472	1.5991	.1661
DIETHYL ETHER	.082627	.208017	.8442	-.0122	16.4590	1.3373	.5232	.0251
DIETHYL SULFIDE	.129285	.224903	1.8993	1.9100	10.0000	.5571	1.5785	.1313
DIETHYL AMINE	.082300	.224030	1.4063	.3948	20.0460	.5849	1.5409	.0822
N-PROPYL ACETATE	.076849	.208546	1.2716	1.1100	7.4800	.7933	1.1839	.0571
ETHYL PROPIONATE	.077903	.201224	1.1631	1.2880	6.9005	1.0458	.7724	.0212
METHYL BUTYRATE	.078133	.201903	1.1794	1.1790	7.5350	.7552	1.2046	.0478
METHYL ISOBUTYRATE	.080231	.203015	1.2195	1.3090	6.5905	.8575	.9742	.0443
N-PENTANE	.086490	.209870	1.0134	12.0000	34.0000	1.2143	.5219	.0264
ISOPENTANE	.085924	.211352	1.0936	12.0000	34.0000	1.0959	.5500	.0212
CHLOROBENZENE	.084662	.218249	.0000	.6767	3.3340	.9005	.7371	.0020
FLUOROBENZENE	.082549	.209647	1.0522	.4236	11.0310	1.0562	.6329	.0315
BENZENE	.085450	.212280	.7751	12.0000	34.0000	1.1372	.5135	.0190
ANILINE	.084738	.201656	.5702	12.0000	34.0000	1.4843	.4913	.0180
CYCLOHEXANE	.088335	.212279	1.0878	12.0000	34.0000	.9204	.7150	.0555
N-HEXANE	.084770	.206910	.8571	12.0000	34.0000	1.6353	.3707	.0020
TOLUENE	.076025	.236174	2.7221	12.9600	31.6800	.5598	2.4989	.2677

Table A.9 (continued)

N-HEPTANE	.082017	.203818	.6643	12.0000	34.0000	1.5885	.4087	.0020
N-OCTANE	.079736	.200792	1.4707	12.0000	34.0000	1.7547	.3889	.0020
ISOOCTANE	.088417	.206659	.7736	12.0000	34.0000	1.1763	.5764	.0223
M-XYLENE	.081960	.215904	2.6407	2.1920	4.1600	1.0335	.7265	.0274
O-XYLENE	.083210	.206226	.7776	12.0000	34.0000	1.4059	.5065	.0357
P-XYLENE	.080616	.205609	.7508	12.0000	34.0000	1.4411	.5337	.0507
ETHYL BENZENE	.084647	.230291	2.2678	2.1100	7.6500	2.1126	.3549	.0559
N-DECANE	.078396	.195171	.2765	12.0000	34.0000	1.3001	.5954	.0076

Appendix B

Summary of Equations of State

In this work, comparisons were made to several equations of state. The expressions of these equations are given below. These equations are all van der Waals type cubic equations and can be rearranged in terms of the general cubic equations expressed by, Eqns (2.2) and (2.5).

$$P=\frac{RT}{V-b}-\frac{a}{V^2+ubV+wb^2} \tag{2.2}$$

$$P=\frac{RT}{V-b_1}-\frac{a}{(V-b_2)(V-b_3)} \tag{2.5}$$

where

$$a=\frac{\Omega_a R^2 T_C^2}{P_C}, \qquad \Omega_a=\Omega_{ac}\alpha \tag{2.6}$$

and

$$b_k=\Omega_{bk}\frac{RT_C}{P_C}, \qquad k=1,2,3 \tag{B.1}$$

B.1 The Soave-Redlich-Kwong (SRK) Equation (Soave, 1972)

The SRK equation has the form

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)} \tag{B.2}$$

This equation can be obtained from Eqn. (2.2) with u=1 and w=0. The critical constants are given by

$$\Omega_{ac}=0.42747$$
$$\Omega_{bc}=0.08664 \tag{B.3}$$

The temperature dependency of α is of the Soave type

$$\alpha=[1+m(1-T_r^{1/2})]^2 \tag{B.4}$$

where m is given by

$$m=0.480+1.574\omega-0.176\omega^2 \tag{B.5}$$

B.2 The Peng-Robinson (PR) Equation (1986)

The PR equation has the form

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)+b(V-b)} \tag{B.6}$$

This equation can be obtained from Eqn. (2.) with u=2 and w=-1. The critical constants are given by

$$\begin{aligned}\Omega_{ac}&=0.45724\\ \Omega_{bc}&=0.07780\end{aligned} \tag{B.7}$$

The temperature dependency of α is of the Soave type, Eqn. (B.2), and m is given by

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

B.3 The Schmidt-Wenzel (SW) Equation (1980)

The SW equation has the general form, Eqn. (2.2), with u = 1-w. The critical constants are given by

$$\Omega_{ac}=[1-\zeta_c(1-\beta_c)]^3 \qquad \Omega_{bc}=\beta_c\zeta_c \tag{B.9}$$

where, β_c and ζ_c were determined from the following expressions

$$\beta_c=0.25989-0.0217\omega+0.0375\omega^2 \qquad \zeta_c=\frac{1}{3(1+\beta_c\omega)} \tag{B.10}$$

The temperature dependency of α is similar to the Soave type, Eqn. (B.2)

$$\alpha=[1+\kappa(1-T_r^{1/2})]^2 \tag{B.11}$$

and κ is a complicated function of T_r and ω. The results listed in Table A.6 were obtained by Margerum (1989). In his work, for $\omega \leq 0.4$, κ was calculated by

$$\kappa=k_1=k_0+(5T_r-3k_0-1)^2/70 \tag{B.12}$$

for $0.4 < \omega < 0.55$, κ was given by

$$\kappa=\frac{w-0.4}{0.15}k_1+\frac{0.55-w}{0.15}k_2 \qquad \textbf{(B.13)}$$

and for $\omega \geq 0.55$, κ was calculated by

$$\kappa=k_2=k_0+0.71(T_r-0.779)^2 \qquad \textbf{(B.14)}$$

k_0 was calculated from

$$k_0=0.465+1.347\omega-0.528\omega^2 \qquad \textbf{(B.15)}$$

for $\omega \leq 0.3671$ and from

$$k_0=0.5361+0.9593\omega \qquad \textbf{(B.16)}$$

for $\omega > 0.3671$.

If $T_r > 1$, κ was evaluated at $T_r = 1$.

B.4 The Patel-Teja (PT) Equation (1982)

The PT equation has the form

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)+C(V-b)} \qquad \textbf{(B.17)}$$

where

$$C=\Omega_c\frac{RT_C}{P_C} \tag{B.18}$$

Ω_c and Ω_{ac} are given by

$$\begin{aligned}\Omega_c&=1-3\zeta_c\\ \Omega_{ac}&=3\zeta_c^2+3(1-2\zeta_c)\Omega_{bc}+\Omega_{bc}^2+1-3\zeta_c\end{aligned} \tag{B.19}$$

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

$$\Omega_{bc}^3+(2-3\zeta_c)\Omega_{bc}^2+3\zeta_c^2\Omega_{bc}-\zeta_c^3=0 \tag{B.20}$$

ζ_c was determined from the following correlation

$$\zeta_c=0.329032-0.076799\,\omega+0.0211947\,\omega^2 \tag{B.21}$$

For the T_r in the range of 0.9-1.0, a correction was used by Patel and Teja (1982)

$$\zeta_c'=\zeta_c-10(\zeta-Z_c)(T_r-0.9) \tag{B.22}$$

The temperature dependency of α is the same as the Soave type, Eqn. (B.2)

and m is given by

$$m = 0.452413 + 1.30982\omega - 0.295937\omega^2 \qquad \text{(B.23)}$$

ζ_c and m can also be component dependent constants.

B.5 The Sugie-Iwahori-Lu (SIL) Equation (1989)

The SIL equation has a general form as shown in Eqn. (2.5). The results listed in Table 5.8 were calculated by Margerum (1989). In his work, Ω_{ac} and Ω_{bc} were determined iteratively from V_L^s correlations at two points, T_r=0.7 and T_r=0.9. The V_L^s correlations used in his work include the Campbell-Thodos (1984) and the Hankinson-Thomson (Reid et al., 1987) expressions. The value of α was determined from P^s correlations using the procedure as mentioned in Section 3.1. The P^s correlations used in Margerum's work include the Gomez-Nieto and Thodos (1977), the Wagner (Reid et al., 1987), and the Frost-Kalwarf-Thodos (Reid et al., 1987) expressions.

Appendix C

Binary Interaction Coefficients and Data Sources for the Mixtures

The binary interaction coefficients obtained for the simulataneous representation of VLE and volumes, or VLE and excess enthalpies in Chapter 5 are listed in this Appendix. The data sources for the six binary systems calculated in Chapter 5.4 are also listed in this Appendix.

Table C.1 Binary interaction coefficients for the simultaneous representation of VLE and volumes for the hydrogen sulfied + n-heptane system

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
277.59 K	SRK	E-W-S	0.45640	-0.84373	-4484.3	2774.2
	PR	E-W-S	0.29647	-1.11780	-2655.3	3035.4
	PT	E-W-S	0.34277	-0.86790	-3405.9	3404.7
	PRSV	E-W-S	0.28580	-0.78799	-3942.7	3626.1
	Modified ALS	Conventional	0.04257	-	-	-
	Modified ALS	Adachi-Sugie	0.041374	-0.011290	-	-
	Modified ALS	SGR	0.032806	-0.016965	0.22890	-
	Modified ALS	E-W-S	0.40182	-0.67750	-3799.4	3590.7
310.93 K	SRK	E-W-S	0.45456	-0.77388	-4484.3	2774.2
	PR	E-W-S	0.31144	-1.07030	-2655.3	3035.4
	PT	E-W-S	0.35799	-0.80338	-3405.9	3404.7
	PRSV	E-W-S	0.30683	-0.76805	-3942.7	3626.1
	Modified ALS	Conventional	0.031570	-	-	-
	Modified ALS	Adachi-Sugie	0.031836	-0.0040172	-	-
	Modified ALS	SGR	0.030332	0.44687	0.31520	-
	Modified ALS	E-W-S	0.38523	-0.68871	-3799.4	3590.7

Table C.1 (Continue)

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
344.26 K	SRK	E-W-S	0.46072	-0.77029	-4484.3	2774.2
	PR	E-W-S	0.35921	-0.99443	-2655.3	3035.4
	PT	E-W-S	0.37484	-0.82787	-3405.9	3404.7
	PRSV	E-W-S	0.35776	-0.74457	-3942.7	3626.1
	Modified ALS	Conventional	0.034041	-	-	-
	Modified ALS	Adachi-Sugie	0.035438	-0.0082183	-	-
	Modified ALS	SGR	0.026931	-0.0090768	0.096062	-
	Modified ALS	E-W-S	0.39135	-0.73507	-3799.4	3590.7
377.59 K	SRK	E-W-S	0.48488	-0.70444	-4484.3	2774.2
	PR	E-W-S	0.40338	-0.79020	-2655.3	3035.4
	PT	E-W-S	0.43305	-0.59270	-3405.9	3404.7
	PRSV	E-W-S	0.40564	-0.63206	-3942.7	3626.1
	Modified ALS	Conventional	-0.19E-10	-	-	-
	Modified ALS	Adachi-Sugie	0.0013179	0.0067899	-	-
	Modified ALS	SGR	0.030330	-0.0044682	0.31524	-
	Modified ALS	E-W-S	0.43985	-0.61272	-3799.4	3590.7

Table C.1 (Continue)

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}
410.93 K	SRK	E-W-S	0.53851	-0.66868	-4484.3	2774.2
	PR	E-W-S	0.45416	-0.80783	-2655.3	3035.4
	PT	E-W-S	0.48209	-0.60490	-3405.9	3405.7
	PRSV	E-W-S	0.45875	-0.61039	-3942.7	3626.1
	Modified ALS	Conventional	0.27E-5	-	-	-
	Modified ALS	Adachi-Sugie	0.14E-5	-0.13E-5	-	-
	Modified ALS	SGR	0.027623	-0.00454	0.31776	-
	Modified ALS	E-W-S	0.50059	-1.06120	-3799.4	3590.7

Table C.2 Binary interaction coefficients for the simultaneous representation of VLE and volumes for the ethane + methanol system

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
323.15	SRK	E-W-S	.41674	.13498	-3053.6	7679.8
	PR	E-W-S	.37367	.11019	-3461.8	8349.9
	PT	E-W-S	.24284	.61784E-01	-3086.8	8506.6
	PRSV	E-W-S	.37836	.11652	-3233.9	8088.7
	Modified ALS	Conventional	.20946E-01			
	Modified ALS	Adachi-Sugie	.22974E-01	.55902E-02		
	Modified ALS	SGR	.32655	.29703	.51771E-01	
	Modified ALS	E-W-S	.38756	.19842	-1495.0	7311.0
348.15	SRK	E-W-S	.63245	.21648	-3720.1	8425.8
	PR	E-W-S	.62144	.22172	-3843.8	8799.6
	PT	E-W-S	-.55934E-01	.24323E-01	-1107.4	8387.6
	PRSV	E-W-S	.61971	.25067	-3301.1	8073.5
	Modified ALS	Conventional	.56729E-01			
	Modified ALS	Adachi-Sugie	.70510E-01	.22310E-01		
	Modified ALS	SGR	.23200	.17360	.11290	
	Modified ALS	E-W-S	.32922	.14286	-1294.3	8140.6

Table C.2 (continue)

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}
373.15	SRK	E-W-S	.68245	.17661	-5600.5	11606.
	PR	E-W-S	.67918	.13656	-7592.7	14636.
	PT	E-W-S	-.13083	.11950	768.43	8140.6
	PRSV	E-W-S	.66367	.13297	-7678.9	14793.
	Modified ALS	Conventional	.90484E-01			
	Modified ALS	Adachi-Sugie	.96910E-01	.80481E-02		
	Modified ALS	SGR	.15432	.63360E-01	.14572	
	Modified ALS	E-W-S	.23721	.20076	630.25	8281.1

Table C.3 Binary interaction coefficients for the simultaneous representation of VLE and volumes for the ammonia + water system

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
277.59	SRK	E-W-S	.26613	-.34676E-01	-1465.2	-10936.
	PR	E-W-S	.44139E-01	-.63307E-02	578.81	-10896.
	PT	E-W-S	-.29498	.18379E-01	960.52	-8881.0
	PRSV	E-W-S	.45626E-01	-.90690E-02	-696.82	-9634.5
	Modified ALS	Conventional	-.34190			
	Modified ALS	Adachi-Sugie	-.33674	-.42062E-01		
	Modified ALS	SGR	-.28974	-.74624E-01	.81509	
	Modified ALS	E-W-S	-.18956	.45340E-01	4483.9	-10298.
288.71	SRK	E-W-S	.26205	-.18916E-01	-485.31	-11605.
	PR	E-W-S	.40743E-01	-.17343E-02	1802.0	-11948.
	PT	E-W-S	-.29493	.20973E-01	806.27	-8396.5
	PRSV	E-W-S	.42429E-01	-.66075E-02	818.15	-10995.
	Modified ALS	Conventional	-.32385			
	Modified ALS	Adachi-Sugie	-.31978	-.38185E-01		
	Modified ALS	SGR	-.27755	-.66735E-01	.82369	
	Modified ALS	E-W-S	-.18317	.45838E-01	4491.5	-10154.

Table C.3 (continue)

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}
299.82	SRK	E-W-S	.25188	-.42534E-01	408.43	-13033.
	PR	E-W-S	.33042E-01	-.97102E-02	2143.5	-12175.
	PT	E-W-S	-.29911	.19815E-01	1575.6	-8757.7
	PRSV	E-W-S	.34587E-01	-.93391E-02	1489.9	-11490.
	Modified ALS	Conventional	-.30750			
	Modified ALS	Adachi-Sugie	-.30433	-.34647E-01		
	Modified ALS	SGR	-.26297	-.63158E-01	.83063	
	Modified ALS	E-W-S	-.18346	.48865E-01	4408.2	-9782.2
310.93	SRK	E-W-S	.24448	-.45840E-01	1021.3	-13686.
	PR	E-W-S	.28174E-01	-.16415E-01	2160.8	-12025.
	PT	E-W-S	-.29980	.22996E-01	1773.2	-8539.6
	PRSV	E-W-S	.29722E-01	-.13022E-01	1886.4	-11709.
	Modified ALS	Conventional	-.29327			
	Modified ALS	Adachi-Sugie	-.29058	-.32845E-01		
	Modified ALS	SGR	-.24968	-.62343E-01	.82877	
	Modified ALS	E-W-S	-.18214	.56264E-01	4399.7	-9373.1

Table C.3 (continue)

T (K)	EOS	Mixing rules	k_{ij}	l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}
322.04	SRK	E-W-S	.23557	-.49133E-01	1508.9	-14176.
	PR	E-W-S	.21882E-01	-.19355E-01	2161.0	-11796.
	PT	E-W-S	-.30103	.17269E-01	5631.4	-11808.
	PRSV	E-W-S	.38474E-02	-.15528E-01	1433.8	-10806.
	Modified ALS	Conventional	-.28067			
	Modified ALS	Adachi-Sugie	-.27819	-.32574E-01		
	Modified ALS	SGR	-.23908	-.59630E-01	.83933	
	Modified ALS	E-W-S	-.20184	.81554E-01	3311.4	-7840.7

Table C.4 Binary interaction coefficients for the simultaneous representation of VLE and H^E of six binary systems

Systems	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
Carbon Tetrachloride + n-Heptane	SRK	E-W-S	-.33299E-01	-2.1558	284.09	825.34
	PR	E-W-S	-.15976	.92288	1421.3	597.64
	PT	E-W-S	-.99867E-01	-.59160	-2199.9	2305.0
	PRSV	E-W-S	-.73495E-01	.92604	1375.7	608.60
	Modified ALS	Conventional	-.28777E-02			
	Modified ALS	Adachi-Sugie	-.26298E-02	-.12890E-02		
	Modified ALS	SGR	-.40076E-03	-.31674E-02	.87463	
	Modified ALS	E-W-S	-.44516E-01	.96055	1289.7	613.75
Benzene + Cyclohexane	SRK	E-W-S	-.99227E-01	.59505	1556.1	1038.5
	PR	E-W-S	-.38781	.32979	2027.3	1454.4
	PT	E-W-S	-.19024	-.32036E-01	-4533.0	6319.1
	PRSV	E-W-S	-.19959	.34488	2025.3	1471.7
	Modified ALS	Conventional	.40406E-01			
	Modified ALS	Adachi-Sugie	.40411E-01	-.14652E-02		
	Modified ALS	SGR	.40411E-01	-.14714E-02	.50002	
	Modified ALS	E-W-S	-.30714	.33449	2033.3	1457.5

Table C.4 (continue)

Systems	EOS	Mixing rules	k_{ij}	l_{ij} α_{ij}	m_{ij} Δg_{ij}	Δg_{ji}
Benzene + n-Heptane	SRK	E-W-S	-.59613E-01	.31153	4446.5	-190.64
	PR	E-W-S	-.28976	.23852	4163.3	441.50
	PT	E-W-S	-.96872E-01	-.30741	-4317.0	4615.4
	PRSV	E-W-S	-.13708	.26204	3951.1	616.10
	Modified ALS	Conventional	.20284E-01			
	Modified ALS	Adachi-Sugie	.20287E-01	-.70559E-03		
	Modified ALS	SGR	.20288E-01	-.70444E-03	.50002	
	Modified ALS	E-W-S	-.19532	.25148	4002.2	555.33
n-Hexane + Ethanol	SRK	E-W-S	.64293	1.0916	31584.	7926.2
	PR	E-W-S	.50133	.65838	6189.5	2140.4
	PT	E-W-S	.75375	.38146	-2618.1	7265.2
	PRSV	E-W-S	.51549	.64002	6330.1	2196.6
	Modified ALS	Conventional	-.43381			
	Modified ALS	Adachi-Sugie	-.43537	.11857		
	Modified ALS	SGR	-.41545	.12375	.40357	
	Modified ALS	E-W-S	-.56022E-01	.19797	15789.	2491.9

Table C.4 (continue)

Systems	EOS	Mixing rules	k_{ij}	l_{ij} / α_{ij}	m_{ij} / Δg_{ij}	Δg_{ji}
Ethanol + Cyclohexane	SRK	E-W-S	.70878	.23145	10720.	-4235.4
	PR	E-W-S	.39741	.60818	2752.4	6005.6
	PT	E-W-S	.69467	.44511	7225.4	-1991.9
	PRSV	E-W-S	.44487	.59951	2827.8	6040.5
	Modified ALS	Conventional	-.27706			
	Modified ALS	Adachi-Sugie	-.27645	-.49467E-01		
	Modified ALS	SGR	-.24545	-.64445E-01	.79872	
	Modified ALS	E-W-S	.49918	-1.9703	1869.9	1106.5
1-Butanol + n-Heptane	SRK	E-W-S	.49186	.53447	1167.8	18163.
	PR	E-W-S	-.11040	.32362	2341.4	13084.
	PT	E-W-S	.46288	.49946	1137.7	20420.
	PRSV	E-W-S	.89212E-01	.34343	2214.0	12528.
	Modified ALS	Conventional	-.42336E-01			
	Modified ALS	Adachi-Sugie	-.28405E-01	-.38038E-01		
	Modified ALS	SGR	.64265E-01	-.11947	.93075	
	Modified ALS	E-W-S	.18147E-01	.33311	2355.8	12639.

Table C.5 VLE data sources for forteen binary systems

SYSTEM	No. Points	T(K)	DATA SOURCE
METHANOL+WATER	12	523.15	Griswold and Wong (1952)
METHANOL+N-HEXANE	24	323.15	Wolff and Hoeppel (1968)
METHANOL+N-HEXANE	24	333.15	Wolff and Hoeppel (1968)
ETHANOL+N-HEXANE	20	323.14	Diaz Pena and Rodrigues Cheda (1970)
ETHANOL+N-HEPTANE	11	343.15	Ramalho and Delmas (1968)
ETHANOL+N-OCTANE	21	328.15	Boublikova and Lu (1969)
N-PROPANOL+N-HEPTANE	14	348.15	Fu and Lu (1966)
N-PROPANOL+N-OCTANE	17	313.15	Oracz (1976)
1-BUTANOL+N-PENTANE	15	303.15	Ronc and Ratcliff (1976)
1-BUTANOL+N-HEXANE	11	298.15	Smirnova and Kurtynina (1969)
1-BUTANOL+N-HEPTANE	8	323.15	Aristovich et al. (1965)
1-BUTANOL+N-OCTANE	14	313.15	Oracz (1976)
1-BUTANOL+N-DECANE	21	373.15	Lee and Scheller (1967)
1-BUTANOL+TOLUENE	17	333.31	Lnenickova and Wichterle (1977)

Table C.6 VLE data sources for six ternary systems

SYSTEM	No. Points	T(K)	DATA SOURCE
ACETONE+METHANOL+WATER	51	373.15	Griswold and Wong (1952)
ACETONE+METHANOL+2-PROPANOL	27	328.15	Freshwater and Pike (1967)
N-HEXANE+ETHANOL+BENZENE	43	328.15	Ho and Lu (1963)
ETHANOL+ACETONITRILE+BENZENE	21	318.15	Nagata (1985)
METHANOL+CARBON TETRACHLORIDE+BENZENE	6	308.15	Scatchard and Ticknor (1952)
METHANOL+CARBON TETRACHLORIDE+BENZENE	8	308.15	Scatchard and Ticknor (1952)

Table C.7 VLE data sources of eighteen constituent binary systems for the six ternary systems

SYSTEM	No. Points	T(K)	DATA SOURCES
ACETONE+METHANOL	14	273.15	Griswold and Wong (1952)
ACETONE+WATER	22	273.15	Griswold and Wong (1952)
METHANOL+WATER	16	273.15	Griswold and Wong (1952)
ACETONE+METHANOL	28	328.15	Freshwater and Pike (1967)
ACETONE+2-PROPANOL	14	328.15	Freshwater and Pike (1967)
METHANOL+2-PROPANOL	20	328.15	Freshwater and Pike (1967)
N-HEXANE+ETHANOL	17	328.15	Ho and Lu (1963)
BENZENE+N-HEXANE	14	328.15	Ho and Lu (1963)
ETHANOL+BENZENE	9	328.15	Ho and Lu (1963)
METHANOL+CARBON TETRACHLORIDE	9	308.15	Scatchard et al. (1946)
METHANOL+BENZENE	9	308.15	Scatchard et al. (1946)
CARBON TETRACHLORIDE+BENZENE	8	313.15	Scatchard et al. (1946)
METHANOL+CARBON TETRACHLORIDE	6	328.15	Scatchard and Ticknor (1952)
METHANOL+BENZENE	9	328.15	Scatchard et al. (1946)
CARBON TETRACHLORIDE+BENZENE	16	323.14	Zawidki (1900)
ETHANOL+ACETONITRILE	8	293.15	Vierk (1950)
ETHANOL+BENZENE	12	318.15	Brown and Smith (1954)
ACETONITRILE+BENZENE	12	318.15	Brown and Smith (1955)

Table C.8 VLE and saturated volume data sources of three binary systems

SYSTEM	No. Points	T(K)	DATA SOURCE
HYDROGEN SULFIDE+N-PENTANE	9	277.59	Sage and Lacey (1955)
	9	310.93	
	9	344.26	
	12	377.59	
	11	410.93	
ETHANE+METHANOL	6	323.15	Ma and Kohn (1964)
	6	348.15	
	6	373.15	
WATER+AMMONIA	11	277.59	Scatchard et al. (1947)
	11	288.71	
	11	299.82	
	11	310.93	
	11	322.04	

Table C.9 Compressed liquid volume data source of the hydrogen sulphide + n-pentane system

SYSTEM	No. Points	T(K)	DATA SOURCE
HYDROGEN SULFIDE+N-PENTANE	198	277.59	Sage and Lacey (1955)
	193	310.93	
	184	344.26	
	173	377.59	
	132	410.93	

Table C.10 VLE and H^E data sources of six binary systems

SYSTEM	Property	No. Points	T(K)	DATA SOURCE
CARBON TETRACHLORIDE+N-HEPTANE	VLE	14	298.15	Bissell and Williamson (1975)
	H^E	21	298.15	Grolier and Inglese (1975)
BENZENE+CYCLOHEXANE	VLE	13	298.15	Tasic et al. (1978)
	H^E	10	298.15	Abello (1973)
BENZENE+N-HEPTANE	VLE	12	298.13	Jain et al. (1973)
	H^E	9	298.15	Hammerl and Raetzsch (1973)
N-HEXANE+ETHANOL	VLE	11	298.15	Smith and Robinson (1970)
	H^E	14	298.15	Brown et al. (1964)
ETHANOL+CYCLOHEXANE	VLE	9	308.15	Scatchard and Satkifwicz (1964)
	H^E	9	308.15	Nagata and Yamada (1974)
1-BUTANOL+N-HEPTANE	VLE	14	313.15	Oracz (1976)
	H^E	20	318.15	Savini et al. (1966)

Table C.11 VLE data source of ethanol + water +salt systems

SYSTEM	No. Points	Pressure (KPa)	Molarity (salt)	DATA SOURCE
ETHANOL+WATER	12	101.325	0.0	Dobroserdov and Ilyina (1965)
ETHANOL+WATER+NACL	15	101.325	1.0	
ETHANOL+WATER+CACL2	12	101.325	0.901	
ETHANOL+WATER+ZNCL2	14	101.325	1.0	

Appendix D

Source Codes of Programs

The source codes of the programs of the determination of the parameters of the modified ALS equation, the buble point temperature calculation and the canonical Monte Carlo simulation are presented in this appendix.

All programs were written in the FORTRAN language. Comments are included to clarify the programs.

D.1 The source codes of the program for the determination of the parameters of the modified ALS equation of state

This program was used to determine the parameters of the modified ALS equation.

```
$DEBUG
*******************************************************************************
* THIS PROGRAM IS USED TO CALCULATE THE PARAMETERS OF MODIFIED ALS
* EQUATION OF STATE BY FITTING THE SATURATED DATA
*
* TR(DZ=0.5) IS CLCULATED BY USING CUBIC SPLINE METHOD
*
* THE UNIT USED IN THE PROGRAM IS OF THE ENGLISH SYSTEM
*******************************************************************************
      PROGRAM MMILP
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER(NPURE=200)
      PARAMETER(NDATA=240)
      CHARACTER NAME*24,FORM*10,NAME1*24,REF*80,TITLE*80,TABLE(3)*80
      CHARACTER IUT*1,IUT1*1,IUTO*1,IUP*4,IUP1*4,IUPO*4,
     1 IUV*10,IUV1*10,IUVO*10,AAA*12,RESFILE*12,QFILE*12
      DIMENSION DZ(NDATA),XX(10),WW(10),T1(NDATA)
      DIMENSION PALF(10)
      COMMON/RETF/RESFILE
      COMMON/CU/CUA(NDATA),CUB(NDATA),CUC(NDATA),CUD(NDATA),
     1 CUS(NDATA),CUH(NDATA)
      COMMON/PPS/CUPA(NDATA),CUPB(NDATA),CUPC(NDATA),CUPD(NDATA)
      COMMON/VLS/CUVA(NDATA),CUVB(NDATA),CUVC(NDATA),CUVD(NDATA)
      COMMON/CONST1/NAME(NPURE),FORM(NPURE)
      COMMON/CONST2/TC(NPURE),PC(NPURE),VC(NPURE),W(NPURE),U(NPURE),
     1 WM(NPURE),TB(NPURE)
      COMMON/DAT1/T(NDATA),P(NDATA),VSL(NDATA),VSV(NDATA)
      COMMON/PAR1/F,G,H,PRTR
      COMMON/PAR2/C,D,E
      COMMON/PAR3/ATT(10)
      COMMON/PAR4/UT(10)
      COMMON/PAR5/XT(10)
      COMMON/PAR6/ZCDRT(10),DZVL2
```

```
      COMMON/PAR7/WIT(10)
      COMMON/PAR8/TCI,PCI,VCI,WI,UI,NK
      COMMON/PAR0/WB0,F0,C0,D0,E0
      COMMON/WW/WA,WB
      COMMON/TP/TRT(10),PRTRT(10)
      COMMON/NM/UM,NTR
      COMMON/OPT/IOPT,LOPT,LALF
      COMMON/RT0/R,T0
      COMMON/TRALF/TRALF(NDATA),ALF(NDATA)
      COMMON/FAULT/LFAULT
      COMMON/ALF0/ALFA,ALFN,ALFM,IALFA,IALFN,IALFM
C --  SETTING PROGRAM UNITS
      IUTO='R'
      IUPO='PSIA'
      IUVO='FT3/LBMOL '
C --  SETTING PURE DATAFILE UNITS
      IUT1='K'
      IUP1='BAR'
      IUV1='ML/GMOL'
      XX(1)=1.0
C --  SET FIXED VALUES
      R=10.7315
      TRM=0.998
      DZVL2=0.5
C     TRM - THE MAXIMUM TR IN THE FITTING
C --  READ AND CONVERT PURE DATA FROM PURE DATAFILE
      OPEN(4,FILE='PURE.DAT')
      READ(4,*)
      READ(4,*)
      I=0
 10   CONTINUE
      I=I+1
      READ(4,1050)NAME(I),FORM(I),WM(I),TC(I),PC(I),W(I),ZC,U(I),TB(I)
1050  FORMAT(T2,A24,A10,20F10.6)
      IF(NAME(I).EQ.'END') GO TO 15
      PC(I)=PCONV(PC(I),IUP1,IUPO)
      TC(I)=TCONV(TC(I),IUT1,IUTO)
      TB(I)=TCONV(TB(I),IUT1,IUTO)
      VC(I)=ZC*R*TC(I)/PC(I)
      GOTO 10
 15   CONTINUE
      CLOSE(4)
      N=I-1
C --  SET UP DATA FILE NAMES
      OPEN(7,FILE='CON')
      WRITE(*,*)' PLEASE INPUT YOUR DATA FILENAME'
```

```
      READ(*,1000)AAA
1000  FORMAT(A)
      OPEN(3,FILE=AAA)
      WRITE(*,*)' PLEASE INPUT YOUR PARAMTER DATA FILENAME'
      READ(*,1000)AAA
      OPEN(5,FILE=AAA)
C --  READ OPTIMAZATION OPTIONS FROM PARAMETER FILE
      READ(5,1000)TITLE
      READ(5,1000)TABLE(1)
      READ(5,*)IOPT,LOPT,LALF,LP,NTR
C     IOPT - THE OPTIMIZATION METHODS
C        IOPT   =1 STEP BY STEP
C               =2 MAQUAT
C     LOPT - THE OPTIMIZATION TYPE
C        LOPT   =0 OPTIMIZATION FOR ALL
C               =1 OPTIMIZATION WITH F=F0+F1*W
C               =2 OPTIMIZATION WITH D,E=CONSTANT(D0,E0)
C               =3 OPTIMIZATION WITH F=F0+F1*W, AND D,E=CONSTANT(D0,E0)
C               =4 ALL PARAMETERS FIXED AT GIVEN VALUE FROM DATAFILE
C     LALF - THE CODE OF ALF FUNCTION
C        LALF>0 AND <=5 QA=[(1.0-F)**3]*ALF
C               =1 ALF=(1+P1(1-TR^0.5))^2
C               =2 ALF=(1+P1(1-TR^0.5)+P2(1-TR)(0.9-TR))^2
C               =3 ALF=EXP(A(1-TR^N)^(2M+1))
C        LALF>5 AND <=10 QA=[(1-F)*G*H/F]*ALF
C               =6 ALF=(1+P1(1-TR^0.5))^2
C               =7 ALF=(1+P1(1-TR^0.5)+P2(1-TR)(0.9-TR))^2
C               =8 ALF=EXP(A(1-TR^N)^(2M+1))
C     LP - THE PRINT TYPE
C        LP     =0 PRINT ORIGENAL RESULTS WITH OUT ALF ERROR MESSAGE
C               =1 PRINT ORIGENAL RESULTS WITH ALF ERROR MESSAGE
C               =2 PRINT ORIGENAL RESULTS WITH OUT ALF ERROR MESSAGE
C                  BUT WITH TU RESULTS
C               =3 PRINT ORIGENAL RESULTS WITH ALF ERROR MESSAGE
C                  AND TU RESULTS
C               =4 PRINT BRIFE RESULTS WITHOUT ALF ERROR MESSAGE
C     NTR - THE NUMBER OF POINTS OF TR USED FOR OPTIMAZATION
C         ( NTR=3 - 5)
      IF(LALF.EQ.3.OR.LALF.EQ.8)THEN
C --  READ INITIAL VALUES FOR FITTING ALF FUNCTION
      READ(5,*)
      READ(5,*)ALFA,ALFN,ALFM
      READ(5,*)IALFA,IALFN,IALFM
      ENDIF
C --  SET UP RESULT FILE NAMES
      LPALF=0
```

```
      IF(LP.EQ.0.OR.LP.EQ.2.OR.LP.EQ.4)LPALF=1
      LPTU=0
      IF(LP.LE.1.OR.LP.EQ.4)LPTU=1
      WRITE(*,*)' PLEASE INPUT YOUR RESULT FILENAME'
      READ(*,1000)RESFILE
      OPEN(6,FILE=RESFILE,STATUS='UNKNOWN')
      WRITE(*,*)' PLEASE INPUT YOUR PARAMETER RESULT FILENAME'
      READ(*,1000)QFILE
      OPEN(7,FILE=QFILE,STATUS='UNKNOWN')
      IF(LPTU.EQ.0)THEN
       WRITE(*,*)'PLEASE INPUT YOUR TU FILENAME'
       READ(*,1000)AAA
       OPEN(9,FILE=AAA,STATUS='UNKNOWN')
      ENDIF
C --  WRITE DATE TO RESULT FILE
      CALL GETDAT(IY,IM,ID)
      WRITE(6,'(4X,''DATE(M/D/Y): '',I2,''/'',I2,''/'',I4)')IM,ID,IY
      WRITE(6,1020)IOPT,LOPT,LALF,LP
1020  FORMAT(/2X,'IOPT=',I2,' LOPT=',I2,' LALF=',I2,' LP=',I2)
      CLOSE(6)
      IF(LPTU.EQ.0)
     1 WRITE(9,'(4X,''DATE(M/D/Y): '',I2,''/'',I2,''/'',I4)')IM,ID,IY
C --  READ SATURATED DATA FORM DATA FILE
      DALFTT=0.0
      TDEVLT=0.0
      TDEVVT=0.0
      READ(3,*)NPT
      WRITE(7,1001)NPT,LALF
1001  FORMAT(2X,'PARAMETERS OF ',I3,' COMPONENTS FOR LALF=',I2)
      CLOSE(7)
      DO 500 K=1,NPT
C --  READING PARAMETERS
      READ(5,1000)TABLE(2)
      READ(5,*)WB0,F0,C0,D0,E0
C     WB0,F0,C0,D0,E0 - THE INITIAL VALUES OF PARAMETER WB,F,C,D,E
C --  READING SATURATED DATA
      READ(3,*)NAME1,REF
      WRITE(*,1002)K,NAME1
1002  FORMAT(2X,'K=',I2,2X,'NAME=',A24)
      READ(3,*)NK,IUT,IUP,IUV
      DO 20 J=1,NK
      READ(3,*)T(J),P(J),VSL(J),VSV(J)
20    CONTINUE
C --  FIND PURE DATA BY COMPARE THE NAME AND GIVE VALUES
      DO 30 KK=1,N
      IF(NAME1.NE.NAME(KK))GOTO 30
```

```
      I=KK
      GOTO 40
30    CONTINUE
      WRITE(*,1030)NAME1
1030  FORMAT(2X,A15,7HNO DATA)
      STOP
40    CONTINUE
      TCI=TC(I)
      PCI=PC(I)
      VCI=VC(I)
      WI=W(I)
      UI=U(I)
C --  CONVERT SATURATED DATA UNITS TO PROGRAM UNITS
      WW(1)=WM(I)
      ND=0
      DO 50 J=1,NK
      T(J)=TCONV(T(J),IUT,IUTO)
      P(J)=PCONV(P(J),IUP,IUPO)
      VSL(J)=VCONV(VSL(J),XX,WW,1,IUV,IUVO)
      VSV(J)=VCONV(VSV(J),XX,WW,1,IUV,IUVO)
      ZV=P(J)/R/T(J)*VSV(J)
      ZL=P(J)/R/T(J)*VSL(J)
      DZ(NK-J+1)=ZV-ZL
      T1(NK-J+1)=T(J)
      TR=T(J)/TCI
      IF(TR.LE.TRM)ND=ND+1
50    CONTINUE
C --  FIND TB OR MINIMUM T
      TB(I)=AMAX1(TB(I),T(1))
C --  FIND TR AT DZ=0.5 BY USING CUBIC SPLINE METHOD
      CALL CUSP(NK,T,P,CUPA,CUPB,CUPC,CUPD,CUS,CUH,DZVL2,TA,4,1,LERR)
      CALL CUSP(NK,T,VSL,CUVA,CUVB,CUVC,CUVD,CUS,CUH,DZVL2,TA,4,1,LERR)
      CALL CUSP(NK,DZ,T1,CUA,CUB,CUC,CUD,CUS,CUH,DZVL2,TA,4,0,LERR)
      IF(LERR.NE.0)THEN
       WRITE(*,*)' CUSP FAIL FOR FIND TR AT DZVL2'
       STOP 'STOP PROGRAM'
      ENDIF
      TRA=TA/TCI
      TRB=TB(I)/TCI
      TRB=TRB+(1.0-TRB)*0.1
      TRT(2)=TRA
C --  SETTING DATA POINTS
      DTR=(TRA-TRB)/(NTR-1)
      TRT(1)=TRT(2)-DTR
      DO 60 J=3,NTR
      J1=J-1
```

```
      TRT(J)=TRA-J1*DTR
60    CONTINUE
C --  CALCULATE PR AND ZL FOR DATA POINTS
      DO 70 J=1,NTR
      TR=TRT(J)
      CALL PRCAL(TR,PR)
      CALL ZLCAL(TR,ZCDR)
      PRTRT(J)=PR/TR
      ZCDRT(J)=ZCDR
70    CONTINUE
C --  SETTING INITIAL VALUES
      WB=WB0
      F=F0
      C=C0
      D=D0
      E=E0
      IF(LOPT.NE.4)CALL MOPT(DDT)
      OPEN(6,ACCESS='APPEND',FILE=RESFILE,STATUS='OLD')
C --  WRITTING TITLE OF TABLE
      WRITE(6,1005)K,NAME(I),FORM(I),WI,UI
1005  FORMAT(1X,'K=',I2,' NAME=',A24,' FORM=',A10,' W=',F7.4,
     1 ' U=',F7.4)
      WRITE(6,1010)REF
1010  FORMAT(1X,A)
      IF(LP.NE.4)THEN
       WRITE(6,*)'    TR    PRexp   PRcal  ZLdev%  ZVdev%   ALF'
      ENDIF
      IF(LPTU.EQ.0)THEN
       WRITE(9,1015)ND,NAME(I)
1015   FORMAT(2X,'ND=',I3,2X,A)
       WRITE(9,1010)REF
       WRITE(9,*)
     1 '    TR      PR       ZLC      ZL      ZVC      ZV     ALF'
      ENDIF
C --  BEGIN CALCULATION
      TDEVL=0
      TDEVV=0
      DO 200 J=1,NK
      TR=T(J)/TCI
      PRE=P(J)/PCI
      IF(TR.GT.0.998)GOTO 975
      PR=PRE
      PRTR=PR/TR
      CALL S60(TR,AT,YV,YL,XRATIO)
      IF(LFAULT.EQ.1)THEN
C --   WRITTING FAULT POINTS
```

```
      WRITE(*,*)'J=',J,' TR=',TR
      GOTO 975
     ENDIF
     IF(LOPT.NE.4)THEN
      WB=UM
     ENDIF
     ZL=P(J)*VSL(J)/R/T(J)
     ZLC=YL+WB*(PR/TR)
     DZL=(ZL-ZLC)/ZL*100.
     ZV=P(J)*VSV(J)/R/T(J)
     ZVC=YV+WB*(PR/TR)
     DZV=(ZV-ZVC)/ZV*100.
     TDEVL=TDEVL+DABS(DZL)
     TDEVV=TDEVV+DABS(DZV)
     TRALF(J)=TR
     ALF(J)=AT*TR
     IF(LP.NE.4)THEN
       WRITE(6,1100)TR,PRE,PR,DZL,DZV,AT*TR
1100  FORMAT(1X,5(F7.3,1X),F7.4)
     ENDIF
     IF(LPTU.EQ.0)THEN
       WRITE(9,1200)TR,PRE,ZLC,ZL,ZVC,ZV,ALF(J)
1200  FORMAT(2X,F7.4,1X,F8.6,4(1X,F8.6),1X,F7.4)
     ENDIF
200  CONTINUE
975  CONTINUE
     ND=J-1
     IF(LPTU.EQ.0)THEN
      WRITE(9,*)' FOR CRITICAL POINT(IF EXIST IN DATA FILE)'
      ZC=P(NK)*VSV(NK)/R/T(NK)
      WRITE(9,1200)1.0,1.0,WB+F,ZC,WB+F,ZC,1.0
     ENDIF
     TDEVL=TDEVL/ND
     TDEVV=TDEVV/ND
C --  WRITTING OVERALL RESULTS
     WRITE(6,*)' ND,AVD%(ZL),AVD%(ZV)'
     WRITE(6,2000)ND,TDEVL,TDEVV
2000  FORMAT(1X,I3,2X,2(F5.2,1X))
C --  WRITTING PARAMETERS
     WRITE(6,2100)WB,F,DDT
2100  FORMAT(1X,'WB,F,DDT',1X,2(F9.7,1X),G12.5)
     WRITE(6,2200)C,D,E
2200  FORMAT(1X,'C,D,E',1X,3(F7.4,1X))
     WRITE(6,2300)'TR   ',TRT(2),TRT(1),(TRT(J),J=3,NTR)
2300  FORMAT(1X,A5,6(1X,F8.5))
C --  FIND THE PARAMETERS OF ALF FUNCTION BY FITTING ALF DATA
```

```
C     AND PRINT OUT ALF FUNCTIONAND IN PASS 6.
      CLOSE(6)
      CALL FITALF(LALF,NA,ND,PALF,DALFT,LPALF,6)
      OPEN(7,ACCESS='APPEND',FILE=QFILE,STATUS='OLD')
      WRITE(7,3105)TABLE(2),NAME1
 3105 FORMAT(A50,' FOR ',A)
      WRITE(7,3100)WB,F,C,D,E,(PALF(I),I=1,NA)
 3100 FORMAT(1X,F8.6,2X,F8.6,3(2X,F8.4),3(2X,F8.4),3(2X,F8.5))
      CLOSE(7)
      TDEVLT=TDEVLT+TDEVL
      TDEVVT=TDEVVT+TDEVV
      DALFTT=DALFTT+DALFT
      OPEN(6,ACCESS='APPEND',FILE=RESFILE,STATUS='OLD')
      WRITE(6,*)
      CLOSE(6)
  500 CONTINUE
      OPEN(6,ACCESS='APPEND',FILE=RESFILE,STATUS='OLD')
      TDEVLT=TDEVLT/NPT
      TDEVVT=TDEVVT/NPT
      DALFTT=DALFTT/NPT
      WRITE(6,5000)NPT,TDEVLT,TDEVVT,DALFTT*100.
 5000 FORMAT(2X,'NPT=',I3,' AVERAGE: dVL%=',F7.2,' dVV%=',F7.2,
     1 ' dALF%=',F7.2)
      CLOSE(6)
      STOP
      END
C
C*********************************************************************
C* THIS SUBROUTINE IS USED TO FIND D AND E VALUES TO LET:
C*   DD=SUM(U2-UI)=MIN.
C* DDT - THE ERROR
C*********************************************************************
      SUBROUTINE MOPT(DDT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(4),AA(4,4),DX(4),OLDX(4),G(4),H(4),XH(4),XL(4)
      DIMENSION FP(6),FM(6),F(6),DFDX(6,4)
      EXTERNAL FUNS
      COMMON/PAR2/C,D,E
      COMMON/PAR0/WB0,F0,C0,D0,E0
      COMMON/PAR8/TCI,PCI,VCI,WI,UI,NK
      COMMON/NM/UM,NTR
      COMMON/OPT/IOPT,LOPT,LALF
C --  SETTING INITIAL VALUE
      N=2
      M=2
      X(1)=E
```

```
      X(2)=D
      H(1)=E*0.1
      H(2)=D*0.1
      IF(IOPT.NE.1)THEN
       H(1)=H(1)*0.01
       H(2)=H(2)*0.01
      ENDIF
      MAX=4
      XH(1)=E0+30
      XL(1)=E0-30
      XH(2)=D0+30.
      XL(2)=D0-30.
      IF(XL(1).LE.0.0)XL(1)=1.D-5
      IF(XL(2).LE.-1.D0)XL(2)=-1.D0+1.D-5
      IF(LOPT.LE.1)THEN
C --  SELECT OPTIMIZATION METHOD AND OPTIMIZATION
      IF(IOPT.EQ.1)THEN
       KEY=0
       WRITE(*,*)'BEFORE STEPS'
       CALL STEPS(N,M,X,F,FUNS,H,S,MAX,KEY,XH,XL,0)
       WRITE(*,*)'AFTER STEPS'
      ELSE
       CALL DAMP(N,M,X,F,FUNS,DERI,H,0,S,1.D-10,1.D-10,100,LMAX,0.9,
     1  0.5,FP,FM,G,DX,OLDX,DFDX,AA,KEY,XH,XL,0)
      ENDIF
     ELSE
C --  CALCULATION
      CALL FUNS(N,M,X,F)
      KEY=0
     ENDIF
C --  CALCULATE ERROR
      DDT=0.0
      DO 20 I=1,N
      DDT=DDT+(F(I)*1.E-3)**2
 20    CONTINUE
      DDT=DDT*1.D5
      IF(KEY.NE.0)THEN
       WRITE(*,*)' KEY!=0 IN MOPT. KEY=',KEY
      ENDIF
      RETURN
      END
C
C     FUNS IS THE SUBROUTINE CALLED BY STEPS
      SUBROUTINE FUNS(N,M,X,F)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),F(M),DD(6)
```

```
      COMMON/PAR2/C,D,E
      COMMON/NM/UM,NTR
      E=X(1)
      IF(N.EQ.2)D=X(N)
      CALL S210
      CALL S340(DD)
      DO 10 I=1,M
      F(I)=DD(I)
10    CONTINUE
      RETURN
      END
C
C     THIS SUBROUTINE IS USED TO CALCULATE DD=SUM(U2-UI)
      SUBROUTINE S340(DD)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DD(6)
      COMMON/PAR4/UT(10)
      COMMON/PAR7/WIT(10)
      COMMON/NM/UM,NTR
      DO 10 I=1,NTR
      WIT(I)=UT(I)-UM
10    CONTINUE
      DD(1)=WIT(1)*1.E3
      DD(2)=WIT(NTR)*1.E3
      RETURN
      END
C
C     THIS SUBROUTINE IS USED TO FIND C VALUE BY FITING DC=U2/UM-1.0=0
      SUBROUTINE S210
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(4),F(4),H(4),XH(4),XL(4)
      EXTERNAL FUNS1
      COMMON/PAR2/C,D,E
      COMMON/PAR0/WB0,F0,C0,D0,E0
      COMMON/TP/TRT(10),PRTRT(10)
      COMMON/OPT/IOPT,LOPT,LALF
      N=1
      XH(1)=C+5.0
      XL(1)=C-5.0
      H(1)=C*0.1
      X(1)=C
      MAX=4
      IF(XL(1).LE.0.0)XL(1)=1.E-5
      IF(LOPT.LT.4)THEN
       CALL STEP(N,1,X,F,FUNS1,H,S,MAX,KEY,XH,XL,0)
      ELSE
```

```
      CALL FUNS1(N,1,X,F)
     ENDIF
     RETURN
     END
C
C --  THIS SUBROUTINE IS CALLED BY STEP
     SUBROUTINE FUNS1(N,M,X,F)
     IMPLICIT REAL*8(A-H,O-Z)
     DIMENSION X(N),F(M)
     COMMON/PAR2/C,D,E
     C=X(1)
     CALL S200
     CALL S330(DC)
     F(1)=DABS(DC)
     RETURN
     END
C
C     THIS SUBROUTINE IS USED TO CALCULATE DC=U2/UM-1
     SUBROUTINE S330(DC)
     IMPLICIT REAL*8(A-H,O-Z)
     COMMON/PAR1/F,G,H,PRTR
     COMMON/PAR3/ATT(10)
     COMMON/PAR4/UT(10)
     COMMON/PAR5/XT(10)
     COMMON/PAR6/ZCDRT(10),DZVL2
     COMMON/TP/TRT(10),PRTRT(10)
     COMMON/NM/UM,NTR
     UM=0.0
     DO 10 I=1,NTR
     IF(I.EQ.2)GOTO 10
     TR=TRT(I)
     PRTR=PRTRT(I)
     CALL S60(TR,AT,YV,YL,XRATIO)
     UT(I)=(ZCDRT(I)-YL/PRTR)
     ATT(I)=AT*TR
     XT(I)=XRATIO
     UM=UM+UT(I)
 10   CONTINUE
     UM=(UM+UT(2))/NTR
     DC=UT(2)/UM-1.0
     RETURN
     END
C
*******************************************************************************
*     THIS SUBROUTINE IS USED TO FIND F BY FITING DZ=DZC AT TR=0.5
*******************************************************************************
```

```
      SUBROUTINE S200
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/PAR1/F,G,H,PRTR
      COMMON/PAR8/TCI,PCI,VCI,WI,UI,NK
      COMMON/PAR0/WB0,F0,C0,D0,E0
      COMMON/OPT/IOPT,LOPT,LALF
      IF(LOPT.EQ.0.OR.LOPT.EQ.2)THEN
       FU=0.2499
       FL=0.15
       F=FL
       CALL S320(DF)
       DFL=DF
       F=FU
       CALL S320(DF)
       DFU=DF
  202   CONTINUE
       F=FL+(FU-FL)*(1.0-0.618)
       F1=F
       CALL S320(DF)
       DF1=DF
       F=FL+(FU-FL)*0.618
       F2=F
       CALL S320(DF)
       DF2=DF
       IF(DABS(DF2).GT.DABS(DF1))THEN
        FU=F2
       ELSE
        FL=F1
       ENDIF
       IF(DABS(FU-FL).GT.0.00001)GOTO 202
       F=(FU+FL)/2.0
      ELSE
       IF(LOPT.EQ.4)THEN
        F=F0
       ELSE
        F=0.225372-0.06176*WI
       ENDIF
       CALL S320(DF)
      ENDIF
      RETURN
      END
C
C     THIS SUBROUTINE IS USED FOR THE CALCULATION OF DF=DZ-DZC
      SUBROUTINE S320(DF)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/PAR1/F,G,H,PRTR
```

```
      COMMON/PAR3/ATT(10)
      COMMON/PAR4/UT(10)
      COMMON/PAR5/XT(10)
      COMMON/PAR6/ZCDRT(10),DZVL2
      COMMON/TP/TRT(10),PRTRT(10)
      TR=TRT(2)
      PRTR=PRTRT(2)
      CALL S60(TR,AT,YV,YL,XRATIO)
      UT(2)=(ZCDRT(2)-YL/PRTR)
      ATT(2)=AT*TR
      XT(2)=XRATIO
      DF=YV-YL-DZVL2
      RETURN
      END
C
C     THIS SUBROUTINE IS USED TO FIND a(T) FROM REAL VAPOR PRESSURE
      SUBROUTINE S60(TR,AT,YV,YL,XRATIO)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/OPT/IOPT,LOPT,LALF
      COMMON/PAR1/F,G,H,PRTR
      COMMON/PAR2/C,D,E
      COMMON/WW/WA,WB
      COMMON/NM/UM,NTR
      COMMON/FAULT/LFAULT
      LFAULT=0
      CALL HGFUN(TR,F,H,G,D,C,E,XRATIO)
      WA=(1.0-F)/F*G*H
      WAC=(1.0-F)**3
      AT=(1.0-F/(1.0-F)*DLOG(PRTR))
      AT2=AT
      DAT=AT*0.01
      IT=0
 80   CONTINUE
      IT=IT+1
      Y=0
      CALL S130(WA,AT2,Y,Q1,Q2)
      IF(DABS(Y).LT.1.E-12)THEN
       LFAULT=1
       RETURN
      ENDIF
      YL=Y
      Y=1
      CALL S130(WA,AT2,Y,Q1,Q2)
      YV=Y
      ATU=YV-YL+DLOG(YL/YV)
      ATL=DLOG((YV+Q1)/(YL+Q1)*(YL+Q2)/(YV+Q2))
```

```
      AT=(G-H)*ATU/ATL/WA
      F2=(AT2-AT)
      IF(DABS(F2).LT.0.00001)GOTO 90
      IF(IT.NE.1)DAT=-(AT2-AT1)*F2/(F2-F1)
      AT1=AT2
      AT2=AT2+DAT
      F1=F2
      GOTO 80
   90 CONTINUE
      IF(LALF.GE.1.AND.LALF.LE.5)AT=AT*WA/WAC
      RETURN
      END
C
C     THIS SUBROUTINE IS USED TO FIND THE ROOT OF CUBIC EQUATION
      SUBROUTINE S130(WA,AT,Y,Q1,Q2)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(3)
      COMMON/PAR1/F,G,H,PRTR
      Q1=PRTR*(G-F)
      Q2=PRTR*(H-F)
      A=WA*AT*PRTR
      S0=Q1*Q2
      S1=Q1*Q2-(Q1+Q2)+A
      S2=(Q1+Q2)-1.0
      CALL RTCUB(S2,S1,-S0,X,NROOT,NNEG)
      NX=NROOT-NNEG
      IF(NX.LT.2)THEN
       WRITE(*,1010)NX,NROOT,NNEG,(X(I),I=1,3)
 1010  FORMAT(2X,'NX,NROOT,NNEG=',3I2,' X=',3(G11.4,1X))
       Y=0.0
       RETURN
      ENDIF
      IF(NX.EQ.2)X(1)=X(2)
      IF(DABS(Y-1.0).LT.0.00001)THEN
       Y=AMAX1(X(1),X(2),X(3))
      ELSE
       Y=AMIN1(X(1),X(2),X(3))
      ENDIF
      RETURN
      END
C
C     THIS SUBROUTINE IS USED FOR THE CALCULATION OF ZL SATURATED
      SUBROUTINE ZLCAL(TR,ZCDR)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER(NDATA=240)
      COMMON/VLS/CUVA(NDATA),CUVB(NDATA),CUVC(NDATA),CUVD(NDATA)
```

```
      COMMON/PAR8/TCI,PCI,VCI,WI,UI,NK
      COMMON/DAT1/T(NDATA),P(NDATA),VSL(NDATA),VSV(NDATA)
      COMMON/RT0/R,T0
      TA=TR*TCI
      CALL CUSP(NK,T,VSL,CUVA,CUVB,CUVC,CUVD,CUS,CUH,TA,VA,4,2,LERR)
      IF(LERR.NE.0)THEN
       WRITE(*,*)' CUSP FAILE AT ZCDR'
       STOP 'STOP PROGRAM'
      ENDIF
      ZCDR=VA*PCI/R/TCI
      RETURN
      END
C
C     THIS SUBROUTINE IS USED FOR THE CALCULATION OF PR SATURATED
      SUBROUTINE PRCAL(TR,PR)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER(NDATA=240)
      COMMON/PPS/CUPA(NDATA),CUPB(NDATA),CUPC(NDATA),CUPD(NDATA)
      COMMON/DAT1/T(NDATA),P(NDATA),VSL(NDATA),VSV(NDATA)
      COMMON/PAR8/TCI,PCI,VCI,WI,UI,NK
      TA=TR*TCI
      CALL CUSP(NK,T,P,CUPA,CUPB,CUPC,CUPD,CUS,CUH,TA,PA,4,2,LERR)
      IF(LERR.NE.0)THEN
       WRITE(*,*)' CUSP FAIL AT PR'
       WRITE(*,1000)TR,TA,T(1),T(NK)
1000   FORMAT(2X,'TR=',F7.4,' TA=',F7.2,' T(1)=',F7.2,' T(NK)=',F7.2)
       STOP 'STOP PROGRAM'
      ENDIF
      PR=PA/PCI
      RETURN
      END
C
C     THIS SUBROUTINE IS USED TO CALCULATE X,Y,H,G
      SUBROUTINE HGFUN(TR,F,H,G,D,C,E,XRATIO)
      IMPLICIT REAL*8(A-H,O-Z)
      X=4.0*F+(1.0-4.0*F)*DEXP(C*TR**D*(1.0-TR**E))
      Y=X
      H=(1.0-F)*(X-DSQRT(Y-4.0*F))/2.0
      XRATIO=(X-DSQRT(Y-4.0*F))/(1.0-DSQRT(1.0-4.0*F))
      G=1.0-F-H
      RETURN
      END

*************************************************************************
*     THIS SUBROUTINE IS USED TO FIND THE PARAMETERS OF ALF FUNCTION
*     BY FITTING TR-ALF DATA
```

```
*    LALF - THE CODE OF ALF FUNCTION              (INPUT)
*    NA - THE NUMBER OF PARAMETERS OF ALF FUNCTION (OUTPUT)
*    ND - THE NUMBER OF POINTS                    (INPUT)
*    PALF(10) - PARAMETERS OF ALF FUNCTION        (OUTPUT)
*    DALFT - AVERAGE DIVIATION (DALF/ALF)         (OUTPUT)
*    LP - PRINT TYPE                              (INPUT)
*       LP      =0 PRINT ALL MESSAGE
*               =1 PRINT WITHOUT ERROR MESSAGE
*    LPASS - WRITTING PASS                        (INPUT)
**********************************************************************
      SUBROUTINE FITALF(LALF,NA,ND,PALF,DALFT,LP,LPASS)
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER RESFILE*12
      PARAMETER (NDATA=240)
      DIMENSION X(10),A(10,10),P(10)
      DIMENSION PALF(10),ICO(10),F(200)
      EXTERNAL FUNALF3
      COMMON/TRALF/TRALF(NDATA),ALF(NDATA)
      COMMON/RETF/RESFILE
      COMMON/ALF0/ALFA,ALFN,ALFM,IALFA,IALFN,IALFM
      DO 1 I=1,10
      PALF(I)=0.0
    1 CONTINUE
      OPEN(LPASS,ACCESS='APPEND',FILE=RESFILE,STATUS='OLD')
      CALL ALFP(LALF,NA,LPASS)
      CLOSE(LPASS)
      IF(LALF.EQ.3.OR.LALF.EQ.8)THEN
       NA=3
       X(1)=ALFA
       X(2)=ALFN
       X(3)=ALFM
       ICO(1)=IALFA
       ICO(2)=IALFN
       ICO(3)=IALFM
       CALL MARQS(NA,ND,FUNALF3,X,ICO,F,1.D-4,1)
      ELSE
       CALL LINFIT(NA,ND,X,A,P,ERR,IER)
      ENDIF
      DO 10 I=1,NA
      PALF(I)=X(I)
   10 CONTINUE
      OPEN(LPASS,ACCESS='APPEND',FILE=RESFILE,STATUS='OLD')
      WRITE(LPASS,1000)NA,ERR,(PALF(I),I=1,NA)
 1000 FORMAT(2X,'NA=',I2,' ERR=',G12.5/2X,' PI=',4(G12.5,1X))
      IF(LP.EQ.0)
     1 WRITE(LPASS,*)' I    ALFC     ALF      DALF     DALF%'
```

```
      DALFT=0.0
      DO 20 I=1,ND
      IF(LALF.EQ.3.OR.LALF.EQ.8)THEN
       ALFC=DEXP(PALF(1)*(1.0-TRALF(I)**PALF(2))*(
     1 (1.0-TRALF(I)**PALF(2))**2.0)**PALF(3))
      ELSE
       ALFC=(1.0+PALF(1)*(1.0-TRALF(I)**0.5)+PALF(2)*(1.0-TRALF(I))*
     1  (0.7-TRALF(I)))**2
      ENDIF
      DALF=ALFC-ALF(I)
      DALFT=DALFT+DABS(DALF/ALF(I))
      IF(LP.EQ.0)THEN
       WRITE(LPASS,2000)I,ALFC,ALF(I),DALF,DABS(DALF/ALF(I))*100.0
 2000  FORMAT(2X,I3,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.2)
      ENDIF
 20   CONTINUE
      DALFT=DALFT/ND
      WRITE(LPASS,3000)ND,DALFT*100.0
 3000 FORMAT(2X,'ND=',I3,' DALF%=',F7.2)
      CLOSE(LPASS)
      RETURN
      END
C
*************************************************************************
*     THIS SUBROUTINE IS USED TO PRINT OUT THE NAME OF ALF FUNCTION
*     AND SETTING NA
*     LALF - THE CODE OF ALF FUNCTION              (INPUT)
*     NA - THE NUMBER OF PARAMETERS OF ALF FUNCTION (OUTPUT)
*     LPASS - WRITTING PASS                        (INPUT)
*************************************************************************
      SUBROUTINE ALFP(LALF,NA,LPASS)
      IMPLICIT REAL*8(A-H,O-Z)
      GOTO(10,20,30,40,50,60,70,80,90,100),LALF
 10   CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)^3]*ALF'
      WRITE(LPASS,*)' ALF^0.5=(1.0+P1(1.0-Tr^0.5))'
      NA=1
      RETURN
 20   CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)^3]*ALF'
      WRITE(LPASS,*)' ALF^0.5=(1.0+P1(1.0-Tr^0.5)+P2(1.0-Tr)(0.7-Tr))'
      NA=2
      RETURN
 30   CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)^3]*ALF'
      WRITE(LPASS,*)' ALF=exp(a(1-Tr^n)^(2m+1))'
```

```
      NA=3
      RETURN
   40 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)^3]*ALF'
      RETURN
   50 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)^3]*ALF'
      RETURN
   60 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)*G*H/F]*ALF'
      WRITE(LPASS,*)' ALF^0.5=(1.0+P1(1.0-Tr^0.5))'
      NA=1
      RETURN
   70 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)*G*H/F]*ALF'
      WRITE(LPASS,*)' ALF^0.5=(1.0+P1(1.0-Tr^0.5)+P2(1.0-Tr)(0.7-Tr))'
      NA=2
      RETURN
   80 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)*G*H/F]*ALF'
      WRITE(LPASS,*)' ALF=exp(a(1-Tr^n)^(2m+1))'
      NA=3
      RETURN
   90 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)*G*H/F]*ALF'
      RETURN
  100 CONTINUE
      WRITE(LPASS,*)' QA=[(1-F)*G*H/F]*ALF'
      RETURN
      END
C
C     THIS FUNCTION IS CALLED BY LINFIT FOR FITTING LINEAR ALF FUNCTION
      SUBROUTINE FUNP(N,K,P0,P)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (NDATA=240)
      DIMENSION P(N)
      COMMON/TRALF/TRALF(NDATA),ALF(NDATA)
      COMMON/OPT/IOPT,LOPT,LALF
      GOTO(10,20,30,40,50,60,70,80,90,100),LALF
   10 CONTINUE
      P0=-DSQRT(ALF(K))+1.0
      P(N)=(1.0-DSQRT(TRALF(K)))
      RETURN
   20 CONTINUE
      P0=-DSQRT(ALF(K))+1.0
      P(1)=(1.0-DSQRT(TRALF(K)))
```

```
      P(N)=(1.0-TRALF(K))*(0.7-TRALF(K))
      RETURN
30    CONTINUE
      RETURN
40    CONTINUE
      RETURN
50    CONTINUE
      RETURN
60    CONTINUE
      P0=-DSQRT(ALF(K))+1.0
      P(N)=(1.0-DSQRT(TRALF(K)))
      RETURN
70    CONTINUE
      P0=-DSQRT(ALF(K))+1.0
      P(1)=(1.0-DSQRT(TRALF(K)))
      P(N)=(1.0-TRALF(K))*(0.7-TRALF(K))
      RETURN
80    CONTINUE
      RETURN
90    CONTINUE
      RETURN
100   CONTINUE
      RETURN
      END
C
C     THIS FUNCTION IS CALLED BY MARQS FOR CALCULATE THE DEVIATIONS
      SUBROUTINE FUNALF3(N,M,X,F)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (NDATA=240)
      DIMENSION X(N),F(M)
      COMMON/TRALF/TRALF(NDATA),ALF(NDATA)
      DO 100 I=1,M
      ALF1=DEXP(X(1)*DABS(1.0-TRALF(I)**X(2))*((1.0-
     1 TRALF(I)**X(2))**2)**X(3))
      F(I)=(ALF1-ALF(I))/ALF(I)
100   CONTINUE
      RETURN
      END
```

D.2 The Source Codes of the Program for the Bubble Point Pressure Calculation

This subroutine was used for the VLE calculation of pure substances and mixtures. In this calculation, the bubble pressure and vapor phase composition can be determined from the given temperature and liquid phase composition.

```
$DEBUG
************************************************************************
*    VLEB IS USED TO CALCULATE BUBBLE POINT PRESSURE P AND VAPOR
* PHASE COMPOSITION Y FOR PURE COMPONENTS OR MIXTURES.
* N - THE NUMBER OF COMPONENTS
* T - TEMPERATURE          K
* P - PRESSURE             Pa
* X(N) - LIQUID PHASE COMPOSITION
* Y(N) - VAPOR PHASE COMPOSITION
* IEER - ERROR CODE
*        IERR  =0     NORMAL
*              =-1    BAD DATA (T OR X) INPUT
*              =-2    PARAMETERS WRONG IN THE VAPOR PRESSURE FUNCTION
*              =-3    NOT CONVERGENCE IN THE CALCULATION
*              =-4    NO VLE EXIST IN THE CALCULATION
*              =-5    CRITICAL OR AZEROTROPIC POINT
*              =-6    SUPER CRITICAL FOR THE CALCULATION OF PURE
*
* THE PROGRAM NEEDS TO CALL SUBROUTINE EOS, WHICH HAS THE FORM
*     EOS(N,T,P,X,V,FU,H,S,IP,IFU)
* IN EOS, FUGASITY COEFFICIENT FU(N) ARE CALCULATED BY USING
* EQUATION OF STATE
************************************************************************
      SUBROUTINE VLEB(N,T,P,X,Y,IEER)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (NCOMP=10)
      EXTERNAL FBUBP,FSAT
      DIMENSION X(N),Y(N),FK(NCOMP)
      COMMON/CONST1/TC(NCOMP),PC(NCOMP),VC(NCOMP),W(NCOMP),U(NCOMP),
```

```
     1 WM(NCOMP)
       COMMON/FBU/XCOM(20),YCOM(20),TCOM,NCOM
       COMMON/VEOR/IVR
       COMMON/LEOR/ILR
       COMMON/IEOR/IEOR
       COMMON/DV/DVGL,VL
       COMMON/QQE/QQE
       IEER=0
C -- SETTING ACCURACIES
       EPS1=1.D-8
       EPS2=1.D-8
C -- CHECK INPUT DATA
       IF(N.GT.NCOMP)THEN
        WRITE(7,*)' N GREATER THAN NCOMP'
        IEER=-1
        RETURN
       ENDIF
       IF(T.LE.2.D0.OR.T.GT.7000.D0)THEN
        WRITE(7,*)' T DATA IS WRONG'
        IEER=-1
        RETURN
       ENDIF
       S=0.0
       SS=0.0
       NRX=N
       DO 5 I=1,N
       IF(DABS(X(I)).LT.1.D-6)NRX=NRX-1
       XCOM(I)=X(I)
       S=S+X(I)
       SS=SS+Y(I)
5      CONTINUE
       IF(DABS(S-1.D0).GT.0.01D0)THEN
        WRITE(7,*)' X DATA IS WRONG'
        IEER=-1
        RETURN
       ENDIF
C      CHECK CRITICAL POINT OR AZEROTROPIC POINT, IF YES RETUREN
       LCRIT=0
       IF(N.EQ.1.AND.(T.GE.TC(1).OR.P.GE.PC(1)))THEN
        IEER=-6
        RETURN
       ENDIF
       IF(NRX.NE.1)THEN
        DO 6 I=1,N
        IF(DABS(X(I)-Y(I)).LT.1.E-6)LCRIT=1
6       CONTINUE
```

```
      ENDIF
      IF(LCRIT.EQ.1)THEN
       IEER=-5
       RETURN
      ENDIF
C -- CHECK INITIAL VALUE OF P AND Y. IF WRONG, USING IDEAL FLUID RULE
      IF(DABS(SS-1.D0).GT.1.E-4.OR.P.LT.1.0)THEN
       CALL IDVLE(3,N,T,P,X,Y,FK,IEER)
       IF(IEER.EQ.-2)THEN
        WRITE(7,*)' PSAT DATA WRONG'
        RETURN
       ENDIF
      ENDIF
      TCOM=T
      NCOM=N
      DO 8 I=1,N
      YCOM(I)=Y(I)
8     CONTINUE
      CALL KCALC(N,T,P,X,Y,FK)
      IF(DVGL.LE.0.75*VL)GOTO 100
      P1=P
      P2=P*0.98
      P=RTSEC(FBUBP,P1,P2,1.D-10)
      DO 10 I=1,N
      Y(I)=YCOM(I)
10    CONTINUE
      IF(DVGL.LE.0.0001*VL)IEER=-4
      RETURN
100   CONTINUE
C --  CALCULATE THE POINT NEAR CRITICAL POINT
      WRITE(*,*)' ENTER THE CRITICAL REGION'
      DL=0.2
      ND=10
      PO=P
      Y1O=YCOM(1)
105   CONTINUE
      P=PO*DL
      DT=T*DL/ND
      P1O=P
      P1=P
      P2=P1*QQE
      TCOM=T-ND*DT
      T1O=TCOM
      IF(TCOM.LT.T*0.5)THEN
       WRITE(*,*)' CAN NOT FIND RIGHT INITAL T'
       IEER=-4
```

```
      RETURN
     ENDIF
     P=RTSEC(FBUBP,P1,P2,1.D-10)
     IF(NRX.EQ.1)THEN
      IF(IVR.NE.0.OR.ILR.NE.0.OR.DABS(DVGL).LT.1.D-10)THEN
       DL=DL*1.2
       ND=ND*1.2
       GOTO 105
      ENDIF
     ELSE
      IF(DABS(YCOM(1)-XCOM(1)).LT.1.D-4)THEN
       DL=DL*1.2
       ND=ND*1.2
       YCOM(1)=Y1O
       YCOM(2)=1.0-YCOM(1)
       GOTO 105
      ENDIF
     ENDIF
     ND1=ND
     P1OO=P1O
     Y1OO=Y1O
107   CONTINUE
     ND=ND1
     IF(ND1.GT.5000)THEN
      WRITE(*,*)' NONCONV. IN ',I,' ND=',ND,' TCOM=',TCOM
      P=P1O
      YCOM(1)=Y1O
      YCOM(2)=1.0-Y1O
      IEER=-3
      GOTO 130
     ENDIF
     DO 110 I=1,ND
     I1=ND-I
     TCOM=T-I1*DT
     P1=P1O
     P2=P1*0.992
     YCOM(1)=Y1O
     YCOM(2)=1.0-Y1O
     P=RTSEC(FBUBP,P1,P2,1.D-10)
     IF(NRX.EQ.1)THEN
      IF(IVR.NE.0.OR.ILR.NE.0.OR.DABS(DVGL).LT.1.D-9)THEN
       ND1=(ND-I+1)*2
       DT=(T-T1O)/ND1
       P1O=P1OO
       GOTO 107
      ENDIF
```

```
      ELSE
       IF(DABS(YCOM(1)-XCOM(1)).LT.1.D-4)THEN
        ND1=(ND-I+1)*2
        DT=(T-T1O)/ND1
        P1O=P1OO
        Y1O=Y1OO
        GOTO 107
       ENDIF
      ENDIF
      T1O=TCOM
      P1OO=P1O
      P1O=P
      Y1OO=Y1O
      Y1O=YCOM(1)
110   CONTINUE
130   CONTINUE
      DO 120 I=1,N
      Y(I)=YCOM(I)
120   CONTINUE
      IF(DABS(DVGL).LT.1.D-10)IEER=-4
      RETURN
      END
*************************************************************************
*     THE FUNCTION USED TO CALCUATE THE SUM Y OF THE MIXTURE FOR
*     THE BUBLE POINT CALCULATION
*************************************************************************
      DOUBLE PRECISION FUNCTION FBUBP(P)
      IMPLICIT REAL*8(A-H,O-Z)
      LOGICAL FLAG
      DIMENSION X(20),Y(20),FK(20),YTEMP(20)
      COMMON/FBU/XCOM(20),YCOM(20),TCOM,NCOM
      T=TCOM
      N=NCOM
      DO 5 I=1,N
      X(I)=XCOM(I)
      Y(I)=YCOM(I)
5     CONTINUE
      ITER=0
10    CONTINUE
      CALL KCALC(N,T,P,X,Y,FK)
      YSUM=0.0
      DO 20 I=1,N
      YTEMP(I)=X(I)*FK(I)
      YSUM=YSUM+YTEMP(I)
20    CONTINUE
      FLAG=.TRUE.
```

```
      DO 30 I=1,N
      YTEMP(I)=YTEMP(I)/YSUM
      FLAG=FLAG.AND.DABS(YTEMP(I)-Y(I)).LT.1.D-6
      Y(I)=YTEMP(I)
30    CONTINUE
      ITER=ITER+1
      IF(ITER.GE.20)FLAG=.TRUE.
      IF(.NOT.FLAG)GOTO 10
      FBUBP=0.0
      DO 40 I=1,N
      YCOM(I)=Y(I)
      FBUBP=FBUBP+X(I)*FK(I)
40    CONTINUE
      FBUBP=DLOG(FBUBP)
      RETURN
      END

*************************************************************************
*     SUBROUTINE KCALC IS USED TO CALCULATE THE VAPOR-LIQUID
*     EQUILIBRIUM CONSTANT OF COMPONENTS
*************************************************************************
      SUBROUTINE KCALC(N,T,P,X,Y,FK)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(N),Y(N),FG(20),FL(20),FK(N)
      COMMON/DV/DVGL,VL
      CALL EOS(N,T,P,X,VL,FL,H,S,2,1)
      CALL EOS(N,T,P,Y,VG,FG,H,S,1,1)
      DVGL=(VG-VL)
1010  FORMAT(1X,A,2(F7.4,1X),2G11.4)
      DO 10 I=1,N
      FK(I)=FL(I)/FG(I)
10    CONTINUE
      RETURN
      END
*************************************************************************
*     SUBROUTINE IDVLE IS USED TO CALCUATE THE VLE FOR IDEAL FLUID
*     AS INITIAL VALUE FOR THE VLE CALCULATION OF MIXTURES WITHOUT
*     EXPERIMENTAL VALUES AS INITIAL VALUES
*************************************************************************
      SUBROUTINE IDVLE(ITP,N,T,P,X,Y,K,IER)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 X(N),Y(N),K(N)
      PARAMETER (NCOMP=10)
      COMMON/CONST1/TC(NCOMP),PC(NCOMP),VC(NCOMP),W(NCOMP),U(NCOMP),
     1 WM(NCOMP)
      COMMON/PS/LEQ(NCOMP),PSA(NCOMP),PSB(NCOMP),PSC(NCOMP),PSD(NCOMP)
```

```
      XT(T,I)=1.0-T/TC(I)
      PV1(T,I)=PC(I)*DEXP((PSA(I)*XT(T,I)+PSB(I)*XT(T,I)**1.5+
     1 PSC(I)*XT(T,I)**3+PSC(I)*XT(T,I)**6)/(1.0-XT(T,I)))
      PV2(T,I)=DEXP(PSA(I)-PSB(I)/T+PSC(I)*DLOG(T)+
     1 PSD(I)*PC(I)/T**2)*1.0E5
      PV3(T,I)=DEXP(PSA(I)-PSB(I)/(T+PSC(I)))*1.0E5
      PV4(T,I)=DEXP(PSA(I)-PSB(I)/(T+PSC(I)))/750.061*1.0E5
      IF(ITP.EQ.5)GOTO 50
      IER=0
      DO 5 I=1,N
      IF(LEQ(I).EQ.0.OR.LEQ(I).EQ.2.OR.DABS(PSA(I)).LE.1.D-10)THEN
       IER=-2
       RETURN
      ENDIF
5     CONTINUE
      IF(ITP.GT.2) GOTO 30
      T=0.D0
      DO 10 I=1,N
      IF(ITP.EQ.1) Z=X(I)
      IF(ITP.EQ.2) Z=Y(I)
10    T=T+Z*(-PSC(I)+PSB(I)/(PSA(I)-DLOG(P)))
      IT=1
13    SS=0.D0
      DO 15 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
      K(I)=PV/P
      IF (ITP.EQ.1) SS=SS+K(I)*X(I)
15    IF (ITP.EQ.2) SS=SS+Y(I)/K(I)
      F=SS-1.
      IF (DABS(F).LE.5.D-6) GOTO 20
      IF (IT.EQ.1) GOTO 14
      BFF=F*(T-T0)/(F-F0)
      IF(DABS(BFF).GT.T*0.3)BFF=DSIGN(T*0.3,BFF)
      T0=T
      T=T-BFF
      F0=F
      DO 16 I=1,N
      BBK=PSA(I)-PSB(I)/(T+PSC(I))
      IF(BBK.GT.120.D0.AND.BBK.LT.-120.D0)GOTO 17
16    CONTINUE
      GOTO 13
17    T=T0
      GOTO 20
```

```
14    T0=T
      T=T*1.01D0
      F0=F
      IT=IT+1
      GOTO 13
20    DO 25 I=1,N
      IF (ITP.EQ.2) GOTO 26
      Y(I)=K(I)*X(I)/SS
      GOTO 25
26    X(I)=Y(I)/K(I)/SS
25    CONTINUE
      RETURN
30    IF(ITP.GT.3) GOTO 40
      P=0.D0
      DO 35 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
      P=P+X(I)*PV
35    CONTINUE
      DO 37 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
      K(I)=PV/P
      Y(I)=X(I)*K(I)
37    CONTINUE
      RETURN
40    P=0.D0
      QQ=0.9D0
      DO 41 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
      P=P+Y(I)*PV
41    CONTINUE
      IT=1
42    SS=0.D0
      DO 43 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
```

```
      K(I)=PV/P
      SS=SS+Y(I)/K(I)
43    CONTINUE
      F=DLOG(SS)
      IF (DABS(F).LT.0.00001D0) GOTO 47
      IF (IT.EQ.1) GOTO 45
      P=(P-F*(P-P0)/(F-F0))*(1.-QQ)+P*QQ
      QQ=QQ*QQ
      GOTO 42
45    P0=P
      F0=F
      P=P*1.01D0
      IT=IT+1
      GOTO 42
47    DO 48 I=1,N
48    X(I)=Y(I)/K(I)/SS
      RETURN
50    CONTINUE
      DO 55 I=1,N
      IF(LEQ(I).EQ.1)PV=PV1(T,I)
      IF(LEQ(I).EQ.2)PV=PV2(T,I)
      IF(LEQ(I).EQ.3)PV=PV3(T,I)
      IF(LEQ(I).EQ.4)PV=PV4(T,I)
      K(I)=PV/P
55    CONTINUE
      RETURN
      END
*****************************************************************************
*                        RTSEC
* USED THE SECANT METHOD TO FIND THE ROOT OF A FUNCTION FUNC
* THOUGHT TO LIE NEAR X1 AND X2, TO AN ACCURACY XACC.
*****************************************************************************
      DOUBLE PRECISION FUNCTION RTSEC(FUNC,X1,X2,XACC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/IEOR/IEOR
      IEOR=0
      MAXIT=200
      QQ=0.0
      FL=FUNC(X1)
      F=FUNC(X2)
C -- PICK BOUND WITH LOWEST FUNCTION VALUE AS MOST RECENT GUESS.
      IF(DABS(FL).LT.DABS(F)) THEN
       RTSEC=X1
       XL=X2
       SWAP=FL
       FL=F
```

```
      F=SWAP
     ELSE
      XL=X1
      RTSEC=X2
     ENDIF
C -- SECANT METHOD
20    CONTINUE
     DO 11 J=1,MAXIT
     DF=F-FL
     IF(DABS(DF).LT.1.D-16)DF=DSIGN(1.D-16,DF)
     DX=(XL-RTSEC)*F/DF
     XL=RTSEC
     FL=F
13    CONTINUE
     IF(DABS(DX).GT.DABS(XL*0.1))THEN
      DX=DX*0.5
      GOTO 13
     ENDIF
     RTSEC=RTSEC+DX*(1.0-QQ)
15    CONTINUE
     F=FUNC(RTSEC)
     IF(DABS(F).LT.XACC) RETURN
11    CONTINUE
     IF(MAXIT.LT.202)THEN
      MAXIT=300
      QQ=0.99
      GOTO 20
     ENDIF
12    CONTINUE
     WRITE(*,*)' *** MAXIT EXCEEDED IN RTSEC'
     IEOR=1
     RETURN
     END
```

D.3 The Source Codes of the Program for the Monte Carlo Simulation in the Canonical Ensembles

This program was used to calculate the properties of the hard core Lennard-Jones fluid in the canonical ensembles.

```
*************************************************************************
* PROGRAM MCNVT IS A MONTE CARLO SIMULATION PROGRAM IN THE
* CONSTANT-NVT ENSEMBLE FOR PURE FLUID.(ENSHENG ZHAO, 1993)
* IT HAS FOLLOWING ADDITIONAL FEAFURE
* 1 - CAN BE CONTINUED AFTER INTERUPTED BY USER.
* 2 - CAN CALCULATE PAIR CORRELATION FUNCTION G(R).
* 3 - CAN SET IOFF TO DISCARD NONEQUILIBRIUM CONFIGURATIONS
*
* THIS PROGRAM NEED AN INITIAL NONOVERLAP CONFIGURATION
*
* THIS PROGRAM TAKES DIFERENT POTENTIAL FUNCTIONS AS:
* LPFU - LPFU= 1 HARD SPHERE
*          = 2 SQUARE WELL
*          = 3 SUTHERLAND
*          = 4 HARD CORE LENNARD JONES
*          = 5 LENNARD JONES
*          = 6 CUTOFF LENNARD JONES
*          =11 NEW POTENTIAL(LINEAR)
*          =12 NEW POTENTIAL(SWL)
*
* THE BOX IS OF UNIT  LENGTH, -0.5 TO + 0.5
*
* PRINCIPAL VARIABLES:
* INTEGER N              NUMBER OF MOLECULES
* INTEGER NSTEP          MAXIMUM NUMBER OF CYCLES
* REAL RX(N),RY(N),RZ(N)  POSITIONS
* REAL DENS              REDUCED DENSITY
* REAL TEMP              REDUCED TEMPERATURE
* REAL SIGMA             REDUCED LJ DIAMETER
* REAL RMIN              MINIMUM REDUCED PAIR SEPARATION
* REAL RCUT              REDUCED CUTOFF DISTANCE
```

```
* REAL DRMAX          REDUCED MAXIMUM DISPLACEMENT
* REAL V              THE POTENTIAL FUNCTION
* REAL W              THE VIRIAL
* REAL PRES           THE PRESSURE
*
* USAGE:
* THE PROGRAN TAKES IN A CONFIGURATION OF ATOMS AND RUNS
* A MONTE CARLO SIMULATION AT THE GIVEN TEMPERATURE FOR THE
* SPECIFIED NIMBER OF CYCLES
*
* UNITS:
* THE PROGRAM USES LENNARD-JONES UNITS FOR USER INPUT AND
* OUTPUT BUT CONDUCTS THE SIMULATION IN A BOX OF UNIT LENGTH.
* FOR EXAMPLE, FOR A BOXLENGTH L, AND LENNARD-JONES PARAMETERS
* EPSILON AND SIGMA, THE UNITS ARE:
*
* PROPERTY      LJ UNITS          PROGRAM UNITS
*  TEMP         EPSILON/K         EPSILON/K
*  PRES         EPSILON/SIGMA**3  EPSILON/L**3
*  V            EPSILON           EPSILON
*  DENS         1/SIGMA**3        1/L**3
*
* ROUTINES REFERENCED:
* SUBROUTINE SUMUPZ(RCUT,RMIN,SIGMA,OVRLAP,V,W,ZIJ)
*   CALCULATIES THE TOTAL POTENTIAL ENERGY FOR A CONFIGURATION
* SUBROUTINE ENERGYZ(RXI,RUI,RZI,I,RCUT,SIGMA,V,W,ZIJ)
*   CACULATES THE POTENTIAL ENERGY OF ATOM I WITH ALL THE OTHER
*   ATOMS IN THE LIQUID
* SUBROUTINE READCN(CNFILE)
*   READS IN A CONFIGURATION
* SUBROUTINE WRITCN(CNFILE)
*   WRITES OUT A CONFIGURATION
*************************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 RANF
      CHARACTER CNFILE*30,KEY*1
      CHARACTER INIFILE*30,RESFILE*30,TMPFILE*30,DATTMP*30
      PARAMETER(PI=3.1415927)
      DIMENSION AVZIJ(100),ROVSM(100)
      LOGICAL OVRLAP,NONOVR
      INTEGER STEP
      INTEGER ZIJ(100),ZIJOLD(100),ZIJNEW(100)
      COMMON/IDATA/ICUT,NSTEP,IPRINT,ISAVE,IRATIO,ISTART,IOFF
      COMMON/RDATA/DENS,TEMP,RCUT,DRMAX
      COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
      COMMON/DELZ/DELR,NZ
```

```
      COMMON/LPFU/LPFU
      COMMON/PAR/R,ALF,BAT,CONV
      WRITE(*,*)'     **** PROGRAM MCIJ ****'
      WRITE(*,*)'  CONSTANT-NVT MONTE CARLO PROGRAM'
C --  READ INPUT DATA --
      WRITE(*,*)' PLEASE INPUT INITIAL FILENAME'
      READ(*,1000)INIFILE
      WRITE(*,*)' PLEASE INPUT RESULT FILENAME'
      READ(*,1000)RESFILE
      WRITE(*,*)' PLEASE INPUT TMP FILENAME'
      READ(*,1000)TMPFILE
      WRITE(*,*)' PLEASE INPUT DATA TMP FILENAME'
      READ(*,1000)DATTMP
C      INIFILE='MCNVT4.INI'
      CALL RDINI(INIFILE)
C --  MAKE SURE THE FIRST RUN
      IF(ISTART.EQ.0)THEN
       WRITE(*,*)' ARE YOU SURE THIS IS THE FIRST RUN?(Y/N)'
       READ(*,1000)KEY
 1000  FORMAT(A)
       IF(KEY.NE.'Y'.AND.KEY.NE.'y')ISTART=1
      ENDIF
C --  GETTING START
      IF(ISTART.EQ.0)THEN
       OPEN(6,FILE=RESFILE,STATUS='UNKNOWN')
       CALL GETDAT(IY,IM,ID)
       WRITE(6,'(4X,''DATE(M/D/Y): '',I2,''/'',I2,''/'',I4)')IM,ID,IY
       CNFILE='MCNVT.DAT'
      ELSE
       CNFILE=DATTMP
      ENDIF
      CALL READCN(CNFILE)
      CNFILE=DATTMP
C --  SET RMIN/SIGMA FOR DIFFERENT POTENTIAL FUNCTIONS
      CALL SETR(LPFU,RMIN)
C --  CONVERT INPUT DATA TO PROGRAN UNITS
      CALL CPROU(N,TEMP,BETA,DENS,DENSLJ,SIGMA,ICUT,RCUT,RMIN,DRMAX)
C --  SETTING DISTANCES FOR CALCULATING PAIR CONTRIBUTION FUNCTION
      NZ=100
      DELR=0.5/SIGMA/REAL(NZ)
C --  WRITE DOWN READING DATA AND SETTING OR READING INITIAL AVERAGE DATA
      IF(ISTART.EQ.0)THEN
       CALL WTITLE(LPFU)
       WRITE(6,1010)N,NSTEP,IPRINT,ISAVE,IRATIO,IOFF,TEMP,DENS*SIGMA**3,
     1 RCUT,DRMAX/SIGMA
 1010  FORMAT(2X,'N=',I3,' NSTEP=',I8,' IPRINT=',I5,' ISAVE=',I4,
```

```
     1 ' IRATIO=',I4/2X,'IOFF=',I5,' TEMP=',F8.3,' DENS=',F8.3,
     1 ' RCUT=',F8.3,' DRMAX=',F8.3)
C *** ZERO ACCUMULATIONS **
      ACV=0.0
      ACVSQ=0.0
      ACW=0.0
      ACP=0.0
      ACPSQ=0.0
      FLV=0.0
      FLP=0.0
      ACM=0.0
      ACATMA=0.0
      DO 10 IJ=1,NZ
      AVZIJ(IJ)=0.0
10     CONTINUE
C ****************************
      ELSE
C *** READ AVERAGE DATA FOR CONTINUE RUN **
      OPEN(3,FILE=TMPFILE)
      READ(3,*)ACV,ACW,ACVSQ,ACP,ACPSQ,FLV,FLP,ACM,ACATMA,DRMAX
      READ(3,*)NSTEPS
      READ(3,*)(AVZIJ(IJ),IJ=1,NZ)
      CLOSE(3)
C ****************************
      ENDIF
C -- CALCULATE LONG RANGE CORRECTIONS --
      CALL LVALUE(LPFU,RCUT,SIGMA,DENSLJ,N,VLRC,WLRC)
C -- CALCULATE INITIAL ENERGY --
      CALL SUMUPZ(RCUT,RMIN,SIGMA,OVRLAP,V,W,ZIJ)
      VS=(V+VLRC)/REAL(N)
      WS=W+DENS*WLRC
      PS=DENS*TEMP+W+WLRC*DENS
      PS=PS*SIGMA**3
C -- CHECK OVRLAP FOR INITIAL CONFIGURATION
      IF(OVRLAP)THEN
       IF(ISTART.EQ.0.)STOP 'OVERLAP IN INITIAL CONFIGURATION'
      ENDIF
C -- WRITE OUT SOME USEFUL INFORMATION --
      IF(ISTART.EQ.0)THEN
       WRITE(6,1020)SIGMA,RMIN,RCUT,VLRC/REAL(N),WLRC/REAL(N)
1020   FORMAT(2X,' SIGMA/BOX        =',F10.4/
     1       2X,' RMIN/BOX         =',F10.4/
     2       2X,' RCUT/BOX         =',F10.4/
     3       2X,' LRC FOR <V>      =',F10.4/
     4       2X,' LRC FOR <W>      =',F10.4)
       WRITE(6,1030)VS,WS,PS
```

```
1030  FORMAT(2X,'INITIAL V=',F10.4,' W=',F10.4,' PS=',F10.4)
      WRITE(6,2000)
2000  FORMAT(2X/2X,'  START OF MARKOV CHAIN ')
      CLOSE(6)
     ENDIF
     OPEN(6,FILE=RESFILE,ACCESS='APPEND',STATUS='OLD')
     CALL GETDAT(ISY,ISMO,ISD)
     CALL GETTIM(ISH,ISM,ISS,ISEED)
     WRITE(6,'(2X,''STARTINGTIME: '',I4,'','',I2,'','',I2,1X,
    1 I2,'':'',I2,'':'',I2)')ISY,ISMO,ISD,ISH,ISM,ISS
     WRITE(6,2010)
2010 FORMAT(2X,'  NMOVE      RATIO       V/N         P')
     CLOSE(6)
*********************************************************************
C --  LOOPS OVER ALL CYCLES AND ALL MOLECULES --
     CALL SEED(ISEED)
     IF(ISTART.EQ.0)NSTEPS=1
     DO 100 STEP=NSTEPS,NSTEP
     WRITE(*,*)' I(IN STEP)=',STEP
     DO 99 I=1,N
     RXIOLD=RX(I)
     RYIOLD=RY(I)
     RZIOLD=RZ(I)
C --  CALCULATE THE ENERGY OF I IN THE OLD CONFIGURATION --
     CALL ENERGYZ(RXIOLD,RYIOLD,RZIOLD,I,RCUT,RMIN,SIGMA,
    1 VOLD,WOLD,NONOVR,ZIJOLD)
C --  MOVE I AND PICKUP THE CENTRAL IMAGE --
     CALL RANDOM(RANF)
     RXINEW=RXIOLD+(2.0*RANF-1.0)*DRMAX
     CALL RANDOM(RANF)
     RYINEW=RYIOLD+(2.0*RANF-1.0)*DRMAX
     CALL RANDOM(RANF)
     RZINEW=RZIOLD+(2.0*RANF-1.0)*DRMAX
     RXINEW=RXINEW-ANINT(RXINEW)
     RYINEW=RYINEW-ANINT(RYINEW)
     RZINEW=RZINEW-ANINT(RZINEW)
C --  CALCULATE THE ENERGY OF I IN THE NEW CONFIGURATION
     CALL ENERGYZ(RXINEW,RYINEW,RZINEW,I,RCUT,RMIN,SIGMA,
    1 VNEW,WNEW,NONOVR,ZIJNEW)
C --  CHECK FOR ACCEPTANCE
     DELTV=VNEW-VOLD
     DELTW=WNEW-WOLD
     DELTVB=BETA*DELTV
     IF(NONOVR)THEN
      IF(DELTVB.LT.75.0)THEN
       IF(DELTVB.LE.0.0)THEN
```

```
      V=V+DELTV
      W=W+DELTW
      RX(I)=RXINEW
      RY(I)=RYINEW
      RZ(I)=RZINEW
      DO 170 IJ=1,NZ
      ZIJ(IJ)=ZIJ(IJ)-ZIJOLD(IJ)+ZIJNEW(IJ)
170    CONTINUE
      ACATMA=ACATMA+1.0
     ELSE
      CALL RANDOM(RANF)
      IF(EXP(-DELTVB).GT.RANF)THEN
       V=V+DELTV
       W=W+DELTW
       RX(I)=RXINEW
       RY(I)=RYINEW
       RZ(I)=RZINEW
       DO 180 IJ=1,NZ
       ZIJ(IJ)=ZIJ(IJ)-ZIJOLD(IJ)+ZIJNEW(IJ)
180     CONTINUE
       ACATMA=ACATMA+1.0
      ENDIF
     ENDIF
    ENDIF
   ENDIF
C -- CALCULATE INSTANTANEOUS VALUES --
   VN=(V+VLRC)/REAL(N)
   WN=W+DENS*WLRC
   PRES=DENS*TEMP+W+DENS*WLRC
C -- CONVERT PRESSURE TO LJ UNITS --
   PRES=PRES*SIGMA**3
C -- ACCUMULATE AVERAGES --
   ACV=ACV+VN
   ACW=ACW+WN
   ACP=ACP+PRES
   ACVSQ=ACVSQ+VN*VN
   ACPSQ=ACPSQ+PRES*PRES
   ACM=ACM+1.0
   DO 190 IJ=1,NZ
   AVZIJ(IJ)=AVZIJ(IJ)+ZIJ(IJ)
190  CONTINUE
C -- ENDS LOOP OVER ATOMS
99   CONTINUE
C -- PERFORM PERIODIC OPERATION --
C -- DISCARD NONEQUILIBRIUM CONFIGRATIONS
   IF(STEP.EQ.IOFF)THEN
```

```
C --  ZERO REACCUMULATIONS --
      ACV=0.0
      ACVSQ=0.0
      ACW=0.0
      ACP=0.0
      ACPSQ=0.0
      FLV=0.0
      FLP=0.0
      ACM=0.0
      DO 110 IJ=1,NZ
      AVZIJ(IJ)=0.0
110    CONTINUE
     ENDIF
C --  ADJUST MAXIMUM DISPLACEMENT --
     IF(MOD(STEP,IRATIO).EQ.0)THEN
      RATIO=ACATMA/REAL(N*IRATIO)
      IF(RATIO.GT.0.5)THEN
       DRMAX=DRMAX*1.05
      ELSE
       DRMAX=DRMAX*0.95
      ENDIF
      ACATMA=0.0
      CALL GETTIM(IH,IM,IS,ISEED)
      CALL SEED(ISEED)
     ENDIF
C --  WRITE OUT RUNTIME INFORMATION --
     IF(MOD(STEP,IPRINT).EQ.0)THEN
      OPEN(6,FILE=RESFILE,ACCESS='APPEND',STATUS='OLD')
      WRITE(6,2020)INT(ACM),RATIO,VN,PRES
2020   FORMAT(2X,I8,3(1X,F12.6))
      CLOSE(6)
     ENDIF
C --  WRITE OUT THE CONFIGURATION AT INTERVALS --
     IF(MOD(STEP,ISAVE).EQ.0)THEN
      OPEN(3,FILE=TMPFILE)
      WRITE(3,*)ACV,ACW,ACVSQ,ACP,ACPSQ,FLV,FLP,ACM,ACATMA,DRMAX
      WRITE(3,*)STEP+1
      WRITE(3,*)(AVZIJ(IJ),IJ=1,NZ)
      CLOSE(3)
      CALL WRITCN(CNFILE)
     ENDIF
C --  ENDS LOOP OVER CYCLES --
100   CONTINUE
     CALL GETDAT(IEY,IEMO,IED)
     CALL GETTIM(IEH,IEM,IES,IE100)
     OPEN(6,FILE=RESFILE,ACCESS='APPEND',STATUS='OLD')
```

```
      WRITE(6,*)' END OF MARKOV CHAIN'
C --  CHECK FINAL VALUE OF THE POTENTIAL ENERGY IS CONSISTENT --
      CALL SUMUPZ(RCUT,RMIN,SIGMA,OVRLAP,VEND,WEND,ZIJ)
      IF(ABS(VEND-V).GT.1.D-3)THEN
       WRITE(6,*)' PROBLEM WITH ENERGY'
       WRITE(6,3000)VEND,V
3000   FORMAT(4X,'VEND=',E12.4,' V=',E12.4)
      ENDIF
C --  WRITE OUT THE FINAL CONFIGURATION FROM THE RUN
      CALL WRITCN(CNFILE)
C --  CALCULATE AND WRITE OUT RUNING AVERGES --
      AVV=ACV/ACM
      ACVSQ=(ACVSQ/ACM)-AVV**2
      AVW=ACW/ACM
      AVP=ACP/ACM
      ACPSQ=(ACPSQ/ACM)-AVP**2
      DO 210 IJ=1,NZ
      AVZIJ(IJ)=AVZIJ(IJ)/ACM/REAL(N)
210   CONTINUE
C --  CALCULATE FLUCTUATIONS --
      IF(ACVSQ.GT.0.0)FLV=SQRT(ACVSQ)
      IF(ACPSQ.GT.0.0)FLP=SQRT(ACPSQ)
      WRITE(6,*)' -- AVERGES --'
      ZP=AVP/DENSLJ/TEMP
      WRITE(6,3010)AVV,AVW,AVP,ZP
3010  FORMAT(3X,'<V/N>=',G12.5/3X,'<W/N>=',G12.5/3X,'<PSp>=',G12.5/
     1 3X,'<Zp>=',G12.5)
      WRITE(6,*)' FLUCTUATIONS'
      WRITE(6,3020)FLV,FLP
3020  FORMAT(2X,' FLUCTUATION IN <V/N> =',F10.6/
     1      2X,' FLUCTUATION IN  <P>  =',F10.6)
      WRITE(6,'(2X,'' ENDINGTIME: '',I4,'','',I2,'','',I2,1X,
     1 I2,'':'',I2,'':'',I2)')IEY,IEMO,IED,IEH,IEM,IES
      WRITE(6,*)'  PAIR DISTRIBUTION FUNCTION G(R/SIGMA)'
      DO 220 IJ=1,NZ
      ROVS=IJ*DELR
      ROVSM(IJ)=ROVS-0.5*DELR
      DELR1=DELR
      IF(IJ.GT.1.AND.ROVSM(IJ-1).LT.1.0.AND.ROVS.GT.1.0)THEN
       ROVSM(IJ)=(ROVS-1.0)/2.0+1.0
       DELR1=ROVS-1.0
      ENDIF
      VOLMI=4.0/3.0*PI*DENS*((SIGMA*ROVS)**3-(SIGMA*(ROVS-DELR1))**3)
      WRITE(6,3030)IJ,ROVSM(IJ),ROVSM(IJ)*SIGMA,AVZIJ(IJ),
     1 AVZIJ(IJ)/VOLMI
3030  FORMAT(2X,'IJ=',I3,' R/SIGMA=',F6.3,' R=',F6.4,' N=',F10.4,
```

```
   1 ' G=',F10.4)
    AVZIJ(IJ)=AVZIJ(IJ)/VOLMI
220  CONTINUE
    CALL FITGC(NZ,ROVSM,AVZIJ,GC)
    CALL CORRZ(LPFU,ZP,Z,GC,DENSLJ)
    WRITE(6,3050)GC,ZP,Z
3050  FORMAT(2X,'GC=',F7.3,' ZP=',F10.4,' Z=',F10.4)
    CLOSE(6)
    STOP
    END

*************************************************************************
*  VWIJ SUBROUTINE IS USED FOR CALCULATING CONFIG. FUNCTION VIJ,
*  VIRIAL FUNCTION WIJ FOR MOLECULE I AND J
*  RIJ - THE DISTANCE OF I AND J, IN BOX UNIT
*  SIGMA - THE DIAMTER OF MOLECULES, IN BOX UNIT
*  VIJ - CONFIGRATION FUNCTION, REDUCED
*  WIJ - VIRIAL FUNCTION, REDUCED
*  R,ALF,BAT,CONV- PARAMETERS
*  LPFU - CODE OF POTENTIAL FUNCTION
*       LPFU= 1 HARD SPHERE
*           = 2 SQUARE WELL
*           = 3 SUTHERLAND
*           = 4 HARD CORE LENNARD JONES
*           = 5 LENNARD JONES
*           =11 NEW POTENTIAL(LINEAR)
*           =12 NEW POTENTIAL(SWL)
*************************************************************************
    SUBROUTINE VWIJ(RIJ,SIGMA,VIJ,WIJ)
    IMPLICIT REAL*8(A-H,O-Z)
    COMMON/PAR/R,ALF,BAT,CONV
    COMMON/LPFU/LPFU
    GOTO(1,2,3,4,5,6,7,8,9,10,11,12),LPFU
1    CONTINUE
    RETURN
2    CONTINUE
    RETURN
3    CONTINUE
    RETURN
4    CONTINUE
    IF(RIJ.LT.R*SIGMA)THEN
     VIJ=-1.0
     WIJ=0.0
    ELSE
     GOTO 5
    ENDIF
```

```
      RETURN
5     CONTINUE
      SR1=SIGMA/RIJ
      SR2=SR1*SR1
      SR6=SR2*SR2*SR2
      VIJ=SR6*(SR6-1.0)
      WIJ=SR6*(SR6-0.5)
      VIJ=4.0*VIJ
      WIJ=48.0*WIJ/3.0
      RETURN
6     CONTINUE
      GOTO 5
      RETURN
7     CONTINUE
      RETURN
8     CONTINUE
      RETURN
9     CONTINUE
      RETURN
10    CONTINUE
      RETURN
11    CONTINUE
      IF(RIJ.GE.ALF*SIGMA)THEN
       VIJ=0.0
       WIJ=0.0
      ELSE
       VIJ=CONV*(RIJ-ALF*SIGMA)/((ALF-1.0)*SIGMA)
       WIJ=CONV*RIJ/((ALF-1.0)*SIGMA)
      ENDIF
      RETURN
12    CONTINUE
      RETURN
      END
*******************************************************************************
* LVALUE SUBROUTINE IS USED TO CALCULATE LONG RANGE OF CONFIG.
* FUNCTION VLRC AND VIRIAL FUNCTION WLRC
* LPFU - CODE OF POTENTIAL FUNCTION
*       LPFU= 1 HARD SPHERE
*           = 2 SQUARE WELL
*           = 3 SUTHERLAND
*           = 4 HARD CORE LENNARD JONES
*           = 5 LENNARD JONES
*           =11 NEW POTENTIAL(LINEAR)
*           =12 NEW POTENTIAL(SWL)
* RCUT - CUT DISTANCE, IN BOX UNIT
* SIGMA - DIAMETER OF MOLECULES, IN BOX UNIT
```

```
*  DENSLJ - DENSITY, REDUCED
*  N - NUMBER OF MOLECULES
*  VLRC - LONG RANGE CORROLATION OF CONFIGRATION FUNCTION, REDUCED
*  WLRC - LONG RANGE CORROLATION OF VIRIAL FUNCTION, REDUCED
*****************************************************************************
      SUBROUTINE LVALUE(LPFU,RCUT,SIGMA,DENSLJ,N,VLRC,WLRC)
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER(PI=3.1415927)
      COMMON/PAR/R,ALF,BAT,CONV
      GOTO(1,2,3,4,5,6,7,8,9,10,11,12),LPFU
1     CONTINUE
      RETURN
2     CONTINUE
      RETURN
3     CONTINUE
      RETURN
4     CONTINUE
      GOTO 5
      RETURN
5     CONTINUE
C --  LENNARD JONES --
      SR3=(SIGMA/RCUT)**3
      SR9=SR3**3
      VLRC12=8.0*PI*DENSLJ*REAL(N)*SR9/9.0
      VLRC6=-8.0*PI*DENSLJ*REAL(N)*SR3/3.0
      VLRC=VLRC12+VLRC6
      WLRC12=4.0*VLRC12/REAL(N)
      WLRC6=2.0*VLRC6/REAL(N)
      WLRC=WLRC12+WLRC6
      RETURN
6     CONTINUE
      RETURN
7     CONTINUE
      RETURN
8     CONTINUE
      RETURN
9     CONTINUE
      RETURN
10    CONTINUE
      RETURN
11    CONTINUE
C --  NEW(LINEAR POTENTIAL FUCTION)
      R1=RCUT/SIGMA
      IF(R1.GT.ALF)THEN
       VLRC=0.0
       WLRC=0.0
```

```
      ELSE
       ALF2=ALF*ALF
       ALF3=ALF2*ALF
       R2=R1*R1
       R3=R2*R1
       VLRC=-PI*DENSLJ*REAL(N)*CONV*(ALF3+ALF2*R1+ALF*R2-3.0*R3)/6.0
       WLRC=PI*DENSLJ*REAL(N)*CONV*(ALF3+ALF2*R1+ALF*R2)/2.0
      ENDIF
      RETURN
12    CONTINUE
      RETURN
      END
C
*******************************************************************************
* THIS SUBROTINE IS USED TO CALCULATION CONFIGURATION ENERGY V,
* VIRAL FUNCTION W AND SURONDING MOLECULAR NUMBER ZIJ
*******************************************************************************
      SUBROUTINE SUMUPZ(RCUT,RMIN,SIGMA,OVRLAP,V,W,ZIJ)
      IMPLICIT REAL*8(A-H,O-Z)
      LOGICAL OVRLAP
      INTEGER ZIJ(100)
      COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
      COMMON/DELZ/DELR,NZ
      OVRLAP=.FALSE.
      NOVER=0
      V=0.0
      W=0.0
C --  LOOP OVER ALL THE PAIRS IN THE LIQUID --
      DO 10 I=1,NZ
      ZIJ(I)=0
10    CONTINUE
      DO 100 I=1,N-1
      RXI=RX(I)
      RYI=RY(I)
      RZI=RZ(I)
      DO 99 J=I+1,N
      RXIJ=RXI-RX(J)
      RYIJ=RYI-RY(J)
      RZIJ=RZI-RZ(J)
C --  MINIMUM IMAGE THE PAIR SEPARATIONS --
      RXIJ=RXIJ-ANINT(RXIJ)
      RYIJ=RYIJ-ANINT(RYIJ)
      RZIJ=RZIJ-ANINT(RZIJ)
      RIJSQ=RXIJ*RXIJ+RYIJ*RYIJ+RZIJ*RZIJ
      RIJ=SQRT(RIJSQ)
      IF(RIJ.LT.RMIN)THEN
```

```
      OVRLAP=.TRUE.
      NOVER=NOVER+1
     ENDIF
     IF(RIJ.LT.RCUT)THEN
      CALL VWIJ(RIJ,SIGMA,VIJ,WIJ)
      V=V+VIJ
      W=W+WIJ
     ENDIF
     IJ=INT((RIJ/SIGMA)/DELR)+1
     IF(IJ.LE.NZ)ZIJ(IJ)=ZIJ(IJ)+2
99    CONTINUE
100   CONTINUE
     IF(NOVER.NE.0)WRITE(*,*)' NOVER=',NOVER
     RETURN
     END
C
     SUBROUTINE ENERGYZ(RXI,RYI,RZI,I,RCUT,RMIN,SIGMA,
    1 V,W,NONOVR,ZIJ)
     IMPLICIT REAL*8(A-H,O-Z)
     LOGICAL NONOVR
     INTEGER ZIJ(100)
     COMMON/DELZ/DELR,NZ
     COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
     NONOVR=.TRUE.
     V=0.0
     W=0.0
C --  LOOP OVER ALL MOLECULES EXCEPT I --
     DO 10 IJ=1,NZ
     ZIJ(IJ)=0
10    CONTINUE
     DO 100 J=1,N
     IF(I.NE.J)THEN
      RXIJ=RXI-RX(J)
      RYIJ=RYI-RY(J)
      RZIJ=RZI-RZ(J)
      RXIJ=RXIJ-ANINT(RXIJ)
      RYIJ=RYIJ-ANINT(RYIJ)
      RZIJ=RZIJ-ANINT(RZIJ)
      RIJSQ=RXIJ*RXIJ+RYIJ*RYIJ+RZIJ*RZIJ
      RIJ=SQRT(RIJSQ)
      IJ=INT((RIJ/SIGMA)/DELR)+1
      IF(IJ.LE.NZ)ZIJ(IJ)=ZIJ(IJ)+2
      IF(RIJ.LT.RMIN)NONOVR=.FALSE.
      IF(RIJ.LT.RCUT)THEN
       CALL VWIJ(RIJ,SIGMA,VIJ,WIJ)
       V=V+VIJ
```

```
      W=W+WIJ
     ENDIF
    ENDIF
100  CONTINUE
    RETURN
    END
*****************************************************************************
* SUBROUTINE CORRZ IS USED TO CORROLATE Z FOR HARD CORE OR SQUARE
* WELL TERM
* LPFU - THE CODE OF POTENTIAL FUNCTION
* ZP - ORIGENAL Z
* Z - ZP + ZCORROLATION
* GC - G(R) AT CONTACT
* DENSLJ - REDUCED DENSITY
*****************************************************************************
    SUBROUTINE CORRZ(LPFU,ZP,Z,GC,DENSLJ)
    IMPLICIT REAL*8(A-H,O-Z)
    PARAMETER(PI=3.1415927)
    GOTO(1,2,3,4,5,6,7,8,9,10,11,12),LPFU
1    CONTINUE
    RETURN
2    CONTINUE
    RETURN
3    CONTINUE
    RETURN
4    CONTINUE
    Z=ZP+2.0/3.0*PI*DENSLJ*GC
    RETURN
5    CONTINUE
    RETURN
6    CONTINUE
    RETURN
7    CONTINUE
    RETURN
8    CONTINUE
    RETURN
9    CONTINUE
    RETURN
10   CONTINUE
    RETURN
11   CONTINUE
    RETURN
12   CONTINUE
    RETURN
    END
```

```
------ ************************************************************************
*  SUBROUTINE FITGC IS USED TO FITTING G(R) AT CONTACT
*  NZ - THE NUMBER OF ZIJ
*  ROVSM(NZ) - R/SIGMA
*  AVZIJ - G(R)
*  GC - G(R) AT CONTACT
************************************************************************
      SUBROUTINE FITGC(NZ,ROVSM,AVZIJ,GC)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION ROVSM(NZ),AVZIJ(NZ)
      DIMENSION A(3,3),X(3),P(3)
      COMMON/GCDATA/R1(20),GC1(20)
C     FIND THREE POINT NEAR CONTACT
      N=3
      M=4
      DO 10 I=1,NZ
      IF(ROVSM(I).GE.1.0)THEN
       DO 20 I1=1,M
       I2=I1-1+I
       R1(I1)=ROVSM(I2)
       GC1(I1)=AVZIJ(I2)
20     CONTINUE
       GOTO 30
      ENDIF
10    CONTINUE
30    CONTINUE
      DO 40 I=1,M
      WRITE(*,*)'I=',I,' R=',R1(I),' G=',GC1(I)
40    CONTINUE
      CALL LINFIT(N,M,X,A,P,ERR,IER)
      GC=X(1)+X(2)+X(3)
      RETURN
      END
************************************************************************
*  SUBROUTINE FUNP IS CALLED BY FITGC FOR FITTING G(R) AT CONTACT
************************************************************************
      SUBROUTINE FUNP(N,I,P0,P)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION P(N)
      COMMON/GCDATA/R1(20),GC1(20)
      P0=-GC1(I)
      P(1)=1.0
      P(2)=R1(I)
      P(N)=R1(I)*R1(I)
      RETURN
      END
```

```
*************************************************************************
* SUBROUTINE READCN IS USED TO READ A CONFIGURATION FROM CNFILE
*************************************************************************
      SUBROUTINE READCN(CNFILE)
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER CNFILE*(*)
      INTEGER CNUMIT
      PARAMETER(CNUMIT=10)
      COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
      OPEN(UNIT=CNUMIT,FILE=CNFILE,STATUS='OLD')
      READ(CNUMIT,*)NN
      IF(NN.NE.N)STOP ' N ERROR IN READCN'
      READ(CNUMIT,*)(RX(I),I=1,N)
      READ(CNUMIT,*)(RY(I),I=1,N)
      READ(CNUMIT,*)(RZ(I),I=1,N)
      CLOSE(UNIT=CNUMIT)
      RETURN
      END
*************************************************************************
* SUBROUTINE WRITCN IS USED TO WRITE A CONFIGURATION TO CNFILE
*************************************************************************
      SUBROUTINE WRITCN(CNFILE)
      IMPLICIT REAL*8(A-H,O-Z)
      CHARACTER CNFILE*(*)
      INTEGER CNUMIT
      PARAMETER(CNUMIT=10)
      COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
      OPEN(UNIT=CNUMIT,FILE=CNFILE,STATUS='UNKNOWN')
      WRITE(CNUMIT,1000)N
1000  FORMAT(1X,I4)
      WRITE(CNUMIT,1100)(RX(I),I=1,N)
      WRITE(CNUMIT,1100)(RY(I),I=1,N)
      WRITE(CNUMIT,1100)(RZ(I),I=1,N)
1100  FORMAT(1X,5F10.7)
      CLOSE(UNIT=CNUMIT)
      RETURN
      END
*************************************************************************
* SUBROUTINE WTITLE IS USED TO WRITE THE TITLE FOR THE POTENTIAL
* FUNCTION INDICATED BY LPFU
*************************************************************************
      SUBROUTINE WTITLE(LPFU)
      IMPLICIT REAL*8(A-H,O-Z)
      GOTO(1,2,3,4,5,6,7,8,9,10,11,12),LPFU
1     CONTINUE
      RETURN
```

```
2    CONTINUE
     RETURN
3    CONTINUE
     RETURN
4    CONTINUE
     WRITE(6,*)'   FOR HARD CORN LENNARD JONES FLUID'
     RETURN
5    CONTINUE
     WRITE(6,*)'   FOR LENNARD JONES FLUID'
     RETURN
6    CONTINUE
     WRITE(6,*)'   FOR CUTOFF LENNARD JONES FLUID'
     RETURN
7    CONTINUE
     RETURN
8    CONTINUE
     RETURN
9    CONTINUE
     RETURN
10   CONTINUE
     RETURN
11   CONTINUE
     WRITE(6,*)'   FOR NEW LINEAR POTENTIAL FUNCTION'
     RETURN
12   CONTINUE
     RETURN
     END
************************************************************************
* RDINI SUBROUTINE IS USED TO READ INITIAL DATA FROM INIFILE
************************************************************************
     SUBROUTINE RDINI(INIFILE)
     IMPLICIT REAL*8(A-H,O-Z)
     CHARACTER TABLE*80,INIFILE*30
     COMMON/BLOCK1/RX(500),RY(500),RZ(500),N
     COMMON/IDATA/ICUT,NSTEP,IPRINT,ISAVE,IRATIO,ISTART,IOFF
     COMMON/RDATA/DENS,TEMP,RCUT,DRMAX
     COMMON/LPFU/LPFU
     COMMON/PAR/R,ALF,BAT,CONV
     OPEN(UNIT=4,FILE=INIFILE)
     READ(4,*)
     READ(4,1000)TABLE
1000 FORMAT(A)
     READ(4,*)N,LPFU,ICUT,NSTEP,IPRINT,ISAVE,IRATIO,ISTART,IOFF
C    N - THE NUMBER OF PATICLES
C    LPFU - THE CODE OF POTENTIAL FUNCTION
C    ICUT - ICUT=1 RCUT IS REFER TO THE ORIGENAL DEFINATION
```

```
C            =2 RCUT IS REFER TO THE FRACTION OF BOX LENGTH
C     NSTEP - NUMBER OF CYCLES
C     IPRINT - NUMBER OF STEP BRTWEEN OUTPUT LINES
C     ISAVE - NUMBER OF STEPS BETWEEN DATA SAVES
C     IRATIO - INTERAL FOR UPDATE OF MAX. DISPL.
C     ISTART - ISTART =0 FIRST RUN
      READ(4,1000)TABLE
      READ(4,*)DENS,TEMP,RCUT,DRMAX,R,ALF,BAT,CONV
C     DENS - DENSITY
C     TEMP - TEMPERATURE
C     RCUT - POTENTIAL CUTOFF DISTANCE
C     R,ALF,BAT - THE PARAMETERS OF THE POTENTIAL FUNCTION
C     CONV - THE CONVERTION FACTOR FOR NEW POTENTIAL FUNCTION
      CLOSE(UNIT=4)
      RETURN
      END
*************************************************************************
* SETR SUBROUTINE IS USED TO SET RMIN AND OTHER PARAMETERS FOR
* DIFFERENT POTENTIAL FUNCTIONS
*************************************************************************
      SUBROUTINE SETR(LPFU,RMIN)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/PAR/R,ALF,BAT,CONV
      GOTO(1,2,3,4,5,6,7,8,9,10,11),LPFU
1     CONTINUE
      GOTO 20
2     CONTINUE
      GOTO 20
3     CONTINUE
      GOTO 20
4     CONTINUE
      RMIN=1.0
      R=2.0**(1.0/6.0)
      GOTO 20
5     CONTINUE
      RMIN=0.7
      GOTO 20
6     CONTINUE
      RMIN=1.0
      GOTO 20
7     CONTINUE
      GOTO 20
8     CONTINUE
      GOTO 20
9     CONTINUE
      GOTO 20
```

```
10    CONTINUE
      GOTO 20
11    CONTINUE
      RMIN=1.0
      GOTO 20
20    CONTINUE
      RETURN
      END
*************************************************************************
*  CPROU SUBROUTINE IS USED TO CONVERT VARIABLES TO PROGRAM UNITS
*************************************************************************
      SUBROUTINE CPROU(N,TEMP,BETA,DENS,DENSLJ,SIGMA,ICUT,RCUT,RMIN,
     1 DRMAX)
      IMPLICIT REAL*8(A-H,O-Z)
      BETA=1.0/TEMP
      SIGMA=(DENS/REAL(N))**(1.0/3.0)
      RMIN=RMIN*SIGMA
      DRMAX=DRMAX*SIGMA
      DENSLJ=DENS
      DENS=DENS/(SIGMA**3)
      IF(ICUT.EQ.1)THEN
       RCUT=RCUT*SIGMA
       IF(RCUT.GT.0.5)STOP 'CUT OFF TOO LARGE'
      ENDIF
      RETURN
      END
*************************************************************************
*   Linear fitting program:
* Litting equation form P0+SUM(Pi*Xi))=Min,i=1,N
* X(N) are equation parameters.P0 and P(N) are known.M is data point
* number.A(N,N) is working array.ERR is average error.Fitting fail-
* ture if IER=-1
*************************************************************************
      SUBROUTINE LINFIT(N,M,X,A,P,ERR,IER)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(N,N),X(N),P(N)
      DO 1 I=1,N
      X(I)=0.0
      DO 1 J=1,N
1     A(I,J)=0.0
      DO 10 K=1,M
      CALL FUNP(N,K,P0,P)
      DO 10 I=1,N
      Q=P(I)
      X(I)=X(I)-P0*P(I)
      DO 10 J=I,N
```

```
      A(I,J)=A(I,J)+Q*P(J)
10    A(J,I)=A(I,J)
      CALL SOLEA(N,A,X,IER)
      IF (IER.EQ.-1) GOTO 45
      ERR=0.0
      DO 35 I=1,M
      CALL FUNP(N,I,P0,P)
      FP=0.0
      DO 40 J=1,N
40    FP=FP+X(J)*P(J)
35    ERR=ERR+DABS((FP+P0)/P0)
      ERR=ERR/M
45    RETURN
      END
*****************************************************************
*  SOLVE LINEAR EQUATION GROUP AX=B                             *
*****************************************************************
      SUBROUTINE SOLEA(N,A,B,IER)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(N,N),B(N)
      IER=0
      DO 10 K=1,N-1
      IF (A(K,K).EQ.0.D0) GOTO 35
      DO 10 I=K+1,N
      C=A(I,K)/A(K,K)
      B(I)=B(I)-B(K)*C
      DO 10 J=K+1,N
10    A(I,J)=A(I,J)-A(K,J)*C
      B(N)=B(N)/A(N,N)
      DO 20 K=1,N-1
      I=N-K
      DO 30 J=I+1,N
30    B(I)=B(I)-A(I,J)*B(J)
20    B(I)=B(I)/A(I,I)
      RETURN
35    IER=-1
      END
```