An Improved Group Contribution
Volume Translated Peng-Robinson
Equation of State

By

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For the degree Master of Science (Chemical Engineering)

Progress Report – May 2009

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF.
ABSTRACT

The description of thermo-physical properties of pure components and mixtures, especially the equilibrium between two or more phases is of great importance for the design and simulation of chemical processes and many other applications.

The Volume Translated Peng-Robinson (VTPR) model provides an accurate means by which to calculate these properties for pure and mixed subcritical, as well as supercritical components, with reliable estimations for symmetric and asymmetric systems. However, VTPR requires group interaction parameters and currently the VTPR group interaction parameter matrix is small, as regression of these parameters using experimental data requires great care in order to obey all known boundary conditions. In contrast though, the modified UNIFAC group interaction parameter matrix, which has been continuously extended and improved since 1983, contains considerably more information and would be of great use in the VTPR method. The modified UNIFAC parameters however are unavailable for use in the VTPR method due to their temperature dependence, which leads to incorrect temperature extrapolations when used together with the VTPR mixing rule.

The new group contribution equation of state VGTPR introduces an excess Gibbs energy translation function into the mixing rule, which allows the combination of the volume translated Peng-Robinson EOS with the modified UNIFAC group contribution method, and allows the use of the large amount of information associated with modified UNIFAC. In the VGTPR method, the equality of $g^E$ is obtained by iterative adjustment of the mixture $a$-parameter of the EOS and is guaranteed at any temperature. A fixed reduced density of the pure components and the mixture is used for extension to supercritical conditions. The pressure difference between this state and the saturated state changes $g^E$ only slightly due to the low pressure dependence of $g^E$ in the liquid state. This model therefore allows the combination of the volume translated Peng-Robinson EOS with the modified UNIFAC method (with temperature dependent group interaction parameters).

The VGTPR method is fairly new and until now little has been done in terms of testing the model thoroughly. The work performed will provide a re-derivation of the $g^E$ translated mixing rule in an attempt to simplify the current algorithm and perform comprehensive tests on the VGTPR method, evaluating its performance utilizing the large amount of experimental data stored in the Dortmund Data Bank (DDB).

This report covers a comprehensive review of a number of existing $g^E$ mixing rules, looking at the theoretical concepts related to their derivations along with the advantages and disadvantages associated with each and follows the development of the field over the last 30 years. The idea behind the VGTPR model is introduced and discussed before laying out a work plan for future research required.
PREFACE

The work presented in this progress report was performed at the University of KwaZulu-Natal, Durban from January 2009 to May 2009. The work was supervised by Prof. D. Ramjugernath and Prof. Dr. J. Rarey.

This progress report is presented as a partial requirement for the degree of MSc in Chemical Engineering. All the work presented in this report is original unless otherwise stated and has not (in whole or part) been submitted previously to any tertiary institute as part of a degree.

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NOMENCLATURE

Letters

\( a \) - Equation of state attraction parameter or Helmholtz energy

\( b \) - Equation of state co-volume

\( B \) - Second virial coefficient

\( c \) - Equation of state volume translation term

\( C \) - Third virial coefficient

\( D \) - Fourth virial coefficient or simplifying function for method of Wong and Sandler (1992) – defined by Equation (2.59)

\( f \) - Function defined in derivation by Mollerup (1986) – equivalent to \( u \) (reduced liquid volume)

\( f_c \) - Function defined in derivation by Mollerup (1986)

\( F \) - Surface area to mole fraction ratio used in UNIFAC

\( g \) - Molar Gibbs free energy

\( G \) - Expression used in method of Twu et al. (1991) – defined by Equation (2.14)

\( h \) - Function used in derivation by Michelsen (1990) – defined by Equation (2.34) or molar enthalpy

\( H \) - Expression used in method of Twu et al. (1991) – defined by Equation (2.13)

\( k \) - Binary-interaction parameter

\( l \) - Binary-interaction parameter

\( m \) - Binary-interaction parameter

\( n \) - Number of moles

\( nc \) - Total number of components

\( P \) - Pressure
\( q \) - Function used in derivation by Michelsen (1990) – defined by Equation (2.33)

or when accompanied by a subscript, the relative van der Waals surface area

\( Q \) - Simplifying function for method of Wong and Sandler (1992) – defined by Equation (2.58)

\( r \) - Relative van der Waals volume

\( R \) - Universal gas constant

\( T \) - Temperature

\( u \) - Reduced liquid phase volume - defined by Equation (2.35)

\( v \) - Molar volume

\( V \) - Volume to mole fraction ratio used in UNIFAC

\( z \) - Mole fraction

\( Z \) - Compressibility factor

**Greek Symbols**

\( \alpha \) - Shortcut notation for \( a/bRT \)

\( \beta \) - Binary-interaction parameter

\( \gamma \) - Activity coefficient

\( \varphi \) - Fugacity coefficient

\( \lambda \) - Relative distribution constant for use in the LCVM mixing rule

\( \Lambda \) - Equation of state specific constant used in g\(^E\) mixing rules

or constant of approximating function used in derivation of MHV1 and MHV2 mixing rules

\( \psi \) - Constant of approximating function used in derivation of MHV1 and MHV2 mixing rules

\( \Gamma \) - Constant of approximating function used in derivation of MHV2 mixing rule

**Subscripts**

\( \infty \) - Infinite pressure reference

\( 0 \) - Zero pressure reference
\( \gamma \) - Property calculated from an activity coefficient/g\( ^E \) model

c - Critical property

calc - Result from a calculation

comb - Combinatorial part

EOS - Property calculated from an equation of state

exp - Result from experimental work

f - Component reference letter

i - Component reference letter

j - Component reference letter

k - Component reference letter

l - Component reference letter

m - Property of the mixture (as a whole)

MHV - Calculated by MHV1 mixing rule

res - Residual part

trans - Translation term

V - Calculated by method of Vidal (1978)

Superscripts

\( E \) - Excess property

\( ^\wedge \) - Property of a particular component in a mixture
1. INTRODUCTION

The description of thermo-physical properties of pure components and mixtures, especially the equilibrium between two or more phases is of great importance for the design and simulation of chemical processes and many other applications. Historically, two different approaches have been used to estimate pure component properties and phase equilibria: the equation of state (EOS) approach and the excess Gibbs energy ($g^E$) model approach. Cubic equations of state are the most popular and widely used type of EOS in industry due to their relative simplicity and accuracy in predicting pure component and mixture thermodynamic properties. A great number of $g^E$ models exist, however recent developments have seen the introduction of fully predictive group-contribution models such as ASOG, UNIFAC and modified UNIFAC which do not require binary-interaction parameters found from binary experimental data and are therefore very attractive to engineers involved in process design and simulation. Obviously both the equation of state method and the activity coefficient method have advantages over the other and outperform the other in specific areas. $g^E$ models are simple and robust while equations of state allow calculations for supercritical systems. A desire to link the two methods and make use of the advantages of both, has driven over 30 years of extensive research aimed particularly at utilizing the $g^E$ model to describe mixture parameters of cubic equations of state.

The main advantage of cubic equations of state is not in their ability to represent pure components but rather their value when representing fluid mixtures. Sengers et al. (2000) believe that representation of properties of fluid mixtures is the main, if not the only, purpose of cubic and generalized van der Waals equations of state and that when a pure fluid component is of interest, equations of this type are not the preferred method for representation. In any case, it is widely regarded that there is little room for improvement in the use of cubic equations of state for pure components as this field has had a vast amount of time and effort invested into it by past researchers. A number of methods have been developed for predictions of various types of pure components and therefore cubic equations of state may be used for many polar and non-polar or associating compounds. This has created an opinion that very little progress can be made with regards to pure component representation by equations of state; however this is by no means the case when it comes to EOS use in multicomponent systems.
In order to extend the pure component EOS models to mixtures one can use the van der Waals one-fluid mixing rule. The one-fluid theory of mixtures is based on the assumption that the EOS for a mixture is the same as that for a hypothetical “pure” fluid that has EOS parameters which depend on the composition of the mixture. The relationship used to establish mixture parameters must describe the concentration dependence of these parameters and is commonly known as a mixing rule. Finding the CEOS mixture parameters is of utmost importance when representing a fluid mixture in order to calculate accurate results. This importance is highlighted by Sengers et al. (2000) which concludes that the establishment of the mixture parameters is more important than the actual PVT relationship embodied within a particular EOS.

A number of different mixing rules have been developed, each one aiming at improving predictions of fluid mixtures using cubic equations of state. Generally each new mixing rule improves on previous rules in certain areas, however they fail in others. Some mixing rules have also been developed to improve predictions of specific types of mixtures but still fail when used to represent other types. Most importantly though, with regards to the work presented in this report, a number of mixing rules have been published which use a $g^E$ model to describe the composition dependence of the EOS parameters; therefore providing the desired link of the two methods mentioned above. The $g^E$ takes into account liquid phase non-ideality of the system under investigation and introduces it into the EOS model. This results in more reliable representation of systems containing polar or associating compounds when using equations of state. Furthermore, it has been shown that should predictive $g^E$ models be used, fully predictive EOS models may be developed.
2. MIXING RULES – A REVIEW

At present one universal mixing rule is not available and research is continuing in order to establish a flexible and uncomplicated rule that could predict properties of most multicomponent systems with a reasonable level of accuracy. The following section investigates a number of methods for extending cubic equations of state to mixtures through the calculation of mixture \( a \), \( b \) and \( c \) (in the case of volume-translated equations of state) coefficients. The review will start with the earliest and most simple mixing rule (the quadratic mixing rule) before investigating some empirical modifications that were introduced to improve flexibility of the mixing rules. The final section provides a comprehensive review of the \( g^E \) mixing rules which use the \( g^E \) models to define the composition dependence of the mixture parameters.

Due to the fact that the cubic Peng-Robinson EOS is used in the current method, only rules describing mixtures in association with cubic equations of state will be discussed below. Mixing rules used in other types of equations of state are not reviewed here.

2.1 Quadratic Mixing Rules

The classical quadratic mixing rule is by far the most popular due mainly to its simplicity and the relatively high level of accuracy achieved for mixtures containing nonpolar or only slightly polar compounds. The origin of this mixing rule lies in basic statistical thermodynamics which is used to describe the composition dependence of the virial coefficients. The composition dependence of the virial coefficients for a mixture containing \( nc \) components is given by:

\[
B_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j B_{ij} \\
C_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} \sum_{k=1}^{nc} z_i z_j z_k C_{ijk} \\
D_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} \sum_{k=1}^{nc} \sum_{l=1}^{nc} z_i z_j z_k z_l D_{ijkl} \\
\quad \text{etc.}
\]  

(2.1)

where \( z_f \) is the mole fraction of component \( f \) and \( B_{ij} \), \( C_{ijk} \), \( D_{ijkl} \) etc. are sets of virial coefficients dependent solely on temperature. Obviously \( B_{ff} \), \( C_{fff} \), \( D_{ffff} \) etc. are just the pure component virial
coefficients of $f$, while the remaining coefficients are known as interaction virial coefficients. The subscript $m$ indicates a mixture property.

The van der Waals equation of state for a fluid mixture can be expanded into a power series around zero density to give an expression closely resembling the virial equation:

$$Z = 1 + \sum_{i=1}^{m} \left( \frac{b_m}{v} \right)^i - \frac{a_m}{RTv}$$

$$= 1 + \left( b_m - \frac{a_m}{RT} \right) \left( \frac{1}{v} \right) + b_m^2 \left( \frac{1}{v} \right)^2 + b_m^3 \left( \frac{1}{v} \right)^3 + .... \quad (2.2)$$

where $Z$ is the compressibility factor, $a$ and $b$ are the substance specific equation of state energy (attraction) and co-volume parameters, the subscript $m$ indicates a mixture property, $R$ is the universal gas constant, $T$ is the temperature and $v$ is the molar volume. Comparison of the density virial equation and Equation (2.2) reveals the following relations between the virial coefficients and the EOS parameters:

$$B_m = b_m - \frac{a_m}{RT}$$

$$C_m = b_m^2$$

$$D_m = b_m^3$$

etc. \quad (2.3)$$

From Equation (2.1) one can see that the second virial coefficient $B_m$ has a quadratic dependence on composition. The EOS coefficients $a_m$ and $b_m$ are linked to $B_m$ by Equation (2.3) and so in order to maintain consistency, the composition dependence of $a_m$ and $b_m$ may be at most a quadratic function. Conversely, the third virial coefficient has a cubic composition dependence which imposes the stricter constraint that the EOS parameter $b_m$ should be only a linear function of composition. Similar results may be found when considering other equations of state; however the simplest function for $a_m$ (from the van der Waals equation) is given by:

$$a_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_f z_j a_{ij}$$

(2.4)

here $z_f$ may be the mole fraction of pure component $f$ in the vapour or liquid phase as cubic equations of state are capable or representing both phases. $a_{ii}$ and $a_{ij}$ are the pure component a
parameters calculated using critical properties and the equation associated with the EOS being used, while \( a_{ij} = a_{ji} \) is the cross term and is related to \( a_{ij} \) and \( a_{ij} \) by the geometric mean rule (a combining rule) which contains one adjustable binary-interaction parameter \( k_{ij} (= k_{ji}) \) and no composition dependence:

\[
a_{ij} = (a_{ii}a_{jj})^{0.5} \left( 1 - k_{ij} \right) \tag{2.5}
\]

When \( i=j \), the binary-interaction parameter equals zero and Equation (2.5) produces the pure component \( a \) parameter.

The \( b_m \) parameter is represented most commonly by the linear mixing rule due to its simplicity:

\[
b_m = \sum_{i=1}^{nc} z_i b_i \tag{2.6}
\]

The equation above is reasonable as the parameter \( b \) only represents the closest packing volume possible for a particular type of molecule in a mixture and does not require a complicated function for extension from pure components to a mixture. The \( b_m \) parameter may also be calculated by an equation similar to (2.4) and using the combining rule:

\[
b_{ij} = \frac{1}{2} \left( b_{ii} + b_{jj} \right) \left( 1 - l_{ij} \right) \tag{2.7}
\]

\( l_{ij} (= l_{ji}) \) is a binary-interaction parameter that must be fitted to experimental data. This added complexity is only required for mixtures containing components that are highly asymmetric with respect to size and is often not utilized.

As stated above, the quadratic mixing rule is, for most cases, suitable for representation of phase equilibria in multicomponent systems which contain either non-polar or slightly polar components, however this mixing rule begins to fail severely when applied to systems that contain strongly polar and associating compounds. In addition it will always require binary-interaction parameters specific to the system being investigated which requires experimental results and a fitting procedure, removing the possibility of a fully predictive model.
2.2 Composition-Dependent Combining Rules

In order to account for the shortcomings of the quadratic mixing rule a number of empirical modifications have been made. These modifications aim at increasing flexibility of the mixing rule to correlate phase behavior of mixtures containing strongly polar or associating compounds (non-ideal solutions), which is a trait greatly lacking in the original quadratic mixing rule. These modifications are implemented to improve the calculation of the cross terms \( a_{ij} \) and in effect introduce some composition dependency into the originally composition-independent combining rule (Equation (2.5)) of the classical quadratic mixing rule. The mixing rule for \( a_m \) (Equation (2.4)) remains the same for most methods and only modifications to the cross term calculation are made.

Chao and Robinson (1986) and Stryjek and Vera (1986) implemented combining rules that require two binary-interaction parameters \( k_{ij} \) and \( k_{ji} \), as opposed to the single binary-interaction parameter \( k_{ij}=k_{ji} \) found in the original quadratic mixing rules. The proposed combining rules were respectively:

\[
a_{ij} = \left( a_i a_j \right)^{0.5} \left( 1 - k_{ij} + \left( k_{ij} - k_{ji} \right) z_i \right) \quad (2.8)
\]

\[
a_{ij} = \left( a_i a_j \right)^{0.5} \left( 1 - \frac{k_{ij} k_{ji}}{k_{ij} z_i + k_{ji} z_j} \right) \quad (2.9)
\]

The combining rule of Chao and Robinson (1986) was later extended by Schwartzentruber et al. (1987) to include a third parameter ultimately increasing the flexibility and accuracy of the quadratic mixing rule but at the same time increasing its complexity. The proposed combining rule was given as:

\[
a_{ij} = \left( a_i a_j \right)^{0.5} \left( 1 - k_{ij} - l_{ij} \frac{m_{ij} z_i - m_{ji} z_j}{m_{ij} z_i + m_{ji} z_j} \right) \quad (2.10)
\]

where \( k_{ij}=k_{ji}, \ l_{ij}=-l_{ij}, \ m_{ij}=1-m_{ij} \) and \( k_{ii}=l_{ii}=0 \).

While the composition-dependent combining rules do provide a simple method for extension of equations of state to mixtures containing non-polar or associating compounds, and do so with a
satisfactory level of accuracy, they have been found to contain a serious defect. Michelson and Kistenmacher (1990) investigated composition-dependent combining rules and found that they provide different results when a system is considered to be composed of its actual components to when it is considered to be composed of subcomponents of the actual components. Sengers et al. (2000) explains the problem as follows: ‘If a binary mixture with composition \((x_1, x_2)\) is treated as a ternary system with composition \((x_1, x_2, x_3)\), where the ternary mixture is formed by dividing component 2 into two pseudocomponents with identical properties, a different value for the parameter \(a\) will result. Therefore, the calculated properties will depend on the number of pseudocomponents, which is in contrast to experimental evidence’. Many researchers attempted to overcome the Michelsen-Kistenmacher problem while maintaining the obvious advantages of the composition-dependent combining rules. Mathias et al. (1991) produced an equation that overcame this problem by adding a new composition-dependent term to the classical quadratic mixing rule and not just altering the combining rule as was done by previous authors associated with the flawed composition-dependent combining rules. The new mixing rule proposed was:

\[
a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j (a_{ai} a_{aj})^{0.5} \left(1-k_{ij}\right) + \sum_{i=1}^{nc} z_i \left[ \sum_{j=1}^{nc} z_j \left[ \left(a_{ai} a_{aj}\right)^{1/2} l_{ij}^{1/3} \right]^3 \right] (2.11)
\]

\(l_{ij}\) may or may not equal \(-l_{ij}\) depending on the level of accuracy and complexity required.

Twu et al. (1991) also proposed a revised mixing rule that overcame the Michelsen-Kistenmacher problem and contained an extra term to that of the classical quadratic one:

\[
a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j \left(1-k_{ij}\right) + \sum_{i=1}^{nc} z_i \left[ \sum_{j=1}^{nc} \left(H_{ij} G_{ij}\right)^{1/3} \left(a_{ai} a_{aj}\right)^{1/6} z_j \right]^3 \sum_{j=1}^{nc} G_{ij} z_j (2.12)
\]

where:

\[
H_{ij} = \frac{k_{ij} - k_{ij}}{T} (2.13)
\]

\[
G_{ij} = \exp\left(-\beta_{ij} H_{ij}\right) (2.14)
\]
This mixing rule can either be used as a 2-parameter model by fitting both $k_{ij}$ and $k_{ji}$ to binary experimental data or it can be used as a more accurate 4-parameter model whereby $\beta_{ij}$ and $\beta_{ji}$ are also fitted.

### 2.3 Mixing Rules Using Excess Gibbs Energy ($g^E$)/ Activity Coefficient Models

The classical quadratic mixing rule can at most only be applied to mixtures of slight solution non-ideality. In order to improve this, alterations to this rule was necessary which required a higher level of complexity along with the fitting of binary experimental data to find binary-interaction parameters and led to the development of the composition-dependent combining rules. In some cases as many as 4 binary-interaction parameters need to be fitted to experimental data, which is obviously not ideal.

Highly non-ideal solutions (containing non-polar and associating compounds) have been described using $g^E$ (or activity coefficient) models with great success. Therefore much effort has been dedicated to combining these models with equations of state in order to extend EOS applicability to non-ideal solutions, and consequently utilize the attractive features of both classes of models.

The $g^E$ of a solution can be calculated in two ways: with the use of an appropriate $g^E$ model (most common) and with the use of an EOS via fundamental thermodynamic equations. Therefore the EOS mixing rule composition dependence for the liquid phase can be reflected by a desirable $g^E$ model if the different expressions are matched as follows:

$$g^E_\gamma = g^E_{EOS} \quad (2.15)$$

The subscript $\gamma$ indicates calculation by a $g^E$ model (activity coefficient $\gamma$ model) while the subscript $EOS$ indicates calculation by means of an EOS. If one assumes that the linear mixing rule for $b_m$ (Equation (2.6)) applies, the $a_m$ parameter may then be found by assuming that Equation (2.15) holds true.
A number of models exist which can be used to calculate $g^E_γ$ such as NRTL, UNIQUAC, UNIFAC and many more. $g^E_{EOS}$ is calculated using a specific EOS and the following equation:

$$g^E_{EOS} = RT \left( \ln \varphi_m - \sum_{i=1}^{\infty} z_i \ln \varphi_i \right)$$  \hspace{1cm} (2.16)$$

where $\varphi_m$ and $\varphi_i$ are the mixture and pure component fugacity coefficients respectively and are calculated from the following equation which is specific to pure components:

$$\ln \varphi = \frac{P_v}{RT} - 1 - \ln \frac{P_v}{RT} + \frac{1}{RT} \int_0^\infty \left( \frac{RT}{v} - P \right) dv$$  \hspace{1cm} (2.17)$$

Equation (2.17) may be used to calculate $\varphi_m$ as the mixture is assumed a pure fluid with pure component EOS parameters equal to $a_m$ and $b_m$. It is important to note that this expression may not be used to calculate fugacity coefficients of a particular component in the mixture. The $P$ term is represented by a pressure explicit EOS and is therefore a function of $v$.

The more recent advancement in the field of $g^E$ models, through ASOG, UNIFAC and modified UNIFAC, has seen the development of accurate models based on the group-contribution concept. These models do not require binary experimental data, they only require group-group interaction parameters, and as a result are fully predictive. If a predictive $g^E$ model is used in Equation (2.15) to develop the $g^E$-mixing rule, a predictive group-contribution EOS (GCEOS) results. If a predictive method is used to determine the composition dependence of the EOS parameters, no binary experimental data is required and the EOS becomes fully predictive too. This is obviously a major advantage that was not evident when the investigation into $g^E$ mixing rules first began due to the immaturity of the field of predictive $g^E$ models, however at present it continues to drive further research into more accurate methods.
Combining cubic equations of state with group-contribution $g^E$ models to obtain a mixing rule extends the applicability of cubic equations of state to the prediction of VLE in three major areas:

1. Polar systems at low pressure, where the GCEOS in essence matches the performance of the $g^E$ model with the $\gamma$-$\phi$ approach.
2. Polar systems at high pressure, where conventional mixing rules have been found to fail.
3. Systems that contain supercritical components, wherein gas molecules are considered as new groups.

The following sections will cover major developments made in the field of $g^E$ mixing rules from the first idea proposed by Vidal (1978) to the development of the most recent VTPR model (developed in early 2000).

2.3.1 Vidal

Vidal (1978) was the first to use a $g^E$ model to establish a mixing rule for an EOS in order to allow modeling of highly non-ideal systems. The Redlich-Kwong EOS was used and as a result application of Equation (2.16) yielded the following expression:

$$
\delta_{EOS} = -RT \left[ \ln \left( \frac{P(v_m - b_m)}{RT} \right) - \sum_{i=1}^{m_c} z_i \ln \left( \frac{P(v_i - b_i)}{RT} \right) \right] + P v_m - \sum_{i=1}^{m_c} z_i P v_i + ... \\
- \frac{a_m}{b_m} \ln \left( \frac{v_m + b_m}{v_m} \right) + \sum_{i=1}^{m_c} \frac{a_i}{b_i} \ln \left( \frac{v_i + b_i}{v_i} \right)
$$

(2.18)

where $v_m$ is the mixture molar volume, $a_i$ and $b_i$ the pure component EOS parameters of component $i$ and $v_i$ is the pure component molar volume of component $i$. Equation (2.18) still contains a number of unknowns (namely $b_m$, $v_m$ and all $v_i$) that would restrict its use in finding a useful expression for $a_m$. In order to eliminate these terms from Equation (2.18) and arrive at an explicit expression for $a_m$ an infinite-pressure limit was applied. Due to the fact that the mixture EOS parameters are independent of pressure, calculations at different pressures should not affect the calculated parameters assuming the parameters calculated away from the system pressure (in this case at infinite pressure) are calculated correctly. The infinite pressure limit allows one to make the assumption that the fluid is compressed to such an extent that the molar volume of the
fluid would be equal to the closest packing volume of the molecules (i.e. the molecules are compressed so as to be in contact with each other, and the only intermolecular space exists between contacting molecules). The \( b \) (co-volume) EOS parameter represents the closest packing volume of the molecules and therefore the following assumption could be made, which effectively removes the unknown fluid molar volumes \((v_m \text{ and } v_i)\) from Equation (2.18):

\[
v_m = b_m \tag{2.19}
\]

\[
v_i = b_i \tag{2.20}
\]

It was also noted that in order for the \( g^E \) to be finite (i.e. not be infinite) as pressure approaches infinity, the excess volume \( v^E \) must be assumed to be zero. If \( v^E \) is not zero then \( g^E \) will approach infinity as pressure approaches infinity. This can be seen by investigating the following expression (which is developed from the fundamental property relations):

\[
g^E = a^E + P v^E \tag{2.21}
\]

where \( a^E \) is the excess Helmholtz energy. The above deduction implies that the linear van der Waals mixing rule must be used for the \( b_m \) parameter.

Substitution of the linear \( b \) mixing rule along with Equation (2.19) and (2.20) into Equation (2.18) followed by rearrangement produces the following expression which applies only at infinite pressure:

\[
a_m = b_m \left( \sum_{i=1}^n \frac{a_i}{b_i} \varepsilon_i - \frac{g^E_{\infty}}{\ln 2} \right) \tag{2.22}
\]

where \( g^E_{\infty} \) is the \( g^E \) at infinite pressure and may be calculated using a \( g^E \) model (assuming Equality (2.15) holds).

In using an infinite pressure limit it was assumed that \( g^E \) is independent of pressure. The recommended model for \( g^E \) calculation was NRTL and the result from using this model was used directly in Equation (2.22) even though the model parameters were fitted using data obtained from low to moderate pressure systems. By making this assumption one could use existing model parameters to calculate the \( g^E_{\infty} \) term without having to refit model parameters to high
pressure data. Although it was known that $g^E$ does have a dependency on pressure it was originally decided that the dependency was so slight that the tedious model parameter fitting process could be avoided.

Obviously this assumption is incorrect and will lead to erroneous results, however the mixing rule can be used to provide satisfactory results for highly non-ideal systems if the $g^E$ model parameters are refitted using high pressure data so that a more correct value for $g^E_{\infty}$ is obtained.

Having said this though, Sengers et al. (2000) points out a number of theoretical and computational difficulties associated with the Vidal mixing rule. These include inaccurate representations for non-polar hydrocarbon mixtures, failure of the second virial coefficient boundary condition at the low-density limit (quadratic composition dependence – see Equation (2.1)) and, as already discussed, the need to refit $g^E$ model parameters to account for elevated pressure conditions. Sengers et al. (2000) also states that the $g^E$ model parameters are strongly dependent on temperature so that, while it is good for correlations, it has limited extrapolative or predictive capability.

### 2.3.2 Huron-Vidal

The work of Vidal was later extended slightly by Huron and Vidal (1979), who did not alter or extend the concepts proposed by Vidal but identified that Equation (2.22) can be generalized to other equations of state. The general form proposed by Huron and Vidal was:

$$a_m = b_m \left( \sum_{i=1}^{\infty} \frac{a_i}{b_i} z_i \right) \frac{g^E_{\infty}}{\Lambda}$$

(2.23)

where $\Lambda$ is a numerical constant that depends on the particular EOS that is used. Huron and Vidal (1979) derived $g^E$ mixing rule expressions for $a_m$ using the van der Waals, Soave-Redlich-Kwong and Peng-Robinson equations of state using the same procedure as Vidal (1978) (which investigated the Redlich-Kwong EOS).
The following expressions for $\Lambda$ were found:

van der Waals: $\Lambda = 1$

Redlich-Kwong: $\Lambda = \ln 2$

Soave-Redlich-Kwong: $\Lambda = \ln 2$

Peng-Robinson: $\Lambda = \frac{1}{2\sqrt{2}} \ln \left( \frac{2 + \sqrt{2}}{2 - \sqrt{2}} \right)$

2.3.3 Mollerup

It soon became evident, following the work of Vidal and Huron and Vidal, that the $g^E$ calculated from an EOS and from a $g^E$ model needed to be linked at low pressure rather than at infinite pressure so that the large amount of existing (low pressure) activity coefficient model parameters could be utilized, therefore removing the need to measure data and refit model parameters at elevated pressures. Mollerup (1986) was the first to move the field in this direction by matching the $g^E$ from the EOS and an appropriate model at zero pressure. In deriving the mixing rule Mollerup managed to avoid the assumptions made by Vidal that $g^E$ calculated from an EOS at infinite pressure equals that calculated by a $g^E$ model (using low pressure parameters) and that the co-volume parameter $b$ equals the volume $v$ at infinite pressure. Mollerup still assumed that $v^E$ is zero, however made the assumption that Equation (2.15) applies at a pressure of a few atmospheres or less which is far more reasonable as the $g^E$ model parameters are most commonly established using low to moderate pressure data.

Mollerup (1986) derived the following expression using the van der Waals EOS:

$$
\frac{g^E_{EOS}}{RT} = -\ln \left( 1 - \frac{b_m}{v_m} \right) - \frac{a_m}{RTv_m} + \sum_{i=1}^{n_c} z_i \ln \left( 1 - \frac{b_i}{v_i} \right) + \sum_{i=1}^{n_c} z_i \frac{a_i}{RTv_i} + \ldots
$$

$$
\ldots + \sum_{i=1}^{nc} z_i \ln \left( \frac{v_i}{v_m} \right) + \frac{Pv^E}{RT}
$$

(2.24)

If one then assumes that saturated liquid volumes are independent of pressure (a reasonable assumption by all accounts), the pressure term in the van der Waals EOS may be neglected ($P = 0$) and the equation can be solved for $b/v$ to give:
which may be applied to both the mixture and pure components. Mollerup (1986) states that at low pressures (less than a few atmospheres) Equation (2.25) is accurate to within 1 percent.

The following terms were defined in the derivation:

\[ f_i = \frac{b_i}{v_i} \]  
\[ f_m = \frac{b_m}{v_m} \]  
\[ f_c = \frac{\left( \frac{v_i}{b_i} - 1 \right)}{\left( \frac{v_m}{b_m} - 1 \right)} \]

which allowed the solution of Equation (2.24) with respect to \((a_m/b_m)\) to be found (also applying the assumption that \(v^E = 0\)):

\[
\frac{a_m}{b_m} = \sum_{i=1}^{\infty} z_i \left( \frac{a_i}{b_i} \right) \left( \frac{f_i}{f_m} \right) - \frac{g_0^E}{f_m} + \frac{RT}{f_m} \sum_{i=1}^{\infty} z_i \ln \left( \frac{f_i b_i}{b_m} \right) \]  

where \(g_0^E\) is \(g^E\) at the zero reference pressure.

\(f\) (for pure components and mixtures) is only a weak function of temperature and in the case of mixtures is also dependent on composition, however Mollerup (1986) states that \(f\) may be regarded as a constant for practical applications. Following this, Mollerup identified that if \(b/v\) for the pure components and for the mixture can be assumed equal, then \(f_i = f_m\) and \(f_c = 1\), and found that at the normal boiling point \(f\) is in the region of 0.8 for liquids when using the van der Waals EOS. All of this applied to Equation (2.29) results in the following explicit expression for \(a_m\):
The assumption that $f_i = f_m$ and the assumption that both are equal to some constant found from experimental data was a huge step forward and has been used in the development of many $g^E$ mixing rules since.

### 2.3.4 Modified Huron-Vidal

Michelsen (1990) extended the idea proposed by Mollerup and matched the $g^E$ at a reference pressure of zero using the Soave-Redlich-Kwong EOS. In doing so the following expression was developed which in contrast to the Huron-Vidal mixing rule is not explicit:

$$
\frac{g^E_0}{RT} + \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) = q(\alpha_m) - \sum_{i=1}^{nc} z_i h(\alpha_i)
$$

where $\alpha$ is a shortcut notation used to combine variables in the following way:

$$
\alpha_m = \frac{a_m}{b_mRT} \quad (2.32)
$$

$$
\alpha_i = \frac{a_i}{b_iRT}
$$

$q$ and $h$ are functions of $\alpha_m$ and $\alpha_i$ respectively and are given by:

$$
q(\alpha_m) = -1 - \ln(u_{m,0} - 1) - \alpha_m \ln \left( \frac{u_{m,0} + 1}{u_{m,0}} \right) \quad (2.33)
$$

$$
h(\alpha_i) = -1 - \ln(u_{i,0} - 1) - \alpha_i \ln \left( \frac{u_{i,0} + 1}{u_{i,0}} \right) \quad (2.34)
$$
\( u_{m,0} \) and \( u_{i,0} \) are the reduced liquid phase volumes of the mixture and pure components at zero pressure respectively:

\[
\begin{align*}
    u_{m,0} & = \left( \frac{v_m}{b_m} \right)_{p=0} \\
    u_{i,0} & = \left( \frac{v_i}{b_i} \right)_{p=0}
\end{align*}
\] (2.35)

Equation (2.33) and Equation (2.34) display the dependence of \( q \) and \( h \) on the parameters \( \alpha_m \) and \( \alpha_i \). \( u_{m,0} \) and \( u_{i,0} \) in these functions can be expressed as functions of \( \alpha \) by first converting the Soave-Redlich-Kwong EOS into the following general form:

\[
\frac{Pb}{RT} = \frac{1}{u-1} - \frac{\alpha}{u(u+1)}
\] (2.36)

At the reference pressure of zero Equation (2.36) reduces to:

\[
0 = \frac{1}{u_0-1} - \frac{\alpha}{u_0(u_0+1)}
\] (2.37)

Solving Equation (2.37) for \( u_0 \) and taking the smallest (liquid) root, produces the following expression for \( u_0 \) as a function of \( \alpha \):

\[
u_0 = \frac{1}{2} \left( \alpha - 1 - \left( \alpha^2 - 6\alpha + 1 \right)^{1/2} \right)
\] (2.38)

valid for \( \alpha > 5.83 \). Equation (2.38) is used to represent both \( u_{m,0} \) and \( u_{i,0} \).

Michelsen (1990) states that \( g^E \) model parameters are based mainly on binary mixtures at or near atmospheric pressure and under these conditions \( \alpha_i \) are far removed from the limiting value, with typical values (at the normal boiling point) ranging from 10 to 13. As a result of this, Michelsen (1990) investigated the behavior of the \( q \) and \( h \)-function within this range, and noticed that they vary almost linearly with respect to \( \alpha \). This can be seen in Figure 1 below.
The idea of Michelsen (1990) was then to replace the q and h-function given by Equations (2.33) and (2.34) with linear approximations:

\[ q(\alpha_m) = q_0 + q_1 \alpha_m \]  
\[ h(\alpha_i) \approx h_0 + h_i \alpha_i \]  

By substituting these straight line approximation into Equation (2.31), the right-hand side of the equation is approximated as:

\[ q(\alpha_m) - \sum_{i=1}^{nc} z_i h(\alpha_i) \approx q_0 + q_m \alpha_m - h_0 - h_1 \sum_{i=1}^{nc} z_i \alpha_i \]  

By comparing Equation (2.39) and Equation (2.33) one can see:

\[ q_0 = -1 - \ln\left(\frac{u_{m,0}}{u_{m,0} - 1}\right) \]  
\[ q_1 = -\ln\left(\frac{u_{m,0} + 1}{u_{m,0}}\right) \]  

\[ \text{FIGURE 1} \] Variation of q or h-function with respect to \( \alpha \) for the SRK EOS also showing the linear fit in the range \( 10 < \alpha < 13 \): (---) q or h-function, (—) linear fit
similarly, for Equation (2.40) and Equation (2.34):

\[
h_0 = -1 - \ln \left( u_{i,0} - 1 \right) \\
h_1 = -\ln \left( \frac{u_{i,0} + 1}{u_{i,0}} \right)
\]  

(2.43)

and following the assumption of Mollerup (1986) that the reduced liquid phase volume (termed \( f \) in the work of Mollerup) is constant and the same for the pure components as for the mixture, i.e.:

\[
u_m = \frac{v_m}{b_m} = \left( \frac{v_i}{b_i} \right)_{p=0}
\]

(2.44)

the following conclusion may be drawn:

\[
q_0 = h_0 = \Psi \\
q_1 = h_1 = \Lambda
\]

(2.45)

where \( \Psi \) and \( \Lambda \) are constants.

This then results in a much simpler version of Equation (2.41):

\[
q(\alpha_m) - \sum_{i=1}^{nc} z_i h(\alpha_i) = \Lambda \left( \alpha_m - \sum_{i=1}^{nc} z_i \alpha_i \right)
\]

(2.46)

Equation (2.31) can therefore be rearranged into the following explicit form for calculation of \( a_m \):

\[
a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_{ii}}{b_i} + \frac{1}{\Lambda} \left( g^E_Y + RT \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) \right) \right)
\]

(2.47)

\( \Lambda \) is found by fitting a straight line to a plot of the q-function (or h-function) between \( \alpha \)-values of 10 and 13 and establishing the slope. \( \Lambda \) depends only on the EOS used as this determines the type of q-function (or h-function) obtained in achieving an expression of form similar to Equation (2.31). The q and h-function of Equation (2.33) and (2.34) are specific to the Soave-Redlich-Kwong EOS and yields a \( \Lambda \) value of -0.593. Michelsen (1990) did a similar analysis to that of the Soave-Redlich-Kwong EOS using the Peng-Robinson EOS and the van der Waals
EOS and found Λ values of -0.53 and -0.85 respectively. Equation (2.47) became known as the Modified Huron-Vidal First-Order mixing rule (MHV1) due to its similarity to the Huron-Vidal mixing rule and the fact that a linear (first order) approximation is used to represent the q and h-function.

A Modified Huron-Vidal Second-Order mixing rule (MHV2) was first proposed by Michelsen (1990) and later implemented by Dahl and Michelsen (1990), wherein a second order (quadratic) approximation is used to represent the q and h-function. This makes sense as these functions are not perfectly linear (see FIGURE 1 above) and may be better approximated by a quadratic expression, therefore producing better results. The quadratic approximations are:

\[
q(\alpha_m) \approx q_0 + q_1 \alpha_m + q_2 \alpha_m^2
\]  
\[
h(\alpha_i) \approx h_0 + h_1 \alpha_i + h_2 \alpha_i^2
\]

Once again one finds that the constants in the pure component and mixture approximations are identical:

\[
q_0 = h_0 = \Psi
\]
\[
q_1 = h_1 = \Lambda
\]
\[
q_2 = h_2 = \Gamma
\]

where Γ is a constant. Use of this approximation in equation (2.31) does provide improved results over the MHV1 method, however there is added complexity as the resultant expression is not explicit and as stated by Michelsen (1990) ‘the neatness associated with a simple explicit mixing rule is lost’.

The MHV2 equation is:

\[
\Lambda \left( \alpha_m - \sum_{i=1}^{nc} z_i \alpha_{ii} \right) + \Gamma \left( \alpha_m^2 - \sum_{i=1}^{nc} z_i \alpha_{ii}^2 \right) = \frac{g^E}{RT} + \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right)
\]

The universal Λ and Γ parameters can be found by fitting a second-order polynomial to the EOS-specific approximation function.
The recommended values are:

Soave-Redlich-Kwong EOS: \( \Lambda = -0.4780 \quad \Gamma = -0.0047 \)

Peng-Robinson EOS: \( \Lambda = -0.4347 \quad \Gamma = -0.003654 \)

Both MHV1 and MHV2 have been found not to satisfy the second-virial coefficient boundary condition. Having said this though, both models provide very reasonable correlations and predictions of data obtained from experiment for systems that are highly non-ideal.

**2.3.5 Wong-Sandler**

Wong and Sandler (1992) proposed a new method to link the \( g^E \) model results with EOS computations in order to obtain a mixing rule for the EOS \( a_m \) and \( b_m \) parameters. Attempts to match \( g^E \) at zero pressure were abandoned and the fact that excess Helmholtz energy \( a^E \) is virtually independent of pressure was investigated, resulting in \( a^E \) calculated from an EOS being used to develop the mixing rule. There are two major advantages of using \( a^E \) instead of \( g^E \). The first is that the assumption that \( \nu^E = 0 \) is no longer required as when using \( g^E \) and the second, as stated already, is that \( a^E \) is not as strongly dependent on pressure as \( g^E \).

The basis of the work done by Wong and Sandler is summarized by the following expression:

\[
a^E_{EOS} (T, P = \infty, z_i) = a^E (T, P = \infty, z_i) \\
= a^E (T, P = low, z_i) \\
= g^E (T, P = low, z_i)
\]  

(2.52)

The following argument is used in order to arrive at Equation (2.52): At sufficiently low pressures the \( P
\nu^E \) term of Equation (2.21) is very small. This implies that \( g^E \) is equivalent to \( a^E \) at low pressure. \( a^E \) is essentially independent of pressure (or density) and as a result \( a^E \) at low pressure is equivalent to \( a^E \) at infinite pressure. Therefore the \( a^E \) of a system calculated at infinite pressure using an EOS may be equated to the \( g^E \) of the system calculated using a \( g^E \) model, which is essentially a low pressure calculation (due to the original fitting of model parameters using low-pressure data).

The equality between the \( g^E \) at low pressure and the \( a^E \) at infinite pressure is used to establish the composition dependence of the mixture EOS parameters. Wong and Sandler had to also use the
composition dependence of the second virial coefficient to relate the pure component $a$ and $b$ parameters to the equivalent mixture parameters. Equation (2.1) and (2.3) may be linked to give an expression representing the second virial coefficient composition dependence:

\[
\frac{b_m}{RT} - \frac{a_m}{RT} = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j B_{ij}
\]

(2.53)

The cross term $B_{ij}$ is calculated by:

\[
B_{ij} = b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2} \left[ \left( b_{ii} - \frac{a_{ii}}{RT} \right) + \left( b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij})
\]

(2.54)

where $k_{ij}$ is a binary parameter which is most commonly regressed using low-pressure experimental data.

Calculation of $a^E$ from a van der Waals type EOS at infinite pressure results in the following expression:

\[
a^E_m = \sum_{i=1}^{nc} \left( \frac{a_i}{b_i} - \frac{a_m}{b_m} \right)
\]

(2.55)

where $\Lambda$ is a constant dependent on the EOS used. For the Soave-Redlich-Kwong and Peng-Robinson EOS $\Lambda$ is equal to −0.693 and -0.623 respectively.

Using Equation (2.52) Wong and Sandler were able to convert Equation (2.55) into the following form:

\[
a^E_m = \frac{a^E_m}{\Lambda} - \sum_{i=1}^{nc} \frac{z_i a_i}{b_i}
\]

(2.56)

The $b_m$ parameter is not calculated by the simple linear mixing rule in the Wong-Sandler method, instead it was ensured that the second virial coefficient composition condition is satisfied. This was achieved by substituting the expression for $a_m$ (Equation (2.56)) into the equation representing the second virial coefficient composition dependence (Equation (2.53)) and rearranging to get an explicit function for $b_m$: 

\[
\frac{b_m}{RT} - \frac{a_m}{RT} = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j B_{ij}
\]
\[ b_m = \frac{\sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j B_{ij}}{1 + \frac{g^E_{ij}(T, \text{low } P, z_i)}{RT} - \sum_{i=1}^{nc} z_i \left( \frac{a_i}{b_i RT} \right)} \]  

(2.57)

If \( Q \) and \( D \) are defined as follows:

\[ Q = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j B_{ij} \]  

(2.58)

\[ D = \frac{1}{RT} \left( \sum_{i=1}^{nc} \frac{a_i}{b_i} + \frac{g^E_{ij}(T, \text{low } P, z_i)}{\Lambda} \right) \]  

(2.59)

then the Wong-Sandler mixing rule may be expressed as:

\[ a_m = RTQ \left( \frac{D}{1-D} \right) \]  

(2.60)

\[ b_m = \frac{Q}{1-D} \]  

(2.61)

### 2.3.6 PSRK

Holderbaum and Gmehling (1991) developed a group-contribution EOS that combined the SRK EOS and the UNIFAC method. The method is known as Predictive Soave-Redlich-Kwong (PSRK) due to its predictive abilities (as there was no introduction of new parameters which would require a fitting procedure, only existing UNIFAC group-interaction parameters and pure component parameters are required). The PSRK model can be used for predictions of VLE over a temperature and pressure range much wider than that possible with UNIFAC, and may also be easily extended for use in supercritical systems, which is not possible with the use of a \( g^E \) model.

Holderbaum and Gmehling (1991) reveals that the PSRK model uses the simple MHV1 mixing rule (Equation (2.47)) differing only in the value of \( \Lambda \) which is changed from -0.593 to -0.64663, however not much insight is provided as to how this value was determined.
The PSRK mixing rule is:

\[
a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} - \frac{1}{0.64663} \left( g_E^E + RT \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) \right) \right)
\]

The new \( \Lambda \) value though was found to provide much improved results at elevated pressure which led Holderbaum and Gmehling (1991) to conclude that ‘the PSRK equation is especially suited for conditions, where use of a \( \gamma-\varphi \)-approach is difficult (i.e. when the real behavior of the vapour phase is unknown and not negligible) or inadequate (i.e. when supercritical components are present)’.

Following the innovative work of Wong and Sandler (1992), Fischer and Gmehling (1996) provided an alternative derivation of the PSRK model which was based on \( a^E \) as opposed to the fugacity coefficients. This derivation provides more insight into the value of \( \Lambda \). In deriving the PSRK equation Fischer and Gmehling (1996) makes two main assumptions:

1. The excess volume \( v^E \) is zero (negligible), which is an assumption made during the derivation of many \( g^E \) mixing rules.
2. The reduced liquid phase volume \( u \) is assumed constant, i.e.:

\[
u_m = u_i = \frac{v_m}{b_m} = \frac{v_i}{b_i} = u
\]

The second assumption was validated by calculating liquid molar volumes of a large number of pure components at normal pressure and boiling temperature and subsequently dividing this value by \( b \) (which is calculated using pure component data). The values of \( u \) were found to vary only slightly from 0.9 for highly polar components (methanol and water) to 1.2 for non-polar components (ethane, propane, butane etc.), with an average value of 1.1. If one considers that at infinite pressure \( u = 1 \), a value of 1.1 at atmospheric pressure is not unreasonable due to the fact that liquids may be compressed only slightly. As a result of \( u \) being estimated at atmospheric pressure the reference pressure of the PSRK model is in the region of 1 atmosphere (and not zero as is the case in the MHV mixing rules).
Through this alternative derivation it is seen that the value of $\Lambda$ in Equation (2.47) is equivalent to a function of $u$ as follows:

$$\Lambda = \ln \left( \frac{u}{u+1} \right)$$  \hspace{1cm} (2.64)

Substitution of $u = 1.1$ results in the value of $\Lambda$ equal to -0.64663 which is the value prescribed earlier by Holderbaum and Gmehling (1991). From Equation (2.64) one can also see that the constant $u$ value assumption inherent in the MHV1 model requires a value of 1.235 for $u$ at zero pressure, which is also not unreasonable as the molar volume of the liquid phase would increase slightly under reduced pressure conditions. So, the MHV1 model uses a zero pressure reference, while the PSRK model assumes a reference state at atmospheric pressure. $g^E$ model parameters are most commonly fitted using low pressure VLE data (not zero pressure data), therefore by using a reference pressure in the region of 1 atmosphere more accurate results will be produced.

In developing the PSRK model, other than altering the mixing rule for $a_m$, Holderbaum and Gmehling (1991) also decided to replace the original temperature dependence of the pure component $a$ parameter ($\alpha$ function) given by Soave (1972) with that given by Mathias and Copeman (1983). This modification was made in order to extend the applicability of the PSRK model to polar mixtures, as the original temperature dependence given by Soave fails to provide sufficiently accurate vapour pressure data for polar substances. The Mathias-Copeman expression is found to provide much improved representation of pure component vapour pressures, which obviously improves the reliability of predictions for polar mixtures. The only downside of this is that the Mathias-Copeman expression requires three adjustable parameters which must be fitted to pure component vapour pressure data (which may not be readily available), while the Soave expression only requires the pure component acentric factors and critical temperatures. As pointed out by Ahlers and Gmehling (2002a), the Mathias-Copeman $\alpha$ function also fails at elevated temperatures.

There are a number of advantages associated with the PSRK model such as the ability to provide accurate predictions of VLE over a large pressure range (i.e. use UNIFAC parameters fitted at low pressure for predictions at high temperature and pressure) and the fact that parameters associated with any $g^E$ model do not have to be altered but may be used directly in the model. For example, should the NRTL model be used instead of UNIFAC, the existing interaction
parameters may be used without modification. Holderbaum and Gmehling (1991) also states that the main advantage of equations of state in comparison to $g^E$ models ($\gamma$-$\phi$ approach) is their ability to represent phase equilibria of systems that contain supercritical components and because of this the UNIFAC interaction parameter table has been extended to include gases (e.g. CO$_2$, CH$_4$, N$_2$ etc.) for use in the PSRK model. This extension has been continuous and had vast amounts of research invested into it by Holderbaum and Gmehling (1991), Fischer and Gmehling (1996), Gmehling et al. (1997), Horstmann et al. (2000) and Horstmann et al. (2005) to name a few, and as a result has seen the addition of well over 30 new groups to the original UNIFAC groups. This extension has obviously greatly increased the range of applicability of the PSRK model and this, along with the fact that it predicts reliable results, has made it a very important tool to chemical engineers. Having said this though, there are also a number of limitations related to the PSRK model. Fischer and Gmehling (1996) identifies two major shortcomings of the method. The first is in the ability of PSRK to describe water-alkane systems (a problem inherent in the UNIFAC method) and second is the prediction of too high bubble point pressures in systems that contain components that differ greatly in size. Ahlers and Gmehling (2002a) identifies 4 major problems with the PSRK model and in doing so strengthens the argument for the development of an improved model (see VTPR below):

1) Predicted liquid densities deviate from experimental values in a similar way to the basic EOS (the SRK EOS).
2) The Mathias-Copeman $\alpha$ function provides unreasonable results at higher reduced temperatures.
3) Predictions of VLE for asymmetric systems are often unsatisfactory.
4) Predictions of excess enthalpies ($h^E$) and infinite dilution activity coefficients ($\gamma^\infty$) are poor.

2.3.7 LCVM

Boukouvalas et al. (1994) proposed an interesting model that made use of both the original $g^E$ mixing rule proposed by Vidal (1978) and that proposed by Michelsen (1990) (MHV1). The $\alpha$-term produced by both models is linked via a linear function, and for this reason the model of Boukouvalas et al. (1994) is called the linear combination of Vidal and Michelsen (LCVM) mixing rule. The LCVM model makes use of a modified and translated Peng-Robinson EOS and
the original UNIFAC g\textsuperscript{E} model, however any EOS and g\textsuperscript{E} model may be used in this mixing rule. The development of this model was driven by the failure of the PSRK model when predicting VLE of mixtures that contain components that differ greatly in size (highly asymmetric systems). As a result the LCVM model has been found to provide satisfactory results for systems of dissimilar component size and systems that contain non-polar and polar components at low and high pressure.

The formulation of the LCVM mixing rule was based on two fundamental observations:

1) Both the Vidal and MHV1 mixing rules may be used at any pressure, irrespective of the reference pressure used in their development (infinite pressure for Vidal, zero pressure for MHV1).

2) The mathematical expression representing both models are very similar (see Equations (2.23) and (2.47)), the only differences being the numerical value represented by \( \Lambda \) and the presence of \( \Sigma z_i(b_m/b_i) \), a Flory-Huggins-type term in the MHV1 mixing rule.

The reason for combining the two methods is due to the fact that in highly asymmetric systems the Vidal model has been found to under-predict bubble point pressures while the MHV1 model has been found to over-predict bubble point pressures which may be seen clearly in FIGURE 3 below. If the two methods were combined in such a way that the over-prediction of the MHV1 model was compensated for by the under-prediction of the Vidal model, accurate results could be obtained overall. It was therefore proposed to have a linear combination of \( \alpha \) calculated from the Vidal model (symbolized by \( \alpha_V \)) and \( \alpha \) calculated from the MHV1 model (symbolized by \( \alpha_{MHV} \)), in order to calculate the true \( \alpha_m \). The proposed combination was:

\[
\alpha_m = \lambda \alpha_V + (1-\lambda) \alpha_{MHV}
\]  

(2.65)

where \( \lambda \) is a constant that determines the relative contributions to \( \alpha_m \) by \( \alpha_V \) and \( \alpha_{MHV} \). When \( \lambda=0 \) \( \alpha_m \) is simply \( \alpha_{MHV} \) and when \( \lambda=1 \) \( \alpha_m \) is simply \( \alpha_V \). The LCVM mixing rule may also be represented as follows by substituting the \( \alpha \)-form of the Vidal and MHV1 mixing rules into Equation (2.65):

\[
\alpha_m = \left( \frac{\lambda}{\Lambda_V} + \frac{1-\lambda}{\Lambda_{MHV}} \right) \frac{g^E}{RT} + \left( \frac{1-\lambda}{\Lambda_{MHV}} \right) \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) + \sum_{i=1}^{nc} z_i \alpha_i
\]  

(2.66)
where $\Lambda_V$ and $\Lambda_{MHV}$ are the $\Lambda$ values of the Vidal and MHV1 mixing rules respectively. $\Lambda_V$ remains unchanged from the originally proposed value of -0.623 for the Peng-Robinson EOS. On the other hand though, Boukouvalas et al. decided to fit the linear approximation of the q-function found in the derivation of the MHV1 mixing rule for the Peng-Robinson EOS over a wider interval of $\alpha$, increasing the interval from (10, 13) to (6, 20). This causes a change in the slope of the straight line approximation (and hence the $\Lambda_{MHV}$ parameter) from -0.53 to -0.52.

In order to determine the value of $\lambda$ (i.e. establish to what degree $\alpha_{MHV}$ and $\alpha_V$ contribute to $\alpha_m$), results for the bubble point pressure of many ethane/n-alkane systems were calculated using values of $\lambda$ ranging from 0 to 1. Systems containing ethane (small) and large alkanes were investigated as the aim of the LCVM method was to overcome the problem associated with representation of systems containing components that differ greatly in size. The average absolute error for each $\lambda$ was then established by comparison with experimental data. The result of this analysis by Boukouvalas et al. may be seen in FIGURE 2 below.

![Average absolute % error (AAE) in predicted bubble point pressure for ethane/n-alkane systems as a function of the $\lambda$ value (taken from Boukouvalas et al. (1994))](image)

**FIGURE 2** Average absolute % error (AAE) in predicted bubble point pressure for ethane/n-alkane systems as a function of the $\lambda$ value (taken from Boukouvalas et al. (1994))

From the results it is obvious that in systems containing components of similar size, such as $C_2/nC_5$, MHV1 ($\lambda=0$) provides the best results but the results provided by Vidal ($\lambda=1$) are still
fairly good with an average absolute error (AAE) well below 10%. However, as the size difference between components begins to increase it becomes evident that there exists a value of $\lambda$ for which the AAE can be minimized as the Vidal and MHV1 models begin to fail severely. For example if one investigates just the $C_2/nC_{28}$ curve of FIGURE 2, the Vidal model produces results with an AAE of around 70% and the MHV1 model yields results with an AAE in excess of 80%, however the correct combination of the two models allows predictions with an AAE in the region of 10%.

Boukouvalas et al. (1994) suggests an optimum value (or reasonable compromise) for $\lambda$ of 0.36 when using UNIFAC which was found by investigating different binary systems (including systems of similar and greatly different component size) at high and low pressure, using varying values of $\lambda$ and focusing specifically on acceptable prediction of bubble point pressures and vapour phase compositions. The result of using $\lambda = 0.36$ for the most asymmetrical system tested, the ethane/$nC_{28}$ system, may be seen in FIGURE 3. In comparison to the Vidal and MHV1 models, the results of the LCVM model are seen to be much more accurate which confirms the reliability of this model for predictions of asymmetric systems. A similar investigation revealed that if modified UNIFAC is used, the value of $\lambda$ falls in the range from 0.65 to 0.75.

**FIGURE 3** Prediction of the bubble point pressure for the system ethane / $nC_{28}$ at 373 K (taken from Boukouvalas et al. (1994))
Voutsas et al. (1996) provides an extensive comparison of the 4 models: MHV2, PSRK, Wong-Sandler and LCVM, investigating the prediction of VLE in asymmetric systems by these models. It was concluded that LCVM was the only model of the four to provide satisfactory results. The same paper also states that the LCVM model has been successfully used to predict VLE in a range of systems of varying complexity.

2.3.8 VTPR

It has long been known that cubic equations of state lack the required accuracy when it comes to representation of saturated liquid densities. Ahlers and Gmehling (2001) identified this and realized that by starting from an improved CEOS (one that was better equipped to calculate saturated liquid densities) an improved group contribution EOS could be developed. It was with this in mind that Ahlers and Gmehling began development of a group contribution EOS that would improve the problems associated with the already highly regarded and successful PSRK model. Over the next 3 years, Ahlers et al. (Ahlers and Gmehling (2002a), Ahlers and Gmehling (2002b), Wang et al. (2003), Ahlers et al. (2004)) developed this concept further in a 5-part series and came up with the already successful Volume Translated Peng-Robinson (VTPR) group contribution EOS capable of completely replacing PSRK.

As stated already, Ahlers and Gmehling (2001) realized that improvements could be made to existing $g^E$ mixing rules by simply using a better EOS. The concept of applying a volume translation to an existing EOS, proposed by Peneloux and Freze (1982), was therefore utilized in conjunction with the Peng-Robinson EOS as follows:

$$P = \frac{RT}{v+c-b} - \frac{a}{(v+c)(v+c+b)+b(v+c-b)}$$

(2.67)

where $c$ is the translation parameter and effectively shifts or translates each $v$ term in the EOS. The volume translation has no effect on VLE calculations and simply provides significant improvements in the description of saturated liquid densities.
The pure component $c$ parameter can be determined by calculating the difference in experimental and calculated densities at a reduced temperature $T_r = 0.7$:

$$c = v_{\text{exp}} - v_{\text{calc}}$$

(2.68)

where the subscripts $\text{exp}$ and $\text{calc}$ represent molar volumes $v$ obtained from experiment and calculated from the EOS respectively. Ahlers and Gmehling (2001) found that, should no experimental data for liquid densities be available, $c$ may also be calculated directly from critical data as follows:

$$c = 0.252 \frac{RT_c}{P_c} \left(1.5448Z_c - 0.4024\right)$$

(2.69)

Equation (2.69) was found by a fitting procedure (explained by Ahlers and Gmehling (2001)) which involved investigating liquid densities of 44 pure components of different families (alkanes, aromatics, ketones, alcohols and refrigerants). The results for predictions of liquid densities by the VTPR EOS were compared to that of the Peng-Robinson and Soave-Redlich-Kwong EOS and it was found to be by far the most accurate model. Over a temperature range $0.3 < T_r < 1$ the VTPR EOS (using Equation (2.69)) was found to have the lowest deviation in liquid density from experimental results with a value of 4.1%. The Soave-Redlich-Kwong and Peng-Robinson equations of state deviated from experimental results by 13.3% and 6.9% respectively.

Near the critical temperature the change in $v$ with change in $T$ (i.e. the slope $dv/dT$) is extreme and as a result the volume translation concept fails, therefore VTPR may not be used for the entire temperature range. Ahlers and Gmehling (2002a) says that it is not recommended to use the VTPR EOS to calculate pure component and mixture liquid densities at reduced temperatures greater than 0.8. Ahlers and Gmehling (2001) also identified this problem and as a result investigated the use of a temperature dependent translation term $c(T)$ as they began exploring the use of volume translation for an improved group contribution EOS. Through this investigation an alternate method to the VTPR EOS was developed which used the temperature dependent volume translation and was called the T-VTPR EOS. The T-VTPR method was found to provide accurate predictions of liquid densities right up to the critical point ($T_r = 1$) however representations of VLE at high pressure proved to be highly unreasonable. As a result it was decided to base future developments on the VTPR EOS and not the T-VTPR EOS.
Obviously the improved description of pure component liquid densities also leads to better representation of mixtures, therefore eliminating one of the major problems found when using the PSRK model. In trying to provide an improved $g^E$ mixing rule and replace PSRK, Ahlers and Gmehling (2002a) identified 3 other areas in which the PSRK shows weaknesses:

1. The Mathias-Copeman $\alpha$ function, used in the calculation of pure component $a$ parameters, is thermodynamically incorrect at higher reduced temperatures

2. The prediction of asymmetric systems often delivers unsatisfactory results.

3. Predictions of excess enthalpies $h^E$ and infinite dilution activity coefficients $\gamma^\infty$ are poor.

In order to ensure that the VTPR model was an improvement over the PSRK model, a number of alterations were made to ideas used in PSRK.

Firstly, the Mathias-Copeman $\alpha$ function (Mathias and Copeman (1983)) was replaced with the Twu $\alpha$ function (Twu et al. (1991), Twu et al. (1995)) for the calculation of pure component EOS $a$ values. The Twu $\alpha$ function provides much more reliable reproduction of pure component vapour pressures and has been shown to operate reasonably at elevated temperatures (i.e. shows reasonable temperature extrapolations). At very high temperatures the $\alpha$ function should approach zero and it is under these conditions that the Mathias-Copeman $\alpha$ function fails.

In order to improve predictions of highly asymmetric systems (weakness 2 above), Ahlers et al. identified that development of the VTPR model required the introduction of improved mixing rules for calculation of the $a_m$ and $b_m$ parameters. Improvements to the mixing rule for $a_m$ revolved around the fact that in the PSRK model there are two parameters which represent a similar property but have different values. These parameters are the co-volume of the pure components $b_i$ (used in the EOS) and the relative van der Waals volume $r_i$ (used in the UNIFAC model). As the degree of asymmetry increases these values are found to become increasingly different (see FIGURE 4 below).
FIGURE 4 Change in the quotients $r_{alkane}/r_{ethane}$ and $b_{alkane}/b_{ethane}$ in dependence of the degree of asymmetry of the system: (o) parameter b (PR EOS); (*) relative van der Waals volume parameter r (taken from Ahlers and Gmehling (2002a))

Ratios relative to ethane are used in FIGURE 4, as the main focus of this study was behavior at different levels of asymmetry. Based on improvements made to the PSRK model by Li et al. (1998), which introduced an empirical correction for more reliable predictions of asymmetric systems, it was decided that the relative van der Waals volume $r_i$ should be replaced by the co-volume $b_i$ in the improved mixing rule model. Using this alteration, Ahlers and Gmehling (2002a) proved that the PSRK mixing rule may be greatly simplified and improved for asymmetric system predictions. The following argument was presented to do so:

i. $g^E$ calculated using the UNIFAC model consist of two parts, the combinatorial and the residual part:

$$g^E = g_{comb}^E + g_{res}^E$$  \hspace{1cm} (2.70)

The combinatorial part is calculated as follows using pure component relative van der Waals volumes $r_i$ and surface areas $q_i$:

$$g_{comb}^E = RT \left( \sum_{i=1}^{nc} z_i \ln V_i + 5 \sum_{i=1}^{nc} z_i q_i \ln F_i \right)$$  \hspace{1cm} (2.71)
where $V_i$ and $F_i$ are the volume to mole fraction ratio and the surface area to mole fraction ratio respectively, calculated by:

$$
F_i = \frac{q_i}{\sum_{j=1}^{nc} z_i q_j} \quad (2.72)
$$

$$
V_i = \frac{r_i}{\sum_{j=1}^{nc} z_j r_j}
$$

ii. The Flory-Huggins term $\sum z_i \ln(b_m/b_i)$ in the PSRK mixing rule (Equation (2.62)) can be rearranged into the following form:

$$
\sum_{i=1}^{nc} z_i \ln\left(\frac{b_m}{b_i}\right) = -\sum_{i=1}^{nc} z_i \ln V_i \quad (2.73)
$$

where:

$$
V'_i = \frac{b_i}{\sum_{j=1}^{nc} z_i b_j} \quad (2.74)
$$

iii. Now applying the fact that $r_i$ is replaced with $b_i$, one can see that the altered form of the Flory-Huggins term (Equation (2.73)) is the negative equivalent of the first summation term in the combinatorial part of the UNIFAC model (Equation (2.71)) and therefore the two terms can be canceled in the PSRK mixing rule. In addition, the second summation in the combinatorial part provides only a small contribution (relative to the first summation term) and is therefore regarded as negligible.

As a result of the above explanation, the $g^E$ term found in the PSRK mixing rule need only be represented by the residual part of the UNIFAC model (which also means that the relative van der Waals volume parameter $r_i$ is no longer required in the mixing rule) as the Flory-Huggins term disappears.
The VTPR mixing rule for $a_m$ is therefore a simplified version of PSRK given by:

$$a_m = b_m \left( \sum_{i=1}^{nc} \frac{z_i}{b_i} a_i - \frac{g_{res}^E}{0.53087} \right)$$  \hspace{1cm} (2.75)$$

$g_{res}^E$ is calculated in the same way as in the UNIFAC model.

The constant $\Lambda$ found in MHV1 (Equation (2.47)) is calculated from a function specific to the EOS used and depends on the reference state of the mixing rule (which affects the reduced liquid phase volume $u$). For the Peng-Robinson EOS $\Lambda$ is calculated from:

$$\Lambda = \frac{1}{2/\sqrt{2}} \ln \left[ \frac{u + (1 - \sqrt{2})}{u + (1 + \sqrt{2})} \right]$$  \hspace{1cm} (2.76)$$

The reference state of the VTPR method is atmospheric pressure (same as PSRK) and under these conditions $u$ was determined for 75 compounds in a similar way to that described for PSRK above, but using the Peng-Robinson EOS instead of the Soave-Redlich-Kwong EOS. $u$ was assumed constant (as in PSRK – Equation (2.63)) and an average value of $u = 1.22498$ was calculated. Using this value of $u$ the $\Lambda$ parameter in VTPR is -0.53087.

To further improve the performance of the VTPR model with respect to asymmetric systems, Ahlers and Gmehling (2002a) applied the work of Chen et al. (2002), which identified that in asymmetric systems the mixing rule for $b_m$ has a larger influence than previously anticipated and as a result proposed a quadratic mixing rule for the $b_m$ parameter:

$$b_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} z_i z_j b_{ij}$$  \hspace{1cm} (2.77)$$

whereby the following combining rule applies:

$$b_{ij} = \left( \frac{b_i^{3/4} + b_j^{3/4}}{2} \right)^{4/3}$$  \hspace{1cm} (2.78)$$

The above mixing rule replaces the linear version used in the PSRK model and has been found to significantly improve predictions of asymmetric systems.
The volume translation parameter $c$ is extended for use in mixtures by a simple linear mixing rule:

$$c_m = \sum_{i=1}^{n_c} z_i c_i$$  \hspace{1cm} (2.79)

No indication is given in the literature covering the development of the VTPR model as to why this rule was selected, however it is very simple and results produced with the model indicate that the rule works adequately.

The last area of weakness found in the PSRK model that Ahlers et al. aimed to eliminate in the new VTPR model was the prediction of excess enthalpies $h^E$ and infinite dilution activity coefficients $\gamma^\infty$. To do this they proposed to use temperature-dependent interaction parameters which would be simultaneously fitted to VLE, $h^E$ and $\gamma^\infty$ data. Ahlers and Gmehling (2002b) give detailed information as to how this fitting procedure was performed and provides insight into the objective function used. The reason for using temperature-dependent interaction parameters is to ensure reliable predictions for gas-alkane systems, which cover a large pressure and temperature range. As a result, the modified UNIFAC model is used in VTPR however the group interaction parameters used are specific to VTPR (i.e. existing modified UNIFAC parameters are not used).
3. THE VGTPR MODEL

To date the PSRK model has become by far the most successful $g^E$ mixing rule developed and is found in most chemical engineering simulation software. Its success may be attributed mainly to its reliability, availability of parameters and range of applicability. However, as pointed out by Ahlers and Gmehling (2002a) and discussed in section 2.4.8 above, the PSRK model does exhibit some serious defects. In order to overcome these, a number of modifications were made to PSRK, resulting in the development of the VTPR model. The modifications made in development of the VTPR model provided an improved mixing rule over PSRK. The VTPR model allowed better: predictions of saturated liquid volumes (through a volume translated EOS), representation of asymmetric systems (by altering the mixing rules), pure component vapour pressure representation (with the use of the Twu $\alpha$ function) and calculations of $h^E$ and $\gamma^\infty$ (by refitting modified UNIFAC (Dortmund) parameters to a larger experimental data base).

Although the VTPR mixing rule provides a major step forward in the field of mixture representation in equations of state, it does contain one major disadvantage which has resulted in PSRK remaining as the mixing rule of choice. VTPR uses the modified UNIFAC (Dortmund) method to calculate $g^E$, however it is unable to utilize the large amount of existing modified UNIFAC (Dortmund) group-group interaction parameters. Cubic equations of state contain their own temperature dependence which in combination with the temperature dependence of the modified UNIFAC (Dortmund) parameters leads to erroneous results. To overcome this problem the modified UNIFAC (Dortmund) group-group interaction parameters have to be re-regressed specifically for use in the VTPR model. In order to improve calculations of a number of properties when using the VTPR model, these parameters are regressed using an objective function that takes into account the differences in experimental and calculated values of the following:

- VLE of normal and high boiling components
- Gas solubilities
- Infinite dilution activity coefficients
- Excess enthalpies
- Excess heat capacities
- Liquid-liquid equilibria
- Solid-liquid equilibria

Looking at the list above, it is understandable that this regression is very complicated and requires great care to obey all specific boundary conditions, which results in a very time-consuming exercise. As a result the VTPR model offers only a very limited number of group-group interaction parameters, which severely limits its availability for use in calculations. Although new parameters are being continuously added, it has taken approximately 8 years for the VTPR parameter matrix to reach its current state displayed in Figure 5 below. The PSRK model on the other hand has a very large parameter matrix (which may be seen in Figure 6) due to continuous extension over the past 18 years and as a result it will take many more years until the VTPR model reaches the maturity level of PSRK. Until this happens VTPR will continue to fall in the shadow of PSRK despite the obvious advantages it has over the PSRK model.
FIGURE 5 Current status of the modified UNIFAC parameters available for use in the VTPR model (taken from DDBSP - Gmehling et al. (2009))
FIGURE 6 Current status of the UNIFAC parameters available for use in the PSRK model (taken from DDBSP - Gmehling et al. (2009))
The idea investigated in this work then involves keeping the VTPR model, while however utilizing the vast amount of existing (and continuously advancing) modified UNIFAC (Dortmund) model parameters instead of undertaking the tedious and difficult task of re-regressing them for use in VTPR. This will ensure that the new model will not only inherit the advantages of VTPR but will also increase its range of applicability up to and even beyond that of PSRK. In other words the limiting factor associated with the VTPR model will be eliminated.
The reason for this concept may be easily illustrated by investigating the differences in existing model parameters for VTPR and modified UNIFAC in Figure 5 and Figure 7 respectively.

This idea was first proposed by Dr. Juergen Rarey (Rarey (2009)) and later investigated by Collinet et al. (2009). It was postulated that the modified UNIFAC (Dortmund) parameters could be used directly if the equality between the $g^E$ calculated from the EOS and from modified UNIFAC (Dortmund) (Equality (2.15)) was ensured, which removes the possibility of the combined double temperature dependence having any influence on the results. To do this the VTPR mixing rule for $a_m$ was altered and a $g^E$ translation $g^E_{\text{trans}}$ term was added as follows:

$$a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} - \frac{g^E_{\text{trans}}}{0.53087} \right)$$

(2.80)

Now, in order to calculate $g^E$ from an EOS the following equation is required which is a different form of Equation (2.16):

$$g^E_{\text{EOS}} = RT \sum_{i=1}^{nc} z_i \ln(\gamma_i)$$

(2.81)

where $\gamma_i$ is the activity coefficient of component $i$. $\gamma_i$ is calculated as follows:

$$\gamma_i = \frac{\hat{\phi}_i}{\phi_i}$$

(2.82)

$\hat{\phi}_i$ is the fugacity coefficient of component $i$ in the mixture calculated from the following equation:

$$\ln \hat{\phi}_i = \frac{1}{RT} \left[ \frac{RT}{v} - \left( \frac{\partial P}{\partial n_i} \right)_{T,v,n_j} \right] dv - \ln Z$$

(2.83)

where $n_j$ and $n_i$ are the number of moles of component $i$ and $j$ respectively. $\phi_i$ in Equation (2.82) is calculated using Equation (2.17). The pressure term $P$ in Equations (2.17) and (2.83) is represented by the EOS and therefore the end result depends heavily on the mixing rules used. Should Equation (2.80) be used without the $g^E_{\text{trans}}$ translation term (i.e. using the VTPR mixing rule) and the modified UNIFAC (Dortmund) group-group interaction parameters be used directly, the
value of $g_E$ that results from Equation (2.81) is different from that calculated using modified UNIFAC (Dortmund) (and substituted into the mixing rule). So what the $g_E$ translation term does is ensure equality between these two calculations, however instead of just trying to match the two $g_E$ terms it was rather suggested to ensure equality between activity coefficients of each component:

$$\gamma_{i,EOS} = \gamma_{i,\gamma}$$ (2.84)

The subscripts $i,EOS$ and $i,\gamma$ indicate activity coefficient of component $i$ calculated from the EOS and from the $g_E$ (activity coefficient) model respectively. This was done due to the fact that there is a possibility that the two $g_E$ values calculated could be identical even when the individual component activity coefficients are not. If the activity coefficients for each component calculated by the two methods are identical, $g_E$ will always be identical. In essence the activity coefficients calculated using modified UNIFAC (Dortmund) are assumed correct and the values calculated from the EOS are matched by making iterative adjustments to the $a_m$ parameter which is done by changing the $g_E$ translation term, which in effect is a correction term.

The Twu $\alpha$-function and the mixing rules for $b_m$ and $c_m$ remain the same as those used in the VTTPR model.

A downside of this approach is that $g_E$ in the EOS approach can only be calculated for subcritical components. It was therefore decided to calculate the equality not along the saturated vapour-pressure curve but at a certain fixed reduced density (reference density) of the pure components and the mixture. The pressure difference between this state and the saturated state changes $g_E$ only slightly due to the low pressure dependence of $g_E$ in the liquid state. The model is now applicable at sub- and supercritical conditions and temperature dependent $g_E$ model parameters regressed previously can be used in the EOS at any temperature. This model therefore allows combination of the volume-translated Peng-Robinson EOS with the modified UNIFAC method (with temperature dependent group interaction parameters).

This model was originally proposed and tested by Collin et al. (2009) and was found to provide very accurate results. VGTPR was found to provide identical predictions to the modified UNIFAC model for vapour-liquid equilibria, excess enthalpies, activity coefficients at infinite dilution and solid-liquid equilibria. Using the reference volume, VGTPR was found to give very
similar results to the PSRK model at subcritical conditions, however under supercritical conditions VGTPR was found to give markedly better results than PSRK.

The outlook of the VGTPR model is promising, however to date little research has been undertaken in the way of testing the model. Therefore, the purpose of this work is to extensively investigate the model using the large amount of experimental data already stored in the Dortmund Data Bank (DDB) with the idea of identifying any problems associated with the model and resolving these problems should they exist. Up until now, this work has not been initiated as a comprehensive review of the literature related to this topic has been undertaken.
4. FUTURE WORK

To date, a comprehensive review of mixing rules for cubic equations of state has been completed so as to establish a better understanding of the topic as a whole and provide a firm foundation from which to develop the VGTPR model. A great deal more work is still required to complete the research. The following section aims to identify what tasks still need to be undertaken and the time frame estimated to perform each.

Completion of literature review

As stated already, a review of the mixing rules for cubic equations of state has been completed and has been presented in this report. A number of other topics still require review for the final thesis. The following topics have been identified as highly important and will be reviewed in the future:

- Fundamental thermodynamic concepts used throughout this work.
- Equations of state (the various types available) and the $\alpha$ functions available for use in the cubic equations of state.
- $g^E$ models.

This should take approximately 1 month to complete, however will be performed intermittently over the forthcoming months.

Implementation of the VGTPR method

At present the algorithm for the VGTPR method has yet to be written. This will be done using MATHCAD initially to test individual systems for investigation of results and identification of any problems associated with the algorithm. It is believed that this should not take too much time; however should there be major problems with the algorithm one could expect the time frame to increase. With all things running smoothly this could take around 2 weeks, however depending on the number of problems encountered this could take up to 1 month. This section of the project is obviously vital so the work required will not be rushed, and should more time be required for completion, it will be duly granted.
Testing the method

Once the algorithm for the VGTPR method is finalized, the testing phase will begin. This will require calculating results for a wide variety of systems followed by comparison of the results with experimental data and predicted results obtained from other well established group contribution equations of state (e.g. PSRK, LCVM and VTPR). The systems to be tested will range from simple (containing nonpolar components) to more complex systems displaying high levels of asymmetry and non-ideality (containing polar or associating components). The performance of the VGTPR model when representing supercritical systems will also be evaluated. Predictions of a number of different properties (e.g. VLE, $h^E$, $\gamma^\infty$ etc.) will be carried out during this testing phase, and compared to results from existing models and experimental data. Results from existing models will be generated with the use of the Dortmund Data Bank software package (DDBSP) (Gmehling et al. (2009)) which has the procedures for these models built-in. Any pure component data, group-group interaction parameters and experimental data that is required will be extracted from the Dortmund Data Bank (Gmehling et al. (2009)).

The modified UNIFAC $g^E$ model is used in the VGTPR mixing rule and as a result the group-group interaction parameters between gases and the structural groups of modified UNIFAC are not available. In order to counter this problem, these missing parameters will be regressed to predictions obtained from the PSRK model which may be utilized for a large variety of gas-containing systems. This is obviously not ideal, however it will provide some ‘ball-park’ values for the missing parameters and allow predictions to be performed on these systems using VGTPR. These parameters can, at a later stage, be more accurately regressed to experimental data.

Apart from just checking and comparing results, the stability of the model will also be tested which will involve investigations at varying conditions. The mathematical workings of the model will also be investigated so as to gain a better understanding of the model which is essential because in order to make improvements one must understand how it works.

It is expected that this part of the project will require a large amount of time, especially when considering that it is during this phase that problems inherent in the model will be identified and hopefully rectified. A large amount of data will need to be generated, organized and examined
which in itself can be a very long procedure. Considering all of this it is expected that this phase should take in the region of 3 to 4 months.

**Thesis write-up**

The final task at hand will be to collect the results of all 3 previous phases and combine them into one coherent document. A clear description of the VGTPR model and how it operates will be provided, while discussions related to the results of the testing phase will also be included. The tedious procedure of compiling a literature review should be finished by this phase; however the discussions will need to be presented in a clear and concise manner. It is estimated that this should take anywhere from 6 weeks to 2 months.
5. REFERENCES


