

THE DEVELOPMENT OF A HYBRID ACTIVITY COEFFICIENT MODEL UTILIZING THE SOLUTION OF GROUPS CONCEPT

By

Brian J. Satola

[BSc (Eng.)]

University of KwaZulu-Natal, Howard College Campus

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ABSTRACT

Models for the description of real non-electrolyte mixture behaviour are of fundamental importance for the synthesis, simulation, design, and operation of many separation processes used in industry (e.g. distillation and extraction). Since often 60-80% of the total costs arise in the separation step, a reliable knowledge of the phase equilibrium behaviour of the system to be separated is of special importance to industrial practitioners (J. Gmehling 2009).

Models like Wilson, NRTL, and UNIQUAC have long been used with great success for the description of the real behaviour of multicomponent mixtures, but they are restricted due to the limited availability of binary interaction parameters. Out of this reason, group contribution methods like ASOG, UNIFAC, and mod. UNIFAC were developed that are based on structural group interactions instead of molecules.

These predictive models however rely on *large* experimental datasets for regression purposes; once the group interaction parameters are determined, there is currently no way of tuning the predicted results. This is viewed as a limitation because group interaction models often can represent binary mixtures more accurately if the group interaction parameters are regressed to experimental data on a case by case basis (Rarey 2008). It is for this reason that the main objective of this work is to test to what extent the group interaction concept is advantageous. If the advantage with respect to correlation and prediction can be verified, a hybrid method will be investigated; whereby the results from group interactions can be adjusted by superimposing component-component-interactions regressed to actual mixture data.

To accomplish this, the NRTL equation will be applied to the solution of groups concept (SOG) formalized by Wilson & Derr (1962). In the course of this report currently accepted methods in industry will be discussed, where the choice of using NRTL will be elucidated. Following the literature review of these methods the proposed methodology will be communicated. The final section will outline the steps required to establish the proposed method, and the work involved in each.

PREFACE

The work presented in this progress report was performed at the University of KwaZulu-Natal, Durban from February 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.

Brian J. Satola (209525595)

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Nomenclature

Latin Letters

$a, b, c, \dots, A, B, C, \dots$	parameters or equations
a	molar Helmholtz energy
A	Helmholtz energy
E	Energy
f	fugacity
$f(\)$	a function of () variables
<i>Final</i>	final state
g	molar Gibbs energy
G	Gibbs energy
h	molar Enthalpy
H	Enthalpy
I, J, K, \dots Group	solution of I, J, K, \dots molecular groups
<i>Initial</i>	initial state
k	Boltzmann constant
$l_i, \theta_i',$ and Φ_i'	convenience variables used in UNIQUAC equation
<i>LLE</i>	liquid-liquid equilibria
M	any intensive thermodynamic property
nM	any extensive thermodynamic property
n, N	number of moles
N	number of particles or molecules
p_i^*	probability of quantum state i of a system's ensemble, where $\sum_i p_i^* = 1$ (summation over all possible quantum states)
P	pressure
q	pure-component area parameter
Q	heat
Q	canonical partition function
Q_k	area parameter group/segment k
r	pure-component volume parameter
R	gas constant
R_k	volume parameter group/segment k

s	molar entropy
S	entropy
SLE	solid-liquid equilibrium
T	absolute temperature
u	molar internal energy
U	internal energy
v	molar volume
V	volume
VLE	vapour-liquid equilibrium
w	interchange energy
W	work
x	mole fraction (liquid)
X	group fraction in liquid solution
z	coordination number (number of nearest touching neighbours for a central molecule)

Greek Letters

α	nonrandomness parameter in NRTL equation
γ	activity coefficient
Γ	group activity coefficient
ε	interaction/potential energy
ξ	local volume fractions
ζ_{mk} and ξ_{mk}	group pair parameters characteristic of groups m and k , independent of temperature, used in ASOG method
θ	component surface area fraction
Θ	group surface area fraction
Φ'_i	component volume correction used in the combinatorial term of the modified UNIFAC method
Ψ_{mk} and T_{mk}	group interaction parameters between group m and group k
Λ	binary interaction parameters in Wilson equation
μ	chemical potential
τ	energetic parameters of the NRTL and UNIQUAC equations
Φ	volume fraction or segment fraction

v_k number of k molecular segments

Symbols and Numbers

1, 2, 3, ... # ... *	system component or group numbers
\Leftrightarrow	Used to show the relationship between an empirical equation, and the fundamental equation used for its development: { <i>empirical equation</i> } \Leftrightarrow { <i>fundamental basis</i> }.
C_p	heat capacity at constant pressure
$g(N_1, N_2, N_{12})$	represents the number of ways molecules of component 1 and 2 can be arranged on a lattice
N_A	Avogadro's number
R_i^*	pure-component group ratio

Sub- and Superscripts: Latin

AZD	azeotropic value/point
C	combinatorial quantity
<i>Comp</i>	total number of system components
E	excess property
FH	identifies the Flory-Huggins relation
FV	free volume
i, j, k	components i, j, k
$(i), (j)$	hypothetical fluids i and j
(i)	pure component i
is	ideal solution property
L	liquid phase
p	phase p
<i>Phase</i>	total number of phases in system
<i>rev</i>	reversible
R	residual quantity
RT and *	identifies a <i>residual tuning</i> quantities/variables used in the proposed method

Sub- and Superscripts: Greek

α, β, π phases α, β , and π

Sub- and Superscripts: Symbols and Numbers

0 standard state, or reference state
1, 2, 3 ... system component identifiers
 ∞ infinite dilution
 \wedge component property
— partial molar mixture property

Introduction

The myriad of methods now available to the practicing engineer is evidence that not any one method is overwhelmingly superior; as our collective understanding grows so do the number of models able to describe real non-electrolyte mixture behaviour. As a result practitioners may use more than one model to obtain an accurate representation of their system.

In a given model it is usually desired to obtain experimental data for the major components in the system under study, this is typically in the form of binary mixture data which, according to current industrial practice, are habitually regressed into binary interaction parameters. Since most industrial systems are composed of 10+ components it is unrealistic to expect enough experimental data to accurately describe the whole system; as a result group contribution methods are used to generate data to regress the missing binary interaction parameters. Using group contribution methods in this way allows practitioners to use the component interaction construct throughout their simulation.

Since group interaction parameters are regressed to reproduce the behaviour of a large number of different mixtures simultaneously—often more than 3000 experimental data points are used to obtain the parameters for one group pair (J. Gmehling 1995)—*they are rarely used in simulations directly although the group interaction concept may prove superior*. Given the potential benefit to industry, a novel *hybrid group contribution method* is proposed. In the context of outlining the proposed method, the following areas will be discussed:

- The thermodynamic formulation used in quantifying phase equilibria
- A methodical review of relevant literature, whereby the pros and cons of key methods used in industry are discussed.

Using this foundation the proposed method will be *formulated*, followed by the proposed *work scope* to establish the methods credibility.

1. The Language of Thermodynamics

The historical development of thermodynamics has been paved by many people throughout history; through the process of trial and error we have come to *accept* certain observations as being *universal* (always true). These observations have resulted in a framework of *abstract* symbols which can playfully be dubbed “the language of thermodynamics”. An important step is to be able to use this common-language to interpret, relate, and predict the behaviour of the world around us whilst obeying these universal-*truths*. In practice these truths are incorporated into *external models* (see LITERATURE REVIEW), which can accurately represent *real mixture behaviour*; accordingly, a brief fundamental review is in order.

1.1. Historical Context

It can be argued that much of the driving force behind the development of thermodynamics resulted from our ever increasing consumption of natural resources (which parallels the continuing importance in the field today).

Much of the foundations can be traced back to the necessity of coal mining, which was an economic alternative to society’s previous major source of “heat” in the 1800’s (wood). As the readily accessible deposits became depleted, surface quarries eventually were developed into mine shafts. As these veins were pursued deeper underground (below water tables) flooding became an obstacle. It was this problem that prompted the re-invention of the steam engine (Falk 1985, Rarey 2006, Müller 2007).

Although the first generation of these engines was highly inefficient (< 5%) they were viewed as a necessity of the *civilized-World*. Their operating costs were accepted at the time, but as these machines were applied to other industries, serious attention was placed on improving their design (Srinivasan 2001, Müller 2007):

“Everyone knows that heat can produce motion. That it posses vast motive power no one can doubt, in these days when the steam engine is everywhere well known. The study of these engines is of great interest, their importance enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world.” (Carnot 2005)

1.2. The Fundamental Foundation

Efficiencies drove people to study the interrelations of heat (Q), work (W), and the *abstract* concept called energy (E). Eventually patterns were identified regarding these variables, and the interrelationships were incorporated into the fundamental theories forming the foundations of thermodynamics.

1.2.1. First Law of Thermodynamics

As touched upon earlier, our collective knowledge has resulted in the identification of certain truths that we consider universal. One such universal-truth is the *conservation of energy*; stated verbatim,

1. Energy can be stored
- Energy can be moved between matter
- Energy can be transformed

These simple statements constitute what is known as the *First Law of Thermodynamics*, and can be mathematically written as

$$E_{\text{stored}} = E_{\text{in}} - E_{\text{out}} \quad (1-1)$$

The concept of *stored* energy (E_{stored}) naturally lends itself to the characteristic expression “internal energy” (U). However in order to calculate this new quantity, some knowledge of the forms of energy that may enter and/or leave the system is required (where *system* refers to some part of the physical world, separated by a conceptual boundary).

Here I take some liberties on the historical development, and simply state that heat and work have been identified as forms of energy.¹ Where *heat* can be considered transient-energy resulting from temperature differences and *work* can be considered a characteristic-form of energy (typically associated with expenditure). These two energy terms may be used to rewrite the 1st Law in its *traditional form*, a closed system which neglects mass transfer across the system boundaries:

$$\underbrace{d(nU)}_{\text{Traditional form}} = \delta Q + \delta W \quad (1-2)$$

However this equation cannot be regarded as giving an explicit definition of internal energy, in fact no such definition is known to exist. The postulated existence of internal energy as a property of the system’s state (a *state-property*) has proven time and time again to be *consistent* with the 1st Law of Thermodynamics; therefore experience *proves* its existence:

¹ For the interested reader Ingo Müller (2007) has written a good book on the historical development of thermodynamics; although some have criticised his depiction, it nonetheless acts as a good springboard for further indulgence.

One such historical test was the application of the 1st Law to nuclear reactions. For a while it was thought that the 1st Law had a “mass defect” (Müller 2007), but Einstein was able to establish a relationship between mass and energy ($E = mc^2$) which further bolstered the 1st Law as a universal-truth. This minor digression makes an important point: an essential part of utilizing the thermodynamic framework, in a consistent manor, lies in the ability to *strictly define* the system being considered.

In accordance, considering a closed system going through a quasi-static change of state (series of very small equilibrium steps where all energy is recovered—considered completely *reversible*), where only expansion or compression of the system and heat transfer can take place, enables the following definitions to be made:

$$\delta W_{rev} = -Pd(nV) \quad (1-3)$$

$$\delta Q_{rev} = Td(nS) \quad (1-4)$$

The total system volume (nV) and entropy (nS) are considered *extensive* state-properties of the system (i.e. dependent on the mass and state of the system, just like internal energy), and can be used to facilitate the calculation of internal energy by making the appropriate substitutions:

$$d(nU) = Td(nS) - Pd(nV) \quad (1-5)$$

Since the internal energy is now in a form that *only* depends on the state of the system (i.e. not on the process or path that produces the state) the relationship is also suitable to describe irreversible systems (*physical reality*).

1.2.2. Second Law of Thermodynamics

As with the conservation of energy, further historical observations have led to an additional universal-truth; specifically,

2. Energy cannot be transformed or moved without wasting some in the process.

This is in reference to the extensive state-property called entropy, a convenience-variable that was introduced by Clausius to represent the quantity $\delta Q/T$; conceptually entropy represents the *wasted effort* (or *lost energy*) involved whenever energy is moved and/or transformed. This is summed up nicely by the following citation (Müller 2007, 71):

Clausius summarized his work in the triumphant slogan

Die Energie der Welt ist konstant.

Die Entroie der Welt strebt einem Maximum zu.

Die Welt (the universe) was chosen in this statement as being the ultimate thermodynamic system, which presumably is not subject to heating and working, so that $dU = 0$ holds, as well as $dS > 0$.

This is known as the *Second Law of Thermodynamics*, and is commonly written symbolically using the definition of entropy as

$$d(nS) \geq \frac{\delta Q}{T} \geq 0 \quad (1-6)$$

Where the equal sign signifies the limiting value of zero (reversibility). This expression is often combined with the 1st law to obtain the *practical form*,

$$\underbrace{d(nU) \leq Td(nS) - Pd(nV)}_{\text{Practical form}} \quad (1-7)$$

The 2nd Law can conveniently be considered as a *constraining relationship* of the 1st Law, which places restrictions on what can and cannot be accomplished in physical reality—nature *naturally* tends towards increasing disorder (entropy).

1.2.3. Third Law of Thermodynamics

The third and last historical observation, like the others, has also proven true 100% of the time; simply stated,

3. It is impossible to remove all of the heat from an object

This statement constitutes the *Third Law of Thermodynamics*, and naturally lends itself to the definition of the lowest point on the *thermodynamic temperature scale* (absolute zero, 0 Kelvin).

The statement implies that it is *impossible* to reach absolute zero, where all of the *heat* (energy) of a system would be removed (creating a perfect crystal). If thought of in terms of the 2nd Law, it is impossible to have a system with zero entropy; in physical reality this minimum is unrealistic and has never been realized—a universal-truth.²

² The current world record for the lowest temperature observed stands at 50 pK (NASA 2003); this is astounding considering that the universe imparts 3 K to bodies through its *background radiation* (Müller 2007).

1.2.4. Expanding Results to Open Systems

In the previous sections the *traditional* and *practical* forms of the 1st Law were derived on the basis of a *closed* system (no mass transfer across system boundaries); however a form that is *open* to the environment (everything outside the system's conceptual boundary) is required for many practical situations (multiple phases, where each phase is considered a system). For a closed system internal energy was found to be a function of the extensive properties entropy and volume, and can therefore be represented by the *total derivative* of the *continuous-function* (via the conservation of energy principle) nU :

$$nU = f(nS, nV) \quad (1-8)$$

$$d(nU) = \underbrace{\left[\frac{\partial(nU)}{\partial(nS)} \right]_{nV} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)} \right]_{nS} d(nV)}_{\text{Traditional form}} \quad (1-9)$$

Comparing the total derivative with the traditional form of the 1st Law allows the *intensive* state-properties (independent of system mass—temperature and pressure) to be readily identified with their partial derivative equivalents. From this mathematical perspective (entirely consistent with observations), the internal energy may be extended to open systems via the *conservation of mass* principle:

$$\text{Conservation of Mass} \Rightarrow n = n_1 + n_2 + \dots + n_{Comp} \quad (1-10)$$

$$nU = f(nS, nV, n_1, n_2, \dots, n_{Comp}) \quad (1-11)$$

$$d(nU) \leq \underbrace{\left[\frac{\partial(nU)}{\partial(nS)} \right]_{nV, n} d(nS) + \left[\frac{\partial(nU)}{\partial(nV)} \right]_{nS, n} d(nV) + \sum_{i=1}^{Comp} \left[\frac{\partial(nU)}{\partial(n_i)} \right]_{nV, nS, n_j \neq i} dn_i}_{\text{Functional form}} \quad (1-12)$$

Where the *chemical potential* is defined for convenience as

$$\mu_i = \left[\frac{\partial(nU)}{\partial(n_i)} \right]_{nV, nS, n_j \neq i} \quad (1-13)$$

Like the temperature and pressure of the system, the chemical potential is independent of the quantity contained within the system (an *intensive* state property).

1.3.Auxiliary Properties

Since no entropy meter is known to exist, researchers have been guided to represent the fundamental law by alternative functions that are more readily determined by practitioners (auxiliary properties). Given the functional dependence of internal energy on the intensive $[T, P, \mu_i]$ and extensive $[nV, nS, n]$ state quantities of a system, new properties may be defined by considering various linear changes of these interrelated-variables on internal energy. Legendre transformations facilitate this process (Alberty 1997, 2001), and can be used to obtain the equivalent potentials of Enthalpy (H), Helmholtz energy (A), and Gibbs energy (G).

1.3.1. Enthalpy (Energy)

$$(nH) \equiv (nU) + P(nV) \quad (1-14)$$

$$d(nH) = d(nU) + Pd(nV) + (nV)dP \quad (1-15)$$

$$nH = f(nS, P, n_1, n_2, \dots, n_{Comp}) \quad (1-16)$$

$$\overbrace{d(nH) \leq \left[\frac{\partial(nH)}{\partial(nS)} \right]_{P,n} d(nS) + \left[\frac{\partial(nH)}{\partial P} \right]_{nS,n} dP + \sum_{i=1}^{Comp} \left[\frac{\partial(nH)}{\partial(n_i)} \right]_{nS,P,n_{j \neq i}} dn_i}^{\text{Functional form}} \quad (1-17)$$

$\underbrace{\hspace{10em}}_{T} \quad \underbrace{\hspace{10em}}_{nV} \quad \underbrace{\hspace{10em}}_{\mu_i}$

1.3.2. Helmholtz Energy

$$(nA) \equiv (nU) - T(nS) \quad (1-18)$$

$$d(nA) = d(nU) - Td(nS) - (nS)dT \quad (1-19)$$

$$nA = f(T, nV, n_1, n_2, \dots, n_{Comp}) \quad (1-20)$$

$$\overbrace{d(nA) \leq \left[\frac{\partial(nA)}{\partial T} \right]_{nV,n} dT + \left[\frac{\partial(nA)}{\partial(nV)} \right]_{T,n} d(nV) + \sum_{i=1}^{Comp} \left[\frac{\partial(nA)}{\partial(n_i)} \right]_{T,nV,n_{j \neq i}} dn_i}^{\text{Functional form}} \quad (1-21)$$

$\underbrace{\hspace{10em}}_{-nS} \quad \underbrace{\hspace{10em}}_{-P} \quad \underbrace{\hspace{10em}}_{\mu_i}$

1.3.3. Gibbs Energy

$$(nG) \equiv \overbrace{(nU) + P(nV) - T(nS)}^{\substack{(nH) - T(nS) \\ P(nV) + (nA)}} \quad (1-22)$$

$$d(nG) = \overbrace{d(nU) + Pd(nV) + (nV)dP - Td(nS) - (nS)dT}^{\substack{=d(nH) - Td(nS) - (nS)dT \\ =Pd(nV) + (nV)dP + d(nA)}} \quad (1-23)$$

$$nG = f(T, P, n_1, n_2, \dots, n_{Comp}) \quad (1-24)$$

$$d(nG) \leq \overbrace{\left[\frac{\partial(nG)}{\partial T} \right]_{P,n} dT + \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \sum_{i=1}^{Comp} \left[\frac{\partial(nG)}{\partial(n_i)} \right]_{T,P,n_{j \neq i}} dn_i}_{\substack{\text{Functional form} \\ -nS \quad nV \quad \mu_i}} \quad (1-25)$$

1.4. Applied Framework

Given the basis upon which the fundamental equations were founded, we have come to believe that fluid properties of homogenous fluids at equilibrium are functions of temperature, pressure, and composition only (Van Ness and Abbott 1982). These observations were formalized by Willard Gibbs; for his numerous contributions to the field, it was in his honour that the most readily applied auxiliary function was named. Building atop the fundamental foundations, Gibbs proved that uniformity of temperature, pressure, and composition between the various phases is a necessary criterion to establish an equilibrium state:

$$dT = dP = \sum_{i=1}^{Comp} \mu_i dn_i = 0 \quad (1-26)$$

Furthermore in order for this condition to be valid over multiple phases, an additional and necessary criterion must be established. Given the framework that has already been constructed, the following must also be true for all components:

$$\sum_{p=1}^{Phase} \mu_i^p dn_i^p = 0 \quad (1-27)$$

In context of the conservation of mass principle, this explicitly requires that the chemical potentials of each component across all phases *must be equal*.

1.4.1. Partial Molar Properties

Given the functional dependence of nG that has been established, the mathematical definition of exactness can be used to obtain

$$d(nG) = n \left[\frac{\partial G}{\partial T} \right]_{P,x} dT + n \left[\frac{\partial G}{\partial P} \right]_{T,x} dP + \sum_{i=1}^{Comp} \left[\frac{\partial (nG)}{\partial n_i} \right]_{T,P,n_{j \neq i}} dn_i \quad (1-28)$$

Here the chemical potential can formally be defined as (for convenience),

$$\mu_i \equiv \left[\frac{\partial (nG)}{\partial n_i} \right]_{T,P,n_{j \neq i}} \equiv \left[\frac{\partial (nA)}{\partial (n_i)} \right]_{T,nV,n_{j \neq i}} \equiv \left[\frac{\partial (nH)}{\partial (n_i)} \right]_{nS,P,n_{j \neq i}} \equiv \left[\frac{\partial (nU)}{\partial (n_i)} \right]_{nV,nS,n_{j \neq i}} \quad (1-29)$$

Some insight into the nature of the chemical potential can be gained by application of Euler's theorem on homogeneous functions, in this case, of degree zero:

$$G = \sum_{i=1}^{Comp} x_i \mu_i \quad (1-30)$$

This explicitly states that the chemical potential must be a function of temperature, pressure, and composition (as is the Gibbs energy); furthermore, the chemical potentials must also be intensive properties of the system.

It should now be apparent that this quantity is important, but its current form is not entirely useful; as stated elsewhere, much of the present work in phase-equilibrium thermodynamics is to relate the *abstract* nature of the chemical potential to physically measurable quantities such as temperature, pressure, and composition (Prausnitz, Lichtenthaler and de Azevedo 1986). This need becomes especially apparent after integrating the differential forms of H , A , and G (ref. Auxiliary Properties):

$$nH = T(nS) + \sum_{i=1}^{Comp} n_i \mu_i \quad (1-31)$$

$$nA = -P(nV) + \sum_{i=1}^{Comp} n_i \mu_i \quad (1-32)$$

$$nG = \sum_{i=1}^{Comp} n_i \mu_i \quad (1-33)$$

So the Gibbs energy is the only auxiliary property that can be *entirely* related through the component contributions within the system—useful.

1.4.1.1. Gibbs-Duhem Relation

In the previous section the astute observer would have noticed *two* different relationships describing the Gibbs energy, one describing a *change* and the other an *equilibrium-state*. Moreover each of these relationships was obtained by different mathematical operations, but are they both thermodynamically consistent within the framework that has been built?

In order for both expressions to be correct, they must prove equivalent. If we consider a homogeneous equilibrium state, then any differential change resulting from changes in T , P , n_i must be given by the total differential of G (energy and matter is *conserved*):

$$dG = d\left(\sum_{i=1}^{Comp} x_i \mu_i\right) = \sum_{i=1}^{Comp} x_i d\mu_i + \sum_{i=1}^{Comp} \mu_i dx_i \quad (1-34)$$

For consistency, this expression *must be equivalent* to the exact differential describing the interrelationships of G , T , P , and composition:

$$dG = \left[\frac{\partial G}{\partial T}\right]_{P,x} dT + \left[\frac{\partial G}{\partial P}\right]_{T,x} dP + \sum_{i=1}^{Comp} \underbrace{\left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_{j \neq i}}}_{\mu_i} dx_i \quad (1-35)$$

Accordingly, the following identity is required in order to avoid any contradictions to the thermodynamic framework (built upon observations that have proven universal-truths)—resulting from equating equations (1-34) and (1-35):

$$\left[\frac{\partial G}{\partial T}\right]_{P,x} dT + \left[\frac{\partial G}{\partial P}\right]_{T,x} dP - \sum_{i=1}^{Comp} x_i d\mu_i = 0 \quad (1-36)$$

This identity is commonly known as the *Gibbs-Duhem equation* (also called the zero-function), and represents a condition that must be obeyed (if you will, a grammatical-law of the language of thermodynamics). So if a system at constant temperature and pressure is considered, we once again obtain a relationship explicitly stating the concentration dependence of the chemical potential (clearly important). Moreover, it places a restriction on the simultaneous behaviour of T , P , and μ_i for a single phase ($Comp + 1$ degrees of freedom).

1.4.2. Fugacity as a Solution Property

Given that temperature and pressure are easily measured, a way to determine the chemical potentials is needed before the framework can be put to practical use. As is often the case with abstract concepts, it is often easiest to generalize from a known condition (ideal).

Lewis was the first to consider the chemical potential for a pure ideal gas, and then generalized the results to all systems (Prausnitz, Lichtenthaler and de Azevedo 1986). Using the Gibbs energy function as a starting point, applying the relation to one mole of a single-phase pure fluid at isothermal conditions, he obtained

$$dG_i = V_i dP \quad (1-37)$$

Since an ideal gas represents the simplest *known* condition/relationship, the component volume was replaced with the ideal gas equation:

$$dG_i = \frac{RT}{P} dP = RT d(\ln P) \quad (1-38)$$

The resulting expression quantifies the relationship between the Gibbs energy and pressure for an ideal gas at constant temperature. To generalize his result Lewis introduced a new function *fugacity* to represent the true system pressure (equation 1-39); integrating this equation from a *known* standard state (designated by a superscript 0) yields equation (1-40),

$$dG_i = RT \overbrace{d(\ln f)}^{\text{Ideal gas correction}} \quad (1-39)$$

$$G - G^0 = RT \ln \frac{f}{f^0} \quad (1-40)$$

It should be noted that in order for the fugacity definition to be universally valid, the relationship must reduce to the ideal gas value at the pressure limit (the basis of the derivation). Thus the following criterion is considered to be a *necessary* component of the fugacity definition:

$$\lim_{P \rightarrow 0} \left(\frac{f}{P} \right) = 1 \quad (1-41)$$

1.4.2.1. An Additional Criterion for Phase Equilibrium

As mentioned earlier, the equality of the chemical potentials across each phase is a criterion for phase equilibrium. Given the abstract nature of chemical potentials a new property was defined for convenience – fugacity. Using the fundamental framework, the fugacity will be shown to be a suitable alternative to chemical potential in describing the state of equilibrium. For each component (*i*) in solution, the fugacity (conveniently thought of as a *utility-function*) can be rewritten as

$$d\mu_i \equiv d\bar{G}_i = RT d \ln \hat{f}_i \quad (1-42)$$

$$\therefore \mu_i = \bar{G}_i = G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0} \quad (1-43)$$

$$\lim_{P \rightarrow 0} \left(\frac{\hat{f}_i}{x_i P} \right) = 1 \quad (1-44)$$

Where the circumflex (^) distinguishes the component-fugacity from the solution property (f). For each component in each phase (p); integration at constant temperature yields

$$\mu_i^p(\text{Final}) = \mu_i^p(\text{Initial}) + RT \ln \frac{\hat{f}_i^p(\text{Final})}{\hat{f}_i^p(\text{Initial})} \quad (1-45)$$

Since the integrand is typically evaluated from a known standard state, the *same* initial state can be selected for each component in each phase of the system (it is completely arbitrary). Given the equality of chemical potentials at equilibrium, it can be easily shown that the fugacities in each phase must also be equivalent. For a hypothetical system consisting of phases α through π it can be easily shown that

$$\hat{f}_i^\alpha(\text{Final}) = \hat{f}_i^\beta(\text{Final}) = \dots = \hat{f}_i^\pi(\text{Final}) \quad (1-46)$$

This constitutes a major justification for the introduction of the fugacity as a thermodynamic variable (Van Ness and Abbott 1982).

1.4.2.2. Ideal Mixture

Given the usefulness of fugacity in representing the chemical potential, we can properly define an *ideal mixture* by integrating the utility-function from the *pure* state to the actual state of the *mixture*:

$$\mu_i - \mu_i^0 = RT \ln \frac{\hat{f}_i^{is}}{f_i} = RT \ln \frac{x_i f_i}{f_i} = RT \ln x_i \quad (1-47)$$

Keeping in mind that the chemical potential is an intensive property that, like the Gibbs energy, depends on temperature, pressure, and composition, an *ideal mixture* can be formally defined as

$$\therefore \mu_i(P, T, x) \equiv \mu_i^0(P, T) + RT \ln x_i \quad (1-48)$$

This definition will prove to be useful in developing the following section.

1.4.3. Excess Properties & Activity Coefficients

Since many of the fundamental properties we wish to use are in the form of derivatives, it is often helpful to adopt a standard datum from which to calculate the change. For this purpose it is common practice to relate properties to their *excess* values – property deviations from their ideal-solution values (known condition to actual condition). This concept can be generalized as

$$M^E = M - M^{is} \quad (1-49)$$

Where M represents any *real/actual* property value, M^{is} the ideal solution value, and M^E the excess of that property value; applying this concept to the chemical potential,

$$\mu^E = \mu - \mu^{is} = \underbrace{[\mu - \mu_i]}_{RT \ln \frac{f_i}{x_i}} - RT \ln x_i \quad (1-50)$$

Given that this relationship has proven quite useful in practice, it is common to introduce a convenience variable known as the *activity coefficient*:

$$\gamma_i \equiv \frac{f_i}{x_i} \quad (1-51)$$

$$\therefore \mu^E = RT \ln \gamma_i \quad (1-52)$$

This means that for a real mixture, the chemical potential can be represented by an augmented ideal mixture value:

$$\mu_i(P, T, x) = \mu_i^0(P, T) + RT \ln x_i + \mu^E \quad (1-53)$$

$$= \mu_i^0(P, T) + RT \ln x_i + \underbrace{RT \ln \gamma_i(T, P, x)}_{\substack{\text{Excess contribution} \\ \text{to the ideal solution} \\ \text{value}}} \quad (1-54)$$

1.5.Lattice Theory

Many of the currently used methods are based, at least in some part, upon Lattice Theory. Here the liquid state is viewed as quasi-crystalline state where the individual molecules are *confined* to a region of space within the system (called a *lattice*). The goal of the theory is to determine the energy of the liquid—in classical thermodynamics is the internal energy U —pure or mixed, by accounting for the energies (E_i) of each probable state (p_i^*) of the mixture:

$$U = E = \sum_i p_i^* E_i \quad (1-55)$$

The last equation can be written as in terms of the *conical partition function*, where the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. For a binary mixture the equation takes the form (Prausnitz, Lichtenthaler and de Azevedo 1986),

$$Q = \sum_{N_{12}} g(N_1, N_2, N_{12}) \exp \left[-\frac{E_{total}}{kT} \right] \quad (1-56)$$

Where $g(N_1, N_2, N_{12})$ represents the number of ways molecules of component 1 and 2 can be arranged on the lattice, and the latter term represents the total energy of the lattice.

Theoretical representation of fluid properties is still one of the most complicated and challenging tasks of chemical physics. An exact solution to the problem would necessitate answering the following questions (Malanowski and Anderko 1992):

1. What are the intermolecular forces between molecules?
 - This falls into the realm of quantum mechanics and can be solved exactly only for very simple cases.
2. What is the effect of intermolecular interactions on the spatial arrangement of molecules and, subsequently, their thermodynamic properties?
 - In principle this can be answered by statistical mechanics if a solution to the first problem is known.

Given that no universal theory has yet been found that meets the needs of industry, methods such as Wilson, NRTL, UNIQUAC are often used. Methods like these tend to include a tuning parameter to account for the intermolecular forces between molecules, along with some kind of assumption on the arrangement of the molecules (e.g. local composition & Guggenheim's quasichemical approximation).

1.5.1. Quasichemical Approximation

Guggenheim constructed a lattice theory for molecules of equal size which form mixtures that are not necessarily random ($s^E \neq 0$). Assumptions on the spatial arrangement of molecules within the mixture were made, which resulted in a simplistic representation of mixtures known as the *quasichemical approximation*; given that the derivation is immaterial for discussion purposes the result will just be simply stated (Prausnitz, Lichtenthaler and de Azevedo 1986):

$$\frac{g^E}{RT} = \left(\frac{w}{RT}\right) x_1 x_2 \left[1 - \frac{1}{2} \left(\frac{2w}{zRT}\right) x_1 x_2 + \dots\right] \quad (1-57)$$

Where w represents the *interchange energy* from each new 1-2 contact formed when pure species-1 is mixed with pure species-2, and z represents the number of nearest touching molecules (called the *coordination number*)—see Figure 1.

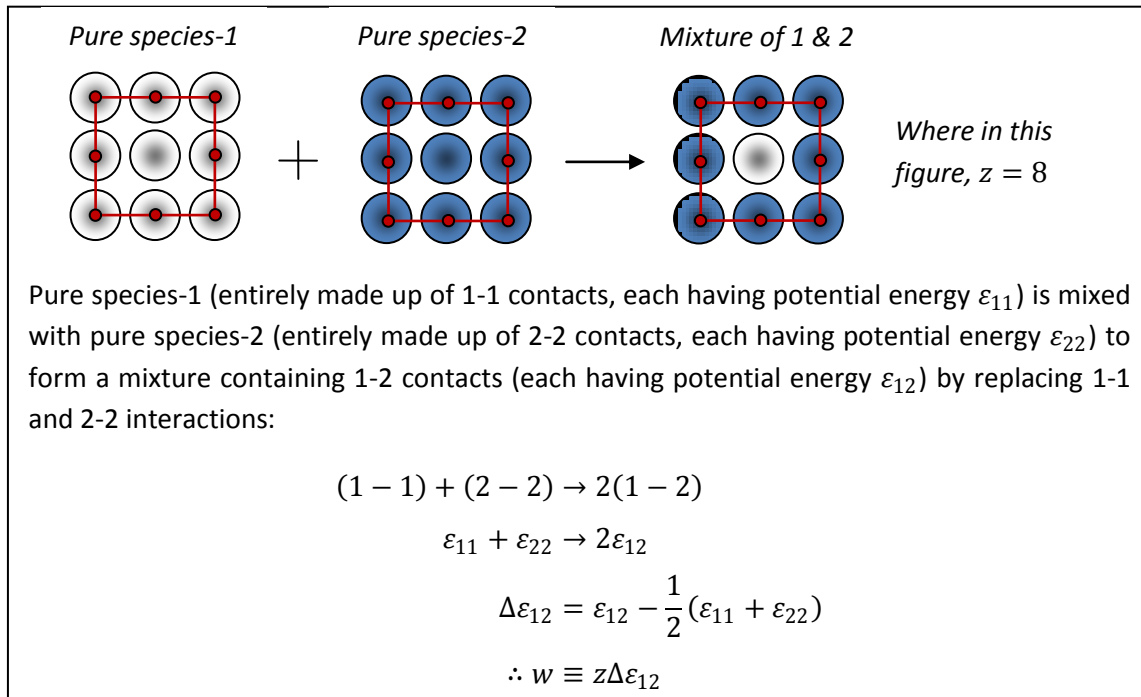


Figure 1: Physical significance of interchange energy. The energy absorbed in the process above is $2w$ (Prausnitz, Lichtenthaler and de Azevedo 1986).

Where the assumption of nonrandomness can be written as (Renon and Prausnitz 1968),

$$x_{21}x_{12} = (1 - x_{21})(1 - x_{12})\exp\left[-\frac{1}{z}(2W_{12} - W_{11} - W_{22})/RT\right] \quad (1-58)$$

It should perhaps be mentioned, priori, that this theory has provided some of the foundations used in the developments of models such as NRTL and UNIQUAC.

2. LITERATURE REVIEW

Given that the main goal of this work is to develop a model that will be of use to industry, an understanding of models currently in use is in order. All proposed equations (no matter the form) are intended to “stand-in” for the Gibbs excess energy relationship

$$g^E = u^E - Ts^E + Pv^E = h^E - Ts^E \quad (2-1)$$

The simplest assumption one can make about g^E is to set it equal to zero (ideal solution) – industrial mixtures are rarely ideal. The next simplest assumption is to set either s^E or h^E equal to zero.

2.1. Algebraic Expressions

If it is assumed that $s^E = 0$ (a concept of regular solutions), then a relationship for h^E that could be solved numerically is needed in order to obtain g^E . Historically h^E was represented by polynomial expansions in the mole fractions or volume fractions, like those resulting in the Margules and Redlich-Kister (1948) expressions.

A general problem with these expansions is that the g^E of a mixture is split into terms corresponding to binary, ternary and higher systems formed by *all* possible components present in the mixture (Malanowski and Anderko 1992):

$$\frac{G^E}{NRT} = g^E = \sum_{i=1}^n \sum_{j=i+1}^n g_{i,j}^E + \sum_{i=1}^n \sum_{j=i+1}^n \sum_{k=j+1}^n g_{i,j,k}^E + \dots \quad (2-2)$$

This relation would require equations describing binary, ternary and higher-order interactions; such a description is highly unrealistic, the number of data increases for each term with the second power of the number of components in the mixture. As with most things complex simplifications are often prudent, and have led to some historically successful relationships (e.g. truncated version of Margules equation).

2.1.1. Pros & Cons

Polynomial expansions were the first models to provide a reasonable representation of *real* mixtures (adhered to the Gibbs-Duhem equation). Many of them can be used today with equal success, but with limitations compared to currently accepted methods. Some observations of their use are listed below for convenience:

- ☒ They are easily applied to two-component systems, and their “tuning” parameters tend to have some physical significance. The equations however do not account for molecular interactions, as will be seen by the local composition methods, which tends to limit their flexibility in accurately describing g^E throughout the entire composition range. Furthermore the equations often lack even a mild temperature dependence term, so they are fundamentally incapable of representing polythermal data
- ☒ Terms can be added as needed and parameters can be defined as functions of temperature to obtain very accurate representation of g^E or phase equilibria data over a wide temperature range; however this would require many experiments to tune the higher-order interactions of the expanded equation, and thus contributes to the limited applicability of such equations—they are not easily extended to mixtures of more than two components.
- ☒ They are often given the merit of being mathematically simple to implement; however given the current state of computing capabilities, it is considered here to be a rather mute point. Yet the equation forms often represent the simplest expressions describing g^E , and their results are rather stable (i.e. predictable). In view of this the methods have found some modern applications in smoothing experimental excess function data (Byer, Gibbs and Van Ness 1973, Malanowski and Anderko 1992, Van Ness 1995).

2.2. Local Composition Methods

An alternate starting point is to assume that $h^E = 0$; this leads to the concept of athermal solutions which has been developed by Flory, Huggins, and others in the study of polymer solutions (Orye and Prausnitz 1965). The Flory-Huggins relationship was successfully modified by Wilson, and has spawned a group of successful models known as *local composition methods*.

2.2.1. Wilson Equation

Although not stated directly in Wilson’s original paper, his development can essentially be considered as an ad-hoc *two-fluid-extension* of a modified Flory-Huggins relationship. He considered mixtures of molecules which not only differ in size, but which also differ in their intermolecular forces (Prausnitz, Lichtenthaler and de Azevedo 1986). The Flory-Huggins equation for athermal mixtures is given by

$$\frac{g^E}{RT} = \sum_{i=1}^{Comp} x_i \ln \frac{\Phi_i}{x_i} \Leftrightarrow \sum_{i=1}^{Comp} x_i \ln x_i \quad (2-3)$$

Where Φ_i is the volume fraction of molecule i and x_i is the mole fraction, and provides a simple measure of a system’s asymmetry; this size affect is given by,

$$\Phi_i = \frac{x_i v_i^L}{\sum_{j=1}^N x_j v_j^L} \quad (2-4)$$

Instead of directly weighting the component sizes to the solution composition, Wilson simply replaced $\ln x_i$ with what he termed the “local composition:”

$$\frac{x_{ij}}{x_{ii}} = \frac{x_j e^{-\varepsilon_{ij}/RT}}{x_i e^{-\varepsilon_{ii}/RT}} \quad (2-5)$$

So that the ratio of i and j around a central i molecule (x_{ii} and x_{ij} respectively) is proportional to their contact energies (ε_{ij} and ε_{ii})—the probability of finding i or j as a neighbour. Wilson used this definition to redefine the volume fractions into the *local* volume fractions ξ_i and ξ_j (Orye and Prausnitz 1965):

$$\xi_i = \frac{x_i v_i^L e^{-\varepsilon_{ij}/RT}}{\sum_{j=1}^N x_j v_j^L e^{-\varepsilon_{ij}/RT}} \quad (2-6)$$

The g^E -form of the Wilson equation is obtained upon substituting the local volume fractions into the Flory-Huggins equation, and introducing the convenience parameter Λ_{ij} :

$$\frac{g^E}{RT} = - \sum_{i=1}^{Comp} x_i \ln \left[\sum_{j=1}^{Comp} x_j \Lambda_{ij} \right] \quad (2-7)$$

Where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} e^{-(\varepsilon_{ij} - \varepsilon_{ii})/RT} \quad (2-8)$$

So instead of directly accounting the *primary* energies of each type of contact (i.e. $\varepsilon_{ij} \{= \varepsilon_{ji}\}$, ε_{ii} , and ε_{jj}) he simplified by introducing *secondary* interaction parameters Λ_{ij} and Λ_{ji} . This enabled Wilson to reduce the number of parameters required for each binary-pair by one (Marcilla, Gomis and Esteban 1995).

Utilizing the language of thermodynamics, the Wilson equation can also be rewritten in terms of activity coefficients as

$$\ln \gamma_i = - \ln \left(\sum_{j=1}^{Comp} x_j \Lambda_{ij} \right) + 1 - \sum_{j=1}^{Comp} \left(\frac{x_j \Lambda_{ji}}{\sum_{k=1}^{Comp} x_k \Lambda_{jk}} \right) \quad (2-9)$$

So like the Flory-Huggins relationship, the Wilson equation contains no explicit part to account for the enthalpic effects of mixing; however unlike the Flory-Huggins equation, the entropic contribution to the Gibbs energy is accounted for by the local composition concept.

2.2.1.1. Pros & Cons

- ☑ As can be seen by the final equation form, this model is easily extended to mixtures of more than two components, and only requires parameters relating to binary interactions.
- ☑ Molecular size differences are taken into account by the ratio of pure component volumes (essentially weighting the binary interaction contributions according to the size of the system components), and has been proven to represent both polar and nonpolar mixtures quite well (Orye and Prausnitz 1965, Bruin 1970, Walas 1985, Prausnitz, Lichtenthaler and de Azevedo 1986, Malanowski and Anderko 1992, Poling, Prausnitz and O'Connell 2001).
- ☑ The parameters $(\varepsilon_{ij} - \varepsilon_{ii})$ are *generally* treated as being temperature independent, thus enabling the equation to be applicable to both isothermal and isobaric data, and even those taken at various pressures and temperatures (Malanowski and Anderko 1992).
 - However mild temperature dependence is built into the equation via $(\varepsilon_{ij} - \varepsilon_{ii})/RT$, and is considered to be an important advantage in the design of isobaric distillation equipment where the temperature varies from plate to plate (Orye and Prausnitz 1965).
 - ☒ Care must be taken when predicting systems exhibiting strong h^E behaviour though; in this case the parameters are highly temperature dependent, and extrapolations necessitate caution. This suggests that a modification where h^E is not assumed zero, and/or inclusion of an explicit temperature dependence would provide an improvement (increased *flexibility*).
- ☒ The Wilson equation, as given, cannot handle liquid-liquid immiscibility.
 - Wilson (1964, Scatchard and Wilson 1964) demonstrated that the g^E prediction could be modified by including an arbitrary multiplier C (later shown to be derivable from the two-liquid theory used to formulate NRTL— (Renon and Prausnitz 1969)):

$$\frac{g^E}{RT} = -C \sum_{i=1}^{Comp} x_i \ln \left[\sum_{j=1}^{Comp} x_j \Lambda_{ij} \right] \quad (1-59)$$

Unfortunately this modification is not easily extended to multicomponent systems; as it has been introduced, the tuning-value would be *unique* for each binary. This suggests an additional area for improvement where sufficient formalism is needed to extend the *concept* to multicomponent LLE systems.

2.2.2. NRTL Equation

Renon & Prausnitz (1968) introduced the concept of the two-fluid model and combined it with Wilson's local composition concept; inclusion of a *nonrandomness* correction laid the foundation for the development of the NRTL equation (non-random, two-liquid).

Scott (1956) proposed that instead of treating mixtures as single-fluids (effectively *averaging* the solution environment), a mixture could be considered as a solution of two *distinct* fluids (one

with molecule i at the centre, and one with molecule j at the centre). Renon adopted this strategy and expressed g^E in terms of two hypothetical fluids, enabling g^E to be calculated *directly* via

$$g^E = x_i \left(g^{(i)} - g_{pure}^{(i)} \right) + x_j \left(g^{(j)} - g_{pure}^{(j)} \right) \quad (2-10)$$

Where $\left(g^{(i)} - g_{pure}^{(i)} \right)$ represents the energy of transferring a pure species into a *hypothetical* mixture environment with energy $g^{(i)}$. In order to account for the number of ji , ii , ij , and jj contacts, this strategy was combined with the local composition construct (the mean local composition around the central i and j molecules). The mixture environments were redefined in terms of local mole fractions as

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \left[\frac{e^{-\alpha g_{ji}/RT}}{e^{-\alpha g_{ii}/RT}} \right] \quad (2-11)$$

Where Renon introduced what he called a *nonrandomness parameter* to scale down the *characteristic* energy differences between j around i and i around i (and vice versa, where $g_{ji} = g_{ij}$); making the appropriate substitutions (see Figure 2), the expressions can be rewritten as

$$x_{ji} = \frac{x_j \exp[-\alpha(g_{ji} - g_{ii})/RT]}{x_j + x_i \exp[-\alpha(g_{ij} - g_{jj})/RT]} \quad (2-1)$$

$$g^E = \sum_{i=1}^{Comp} x_i x_{ji} (g_{ji} - g_{ii}) \quad (2-2)$$

Upon the appropriate differentiation, the NRTL expression for activity coefficients is obtained:

$$\ln \gamma_i = \frac{\sum_{j=1}^{Comp} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{Comp} G_{ki} x_k} + \sum_{j=1}^{Comp} \frac{x_j G_{ji}}{\sum_{k=1}^{Comp} G_{ki} x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{Comp} \tau_{kj} G_{kj} x_k}{\sum_{k=1}^{Comp} G_{kj} x_k} \right) \quad (2-3)$$

Using convenience-variables,

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT} \quad (2-4)$$

$$G_{ji} = \exp(-\alpha \tau_{ji}) \quad (2-5)$$

These definitions can also be used to redefine the excess Gibbs function of NRTL; expressed for a multicomponent mixture as

$$\frac{g^E}{RT} = RT \sum_{i=1}^{Comp} x_i x_{ji} (g_{ji} - g_{ii}) = \sum_{i=1}^{Comp} x_i \frac{\sum_{j=1}^{Comp} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{Comp} G_{ki} x_k} \quad (2-6)$$

So unlike Wilson's equation, the NRTL equation directly calculates the deviation in the Gibbs energy from the ideal Gibbs energy (i.e. it never calculates the entropic part of mixing), and is able to represent multicomponent mixtures with two liquid phases.

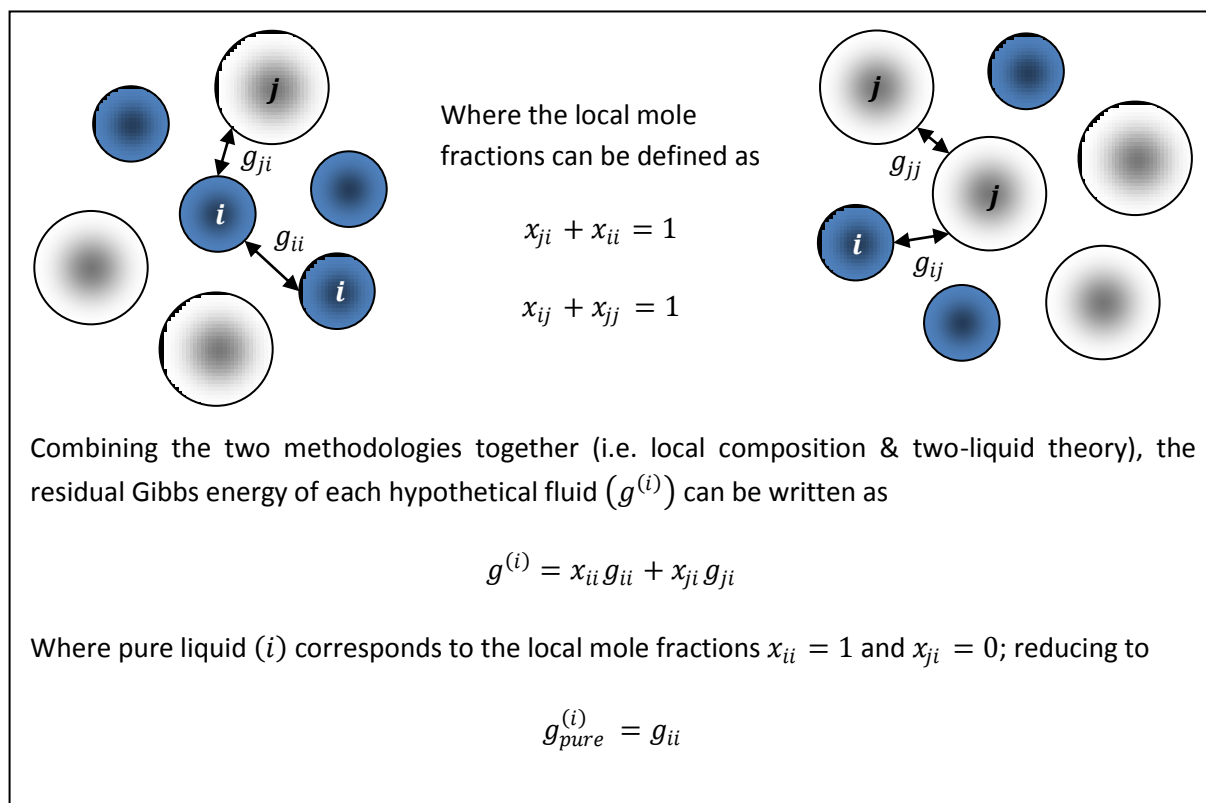


Figure 2: Two cells according to Scott's two-liquid theory of binary mixtures, including the relationships enabling its application to the local composition concept.

2.2.2.1. Nonrandomness Parameter

One of the main benefits of the NRTL equation is its ability to represent mixtures exhibiting partial miscibility. Unlike the empirically modified Wilson equation (G. M. Wilson 1964, Scatchard and Wilson 1964) the NRTL equation is able to represent multicomponent mixtures (i.e. not just binary mixtures) if given an appropriate nonrandomness factor.

In the original derivation of the NRTL equation, relationships were drawn between the nonrandomness factor (α) and Guggenheim's quasichemical approximation—it was shown that α was related to the inverse of the coordination number ($1/z$) that appeared in Guggenheim's expression (which can be *conceptually* considered as $2/z$). Renon made an effort to explicitly mention that the nonrandomness parameter was entirely *empirical*; however it appears that he was clearly guided by the *idea* that the two quantities were related. The defining NRTL relations can be manipulated into a form explicitly showing the nonrandomness as (Renon and Prausnitz 1968):

$$x_{ji}x_{ij} = (1 - x_{ji})(1 - x_{ij}) \exp(-\alpha(2g_{ij} - g_{ii} - g_{jj})/RT) \quad (2-7)$$

Since the coordination number is typically found to be within the range of 6-12 (Renon and Prausnitz 1968, Abrams and Prausnitz 1975, Prausnitz, Lichtenthaler and de Azevedo 1986), the alpha parameter was expected to be on the order 0.1 – 0.3 (later revised to 0.2 – 0.47 based on experimental fittings). He even went so far as to suggest values based on the chemical natures of the mixtures being considered (Renon and Prausnitz 1968)—clearly influenced by the *idea* that alpha was a property of the mixture, but subsequent studies in the field have *eliminated any physical significance* originally attributed to the parameter (Marina and Tassios 1973, Heidemann and Mandhane 1973, Tassios 1976).

2.2.2.2. Pros & Cons

- ☑ Retains the beneficial attributes exhibited by the Wilson equation, and has the additional advantage of being able to describe LLE with a suitable value for α . Moreover the LLE tuning was introduced in a consistent way, thus enabling readily extensions to multicomponent systems (unlike the modification originally proposed by Wilson).
- ☑ Like Wilson's equation there is mild temperature dependence built-in (τ_{ji}).
 - Explicit temperature dependence was later formulated where all three parameters of the NRTL equation were treated as linear functions of temperature (Nagata and Yamada 1973, Walas 1985, Malanowski and Anderko 1992); however for the simultaneous correlation of VLE, γ^∞ , H^E , C_p , y_{AZD} , SLE, and LLE data a quadratic dependence is often required (Rarey 2009). Since explicit temperature dependence increases the number of parameters, it is generally only used on an *as needed basis* in practice.
- ☒ Compared to the original Wilson equation the NRTL model requires the regression of three parameters instead of just two (i.e. conventional wisdom tells us that more experimental data is required to obtain an accurate fit).
 - Renon tried to address this issue by attempting to *predict* the nonrandomness based on the *types* of mixtures being evaluated (Renon and Prausnitz 1968, Renon and Prausnitz 1969, Bruin and Prausnitz 1971), however as mentioned, subsequent studies have eliminated any physical significance originally attributed to the parameter (e.g. Tassios 1976, even showed that $\alpha = -1$ works in many cases). In practice the nonrandomness factor (α) is unceremoniously set to 0.3 (typically results in *stable* predictions with the NRTL equation), and is typically only treated as an adjustable parameter when warranted (i.e. to fit LLE, or in order to stabilize the prediction)—it is entirely considered an *empirical factor*.
 - Further work was even done in an attempt to reduce the NRTL expression to only one parameter by introducing predictions based on pure component properties and molecular structure (Bruin and Prausnitz 1971, Hála 1972); however the simplification leads to a loss in accuracy, as compared to the original form of the NRTL equation.

- ☑ One of the major benefits of the NRTL model is its increased flexibility in representing the g^E curve over the entire composition range (Morisue, Noda and Ishida 1972, Walas 1985).
- ☞ However its flexibility has also led to some instability whereby two two-phase regions are sometimes predicted (Katayama, Kato and Yasuda 1973), hence the range of its intended application should be evaluated for any instability. Any instability is often overcome by setting/changing the value of alpha for the particular regression-run in question.

2.2.3. UNIQUAC Equation

To combine the advantages of the Wilson and NRTL equations Abrams and Prausnitz (1975) proposed a two-parameter equation that extends the quasi-chemical theory of Guggenheim (Malanowski and Anderko 1992)—the universal quasi-chemical (UNIQUAC) equation. Like the NRTL equation, the UNIQUAC equation can be derived from Scott's two-fluid theory; a brief derivation following Maurer and Prausnitz (1978) will be made.

The energy of mixing u^E , the total change in energy in transferring x_1 moles of species 1 from pure liquid 1 and x_2 moles of species 2 from pure liquid 2, is given by:

$$u^E = \underbrace{\frac{1}{2} z x_1 N_A [\theta_{11} U_{11}^{(1)} + \theta_{21} U_{21}^{(1)} - U_{11}^{pure 1}]}_{\text{Hypot hetical fluid (1)}} + \underbrace{\frac{1}{2} z x_2 N_A [\theta_{22} U_{22}^{(2)} + \theta_{12} U_{12}^{(2)} - U_{22}^{pure 2}]}_{\text{Hypot hetical fluid (2)}} \quad (2-8)$$

Where z is the coordination number, N_A is Avogadro's number, $U_{21}^{(1)}$ represents the potential energy of 2-1 neighbours in hypothetical fluid (1)—similar explanations for other combinations—and where the *local* surface fractions (θ) obey the following conservation equation for *each* component i in the mixture ($i = 1$ to *Comp*):

$$\sum_{j=1}^{Comp} \theta_{ji} = 1 \quad (2-9)$$

And similar to Wilson (1964), the *local* surface fractions are defined by (and vice versa for $\theta_{ij} / \theta_{jj}$),

$$\frac{\theta_{ji}}{\theta_{ii}} = \frac{\theta_j}{\theta_i} \exp\left(-\frac{\frac{1}{2} z (U_{ji} - U_{ii})}{kT}\right) \quad (2-10)$$

Where the surface area fractions is given by

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{Comp} q_j x_j} \quad (2-11)$$

$$q_i = \sum_{k=1}^{\text{Group}} \nu_k Q_k \quad (2-12)$$

Given the conservation equations, and assuming that $U_{11}^{(1)} = U_{11}^{\text{pure } 1}$ and $U_{22}^{(2)} = U_{22}^{\text{pure } 2}$, equation (2-8) can be simplified as

$$u^E = x_1 \theta_{21} q_1 \underbrace{\left\{ \frac{1}{2} z N_A (U_{21} - U_{11}) \right\}}_{\Delta u_{21}} + x_2 \theta_{12} q_2 \underbrace{\left\{ \frac{1}{2} z N_A (U_{12} - U_{22}) \right\}}_{\Delta u_{12}} \quad (2-13)$$

Although internal energy is more intuitive, an expression for g^E is needed for practical calculations. This translation can be made by using one of the subtleties of classical thermodynamics (Elliott and Lira 1999),

$$T \left(\frac{\partial(A/RT)}{\partial T} \right)_V = \frac{T}{RT} \left(\frac{\partial U}{\partial T} \right)_V - \frac{TU}{RT^2} - \frac{T}{R} \underbrace{\left(\frac{\partial S}{\partial T} \right)_V}_{= \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V} = - \frac{U}{RT} \quad (2-14)$$

Integration of equation (2-14) and substituting equation (2-13)—assuming that Δu_{ji} and Δu_{ij} are independent of temperature—yields:

$$\int_{\infty}^T d \left(\frac{a^E}{RT} \right) = \frac{a^E}{RT} - \frac{a^E}{RT} \Big|_{\infty} = - \int_{\infty}^T d \left(\frac{u^E}{RT^2} \right) dT \quad (2-15)$$

$$\frac{a^E}{RT} - \underbrace{\frac{a^E}{RT} \Big|_{\infty}}_{\substack{\text{forms an} \\ \text{athermal} \\ \text{mixture}}} = - \sum_{i=1}^{\text{Comp}} \left[\sum_{j=1}^{\text{Comp}} x_i q_i \theta_j \underbrace{\exp \left(- \frac{\Delta u_{ji}}{RT} \right)}_{\substack{\text{energy} \\ \text{parameter} \\ \equiv \tau_{ji}}} \right] \quad (2-16)$$

Where at very high temperatures the enthalpic contribution becomes very small compared to entropic one, and it is assumed that components i and j form an athermal mixture; the equation of Guggenheim is used for molecules of arbitrary size and shape (Maurer and Prausnitz 1978):

$$\begin{aligned} \frac{a^E}{RT} \Big|_{\infty} &= \left(\frac{a^E}{RT} \right)_{\text{athermal}} = - \left(\frac{S^E}{R} \right)_{\text{combinatorial}} \\ &= \sum_{i=1}^{\text{Comp}} \left(x_i \ln \frac{\Phi_i}{x_i} \right) + \frac{z}{2} \sum_{i=1}^{\text{Comp}} \left(q_i x_i \ln \frac{\theta_i}{\Phi_i} \right) \end{aligned} \quad (2-17)$$

Where the segment/volume fractions (Φ_i) are calculated as

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{\text{Comp}} r_j x_j} \quad (2-18)$$

$$r_i = \sum_{k=1}^{\text{Group}} \nu_k R_k \quad (2-19)$$

At low pressures the excess volume of mixing liquids, relative to the other contributions, is quite small (Elliott and Lira 1999), and the assumption of Hildebrand and Scott can be reasonably be applied:

$$(a^E)_{T,P} \approx (g^E)_{T,P} = g^{E(C)} + g^{E(R)} \quad (2-20)$$

Where the *combinatorial* term ($g^{E(C)}$) represents the entropic contributions to the mixture property (interactions resulting from molecular differences in size and shape), and where the *residual* ($g^{E(R)}$) accounts for the enthalpic contributions (energetic interactions of the solution). With the appropriate partial differentiation, the activity coefficients can be obtained as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2-21)$$

$$\begin{aligned} \ln \gamma_i^C &= \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{\text{Comp}} (x_j l_j) \\ &= \ln \Phi'_i + \frac{z}{2} q_i \ln \frac{\theta'_i}{\Phi'_i} + l_i - \Phi'_i \sum_{j=1}^{\text{Comp}} (x_j l_j) \end{aligned} \quad (2-22)$$

$$\begin{aligned} \ln \gamma_i^R &= q_i \left[1 - \ln \left(\sum_{j=1}^{\text{Comp}} \theta_j \tau_{ji} \right) - \sum_{j=1}^{\text{Comp}} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{\text{Comp}} \theta_k \tau_{kj}} \right] \\ &= q_i \left[1 - \ln \left(\sum_{j=1}^{\text{Comp}} x_j \theta'_j \tau_{ji} \right) - \sum_{j=1}^{\text{Comp}} \frac{x_j \theta'_j \tau_{ij}}{\sum_{k=1}^{\text{Comp}} x_k \theta'_k \tau_{kj}} \right] \end{aligned} \quad (2-23)$$

Where l_i has been defined for convenience, and where θ'_i and Φ'_i are often introduced to remove the singularity that develops at $x_i = 0$.

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (2-24)$$

$$\theta'_i = \frac{\theta_i}{x_i} \quad (2-25)$$

$$\Phi'_i = \frac{\Phi_i}{x_i} \quad (2-26)$$

2.2.3.1. Pros & Cons

- ☑ Like Wilson and NRTL there is a built in temperature dependence that is assumed valid over moderate ranges.
- ☑ Like the NRTL equation UNIQUAC can represent LLE; however it only requires two adjustable parameters per binary (versus the three needed for NRTL).
- ☑ Given its theoretical basis, the UNIQUAC model is generally accepted as being more widely applicable (there is a greater *comfort-factor* in its use), and it is capable of representing mixtures exhibiting different types of interactions between molecules (possibly superior representation of mixtures of widely different molecular sizes).
 - ☒ However the UNIQUAC equation is more complicated, and has been shown to be less accurate than the NRTL and Wilson equations (Malanowski and Anderko 1992). Likely much of its support stems from its use in group contribution methods such as UNIFAC, where there is a great deal of effort being expended.

2.2.4. General Discussion

Wilson's concept of local composition has resulted in several successful methods that are still most widely used in industry today (i.e. Wilson, NRTL, and UNIQUAC equations). Given the importance of these methods much effort has been spent on trying to understand Wilson's use of *local composition* and the equations based on it (McDermott and Ashton 1977, Maurer and Prausnitz 1978, Mollerup 1981, Kemény and Rasmussen 1981, Hu, Azevedo and Prausnitz 1983, Hoheisel and Kohler 1984, Mansoori 1985, Góral 1995). Given UNIQUAC's stronger theoretical foundation it is often viewed in a more favourable light than Wilson or NRTL, although the method typically underperforms in comparison tests (Lafyatis, et al. 1989, Malanowski and Anderko 1992).

Practitioners will often have their *favourites* for one reason or another; however choices should be made based on which method provides the best results on a case by case basis. When considering modelling applications on the other hand, *generalizations* are often tactfully employed since individual unit operations must use a *single* g^E model to represent the phase behaviour of multicomponent streams in a consistent manner. A judicious choice must often be made; in the context of the pros and cons already stated for each method, these additional *guidelines* seem appropriate for practical use:

- If it is known a priori that LLE does not exist then either Wilson or NRTL can be used with equivalent results. Wilson describes steep ascending slopes towards γ_i^∞ better than NRTL; else, preference is often given to the NRTL equation in view of its greater flexibility in representing the intricacies of various g^E shapes.
- If it is known, or not known, a priori that LLE exists then either NRTL or UNIQUAC can be employed. Preference in this case is usually given to NRTL, given that its increased flexibility (Morisue, Noda and Ishida 1972, Walas 1985) tends to give superior results over those of UNIQUAC (Lafyatis, et al. 1989, Malanowski and Anderko 1992).

- Although the Wilson equation cannot predict phase splitting, it can still predict realistic VLE behaviour inside the miscibility gap without stability tests (Rarey 2009).

2.3. Group Contribution Methods

The idea that solutions can be represented by a mixture of molecular-groups is generally credited to Langmuir (Deal and Derr 1968, Fredenslund, Jones and Prausnitz 1975, Kojima and Tochigi 1979), with contributing work performed by Brønsted & Koefoed (Hála 1978). This concept was later formalized into the *solution of groups* (SOG) concept by Wilson & Deer (1962), and provides a common foundation on which all group contribution g^E models are based. Given the industrial importance of these methods, a derivation following Hála (1978) will be presented here.

A solution can conceptually be considered a solution of pure components ($X, Y, \dots Comp$) at constant temperature and pressure:

$$n_1X + n_2Y + \dots + n_{\#}Comp; [T, P] \quad (2-27)$$

The components can be conceptually *fragmented* and represented as a combination of molecular-groups ($I, J, \dots Group$)

$$\begin{aligned} n_1X &= v_1^{(1)}I + v_2^{(1)}J + \dots + v_3^{(1)}Group \\ n_2Y &= v_1^{(2)}I + v_2^{(2)}J + \dots + v_3^{(2)}Group \\ &\vdots \\ n_{\#}Comp &= v_1^{(\#)}I + v_2^{(\#)}J + \dots + v_{*}^{(\#)}Group \end{aligned} \quad (2-28)$$

Where $v_{Group}^{(Comp)}$ represents the number of molecular group types in each pure component (in mols); considering this we can equally write the overall balance in terms of the molecular groups as

$$\underbrace{[n_1X + n_2Y + \dots + n_{\#}Comp]}_{\text{Solution of components}} = \underbrace{[v_1I + v_2J + \dots + v_kK + \dots + v_{*}Group]}_{\text{Solution of groups}} \quad (2-29)$$

Where v_k represents the total number of k -groups within the mixture (also in moles)

$$v_k = v_k^{(1)} + v_k^{(2)} + \dots + v_k^{(\#)} \quad (2-30)$$

In a similar stepwise fashion, we can equally write the excess Gibbs energy in terms of groups for a constant temperature and pressure process:

$$G^E = G - G^{is} \equiv \underbrace{\sum_{k=1}^{Group} \nu_k \hat{\mu}_k^E}_{\text{SOG of the mixture (mixture value)}} - \underbrace{\sum_{k=1}^{Group} \sum_{j=1}^{Comp} \nu_k^j \hat{\mu}_k^{E(j)}}_{\text{Solution of pure groups (ideal solution value)}} ; [T, P] \quad (2-31)$$

The excess Gibbs energy now needs to be transformed into something more readily applied in VLE calculations – the activity coefficient,

$$\mu^E = \sum_{i=1}^{Comp} \left[\frac{\partial(G^E)}{\partial n_i} \right]_{T,P,n_{j \neq i}} dn_i \equiv RT \sum_{i=1}^{Comp} \ln \gamma_i \quad (2-32)$$

This defining-relationship is now applied to each term in the G^E expression of SOG,

$$\frac{\partial}{\partial n_i} \left(\sum_{k=1}^{Group} \nu_k \hat{\mu}_k^E \right) = \sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \hat{\mu}_k^E \quad (2-33)$$

$$\frac{\partial}{\partial n_i} \left(\sum_{k=1}^{Group} \sum_{j=1}^{Comp} \nu_k^j \hat{\mu}_k^{E(j)} \right) = \sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \hat{\mu}_k^{E(i)} \quad (2-34)$$

Making the appropriate substitutions into the activity coefficient expression results in the fundamental relationship of the SOG construct:

$$\begin{aligned} \mu^E &= \left[\sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \hat{\mu}_k^E - \sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \hat{\mu}_k^{E(i)} \right] \quad (2-35) \\ &= \sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \left(\hat{\mu}_k^E - \hat{\mu}_k^{E(i)} \right) \\ &\equiv RT \sum_{i=1}^{Comp} \ln \gamma_i \end{aligned}$$

This is often cited in literature as

$$RT \sum_{i=1}^{Comp} \ln \gamma_i = \sum_{k=1}^{Group} \sum_{i=1}^{Comp} \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (2-36)$$

By making the following definitions for convenience:

$$\mu_i^E = RT \ln \gamma_i \quad [=] \text{ Mixture property} \quad (2-37)$$

$$\hat{\mu}_k^E = RT \ln \Gamma_k \quad [=] \text{ SOG property} \quad (2-38)$$

$$\hat{\mu}_k^{E(i)} = RT \ln \Gamma_k^{(i)} [=] \text{ Pure-Group property} \quad (2-39)$$

The big assumption here is that group contributions are taken to be additive, and that the groups are not changed when combining them into different molecules (proximity effect).

2.3.1. ASOG Method

Wilson & Dear (1962) showed that the SOG construct could successfully be used for making estimates from limited amounts of data – a large monetary incentive for industry. This early success paved the way for the analytical solution of groups' equation (ASOG), arguably the first method sufficiently developed for direct use by industry (Kojima and Tochigi 1979).

Like Wilson & Dear it was assumed that the excess chemical potential ($RT \ln \gamma_i$) is comprised of two separate contributions:

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{Combinatorial contribution}} + \underbrace{\ln \gamma_i^R}_{\text{Residual contribution}} \quad (2-40)$$

Where like UNIFAC, the *combinatorial* term accounts for differences in molecular size, and the *residual* term accounts for the intermolecular forces of the molecules. Differences in molecular size were taken into account using a modified Flory-Huggins relation:

$$\ln \gamma_i^C \equiv \ln \gamma_i^{FH} = \ln R_i^* + 1 - R_i^* \quad (2-41)$$

Where the convenience variable R_i^* is defined as (Naidoo 2007),

$$R_i^* \equiv \frac{\sum_{k=1}^{Group} v_{ki}}{\sum_{k=1}^{Group} \sum_{j=1}^{Comp} v_{kj} x_j} [=] \text{ Pure-component group ratio of the SOG} \quad (2-42)$$

And the residual term is calculated using the fundamental SOG relationship that was derived in the preceding section:

$$\ln \gamma_i^R = \sum_{k=1}^{Group} v_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (2-43)$$

The Wilson equation was adapted to the SOG construct and used to calculate the pure-group activities and the activities of the groups in solution:

$$\ln \Gamma_k = 1 - \ln \left(\sum_{m=1}^{\text{Groups}} X_m \Psi_{mk} \right) - \sum_{n=1}^{\text{Groups}} \left(\frac{X_n \Psi_{kn}}{\sum_{m=1}^{\text{Groups}} X_m \Psi_{mn}} \right) \quad (2-44)$$

$$\ln \Gamma_k^{(i)} = 1 - \ln \left(\sum_{m=1}^{\text{Groups}} X_{mi}^{(i)} \Psi_{mk} \right) - \sum_{n=1}^{\text{Groups}} \left(\frac{X_{ni}^{(i)} \Psi_{kn}}{\sum_{m=1}^{\text{Groups}} X_{mi}^{(i)} \Psi_{mn}} \right) \quad (2-45)$$

Where

$$X_m = \frac{\sum_{i=1}^{\text{Comp}} X_i v_{mi}}{\sum_{i=1}^{\text{Comp}} \sum_{m=1}^{\text{Group}} X_i v_{mi}} \quad [=] \text{ Mixture group-fractions} \quad (2-46)$$

$$X_{mi}^{(i)} = \frac{v_{ki}}{\sum_{m=1}^{\text{Groups}} v_{mi}} \quad [=] \text{ Pure-group fractions} \quad (2-47)$$

And the group interaction energies are obtained from

$$\Psi_{mk} = \exp \left(\zeta_{mk} + \frac{\xi_{mk}}{T} \right) \quad (2-48)$$

Where Ψ_{mk} are the group interaction parameters attributed to groups m and k , where $\Psi_{mk} \neq \Psi_{km}$ and $\Psi_{mm} = 1$. So here the temperature dependence is explicitly correlated using two group interaction parameters ζ_{mk} and ξ_{mk} (Tochigi and Kojima 1976, Tochigi, Minami and Kojima 1977, Kojima and Tochigi 1979) whereas LC-equations *typically* only make use of an implied temperature relationship.

2.3.2. UNIFAC Method

The UNIFAC method is similar to the ASOG method except for the equations used to represent the combinatorial and residual contributions of the solute-activity. The UNIQUAC method was adopted as an alternative to the Flory-Huggins and Wilson adaptations used in ASOG; it was from this extension of UNIQUAC that gave UNIFAC its name (*UNIQUAC Functional-group Activity Coefficient model*). Given the promising results of UNIQUAC at the time, the decision was made to see if the benefits would extend into the SOG concept (Fredenslund, Jones and Prausnitz 1975).

The group fractions in the mixture and the pure component group fractions are calculated as in ASOG, and likewise with the residual term but without the built-in temperature dependence:

$$\Psi_{mk} = \exp \left(-\frac{(\varepsilon_{mk} - \varepsilon_{kk})}{T} \right) \quad (2-49)$$

As in the ASOG method the application of UNIQUAC to SOG requires *adaptations* to the standard UNIQUAC terms. The pure component properties are transformed into the sum of the group volume and area parameters (R_k and Q_k):

$$r_i = \sum_{k=1}^{\text{Group}} v_k^{(i)} R_k \quad [=] \text{ pure group volumes} \quad (2-50)$$

$$q_i = \sum_{k=1}^{\text{Group}} v_k^{(i)} Q_k \quad [=] \text{ pure group surface areas} \quad (2-51)$$

And the group activity coefficient Γ_k in the mixture, and pure group activity coefficients $\Gamma_k^{(i)}$ are represented as

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_{m=1}^{\text{Group}} \Theta_m \Psi_{mk} \right) - \sum_{m=1}^{\text{Group}} \frac{\Theta_m \Psi_{km}}{\sum_{n=1}^{\text{Group}} \Theta_n \Psi_{nm}} \right] \quad (2-52)$$

$$\ln \Gamma_k^{(i)} = Q_k \left[1 - \ln \left(\sum_{m=1}^{\text{Group}} \Theta_m^{(i)} \Psi_{mk} \right) - \sum_{m=1}^{\text{Group}} \frac{\Theta_m^{(i)} \Psi_{km}}{\sum_{n=1}^{\text{Group}} \Theta_n^{(i)} \Psi_{nm}} \right] \quad (2-53)$$

Where

$$\Theta_m = \frac{Q_m X_m}{\sum_{n=1}^{\text{Group}} Q_n X_n} \quad (2-54)$$

$$\Theta_m^{(i)} = \frac{Q_m X_{mi}^{(i)}}{\sum_{n=1}^{\text{Group}} Q_n X_{ni}^{(i)}} \quad (2-55)$$

2.3.3. General Discussion

Both ASOG and UNIFAC have been amply tested in literature, but considerably more effort has been expended on the UNIFAC model (and its modifications). In this section the general differences between the two methods will be discussed: concentration dependence, temperature dependence, and group definitions.

2.3.3.1. Concentration Dependence

Since the formalization of the SOG concept in 1962 improvements have been made by incorporating better concentration dependent relationships. Up until the introduction of the Wilson

equation in 1964 industry had to rely on cumbersome algebraic and empirical equations (usually derived on a case by case basis); given that the Wilson equation was proving superior to other methods in practice at the time, it seems quite logical that the Wilson equation was extended to the SOG concept. This extension (ASOG) was being formulated as early as 1968 (Deal and Derr 1968), and eventually was further developed with practitioners in mind (Kojima and Tochigi 1979).

As previously discussed the success of Wilson paved the way for other local-composition models like NRTL (Renon and Prausnitz 1968) and UNIQUAC (Abrams and Prausnitz 1975). In view of the benefits of UNIQUAC previously discussed, and given that the expression is written as a combination of combinatorial and residual contributions, it seems natural to extend the expression to the SOG concept (Fredenslund, Jones and Prausnitz, Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures 1975). Like ASOG the method was further developed with practitioners in mind (Fredenslund, Gmehling, et al. 1977).

The *original* methods as presented seem to give about equal reliability, but the UNIFAC method was singled out for further development (J. Gmehling 2009). One can only surmise that this decision was likely based on the broader applicability of the UNIQUAC LC-equation as compared to Wilson, given that Wilson's inability to represent LLE becomes mute upon application of the SOG construct (Rizzi and Huber 1981).

2.3.3.2. Combinatorial Contribution

The effect of combinatorial expressions on the ASOG and UNIFAC predictions does not seem to have been the subject of much research; the limited amount of work that has been done has historically been limited to the UNIFAC method. Early work to address the predictive results for asymmetric systems led to the following UNIFAC modification of the combinatorial expression (Weidlich and Gmehling 1987):

$$\ln \gamma_i^C = 1 - \Phi_i' + \ln \Phi_i' - 5q_i \left(1 - \frac{\Phi_i}{\theta_i} + \ln \frac{\Phi_i}{\theta_i} \right) \quad (2-56)$$

Where the $\frac{3}{4}$ term was introduced into Φ_i' to correct for the overly large combinatorial contribution of the original UNIFAC expression (Thomas and Eckert 1984):

$$\Phi_i' = \frac{r_i^{3/4} x_i}{\sum_{j=1}^{Comp} r_j^{3/4} x_j} \quad (2-57)$$

2.3.3.3. Temperature Dependence

A major difference between the ASOG and the *original* UNIFAC equation was their treatment of the group-temperature-dependence. Seemingly influenced by work done on the temperature dependence of ASOG (Tochigi and Kojima 1976, Tochigi, Minami and Kojima 1977, Kojima and

Tochigi 1979, Tochigi, et al. 1981), the temperature dependence of UNIFAC was expanded (Weidlich and Gmehling 1987):

$$\Psi_{mk} = \exp \left[- \left(\frac{(\varepsilon_{mk}^a - \varepsilon_{kk}^a)}{a_{mk}} + \frac{(\varepsilon_{mk}^b - \varepsilon_{kk}^b)}{b_{mk}} T + \frac{(\varepsilon_{mk}^c - \varepsilon_{kk}^c)}{c_{mk}} T^2 \right) / T \right] \quad (2-58)$$

2.3.3.4. Definition of Groups

Another major difference between ASOG and UNIFAC relations are the group definitions used by each. This difference is especially boisterous considering that the whole principle behind SOG rests on the *additivity* of functional groups; given the historic ambiguity of defining functional groups, the specific details concerning the differences are inconsequential.

It is of interest to note, however, that the lack of theoretical basis has been given some attention (Wu and Sandler 1991)^{a, b}. Unfortunately it appears that little consideration has been given to the promising results...

2.3.3.5. Present Status

The *modified UNIFAC* (Dortmund) method encompasses the changes to the combinatorial and temperature-dependent expressions that were covered in the preceding sections (Weidlich and Gmehling 1987). This modification has essentially narrowed the fundamental differences between the ASOG and UNIFAC methodologies; the modified combinatorial expression basically provides a middle-of-the-road representation between the two *original* methods, and the temperature-dependence was subsequently extended to include a quadratic dependence.

The largest difference left between ASOG and modified UNIFAC (Do.) is the quality of the data used to determine their parameters; clearly in this regards the UNIFAC and modified UNIFAC (Do.) methods have exceedingly benefited (Weidlich and Gmehling 1987, Gmehling, Li and Schiller 1993, Gmehling, et al. 1993, Gmehling, Lohmann, et al. 1998, Lohmann, Joh and Gmehling 2001, Gmehling, Wittig, et al. 2002, Fischer, Kleiber and de Loos 2007, J. Gmehling 2009).

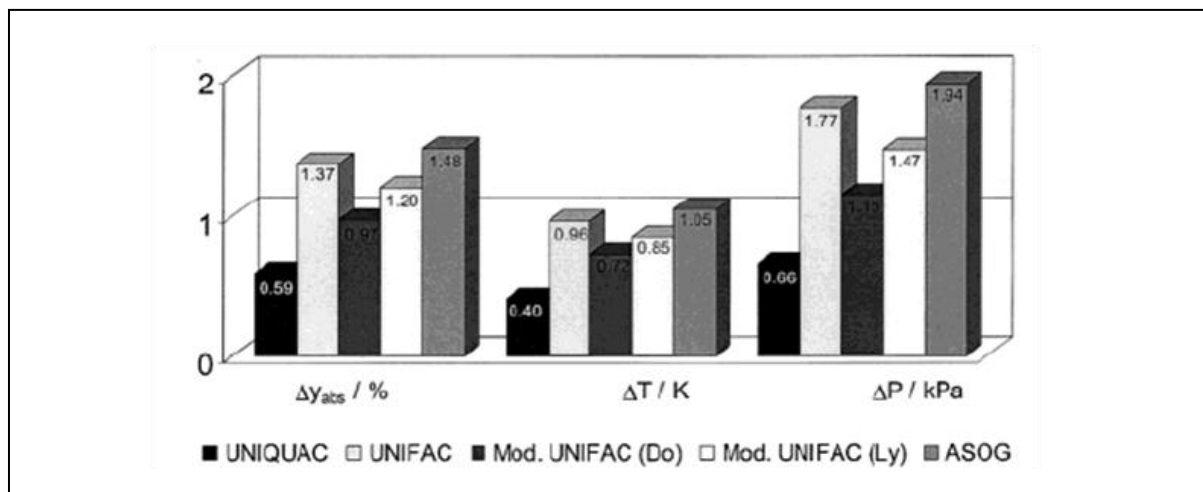


Figure 3: Mean deviations between experimental and predicted VLE data for 2400 consistent VLE data sets (Lohmann, Joh and Gmehling 2001)

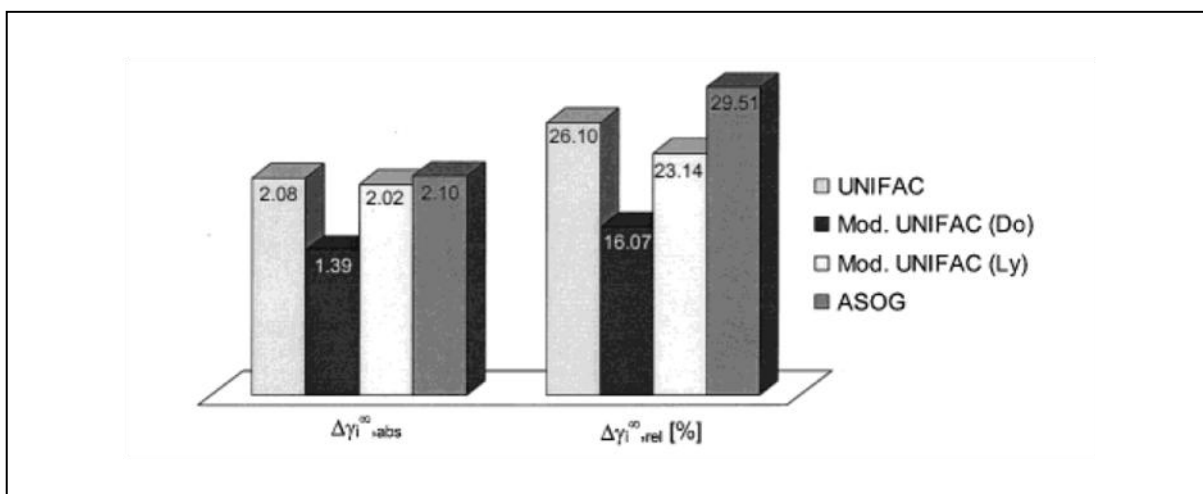


Figure 4: Mean deviations between experimental and predicted activity coefficients at infinite dilution for 13,500 data points (Lohmann, Joh and Gmehling 2001).

3. Proposed Method

Since the goal is to develop a useful method for industry, the formulation of a *hybrid method* should incorporate the following features:

1. The method should reduce to the *standard* from of the SOG concept when no experimental data exists. This will facilitate a drop in replacement (or at least an alternative) of current group contribution methods used by practitioners.
2. The hybrid method should also be kept as *simple* as possible to facilitate its incorporation into existing industrial-software (assuming that the concept is proven advantageous).
3. In order for the hybrid method to be *generally applicable*, the formulation should obey the formalism of the SOG concept throughout the entire composition range.

A simple augmentation meeting all of the above criteria is

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{Combinatorial contribution}} + \overbrace{\underbrace{\ln \gamma_i^R}_{\text{Residual contribution}} + \underbrace{\ln \gamma_i^{RT}}_{\text{Residual Tuning}}}_{\text{Residual affects}} \quad (3-1)$$

3.1. Combinatorial Term

Recent work performed by Bruce Moller (2008) compared various combinatorial expressions. The study evaluated the combinatorial equations of Guggenheim-Staverman, mod. UNIFAC, and a free volume expression named GK-FV. Given that the tested solutes were not polymers, it was surprising that GK-FV generally proved superior. At face value this suggests that combinatorial contributions should include free volume (FV) effects, even though this concept was initially developed for polymer applications (Moller 2008):

$$\ln \gamma_i^C \equiv \ln \gamma_i^{C(FV)} = \ln \frac{\Phi_i^{FV}}{x_i} + 1 - \frac{\Phi_i^{FV}}{x_i} - q_i \frac{z}{2} \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (3-2)$$

Here the free volume represents the volume not occupied by the solution molecules; defined by,

$$\Phi_i^{FV} = \frac{x_i V_i^{FV}}{\sum_{j=1}^{\text{Comp}} x_j V_j^{FV}} \quad (3-3)$$

$$V_i^{FV} = v_i - \Phi_i \quad (3-4)$$

During the study large negative deviations were predicted with the GK-FV equation when the size of the solute became larger than the size of the solvent, to overcome this limitation a modification to the GK-FV was proposed (Moller 2008); generalizing the result,

$$\ln \gamma_i^{C(FV^*)} = \ln \frac{V_i^{FV}}{x_i} + 1 - \frac{V_i^{FV^*}}{x_i} - q_i \frac{z}{2} \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (3-5)$$

Where

$$V_i^{FV^*} = (v_i)^{2/3} - (\Phi_i)^{2/3} \quad (3-6)$$

Since the modification provides a far better prediction for large solutes in small solvents, while maintaining near-equivalent results for small solutes in larger solvents, the combinatorial expression will be incorporated in the study of the proposed hybrid method.

3.2. Residual Term

Given that the UNIQUAC tends to greatly over predict two-phase regions (Lafyatis, et al. 1989) this study opts to use the NRTL equation to develop the concept of the hybrid group contribution model. Furthermore, the increased flexibility of the NRTL equation seems amply suited for the tuning portion of the hybrid method:

$$\ln \gamma_i^R = \sum_{k=1}^{Group} v_{ki} \left[\underbrace{\left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right)}_{\text{Standard group contributions}} + \underbrace{\left(\ln \Gamma_k^* - \ln \Gamma_k^{*(i)} \right)}_{\text{Group adjustments}} \right] \quad (3-7)$$

Where $\ln \Gamma_k$ and $\ln \Gamma_k^{(i)}$ would represent the *standard* group predictions obtained for group parameters fitted to the NRTL expression over *many* experimental datasets.

$$\ln \Gamma_k = \frac{\sum_{m=1}^{Group} T_{mk} \Psi_{mk} X_m}{\sum_{m=1}^{Group} \Psi_{mk} X_m} + \sum_{m=1}^{Group} \frac{X_m \Psi_{mk}}{\sum_{n=1}^{Group} \Psi_{nk} X_n} \left(\tau_{km} - \frac{\sum_{n=1}^{Group} T_{nm} \Psi_{nm} X_m}{\sum_{n=1}^{Group} \Psi_{nm} X_n} \right) \quad (3-8)$$

$$\ln \Gamma_k^{(i)} = \frac{\sum_{m=1}^{Group} T_{mk} \Psi_{mk} X_{mi}^{(i)}}{\sum_{m=1}^{Group} \Psi_{mk} X_{mi}^{(i)}} + \sum_{m=1}^{Group} \frac{X_{mi}^{(i)} \Psi_{mk}}{\sum_{n=1}^{Group} \Psi_{nk} X_{ni}^{(i)}} \left(\tau_{km} - \frac{\sum_{n=1}^{Group} T_{nm} \Psi_{nm} X_{ni}^{(i)}}{\sum_{n=1}^{Group} \Psi_{nm} X_{ni}^{(i)}} \right) \quad (3-9)$$

Using *convenience-variables* for the standard group contributions

$$T_{mk} = - \left(\underbrace{(\varepsilon_{mk}^a - \varepsilon_{kk}^a)}_{a_{mk}} + \underbrace{(\varepsilon_{mk}^b - \varepsilon_{kk}^b)}_{b_{mk}} T + \underbrace{(\varepsilon_{mk}^c - \varepsilon_{kk}^c)}_{c_{mk}} T^2 \right) / T \quad (3-10)$$

$$\Psi_{mk} = \exp(-T_{mk}) \quad (3-11)$$

Where Ψ_{mk} are the group interaction parameters attributed to groups m and k ($\Psi_{mk} \neq \Psi_{km}$).

In fitting the parameter matrix for the *standard* groups, it seems prudent to fix the nonrandomness parameter; given that typical values of α vary from 0.2 – 0.47, a fixed value of 0.3 will be used. If the use of a fixed value ($\alpha = 0.3$) leads to erroneous results, the parameter will need to be included in the regression of the regression of the standard groups. This should support the regression of group parameters that will be *generally applicable*, a requirement dictated by industrial use of such methods (in accordance with feature no.1).

As mentioned $\ln \Gamma_k^*$ and $\ln \Gamma_k^{*(i)}$ will represent the *corrections* to the standard group values, thus enabling practitioners to tune parameters on a system by system basis. The corrections will use a slightly altered form (distinguished by the $*$ superscript):

$$\ln \Gamma_k^* = \frac{\sum_{m=1}^{Group} T_{mk} \Psi_{mk}^* X_m}{\sum_{m=1}^{Group} \Psi_{mk}^* X_m} + \sum_{m=1}^{Group} \frac{X_m \Psi_{mk}^*}{\sum_{n=1}^{Group} \Psi_{nk}^* X_n} \left(\tau_{km} - \frac{\sum_{n=1}^{Group} T_{nm} \Psi_{nm}^* X_m}{\sum_{n=1}^{Group} \Psi_{nm}^* X_n} \right) \quad (3-12)$$

$$\ln \Gamma_k^{*(i)} = \frac{\sum_{m=1}^{Group} T_{mk} \Psi_{mk}^* X_{mi}^{(i)}}{\sum_{m=1}^{Group} \Psi_{mk}^* X_{mi}^{(i)}} + \sum_{m=1}^{Group} \frac{X_{mi}^{(i)} \Psi_{mk}^*}{\sum_{n=1}^{Group} \Psi_{nk}^* X_{ni}^{(i)}} \left(\tau_{km} - \frac{\sum_{n=1}^{Group} T_{nm} \Psi_{nm}^* X_{ni}^{(i)}}{\sum_{n=1}^{Group} \Psi_{nm}^* X_{ni}^{(i)}} \right) \quad (3-13)$$

Where the nonrandomness parameter (α) is reintroduced into *convenience* expression for the energy contributions, thus retaining the flexibility characteristics of the NRTL expression:

$$\Psi_{mk}^* = \exp(-\alpha T_{mk}) \quad (3-14)$$

Ψ_{mk}^* are the group interaction parameters attributed to groups m and k ($\Psi_{mk}^* \neq \Psi_{km}^*$).

4. Proposed Work Scope

The following sections list a tentative work scope that will facilitate in quantifying current industrial methods; in turn, the results can be used for comparison to either bolster or refute the proposed hybrid method.

4.1. Quantify SOG Advantage

The reasoning behind formalizing a hybrid group contribution method appears sound; the method is designed to address industrial needs (as should be the case in research). It is a new *twist* on an *old idea* that will need to be quantified in order to determine its usefulness, and perhaps some measure of its *potential* staying power.

- Test cases will be conducted to quantify the differences between commonly accepted models (e.g. Wilson, NRTL, and UNIQUAC) and the proposed hybrid group method.
 - In this step the *standard* contributions to the proposed method can be taken as zero, while the tuning contributions can be regressed in order to quantify the ability of the SOG concept to represent mixtures on a case by case basis.

4.2. Prediction of Gammas at Infinite Dilution

In the projected work it should also be tested if this improvement can be observed when predicting ternary mixture behaviour; as test data, activity coefficients at infinite dilution in solvent mixtures (stored in the data bank DDB-ACM) and for a few ternary LLE mixtures should be used.

- An up to date version of the DDB-ACM has been received from Prof. Jürgen Rarey, and will be used in the proposed work (Rarey 2009).
 - The DDB-ACM is in the form of a text file that will have to be imported into an Access table before use.
- The PEQ COM-server delivered with the DDB software package will be used to calculate values using the published and consortium versions of UNIFAC and mod. UNIFAC as a first step.
 - For comparison the ternary results will be “decoupled” from the binary results, otherwise the test results would be influenced by the results for the gamma infinite in the component binaries (Rarey 2009).
 - Depending on the results, a paper could be written comparing the performance of the different predictive models in predicting ternary data (industrially important, where little literature is known to exist).

- The practice of using frequency plots will be adopted (Mu, Rarey and Gmehling 2007), and any other methods used will be formalized into a procedure to facilitate future work.

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