GLOBAL OPTIMIZATION AND ANALYSIS
FOR THE GIBBS FREE ENERGY FUNCTION
USING THE UNIFAC, WILSON AND ASOG EQUATIONS

Conor M. McDonald and Christodoulos A. Floudas*

Department of Chemical Engineering
Princeton University
Princeton, N.J. 08544-5263


Abstract
The Wilson equation for the excess Gibbs energy has found wide use in successfully representing the behavior of polar and nonpolar multicomponent mixtures with only binary parameters, but was incapable of predicting more than one liquid phase. The UNIFAC and ASOG group contribution methods do not have this limitation and can predict the presence of multiple liquid phases. The most important area of application of all these equations is in the prediction of phase equilibrium. The calculation of phase equilibrium involves two important problems: (i) the minimization of the Gibbs free energy, and (ii) the tangent plane stability criterion. Problem (ii), which can be implemented as the minimization of the tangent plane distance function, has found wide application in aiding the search for the global minimum of the Gibbs free energy. However, a drawback of all previous approaches is that they could not provide theoretical guarantees that the true equilibrium solution will be obtained. The goal of this work is to find the equilibrium solution corresponding to the global minimum of the Gibbs free energy. A proof that the Wilson equation leads to a convex formulation for the minimization of the Gibbs energy is provided so that a local optimization technique will always converge to a global minimum. In addition, new expressions are derived for the molar Gibbs free energy function when the UNIFAC, ASOG and modified Wilson equations are employed. These expressions are then transformed so that application of a branch and bound based global optimization algorithm originally due to Falk and Soland (1969) is possible. This allows global solutions to be obtained for both the minimization of the Gibbs free energy and the minimization of the tangent plane distance function. The algorithm is implemented in C as part of the package GLOPEQ, GlObal Optimization for the Phase EQuilibrium problem (McDonald and Floudas, 1994d). Results for several examples are presented.

*Author to whom all correspondence should be addressed.
1 Introduction

Reliable prediction of phase and chemical equilibrium is extremely important in many separation applications such as distillation towers and liquid–liquid extraction. The equation of Wilson (1964) provided a much improved representation of vapor–liquid phase equilibrium for polar and nonpolar multicomponent systems with binary parameters. However, the main drawback of the Wilson equation is its inability to predict liquid–liquid immiscibility. The modified Wilson equation of Tsuboka and Katayama (1975) was one attempt to overcome this limitation by incorporating positive contributions to the excess Gibbs free energy function through the addition of a volume term. The NRTL equation of Renon and Prausnitz (1968) and the UNIQUAC equation of Abrams and Prausnitz (1975) were important advances in the representation of vapor–liquid and liquid–liquid equilibrium. The next important fundamental advance was the development of group contribution methods, namely the UNIFAC equation of Fredenslund et al. (1975) and the ASOG equation of Kojima and Tochigi (1979). In the absence of reliable experimental data, they represent a theoretically based approach by which to obtain estimates of activity coefficients, and hence the prediction of phase equilibrium.

This work is concerned with seeking global solutions to the phase and chemical equilibrium problem. One approach is to minimize the Gibbs free energy function, assuming conditions of constant temperature and pressure. A global minimum will then correspond to the true equilibrium solution. Previous optimization approaches typically have employed Newton type methods so that the solutions found are highly dependent on starting point, and local solutions can at best be guaranteed. Seider et al. (1980) provide a review of these methods. Paules and Floudas (1989) utilized the Global Optimal Search algorithm of Floudas et al. (1989). The tangent plane distance criterion first proposed by Gibbs (1873) has also become an important problem in the search for equilibrium solutions corresponding to a global minimum of the Gibbs free energy. Given an equilibrium solution that satisfies the condition of equipotentials, it is possible to determine if the Gibbs free energy associated with this solution can be reduced to provide an improved solution. This is described fully by Baker et al. (1982) and Michelsen (1982a, 1982b). A number of algorithms use the tangent plane criterion in conjunction with the minimization of the Gibbs free energy. Gautam and Seider (1979) used a combined phase-splitting algorithm to improve the reliability of their approach. Michelsen (1982a, 1982b) proposed a two–stage approach where the compositions obtained from the stability test were used to initiate the search for a solution with a lower Gibbs free energy. Swank and Mullins (1986) provide a comparative review of these and other methods designed for use in the modeling of distillation trays with more than one liquid phase. Sun and Seider (1994) use homotopy continuation methods to obtain equilibrium solutions.

However, none of the above approaches can provide any theoretical guarantee that the global minimum of the Gibbs free energy will be obtained in all cases. In more recent work, McDonald and Floudas (1994a) showed how the Global OPerationization method (GOP) of Floudas and Visweswaran (1990, 1993) could be used to guarantee obtaining ε-global solutions when the liquid phase can be modeled by the NRTL equation. A global optimization branch and bound algorithm of Falk
and Soland (1969) can be used to make the same guarantees for the UNIQUAC equation and this is described in McDonald and Floudas (1994b). For the phase stability problem, McDonald and Floudas (1994c) showed how global solutions could be obtained for the minimization of the tangent plane distance function for challenging examples where the NRTL and UNIQUAC equations are used. This allowed the verification of equilibrium solutions corresponding to global minima in the Gibbs free energy function in reasonable time.

In this work, it will be shown that the Wilson equation leads to a convex formulation for the minimization of the Gibbs free energy. This has the important implication that a local optimization technique will always find a global minimum. Therefore, a global optimization algorithm is not necessary. The difficulties associated with using the UNIFAC, modified Wilson or ASOG activity coefficient correlations is that because of their complexity, multiple solutions may be obtained for the phase equilibrium problem. One of these solutions will then correspond to a global minimum. Conventional methods can provide no guarantee of finding the equilibrium solution, leading to erroneous prediction of phase equilibrium. New properties and simplifications of the molar Gibbs free energy functions are presented for these equations. By manipulating these expressions, they can be altered into a form suitable for the application of a global optimization algorithm for both the minimization of the Gibbs free energy and the tangent plane distance function. This represents the first approach that can offer such theoretical guarantees.

In the following section, the two optimization problems of direct relevance to this work are described. Then the analysis for the UNIFAC, Wilson, modified Wilson and ASOG equations is presented. This shows how the molar Gibbs free energy functions are simplified and transformed so that the branch and bound algorithm of Falk and Soland (1969) can be applied. The proposed approach provides guarantees that the equilibrium solution corresponding to a global minimum in the Gibbs free energy function can be obtained for this class of problems. The molar Gibbs free energy functions are altered so that they are expressed as the difference of two convex functions, where the concave portion is separable. This permits valid underestimators to be generated very simply. Examples for all models analyzed are then presented.

2 Problem Description

It is required to obtain the equilibrium solution corresponding to a global minimum in the Gibbs free energy for multicomponent and multiphase mixtures whose liquid phases can be modeled using the UNIFAC, Wilson, modified Wilson or ASOG equations, and where the vapor phase is assumed to behave ideally. The Gibbs function is the proper thermodynamic measure of equilibrium under conditions of constant temperature and pressure. There are two problems of interest:

(i) Minimization of the Gibbs free energy.

(ii) Minimization of the tangent plane distance function (stability problem)
In terms of the notation to be used, the set of components is described by the set \( C \equiv \{i\} \), the set of elements is represented by the set \( E \equiv \{e\} \), and the set of phases is given by \( P \equiv \{k\} \) where \( P = P_L \cup P_V \), with \( P_L \) and \( P_V \) denoting the liquid phases and vapor phase respectively. The vapor phase is treated ideally in this work, although it is possible to extend the approach to treat cases where the \( B \)–truncated virial equation of state can adequately represent vapor nonidealities. The variables of the problem are \( n \equiv \{n^k_i\} \), representing the number of mols of component \( i \) in phase \( k \), and the corresponding mol fractions \( x \equiv \{x^k_i\} \) defined as \( x^k_i = n^k_i / \sum_j n^k_j \). In addition, the phase fractions are defined as \( \phi^k = \sum_i n^k_i / n_T \) where \( n_T \) is the total number of mols of substance in the system.

The phase equilibrium problem then corresponds to globally minimizing the Gibbs free energy function while satisfying the material balance constraints. The global solution to this problem supplies the true phase and component distribution at equilibrium:

\[
\begin{align*}
\min \quad & G(n) \\
\text{s.t.} \quad & \sum_{k \in P} n^k_i = n^T_i \quad \forall \ i \\
& 0 \leq n \leq n_T
\end{align*}
\]

where \( G(n) \) is the total Gibbs free energy of the system expressed in terms of mol numbers and \( n^T_i \) represents the total number of mols of component \( i \) in the system. If reaction occurs in the system, then mass must be conserved over the elements so that the following linear constraint set replaces the component mass balance constraints of (G):

\[
\sum_{i \in C} \sum_{k \in P} a_{ei} n^k_i = b_e \quad \forall \ e \in E
\]

where \( a_{ei} \) is the number of gram–atoms of element \( e \) in component \( i \), and \( b_e \) the total number of gram–atoms of element \( e \) in the system.

An equilibrium solution to (G) must satisfy the necessary first order equilibrium condition of equipotentials, namely:

\[
\mu^k_i = \mu^{k'}_i \quad \forall \ k, k'
\]

The global minimum will obviously satisfy Eqn. (2). However, for the class of problems considered here, there can be more than one solution satisfying Eqn. (2) corresponding to local extrema which represent false predictions of phase equilibrium. This is the main difficulty associated with the phase equilibrium problem and it is an area where the tangent plane criterion finds important application. Solutions generated by solving (G) can be tested for stability with the tangent plane criterion, as first suggested by Gibbs (1873). Denote the mol fractions in one of the phases of the equilibrium solution to (G) as \( z \equiv \{z_i\} \). Then for this equilibrium solution to correspond to a global minimum of (G), the tangent hyperplanes to the Gibbs surface constructed at \( z \) must lie below this surface
everywhere. These hyperplanes are defined by the chemical potentials, \( \mu_i^0(z) \) constructed at \( z \).

The tangent plane distance function, \( F(x) \), represents the difference between the Gibbs surface and
the tangent hyperplane. If this distance is negative anywhere over the feasible domain, then the
postulated solution represented by \( z \) is not the global solution of (G). Baker et al. (1982) supply a
detailed derivation and proof of the tangent plane criterion. The problem is given below:

\[
\begin{align*}
\min & \quad F(x) = g(x) - \sum_{i \in C} x_i \mu_i^0(z) \\
\text{s.t.} & \quad \sum_{i \in C} x_i = 1 \\
& \quad 0 \leq x_i \leq 1 \forall i
\end{align*}
\]

This problem has the same essential structure as (G) and therefore previous approaches cannot
guarantee that a global solution will be obtained in all cases for (S) either. Recently, McDonald
and Floudas (1994c) showed how global solutions could be obtained for (S) when the liquid phases
are modeled using the NRTL or UNIQUAC equations. In other words, if a local approach finds a
nonnegative tangent plane distance function, then this does not imply that the equilibrium solution
associated with \( z \) corresponds to a global minimum of the Gibbs free energy.

Both problems (G) and (S) can be expressed in terms of the molar Gibbs free energy function
which is obtained by adding the excess Gibbs free energy, \( g^E(x) \), to the ideal Gibbs energy, \( g^I(x) \),
as follows:

\[
g(x) = g^I(x) + g^E(x)
\]

(3)

where

\[
\frac{g^I(x)}{RT} = \sum_{i \in C} x_i \left\{ \frac{\Delta C_i'}{RT} + \ln x_i \right\}
\]

(4)

The Gibbs free energy per phase can be obtained by using mol numbers over mol fractions. A
summation of the Gibbs energies per phase then yields \( G(n) \).

3 Analysis for the UNIFAC Equation

In this section, the expressions for the molar Gibbs free energy function of the UNIFAC equation
will be supplied. New properties are described that allow this function to be transformed into the
difference of two convex functions where the convex function that is subtracted is separable.

3.1 Definition of the molar Gibbs energy

The UNIFAC group contribution model for predicting activity coefficients was proposed by Fre-
denslund et al. (1975), and is based on the UNIQUAC equation of Abrams and Prausnitz (1975).
The expressions of the activity coefficients are given in Appendix A. A full description of the model
can be found in Fredenslund et al. (1977). In what follows, the indices $i$ and $j$ run over the set of components $C$, and the indices $l$, $m$ and $n$ run over the set of groups $G$. The excess Gibbs free energy function is composed of two contributions. The first is a combinatorial part, representing differences in the size and shape of the molecules, and the second is a residual part, which is due to the energies of interaction between them. The excess molar Gibbs free energy for the combinatorial part, $g^E_C(x)$, is given by Abrams and Prausnitz (1975) as:

$$
\frac{g^E_C(x)}{RT} = \sum_{i \in C} x_i \left\{ -\ln x_i + \left[ 1 - \frac{z}{2q_i} \right] \ln \phi_i + \frac{z}{2q_i} \ln \theta_i \right\}
$$

(5)

where $z$, $q_i$, $\phi_i$ and $\theta_i$ are defined in Appendix A. The residual molar excess Gibbs free energy function, labeled $g^E_R(x)$, is given as:

$$
\frac{g^E_R(x)}{RT} = \sum_{i \in C} x_i \ln \gamma_i^R = \sum_{i \in C} x_i \sum_{l \in G} v_{li} \left\{ \ln \Gamma_l - \ln \Gamma_l^{(i)} \right\}
$$

(6)

where $v_{li}$, $\Gamma_l$ and $\Gamma_l^{(i)}$ are defined in Appendix A. The definition of the molar Gibbs free energy is given by the addition of the ideal portion and the excess combinatorial and residual portions as follows:

$$
\frac{g(x)}{RT} = \frac{g^I(x)}{RT} + \frac{g^E_C(x)}{RT} + \frac{g^E_R(x)}{RT}
$$

$$
= \sum_{i \in C} x_i \left\{ \frac{\Delta G^I_i}{RT} + \left[ 1 - \frac{z}{2q_i} \right] \ln \phi_i + \frac{z}{2q_i} \ln \theta_i + \sum_{l \in G} v_{li} \left[ \Gamma_l - \Gamma_l^{(i)} \right] \right\}
$$

(7)

where it is seen that the logarithmic mol fraction term of the ideal Gibbs free energy cancels with the leading term of the excess combinatorial Gibbs free energy. This function is highly nonlinear and nonconvex. The next section will demonstrate the underlying structure associated with Eqn. (7).

### 3.2 Transformation of the molar Gibbs free energy

The following property will help considerably in the analysis of the convexity characteristics of Eqn. (7).

**Property 3.1** Let $\rho_i$ be a positive parameter defined $\forall \ i$. If the real-valued functions, $f^1_i(x)$ and $f^2(x)$, are defined as follows:

(i) $f^1_i(x) = x_i \ln \frac{x_i}{\sum_j x_j \rho_j}$

(ii) $f^2(x) = \left[ \sum_i x_i \rho_i \right] \ln \left[ \sum_i x_i \rho_i \right]$  

then $f^1_i(x)$ and $f^2(x)$ are both convex functions.
**Proof:** See McDonald and Floudas (1994c).

The individual terms of Eqn. (7) are now examined.

(i) **Surface volume term** ($\phi_i$)

Firstly, the following parameter is introduced:

$$z_i^R = \frac{\hat{z}_i q_i - 1}{r_i}$$

(10)

This parameter will always be positive. Then define $A$ as:

$$A = \sum_{i \in C} z_i^R r_i x_i \ln \phi_i = \sum_{i \in C} z_i^R r_i x_i \ln \frac{r_i x_i}{\sum_{j \in C} r_j x_j}$$

(11)

after substituting Eqn. (A.4). Note that $A$ is seen to be convex by substituting $r_j$ for $\rho_j$ in Part (i) of Property 3.1. Because $z_i^R$ and $r_i$ are positive, $A$ is the summation of convex and linear terms, that is, it is a convex function.

The terms involving $\phi_i$ of Eqn. (7) can then be written as:

$$\sum_{i \in C} x_i \left[ 1 - \frac{z}{2 q_i} \right] \ln \phi_i = -A$$

(12)

which is a concave, but nonseparable, function. In order that $-A$ be expressed as the difference of two convex functions, where the concave portion will be separable, the following definitions are introduced:

$$z_M^R = \min_i \{z_i^R \}$$

(13)

$$z^A = z_M^R + \sum_{i \in C} [z_i^R - z_M^R]$$

(14)

$$z_i^B = \sum_{j \neq i} [z_j^R - z_M^R] \quad \forall \ i \in C$$

(15)

The following property gives the required result:

**Property 3.2** If $A_+$ and $A_-$ are defined as follows:

$$A_+ = z^A \cdot \sum_{i \in C} r_i x_i \ln \sum_{i \in C} r_i x_i + \sum_{i \in C} z_i^B r_i x_i \ln \frac{x_i}{\sum_{j \in C} r_j x_j} - \sum_{i \in C} z_i^R r_i \ln r_i \cdot x_i$$

$$A_- = \sum_{i \in C} r_i [z_i^R + z_i^B] \cdot x_i \ln x_i$$

then $A_+$ and $A_-$ are convex functions. Further, $-A$ can be expressed as the difference of these two convex functions:

$$-A = A_+ - A_-$$

(16)
**Proof:** See McDonald and Floudas (1994b).

McDonald and Floudas (1994b) describe these transformation steps in detail. The key point is that the concave term \(-A\) has now been expressed as the difference of two convex functions, where the concave portion \((-A_-)\) is separable.

(ii) **Surface area terms (\(\theta_i\))**

Define \(B\) as:

\[
B = \frac{z}{2} \sum_{i \in C} q_i x_i \ln \theta_i
\]  

(17)

Note that \(B\) is seen to be convex by substituting \(q_j\) for \(\rho_j\) in Part (i) of Property 3.1. Because \(z\) and \(q_i\) are positive, \(B\) is the summation of convex and linear terms, that is, it is a convex function. No further transformations are required.

(iii) **Residual activity coefficient terms (\(\Gamma_l\))**

Before proceeding with the analysis, the following new parameters are introduced so as to simplify the notation of the development:

\[
\hat{v}_{li} = \sum_{m \in G} Q_m v_{mi} \Psi_{ml}
\]  

(18)

\[
\psi^{(i)} = \sum_{l \in G} v_{li} \Gamma_l^{(i)}
\]  

(19)

In order to examine the structure of Eqn. (6), the definition of the residual activity coefficient will be expanded out in terms of the mol fractions. The first step is to substitute Eqn. (A.8) into Eqn. (A.10) to redefine the group area fractions in terms of the mol fractions as:

\[
\Theta_l = \frac{\sum_{i \in C} x_i Q_l v_{li}}{\sum_{i \in C} x_i \sum_{m \in G} Q_m v_{mi}} = \frac{\sum_{i \in C} x_i Q_l v_{li}}{\sum_{i \in C} x_i q_i}
\]  

(20)

noting that the denominators of \(X_l\) cancel. The following property provides an important simplification of Eqn. (6):

**Property 3.3**

\[
\sum_{i \in C} x_i \sum_{l \in G} \psi_{li} Q_l \left\{1 - \frac{\Theta_m \Psi_{lm}}{\sum_{n \in G} \Theta_n \Psi_{nm}}\right\} = 0
\]  

(21)

**Proof:** See Appendix B.
The effect of Property 3.3 is that a large number of nonconvex bilinear fractional terms are removed from the definition of \( g^E_R(x) \). The remaining logarithmic term of Eqn. (A.9) that involves \( \Theta_I \) can then be expanded as:

\[
\sum_{m \in G} \Theta_m \Psi_{ml} = \frac{\sum_{i \in C} x_i \sum_{m \in G} Q_m v_{mi} \Psi_{ml}}{\sum_{i \in C} x_i \sum_{m \in G} Q_m v_{mi}} = \frac{\sum_{i \in C} x_i \hat{v}_i}{\sum_{i \in C} x_i q_i}
\]  

(22)

The simplification of Property 3.3 combined with Eqn. (22) means that the residual excess Gibbs free energy can now be formulated as:

\[
\frac{g^E_R(x)}{RT} = \sum_{i \in C} x_i \ln \left\{ \ln \Gamma_i - \ln \Gamma_i^{(i)} \right\}
\]

\[
= - \sum_{i \in C} x_i \sum_{l \in G} v_l Q_l \ln \sum_{m \in G} \Theta_m \Psi_{ml} - \sum_{i \in C} x_i v_i \ln \Gamma_i^{(i)}
\]

\[
= - \sum_{i \in C} x_i \sum_{l \in G} v_l Q_l \ln \left( \sum_{j \in G} \frac{x_j \hat{v}_j}{x_j q_j} \right) - \sum_{i \in C} x_i v_i^{(i)}
\]

\[
= \sum_{i \in C} x_i \ln \sum_{i \in C} x_i q_i - \sum_{i \in C} x_i \sum_{l \in G} v_l Q_l \ln \sum_{j \in G} \frac{x_j \hat{v}_j}{x_j q_j} - \sum_{i \in C} x_i v_i^{(i)}
\]  

(23)

Eqn. (23) is a new expression for the residual excess Gibbs free energy defined in terms of the mol fractions. It represents a much simpler expression than that customarily employed as Eqn. (6) although it is still a nonconvex function. To progress further, the following definitions of the terms in Eqn. (23) are made:

\[
C = \sum_{i \in C} x_i q_i \ln \sum_{i \in C} x_i q_i
\]  

(24)

\[
D = - \sum_{i \in C} x_i \sum_{l \in G} v_l Q_l \ln \sum_{j \in G} \frac{x_j \hat{v}_j}{x_j q_j}
\]  

(25)

Note that \( C \) is convex by simply substituting \( q_i \) for \( \rho_i \) in Part (ii) of Property 3.1. The term \( D \) is nonconvex but can be transformed into the difference of two convex functions as is shown in the following property.

**Property 3.4** Define \( D_+ \) and \( D_- \) as follows:

\[
D_+ = \sum_{i \in C} x_i \sum_{l \in G} v_l Q_l \ln \frac{x_i}{x_j \hat{v}_j} \sum_{j \in G} x_j q_j
\]

\[
D_- = \sum_{i \in C} q_i x_i \ln x_i
\]
then \( D_+ \) and \( D_- \) are convex functions. Further, \( D \) can be equivalently expressed as the difference of these two functions:

\[
D = D_+ - D_-
\]  

(26)

**Proof:** Simply add the term \( D_- \) to \( D \) to give \( D_+ \). By subtracting the same term, the equality of Eqn. (26) is seen to be valid. The result follows from the fact that \( D_+ \) is convex by Part (i) of Property 3.1, because all the parameters involved in the definition of \( D \) are positive. \( D_- \) is also convex and separable because \( q_i \) is never negative.

Thus, the original expression for the molar Gibbs free energy has been recast as the difference of two convex functions:

\[
g(x) = \sum_{i \in C} x_i \Delta G_i + \{A_+ + B + C + D_+\} - \{A_- - D_-\}
\]

\[
= C^U(x) - \sum_{i \in C} \varphi_i \cdot x_i \ln x_i
\]

where

\[
C^U(x) = \sum_{i \in C} x_i \left\{ \frac{\Delta G_i}{RT} - z_i^R r_i \ln r_i + \frac{z}{2} q_i \ln q_i - v^{(i)} \right\} + z^A \cdot \sum_{i \in C} r_i x_i \ln \sum_{i \in C} r_i x_i
\]

\[
+ \sum_{i \in C} z_i^R r_i x_i \ln \sum_{j \in C} r_j x_j + \frac{z}{2} \sum_{i \in C} q_i x_i \ln \sum_{j \in C} q_j x_j
\]

\[
+ \sum_{i \in C} z_i q_i \ln \sum_{i \in C} z_i q_i + \sum_{i \in C} x_i \sum_{i \in C} v_{ii} q_i \ln \sum_{j \in C} x_j v_{ij}
\]

and \( \varphi_i = r_i [z_i^R + z_i^U] + q_i \)

Note that \( C^U(x) \) is convex since it is a summation of convex and linear functions. The parameters \( \varphi_i \) are never negative so that the excess Gibbs free energy is now expressed as the difference of two convex functions.

### 4 The Wilson and modified Wilson Equations

#### 4.1 Analysis for the Wilson Equation

Wilson (1964) proposed the following expression for the excess Gibbs free energy function:

\[
g^E(x) = \sum_{i \in C} x_i \ln \sum_{j \in C} x_j \Lambda_{ij}
\]

(27)

where \( \Lambda_{ij} \) is a nonsymmetric binary interaction parameter between \( i \) and \( j \) with \( \Lambda_{ii} = 1 \). This represented an important advance in the representation of vapor–liquid equilibrium for a very large
number of systems. To obtain the expression for the molar Gibbs free energy, Eqn. (27) is substituted into Eqn. (3) to yield:

\[
\frac{g(x)}{RT} = \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln \frac{x_i}{\sum_{j \in C} x_j \Lambda_{ij}} \right\}
\]

(28)

Note that the logarithmic terms of Eqn. (28) are convex by Property 3.1. The Gibbs function is therefore the summation of linear and convex terms, that is, it is convex. This is confirmation of the well known fact that the Wilson equation cannot predict liquid–liquid immiscibility. One property of convex functions is that the linearization of the function at any point will always underestimate the function. In the context of the tangent plane criterion (Baker et al., 1982), it is obvious then that any tangent drawn to the Gibbs surface will *always* underestimate it, which implies as a direct consequence that the Wilson equation cannot predict liquid phase splitting. Thus, there is no need for global optimization techniques for the Wilson equation. Any local minimum of the Gibbs free energy function will be a global one.

### 4.2 Analysis for the Modified Wilson Equation

There have been a number of attempts to extend the Wilson equation so that it can predict the appearance of more than one liquid phase. Wilson (1964) suggested multiplying the excess Gibbs function by a number greater than one. Extension to multicomponent mixtures is unsatisfactory however. The modified Wilson equation, proposed by Tsuboza and Katayama (1975), was one attempt to overcome this limitation of the Wilson equation, and they derived the following expression for the excess Gibbs free energy using local volume compositions;

\[
\frac{g^E(x)}{RT} = - \sum_{i \in C} x_i \ln \sum_{j \in C} x_j \Lambda_{ji} + \sum_{i \in C} x_i \ln \sum_{j \in C} x_j \rho_{ji}
\]

(29)

where

\[
\Lambda_{ij} = \rho_{ij} \exp \left( \frac{\lambda_{ij} - \lambda_{ji}}{RT} \right) \quad \text{with} \quad \rho_{ij} = \frac{\nu_i}{\nu_j}
\]

where \( \lambda_{ij} \) is a binary interaction parameter for an \( i - j \) pair, and \( \nu_i \) is the molar liquid volume of component \( i \). There are two interaction parameters per binary. Substitution of Eqn. (29) into Eqn. (3) gives the following expression for the molar Gibbs free energy function:

\[
\frac{g(x)}{RT} = \sum_{i \in C} x_i \left\{ \Delta G_i^f + \ln \frac{x_i}{\sum_{j \in C} x_j \Lambda_{ij}} + \ln \sum_{j \in C} x_j \rho_{ji} \right\}
\]

(30)

The nonconvex term of Eqn. (30) involves the volume ratios and this term is defined as:

\[
\mathcal{A} = \sum_{i \in C} x_i \ln \sum_{j \in C} x_j \rho_{ji}
\]

(31)

The following property allows the nonconvex function \( \mathcal{A} \) to be transformed into the difference of two convex functions:
Property 4.1 If $A_+$ and $A_-$ are defined as follows:

$$A_+ = \sum_{i \in C} \left[ \sum_{j \in C} x_j \rho_{ji} \right] \ln \left( \sum_{j \in C} x_j \rho_{ji} \right) + \sum_{i \in C} z_i \ln \frac{z_i}{\sum_{i \in C} x_i \rho_{i}}$$

$$A_- = \sum_{i \in C} z_i \ln z_i \cdot \sum_{j \neq i} \rho_{ji}$$

then $A_+$ and $A_-$ are convex functions. Further, $A$ can be expressed as the difference of these two convex functions:

$$A = A_+ - A_- \quad \text{(32)}$$

Proof: See Appendix C.

The excess Gibbs free energy function can then be expressed as the difference of two convex functions as follows:

$$\frac{g(x)}{RT} = C^T(x) - \sum_{i \in C} \varphi_i \cdot z_i \ln z_i$$

(33)

where

$$C^T(x) = \sum_{i \in C} x_i \left\{ \Delta G_i^T + \ln \frac{x_i}{\sum_{j \in C} x_j \Lambda_{ji}} \right\} + \sum_{i \in C} \left[ \sum_{j \in C} x_j \rho_{ji} \right] \ln \left[ \sum_{j \in C} x_j \rho_{ji} \right]$$

$$+ \sum_{i \in C} \sum_{j \neq i} x_j \rho_{ji} \ln \frac{x_j}{\sum_{i \in C} x_i \rho_{i}}$$

with $\varphi_i = \sum_{j \neq i} \rho_{ji}$

The expression for $C^T(x)$ when expressed in terms of the mol numbers will contain an extra term arising from the denominator of the equation $z_i = n_i / \sum_j n_j$. For the corresponding expression for the total Gibbs free energy expressed in mol numbers, simply replace $z_i$ by $n_i$ in the definition of $C^T$; then the term $\sum_j n_j \ln \sum_j n_j$ must be subtracted from $C^T$. This is the only model for which this extra term is required.

5 Analysis for the ASOG Equation

The origin and underlying basis of the Analytical Solution Of Groups (ASOG) method is described in the monograph of Kojima and Tochigi (1979), which concentrates on vapor–liquid phase equilibrium. Tochigi et al. (1980) discuss the application of the ASOG method to liquid–liquid equilibria. It is now described in detail.
5.1 Model Definition

The activity coefficient expression is assumed to be made up of two contributions, one associated with the size of the molecules, the other with the various groups that make up the molecules, so that:

\[
\ln \gamma_i = \ln \gamma_i^S + \ln \gamma_i^G
\]

(34)

The contributions of both these terms is now described.

(i) Size Contribution:

A Flory–Huggins type term describes the size contribution of molecule \( i \) as follows:

\[
\ln \gamma_i^S = \sum_{i \in C} x_i \ln \gamma_i^S = \ln \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}} + 1 - \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}}
\]

(35)

where \( \nu_i \) is the number of atoms other than hydrogen in the molecule \( i \), and \( x_i \) is the mol fraction of component \( i \) in the liquid solution. The excess molar Gibbs free energy function is then defined as:

\[
\frac{g_E^E(x)}{RT} = \sum_{i \in C} x_i \left\{ \ln \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}} + 1 - \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}} \right\}
\]

(36)

The following property simplifies Eqn. (36):

**Property 5.1**

\[
\sum_{i \in C} x_i \left\{ 1 - \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}} \right\} = 0
\]

(37)

**Proof:** Simply expand out the sum as follows:

\[
\sum_{i \in C} x_i - \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}} = \sum_{i \in C} x_i - \frac{\sum_{i \in C} x_i \nu_i}{\sum_{j \in C} x_j \nu_j} = \sum_{i \in C} x_i - 1 = 0
\]

This completes the proof.

At this point, it is convenient to add the ideal Gibbs energy function to the excess molar Gibbs energy associated with the size contribution to yield:

\[
\frac{g^I(x)}{RT} + \frac{g_E^E(x)}{RT} = \sum_{i \in C} x_i \ln x_i + \sum_{i \in C} x_i \ln \frac{\nu_i}{\sum_{j \in C} \frac{x_j \nu_j}{\nu_j}}
\]

\[
= \sum_{i \in C} x_i \ln \frac{x_i \nu_i}{\sum_{j \in C} x_j \nu_j} = A
\]

(38)
This has been done because \( A \) as defined by Eqn. (38) is convex due to Property 3.1.

(ii) Group Contribution:

The notation and definitions for the residual activity coefficient are very similar to that used for the UNIFAC equation. One major difference is in the definition of \( v_i \) which for the ASOG equation represents the number of atoms other than hydrogen in group \( l \) in molecule \( i \). The group residual activity coefficient is defined by the Wilson (1964) equation with the mol fractions replaced by group fractions:

\[
\ln \Gamma_l = -\ln \sum_{l \in G} X_m a_{lm} + 1 - \sum_{m \in G} \frac{X_m a_{ml}}{\sum_{n \in G} X_n a_{mn}} \tag{39}
\]

where \( a_{lm} \) is the group interaction parameter between groups \( l \) and \( m \); and \( X_l \) is defined by Eqn. (A.8) as for the UNIFAC equation. The temperature dependence of the group interaction parameters is described by:

\[
\ln a_{lm} = m_{lm} + \frac{n_{lm}}{T} \tag{40}
\]

where \( T \) is the temperature of the system in K. The parameters \( m_{lm} \) and \( n_{lm} \) are tabulated for a number of groups in the monograph of Kojima and Tochigi (1979).

The excess molar Gibbs free energy of the group contribution is given by Eqn. (6). The following parameters are defined so as to simplify the foregoing analysis:

\[
\phi_i^S = \sum_{l \in G} v_{li} \tag{41}
\]

\[
\phi_i = \sum_{m \in G} v_{mi} a_{lm} \tag{42}
\]

Eqn. (6) can be simplified for the ASOG equation using the following property.

**Property 5.2**

\[
\sum_{i \in C} \sum_{l \in G} v_{li} \left\{ 1 - \sum_{m \in G} \frac{X_m a_{ml}}{\sum_{n \in G} X_n a_{mn}} \right\} = 0 \tag{43}
\]

**Proof:** Note the similarity of Eqn. (43) to Eqn. (21) for the UNIFAC equation. The proof is obtained by setting \( Q_l = 1 \ \forall \ l \) and swapping the indices on the binary interaction parameters in Appendix B.

The terms of Eqn. (43) are thus removed from the Gibbs free energy expression. The remaining logarithmic term of Eqn. (39) can then be written in terms of the parameters of Eqns. (41) and (42) as:

\[
\sum_{m \in G} X_m a_{lm} = \frac{\sum_{i \in C} \sum_{m \in G} v_{mi} a_{lm}}{\sum_{i \in C} \sum_{n \in G} v_{ni}} = \frac{\sum_{i \in C} \sum_{i \in C} \phi_i}{\sum_{i \in C} \sum_{i \in C} \phi_i^S} \tag{44}
\]
This allows the excess Gibbs free energy associated with the group terms to be written as:

\[
\frac{g_E(x)}{RT} = \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \left\{ \ln \Gamma_l - \ln \Gamma_l^{(i)} \right\}
\]  

(45)

\[
= - \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \ln \sum_{i \in G} x_i v_{l_i}^{(i)} - \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \ln \Gamma_l^{(i)}
\]  

(46)

\[
= \sum_{i \in G} x_i v_i^S \ln \sum_{i \in G} x_i v_i^S - \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \ln \sum_{j \in G} x_j \hat{v}_{lj} - \sum_{i \in G} x_i v_i^{(i)}
\]  

(47)

Note that this is very similar to Eqn. (23). The following definitions are made to better see the structure of Eqn. (47):

\[
B = \sum_{i \in G} x_i v_i^S \ln \sum_{i \in G} x_i v_i^S
\]  

(48)

\[
C = - \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \ln \sum_{j \in G} x_j \hat{v}_{lj}
\]  

(49)

The term \( B \) is convex by Property 3.1. The term \( C \) as defined by Eqn. (49) is nonconvex. To transform it into the difference of two convex functions, where the concave portion is separable, the following property is used.

**Property 5.3** Define \( C_+ \) and \( C_- \) as follows:

\[
C_+ = \sum_{i \in G} x_i \sum_{l \in G} v_{l_i} \ln \frac{x_i}{\sum_j \hat{v}_{lj} x_j}
\]

\[
C_- = \sum_{i \in G} v_i^S x_i \ln x_i
\]

then \( C_+ \) and \( C_- \) are convex functions. Further, \( C \) can be equivalently expressed as the difference of these two functions:

\[
C = C_+ - C_-
\]  

(50)

**Proof:** Set \( Q_l = 1 \) in the proof of Property 3.3. \( \square \)

### 5.2 Expression for the molar Gibbs free energy

This means that the excess molar Gibbs free energy for the group interaction portion can be written as:

\[
\frac{g(x)}{RT} = A + B + C_+ - C_-
\]  

(51)

\[
= C^A(x) - \sum_{i \in G} \varphi_i \cdot x_i \ln x_i
\]  

(52)
where
\[
C^A(x) = \sum_{i \in C} x_i \left\{ \Delta G_i' + \ln \nu_i - v^{(i)} \right\} \\
+ \sum_{i \in C} x_i \ln \frac{x_i}{\sum_{j \in C} x_j \nu_j} + \sum_{i \in C} x_i v_i^S \ln \left( \sum_{i \in C} x_i v_i^S \right) + \sum_{i \in C} x_i \sum_{i \in C} u_i \ln \frac{x_i}{\sum_{j \in C} x_j \nu_j}
\]
and \( \varphi_i = v_i^S \)

6 Branch and Bound Algorithm

In the preceding sections, the expressions for the molar Gibbs free energy were transformed so that the final formulations were cast in the form of the difference of two convex functions, where the concave portion was separable. This allows application of a branch and bound algorithm first developed by Falk and Soland (1969). McDonald and Floudas (1994b) and McDonald and Floudas (1994c) have described this algorithm in detail when the liquid phase is modeled using the UNIQUAC equation for nonideal liquid phases. It works by partitioning the initial feasible region into subdomains in which the convex envelope of the Gibbs free energy or the tangent plane distance function is constructed so as to provide valid underestimators of the global solution. A sequence of nondecreasing lower bounds is then generated until \( \epsilon \)-global convergence is obtained. The variations of the original algorithm and its generalization are discussed in the book of Horst and Tuy (1990). In the discussion to follow, the algorithm is described in terms of a general set of variables \( x = \{x_i\} \), so that the problem of interest is of the following form:

\[
\begin{align*}
& \min_{x} \quad C(x) - \sum_{i} \varphi_i x_i \ln x_i \\
& \text{s.t.} \quad 0 \leq x_i \leq u_i \quad \forall \; i \\
& \quad A \; x - b = 0
\end{align*}
\]

(DC)

where the last equation is the linear constraint set representing the mass or elemental constraints for the minimization of the Gibbs free energy, or the mol fraction constraints for the minimization of the tangent plane distance function, and \( u_i \) is the appropriate upper bound depending on the problem being solved.

6.1 Convex Underestimation

The convex envelope of a separable concave function is simply the line that joins the endpoints of the function in the current partition, with \( \mathcal{L}_i^B \) and \( \mathcal{U}_i^B \) representing these lower and upper bounds on the \( x \) variables. How these domains are determined will be discussed in the next section. The convex envelope of the separable concave portion of (DC) is labeled \( \Psi_i \) and is defined as:

\[
\Psi_i = -\mathcal{L}_i^B \ln \mathcal{L}_i^B + \left[ \frac{\mathcal{L}_i^B \ln \mathcal{L}_i^B - \mathcal{U}_i^B \ln \mathcal{U}_i^B}{\mathcal{U}_i^B - \mathcal{L}_i^B} \right] \cdot [x_i - \mathcal{L}_i^B] \quad \forall \; i \in C
\]

(53)
This is simply the equation of the line that joins the endpoints of the function in the given box partition. The convex portion of the objective function of (DC) need not be underestimated (the convex envelope of a convex function is the function itself), so the problem that provides a valid underestimation of the global solution in this partition, labeled (UES), is given as follows:

\[
\begin{align*}
&\min \quad C + \sum_i \varphi_i \Psi_i \\
&s.t. \quad L^B_{x_i} \leq x_i \leq U^B_{x_i}, \quad \forall i \\
&\quad A x - b = 0
\end{align*}
\]

(UES) is a convex problem and a local optimization solver can be used to find its global minimum.

6.2 Partitioning scheme

Given a partition, it has been shown how to obtain a lower bound on the global solution within it. To construct the partitions so that convergence to the global solution will be achieved is relatively simple. At the start of every iteration, assume there is a current point, \(x^K\), about which partitioning will occur, and a parent region with associated regional bounds on the variables as \(\{L^R_{x_i}, U^R_{x_i}\}\). This parent region is divided into two or more box regions, with associated box bounds denoted \(\{L^B_{x_i}, U^B_{x_i}\}\). The parent region is therefore partitioned by a set of \(N_P\) orthogonal hyperplanes passing through the current point, so that \(2^{N_P}\) box regions are created at every iteration. \(N_P\) must be at least one. To decide about which facets of the \(n\)-rectangle the partitioning will occur, the distance, labeled \(\delta_i\), between the function and its convex envelope at the current point is used:

\[
\delta_i = \left| -x_i^K \ln x_i^K - \Psi_i(x_i^K) \right|
\]

The larger this distance the greater the need for further refinement along this edge. As long as the partitioning occurs along the variable with the largest \(\delta_i\) then the branch and bound algorithm will converge to an \(\epsilon\)-global solution of (DC), as proved by Horst and Tuy (1990). Of course, the partitioning can occur along additional facets of the current \(n\)-rectangle. The trade-off is then tighter underestimators for higher \(N_P\), but a fewer number of subproblems need be solved for lower \(N_P\). The user can choose the value of \(N_P\) which can vary from one iteration to the next.

The parameter \(s_i^{B_i}\) is used to determine the box bounds for a given problem (UES), where \(B_i\) is one possible combination of the box bounds from the set of all possible combinations \(CB\). For the \(N_P\) variables with the largest values of \(\delta_i\), \(s_i^{B_i} = \pm 1\), depending on the current box region. If \(s_i^{B_i} = 0\) then no partitioning will take place around \(x_i^K\). The partitioning scheme is then as follows:

\[
\begin{align*}
&\text{If } s_i^{B_i} = +1 \text{ then } (x_i - x_i^K) \geq 0 \Rightarrow L^B_{x_i} = x_i^K, \quad U^B_{x_i} = U^R_{x_i} \\
&\text{If } s_i^{B_i} = -1 \text{ then } (x_i - x_i^K) \leq 0 \Rightarrow L^B_{x_i} = L^R_{x_i}, \quad U^B_{x_i} = x_i^K \\
&\text{If } s_i^{B_i} = 0 \text{ then } L^B_{x_i} = L^R_{x_i}, \quad U^B_{x_i} = U^R_{x_i}
\end{align*}
\]

∀ \(i \in C\)

17
The cardinality of the set $CB$ is then seen to equal $2^{N_p}$. A brief description of the algorithm at some iteration $K$ is now provided:

1. Use $x^K$ to evaluate $C(x^K) - \sum_i \varphi_i z_i^K \ln z_i^K$ to yield an upper bound on the global solution.
2. Solve an underestimating problem of type (UES) in each of the $2^{N_p}$ box regions.
3. Store the solutions of (UES) if they lie below the current best upper bound.
4. The region associated with the infimum of all available lower bounds supplies $x^{K+1}$ and the parent region for the next iteration.

Note that at the first iteration, the initial parent region consists of the entire feasible region, defined by the simple rectangular bounds on the $x$ variables. For a detailed discussion of the algorithm, see McDonald and Floudas (1994b).

7 Computational Results

In this section, several examples are considered. They are implemented in C as part of the package GLOPEQ (GLocal Optimization for the Phase and chemical EQuilibrium problem). All times represent total time to convergence using a Hewlett Packard HP9000/730 machine. GLOPEQ is capable of (i) minimizing the Gibbs free energy function – solving problem (G), (ii) minimizing the tangent plane distance function – solving problem (S), and (iii) generating the global minimum of the Gibbs free energy function using a combination of both these algorithms in order to maximize efficiency. Feature (iii) of GLOPEQ is described in McDonald and Floudas (1994d).

7.1 Examples for the UNIFAC

Example 1: $n$-Butyl-Acetate – Water

This binary example has been studied by several authors. Heidemann and Mandhane (1973) calculated binary parameters using the NRTL equation, as did Block and Hegner (1976) in their study of three-phase distillation towers. There are two potential liquid phases at a temperature of 298K and 1 atm pressure. This example is interesting as it contains a small number of components but yields multiple local solutions satisfying Eqn. (2), as discussed by McDonald and Floudas (1994a). The structural and binary interaction parameters for the UNIFAC equation were obtained from Magnusen et al. (1981). There are four groups and these are shown in Table 1 along with the notational parameters of Eqns. (18)–(19).

The molar Gibbs free energy function as defined by Eqn. (3) can be used to calculate the actual Gibbs free energy of a single liquid phase by replacing the mol fractions $x_i$ by the mol numbers $n_i^k$ in a phase $k$. The problem of the minimization of the Gibbs free energy is then seen to be exactly the same in structure as the minimization of the tangent plane distance function. The difference is in the increased number of variables in the problem due to the incorporation of two phases. The mass
balance constraints of (G) replace the summation of mol fraction constraints of (S). When GLOPEQ is used to minimize the Gibbs free energy for two postulated liquid phases, the global LL solution is obtained in 461 iterations and a total time of 5.3 cpu sec. This solution is supplied in Table 2.

Example 2: Water – n-Propanol – n-Hexane

This example was given in Appendix 2 of Fredenslund et al. (1977) as an example of liquid–liquid phase equilibrium calculations. The temperature was 311 K and two feed conditions are considered here as (i) \( n^L_T = \{0.5, 0.3, 0.25\} \), and (ii) \( n^T_T = \{0.5, 0.5, 0.25\} \). A two phase solution is obtained by Fredenslund et al. (1977) for both these feed charges. In this work, there is an equilibrium solution with three liquid phases that has a lower value of the Gibbs free energy for both feed conditions. Solutions satisfying the first order conditions of equal chemical potentials are given in Table 3 and Table 4 for Conditions (i) and Conditions (ii) respectively, and there are three solutions reported for each set of conditions, two local LL and one global LLL, and they are given in order of decreasing Gibbs free energy. The local equilibrium solutions reported by Fredenslund et al. (1977) are marked with a dagger. The values of the corresponding value of the Gibbs free energy are given as \( G^* \) in these tables. Also supplied are the values of the chemical potentials associated with these solutions which were used in this example to test the minimization of the tangent plane distance function. For Conditions (i), and using \( \mu_0^L(z) \) associated with the local LL solution reported by Fredenslund et al. (1977), the global solution of \( \mathcal{F}^* = -0.00728 \) with mol fractions \( \mathbf{x}^* = \{0.93118, 0.06872, 0.00010\} \), indicating instability and was obtained in 10990 iterations and 139 cpu sec. For the other local LL solution of Table 3, the global minimum was \( \mathcal{F}^* = -0.06108 \) with mol fractions \( \mathbf{x}^* = \{0.00223, 0.05710, 0.94066\} \) and was obtained in 1220 iterations and 13.4 cpu sec. Similarly, using the local LL solution for Conditions (ii) with the lowest value of the Gibbs free energy, the global minimum of the tangent plane distance function is \( \mathcal{F}^* = -0.08406 \) with \( \mathbf{x}^* = \{0.00199, 0.05192, 0.94609\} \), obtained in 902 iterations and 10.5 cpu sec. Using the chemical potentials associated with the local LL solution reported by Fredenslund et al. (1977), the global minimum of the tangent plane distance function is \( \mathcal{F}^* = -0.00293 \) with \( \mathbf{x}^* = \{0.92633, 0.07355, 0.00012\} \), obtained in 13083 iterations and 185 cpu sec. This example is particularly tough as there is a strong local minimum with \( \mathcal{F}^* = 0.0 \). If a local optimization technique converges to this solution, it will mistakenly report that the local LL solution is stable when this is not the case. MINOS5.4 converged only 35 times in every 100 to the negative value of \( \mathcal{F}^* \). This is an unacceptable degree of unreliability and emphasizes the need for a global optimization approach. To verify that the global minimum of the tangent plane distance function associated with the LLL solution was nonnegative, the algorithm took 16012 iterations to converge to the global solution of \( \mathcal{F}^* = 0.0 \) in 253 cpu sec for both Conditions (i) and Conditions (ii). Note that only the phase fractions differ at the global minimum of the Gibbs free energy function. The mol fractions are identical so that the same values for \( \mu_0^L(z) \) are obtained.

The UNIFAC equation is therefore capable of predicting very complex behavior and this example
demonstrates the difficulty of obtaining the equilibrium solution corresponding to a global minimum in the Gibbs free energy. It should be noted that it is experimentally known that there are two liquid phases. Magnussen et al. (1981) observed that the UNIFAC equation could predict extraneous liquid phases for systems containing propanol. For this reason, they obtained interaction parameters for both 1-propanol and 2-propanol. If the LL interaction parameters of Magnussen et al. (1981) are used, then a solution with two liquid phases is obtained. When the equilibrium solution corresponding to a global minimum of the Gibbs free energy is used to calculate the chemical potentials, minimization of the tangent plane distance function took 13390 iterations and 207 cpu sec for Conditions (i) and 13945 iterations and 224 cpu sec for Conditions (ii). These solutions are reported in Table 5 for the two feed charges considered.

Example 3: Ethanol – Benzene – Water

This is a commonly studied example in the literature due to the importance of the dehydration of ethanol using benzene as an entrainer. Kovach and Seider (1983) used the UNIQUAC equation to model this azeotropic distillation tower. The authors reported multiple steady states for this column. This system was also studied by Cairns and Furzer (1990) who emphasize the importance of modeling the third liquid phase in the column. In fact, they found that the two phase solution associated with the column actually led to the prediction of infeasible temperatures at the top of the tower. This emphasizes the need for reliable prediction of phase equilibrium. The UNIFAC interaction parameters were obtained from Gmehling et al. (1982). The saturated pressures were calculated using the data of Reid et al. (1977). For a feed charge of \( \eta_1^T = \{0.20, 0.35, 0.45\} \), the global minimum Gibbs free energy is attained at a value of \( -1.235895 \) with two liquid phases and a single vapor phase. This solution is given in Table 6 along with the associated chemical potentials and local LL and LV solutions. If the tangent plane distance function is minimized using the chemical potentials associated with the local LL solution, convergence to the global minimum \( J^* = 0.0 \) with takes 419 iterations and 5.2 sec. This solution is unstable with respect to a vapor phase, and is therefore not the globally equilibrium solution. For the LV solution, a global minimum of the tangent plane distance function is attained at \( J^* = -0.02445 \) with \( \bar{x}^* = \{0.00480, 0.99138, 0.00381\} \), taking 252 iterations and 3.2 cpu sec. To converge to \( J^* = 0.0 \) with \( \bar{x}^* = \{0.00565, 0.99054, 0.00381\} \) using the chemical potentials corresponding to a global minimum of the Gibbs free energy function took 410 iterations and 5.0 cpu sec.

7.2 Examples for the Wilson equation

Example 4: Esterification Reaction

This example is for an esterification reaction involving an equimolar mixture of ethanol and acetic acid reacting reversibly to form ethyl-acetate and water:

\[
EtOH + HAc \rightleftharpoons EtAc + H_2O
\]
It has been used to test several proposed methods in the literature, including those of Sanderson and Chien (1973), George et al. (1976), Castillo and Grossmann (1981), Lantagne et al. (1988), Castier et al. (1989), Xiao et al. (1989), and Paules and Floudas (1989). The liquid phase has been modeled by the above authors using the Wilson activity coefficient model. Xiao et al. (1989) used the UNIQUAC model which does not account for the polymerization of acetic acid in the vapor phase. McDonald and Floudas (1994a) obtained NRTL parameters using infinite dilution coefficients calculated from the Wilson equation. Data for the liquid activity binary parameters used in the Wilson equation are taken from Suzuki et al. (1969). These are supplied in Table 7. These parameters do take into account the formation of dimers and trimers of acetic acid in the vapor phase. Stoichiometric information is supplied in Table 8.

The vapor Gibbs free energies of formation were calculated for the vapor phase by integrating the van't Hoff equation from 298K to the temperature of the system:

\[
\frac{\partial \Delta C^0_{f,p}}{\partial T} = -\frac{\Delta H^0_{f,p}}{T^2}
\]

(54)

where \(\Delta H^0_{f,p}\) is also a function of temperature and is calculated from Kirchoff's equation. The required heat capacity data is obtained from Reid et al. (1977). These Gibbs free energies of formation for the vapor phase are given in Tables 9 and 10 for the two temperature conditions studied here and the saturated pressures are calculated using the Antoine coefficients supplied by Xiao et al. (1989).

There are 4 components and there can only be one liquid phase as the Wilson equation cannot predict the formation of additional liquid phases. At 355 K the global solution contains a liquid and a vapor phase and this solution is given in Table 9. At 358 K, the global solution is a single vapor phase as shown in Table 10. Any solution found must be checked to ensure that the equilibrium constant, \(K_{ran}\) as expressed for the vapor phase matches the experimental one as reported by Stull et al. (1969) at the temperature of the system:

\[
K_{ran} = \frac{\mu_{H_2A_c}}{\mu_{H_2O}} \frac{\mu_{H_2O}}{\mu_{H_2A_c}}
\]

(55)

For example, as pointed out by George et al. (1976), Sanderson and Chien (1973) report a liquid-vapor solution which violates the chemical reaction constraint by an order of magnitude. Because the vapor phase is assumed to behave ideally, the chemical potentials of Eqn. (55) can be replaced by mol numbers so that for \(T = 355\) K, \(K_{ran} = 33.12\), which agrees well with the value of 31.75 as reported by Stull et al. (1969). At \(T = 358\) K \(K_{ran} = 31.80\) which also agrees excellently with the value of 31.75 reported by Stull et al. (1969).

**Example 5: The modified Wilson equation**

A binary liquid-liquid example for methanol and cyclohexane is considered. Tsuboka and Katayama (1975) supply the parameters for this example and at a temperature of 298 K they are:

\[
\Lambda_{12} = 0.30384, \quad \Lambda_{21} = 0.09517, \quad \rho_{12} = 0.374
\]
The global minimum of the Gibbs free energy function contains two liquid phases and is supplied in Table 11. It was obtained in 141 iterations and 1.9 cpu sec.

7.3 An Example for the ASOG equation

Example 6: Toluene – \( n \)-Heptane – Acetonitrile

This example was tested by Tochigi et al. (1980). The binary interaction parameters are supplied by Kojima and Tochigi (1979). The introduced parameters of the ASOG are given in Table 12. The global solution has two liquid phases and it is given in Table 13. If two liquid phases are postulated then the global solution to the minimization of the Gibbs free energy is obtained in 1407 iterations and 43.5 cpu sec.

8 Conclusions

New properties of the molar Gibbs free energy function for nonideal liquid phases that are modeled using the UNIFAC, modified Wilson and ASOG equations have been presented. Simplifications and transformations were also provided for these equations which allow the Gibbs function to be expressed as the difference of two convex functions where the concave portion is separable. These have provided new expressions that allow the application of a global optimization algorithm for the minimization of the Gibbs free energy function and the tangent plane distance function. This algorithm guarantees convergence to an \( \epsilon \)-global solution to both of these problems. The Wilson equation is shown to lead to a convex formulation of the Gibbs free energy. The package GLOPEQ (McDonald and Floudas, 1994d) was used to obtain global solutions for a variety of examples.

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References


Appendix A

The activity coefficient, \( \gamma_i \), is assumed to be composed of combinatorial and residual contributions:

\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R
\]

The combinatorial activity coefficient is given as follows:

\[
\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in G} l_j x_j
\]

(A.2)

where \( z \) is a lattice coordination number usually taken as 10, \( \theta_i \) and \( \phi_i \) are the molecular surface area and volume fractions respectively, and given by:

\[
\theta_i = \frac{q_i x_i}{\sum_{j \in G} q_j x_j}
\]

(A.3)

\[
\phi_i = \frac{r_i x_i}{\sum_{j \in G} r_j x_j}
\]

(A.4)

where \( q_i \) and \( r_i \) are the surface area and volume constants associated with each component \( i \) and are defined as:

\[
q_i = \sum_{l \in G} v_l Q_l \quad \text{and} \quad r_i = \sum_{l \in G} v_l R_l
\]

(A.5)

where \( Q_l \) and \( R_l \) are the group surface area and volume constants respectively and \( v_l \) represents the number of groups of type \( l \) in molecule \( i \). \( l_i \) is another pure component parameter that is defined in the following way:

\[
l_i = \frac{z}{2} \cdot (r_i - q_i) - (r_i - 1)
\]

(A.6)

The residual part of the activity coefficient is given by the following equation:

\[
\ln \gamma_i^R = \sum_{l \in G} v_l \left[ \ln \Gamma_l - \ln \Gamma_l^{(i)} \right]
\]

(A.7)

where \( \Gamma_l \) is the residual activity coefficient of group \( l \) in molecule \( i \) and \( \Gamma_l^{(i)} \) is this quantity in the reference state of pure \( i \), which ensures that \( \ln \gamma_i \rightarrow 0 \) as \( x_i \rightarrow 1 \). These residual activity coefficients are supplied as functions of the effective group fractions, \( X_l \), defined as:

\[
X_l = \frac{\sum_{i \in G} x_i v_l}{\sum_{i \in G \sum_{m \in G} x_i v_{mi}} \quad \forall \ l \in G
\]

(A.8)

The residual activity coefficient is given by the following equation:

\[
\ln \Gamma_l = Q_l \left\{ 1 - \ln \sum_{m \in G} \Theta_m \Psi_{ml} - \sum_{m \in G} \frac{\Theta_m \Psi_{lm}}{\sum_{n \in G} \Theta_n \Psi_{nm}} \right\} \quad \forall \ l \in G
\]

(A.9)
where $\Theta_l$ is the group surface area fraction defined as:

$$\Theta_l = \frac{Q_l X_l}{\sum_{m \in G} Q_m X_m} \quad \forall \ l \in G \quad (A.10)$$

The binary group interaction parameter $\Psi_{lm}$ is given as:

$$\Psi_{lm} = \exp \left( - \frac{a_{lm}}{T} \right) \quad (A.11)$$

where $a_{lm}$ measures the energy of interaction between the groups $l$ and $m$. It is not symmetric so that $a_{lm} \neq a_{ml}$ and it is assumed to be independent of temperature. Eqn. (A.9) is also valid for $\Gamma^{(i)}$ by setting $X_l = 1$ with $X_m \neq l = 0$. 
Appendix B

It is required to prove the following relation:

\[
\sum_{i \in C} x_i \sum_{l \in G} v_{kl} Q_l = \sum_{i \in C} x_i \sum_{l \in G} v_{kl} Q_l \cdot \sum_{m \in G} \frac{\Theta_m \Psi_{lm}}{\sum_{n \in G} \Theta_n \Psi_{nm}}
\] (B.1)

Firstly, the terms involving the area fraction on the RHS of Eqn. (B.1) are expanded:

\[
\sum_{m \in G} \frac{\Theta_m \Psi_{lm}}{\sum_{n \in G} \Theta_n \Psi_{nm}} = \sum_{m \in G} \sum_{i \in C} x_i Q_m v_{mi} \Psi_{lm}
\] (B.2)

Then the following series of steps are used:

(i) Extract the denominator of Eqn. (B.1) to give Eqn. (B.3). This has the important effect of changing the order of indexing from \( \Psi_{lm} \) to \( \Psi_{ml} \) in the numerator.

(ii) This change in the order of indexing implies that the two terms involving \( \Psi_{ml} \) cancel, as the indices \( m \) and \( n \) run independently of each other, so that Eqn. (B.4) is obtained.

\[
\sum_{i \in C} x_i \sum_{l \in G} v_{kl} Q_l \cdot \sum_{m \in G} \frac{\sum_{i \in C} x_i Q_m v_{mi} \Psi_{lm}}{\sum_{n \in G} Q_n v_{ni} \Psi_{nm}}
\]

\[
= \sum_{l \in G} \sum_{i \in C} x_i \sum_{n \in G} Q_n v_{ni} \Psi_{nl} \cdot \sum_{i \in C} x_i \sum_{m \in G} v_{mi} Q_m \cdot \sum_{l \in G} x_j Q_l v_{lj} \Psi_{ml}
\] (B.3)

\[
= \sum_{l \in G} \sum_{i \in C} x_i \sum_{n \in G} Q_n v_{ni} \Psi_{nl} \cdot \sum_{i \in C} x_i \sum_{m \in G} v_{mi} Q_m \Psi_{ml} \cdot \sum_{l \in G} x_j Q_l v_{lj}
\]

\[
= \sum_{l \in G} \sum_{j \in G} x_j Q_l v_{lj} = \sum_{i \in C} x_i \sum_{l \in G} Q_l v_{li}
\] (B.4)

Eqn. (B.4) is therefore equal to the LHS of Eqn. (B.1), and the proof is complete. \( \square \)
Appendix C

The term $A$ of Eqn. (31) is defined as:

$$A = \sum_{i \in C} x_i \ln \sum_{j \in C} x_j \rho_{ij}$$  \hspace{1cm} (C.1)

A term is added and subtracted from Eqn. (C.1) as follows:

$$\sum_{i \in C} x_i \ln \sum_{j \in C} x_j \rho_{ij}$$

$$= \sum_{i \in C} x_i \ln \left( \sum_{j \in C} x_j \rho_{ij} \right) + \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln \sum_{i \in C} x_i \rho_{il} - \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln \sum_{i \in C} x_i \rho_{il}$$

$$= \sum_{i \in C} \left( \sum_{j \in C} x_j \rho_{ji} \right) \ln \left( \sum_{j \in C} x_j \rho_{ji} \right) - \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln x_j$$  \hspace{1cm} (C.2)

The last term of Eqn. (C.3) is then transformed by adding and subtracting the following term:

$$- \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln \sum_{i \in C} x_i \rho_{il}$$

$$= - \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln \sum_{i \in C} x_i \rho_{il} + \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln x_j - \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln x_j$$

$$= \sum_{i \in C} \rho_{ji} x_j \ln \frac{x_j}{\sum_{i \in C} x_i \rho_{il}} - \sum_{i \in C} \sum_{j \in C, j \neq i} x_j \rho_{ji} \ln x_j$$

$$= \sum_{i \in C} \sum_{j \in C, j \neq i} \rho_{ji} x_j \ln \frac{x_j}{\sum_{i \in C} x_i \rho_{il}} \sum_{i \in C} x_i \ln x_i \cdot \sum_{j \in C, j \neq i} \rho_{ji}$$  \hspace{1cm} (C.4)

Substitution of Eqn. (C.4) into Eqn. (C.3) then yields the final result:

$$\sum_{i \in C} x_i \ln \sum_{j \in C} x_j \rho_{ij}$$

$$= \sum_{i \in C} \left[ \sum_{j \in C} x_j \rho_{ji} \right] \ln \left( \sum_{j \in C} x_j \rho_{ji} \right) + \sum_{i \in C} \sum_{j \in C, j \neq i} \rho_{ji} x_j \ln \frac{x_j}{\sum_{i \in C} x_i \rho_{il}} - \sum_{i \in C} x_i \ln x_i \cdot \sum_{j \in C, j \neq i} \rho_{ji}$$  \hspace{1cm} (C.5)

The first term of Eqn. (C.6) is convex by Part (ii) of Property 3.1. The second term is also convex using Part (i) of Property 3.1 as $\rho_{ji}$ is always positive. The summation of these convex functions is itself a convex function and corresponds to the definition of $A_+$ in Eqn. (32). The third and last term of Eqn. (C.6) corresponds to the definition of $A_-$ supplied by Eqn. (32) and is clearly a concave and separable function. This completes the proof.

$\Box$

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UNIFAC data for $n$-Butyl-Acetate (1) – Water (2)

<table>
<thead>
<tr>
<th>Component</th>
<th>$q_i$</th>
<th>$v^{(i)}$</th>
<th>$\tilde{v}_k$ ($v_k$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CH_2$</td>
</tr>
<tr>
<td>$C_6H_{12}O_2$ (1)</td>
<td>4.196</td>
<td>-0.00108</td>
<td>7.52678 (3)</td>
</tr>
<tr>
<td>$H_2O$ (2)</td>
<td>1.4</td>
<td>0</td>
<td>0.44374 (0)</td>
</tr>
</tbody>
</table>

Table 1: Data for Example 1

Solution for $n$-Butyl-Acetate (1) – Water (2)

$G^* = -0.03407$, $T = 298K$, $P = 1.0$ atm

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (mols)</th>
<th>Liquid I $x_i^I$</th>
<th>Liquid II $x_i^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_{12}O_2$ (1)</td>
<td>0.50</td>
<td>0.91717</td>
<td>0.00036</td>
</tr>
<tr>
<td>$H_2O$ (2)</td>
<td>0.50</td>
<td>0.08283</td>
<td>0.99964</td>
</tr>
<tr>
<td>$\phi^k$</td>
<td></td>
<td>0.544979</td>
<td>0.455021</td>
</tr>
</tbody>
</table>

Table 2: Global Solution for Example 1

30
<table>
<thead>
<tr>
<th>Components</th>
<th>Solution (G*)</th>
<th>$\mu^0_i(z)$</th>
<th>Liquid I $x_i^I$</th>
<th>Liquid II $x_i^{II}$</th>
<th>Liquid III $x_i^{III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$ (1)</td>
<td>Local LL</td>
<td>-0.03388</td>
<td>0.92236</td>
<td>0.10717</td>
<td>(—)</td>
</tr>
<tr>
<td>$C_3H_7OH$ (2)</td>
<td>(−0.19155)</td>
<td>-0.59875</td>
<td>0.07749</td>
<td>0.45793</td>
<td>(—)</td>
</tr>
<tr>
<td>$C_6H_{14}$ (3)</td>
<td></td>
<td>0.02007</td>
<td>0.00015</td>
<td>0.43490</td>
<td>(—)</td>
</tr>
<tr>
<td>$\phi^k$</td>
<td></td>
<td></td>
<td></td>
<td>0.45268</td>
<td>0.54732</td>
</tr>
<tr>
<td>$H_2O$ (1)</td>
<td>Local LL †</td>
<td>-0.02527</td>
<td>0.62647</td>
<td>0.06277</td>
<td>(—)</td>
</tr>
<tr>
<td>$C_3H_7OH$ (2)</td>
<td>(−0.20626)</td>
<td>-0.60830</td>
<td>0.35571</td>
<td>0.06520</td>
<td>(—)</td>
</tr>
<tr>
<td>$C_6H_{14}$ (3)</td>
<td></td>
<td>-0.04454</td>
<td>0.01781</td>
<td>0.93203</td>
<td>(—)</td>
</tr>
<tr>
<td>$\phi^k$</td>
<td></td>
<td></td>
<td></td>
<td>0.75905</td>
<td>0.24095</td>
</tr>
<tr>
<td>$H_2O$ (1)</td>
<td>Global LLL</td>
<td>-0.03385</td>
<td>0.45295</td>
<td>0.00282</td>
<td>0.92272</td>
</tr>
<tr>
<td>$C_3H_7OH$ (2)</td>
<td>(−0.20792)</td>
<td>-0.59902</td>
<td>0.48501</td>
<td>0.06676</td>
<td>0.07715</td>
</tr>
<tr>
<td>$C_6H_{14}$ (3)</td>
<td></td>
<td>-0.04518</td>
<td>0.06204</td>
<td>0.93042</td>
<td>0.00013</td>
</tr>
<tr>
<td>$\phi^k$</td>
<td></td>
<td></td>
<td></td>
<td>0.51700</td>
<td>0.22139</td>
</tr>
</tbody>
</table>

† Solution obtained by Fredenslund et al. (1977)

Table 3: Solutions for Example 2 at Conditions (i)
### Solution for Water (1) – n-Propanol (2) – n-Hexane (3)

\( n_i^T = \{0.5, 0.5, 0.25\} \), \( T = 311K \), \( P = 1.0 \text{ atm} \)

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>( \mu_i^0(z) )</th>
<th>Liquid I ( x_i^I )</th>
<th>Liquid II ( x_i^H )</th>
<th>Liquid III ( x_i^{III} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O ) (1)</td>
<td>Local LL</td>
<td>-0.03235</td>
<td>0.19565</td>
<td>0.93223</td>
<td>(—)</td>
</tr>
<tr>
<td>( C_3H_7OH ) (2)</td>
<td>((-0.31402))</td>
<td>-0.61847</td>
<td>0.52760</td>
<td>0.06767</td>
<td>(—)</td>
</tr>
<tr>
<td>( C_6H_{14} ) (3)</td>
<td></td>
<td>0.04557</td>
<td>0.27675</td>
<td>0.00010</td>
<td>(—)</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td>0.72257</td>
<td>0.27743</td>
<td>(—)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>( \mu_i^0(z) )</th>
<th>Liquid I ( x_i^I )</th>
<th>Liquid II ( x_i^H )</th>
<th>Liquid III ( x_i^{III} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O ) (1)</td>
<td>Local LL †</td>
<td>-0.03040</td>
<td>0.48006</td>
<td>0.00280</td>
<td>(—)</td>
</tr>
<tr>
<td>( C_3H_7OH ) (2)</td>
<td>((-0.32765))</td>
<td>-0.60242</td>
<td>0.46729</td>
<td>0.06618</td>
<td>(—)</td>
</tr>
<tr>
<td>( C_6H_{14} ) (3)</td>
<td></td>
<td>-0.04494</td>
<td>0.05265</td>
<td>0.93102</td>
<td>(—)</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td>0.83224</td>
<td>0.16776</td>
<td>(—)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>( \mu_i^0(z) )</th>
<th>Liquid I ( x_i^I )</th>
<th>Liquid II ( x_i^H )</th>
<th>Liquid III ( x_i^{III} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O ) (1)</td>
<td>Global LLL</td>
<td>-0.03385</td>
<td>0.45295</td>
<td>0.00282</td>
<td>0.92272</td>
</tr>
<tr>
<td>( C_3H_7OH ) (2)</td>
<td>((-0.32773))</td>
<td>-0.59902</td>
<td>0.48501</td>
<td>0.06676</td>
<td>0.07715</td>
</tr>
<tr>
<td>( C_6H_{14} ) (3)</td>
<td></td>
<td>-0.04518</td>
<td>0.06204</td>
<td>0.93042</td>
<td>0.00013</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td>0.79569</td>
<td>0.16190</td>
<td>0.04241</td>
<td></td>
</tr>
</tbody>
</table>

† Solution obtained by Fredenslund et al. (1977)

Table 4: Solutions for Example 2 at Conditions (ii)
### Solution for Water (1) – n-Propanol (2) – n-Hexane (3)

\[ T = 311K, \ P = 1.0 \ \text{atm} \]

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ( (G^*) )</th>
<th>( \mu_i^0(z) )</th>
<th>Feed ( n_i^T )</th>
<th>Liquid I ( x_i^I )</th>
<th>Liquid II ( x_i^{II} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O ) (1)</td>
<td>Global LL</td>
<td>-0.04933</td>
<td>0.50</td>
<td>0.22781</td>
<td>0.85570</td>
</tr>
<tr>
<td>( C_3H_7OH ) (2)</td>
<td>(-0.39268)</td>
<td>-1.11367</td>
<td>0.30</td>
<td>0.38067</td>
<td>0.14062</td>
</tr>
<tr>
<td>( C_6H_{14} ) (3)</td>
<td></td>
<td>-0.13565</td>
<td>0.25</td>
<td>0.39152</td>
<td>0.00367</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td></td>
<td></td>
<td>0.60442</td>
<td>0.39558</td>
</tr>
<tr>
<td>( H_2O ) (1)</td>
<td>Global LL</td>
<td>-0.05055</td>
<td>0.50</td>
<td>0.37951</td>
<td>0.82571</td>
</tr>
<tr>
<td>( C_3H_7OH ) (2)</td>
<td>(-0.61464)</td>
<td>-1.10665</td>
<td>0.50</td>
<td>0.41115</td>
<td>0.16830</td>
</tr>
<tr>
<td>( C_6H_{14} ) (3)</td>
<td></td>
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<td>0.25</td>
<td>0.20934</td>
<td>0.00599</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td></td>
<td></td>
<td>0.95409</td>
<td>0.04591</td>
</tr>
</tbody>
</table>

Table 5: Example 2 using parameters of Magnussen \textit{et al.} (1981)
### Solution for Ethanol (1) – Benzene (2) – Water (3)

\( n_i^T = \{0.20, 0.35, 0.45\}, T = 338K, P = 1.0 \text{ atm} \)

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>(\mu_i^0(z))</th>
<th>Liquid I (x_i^L)</th>
<th>Liquid II (x_i^{II})</th>
<th>Vapor (y_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_5OH) (1)</td>
<td>Local LV</td>
<td>-1.71936</td>
<td>0.22661</td>
<td>(—)</td>
<td>0.17918</td>
</tr>
<tr>
<td>(C_6H_6) (2)</td>
<td>((-1.23329))</td>
<td>-0.47832</td>
<td>0.00506</td>
<td>(—)</td>
<td>0.61982</td>
</tr>
<tr>
<td>(H_2O) (3)</td>
<td></td>
<td>-1.60446</td>
<td>0.76833</td>
<td>(—)</td>
<td>0.20100</td>
</tr>
<tr>
<td>(\phi^k)</td>
<td></td>
<td>0.43890</td>
<td>(—)</td>
<td>0.56110</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>(\mu_i^0(z))</th>
<th>Liquid I (x_i^L)</th>
<th>Liquid II (x_i^{II})</th>
<th>Vapor (y_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_5OH) (1)</td>
<td>Local LL</td>
<td>-1.52310</td>
<td>0.00612</td>
<td>0.30357</td>
<td>(—)</td>
</tr>
<tr>
<td>(C_6H_6) (2)</td>
<td>((-1.23481))</td>
<td>-0.50381</td>
<td>0.99016</td>
<td>0.00802</td>
<td>(—)</td>
</tr>
<tr>
<td>(H_2O) (3)</td>
<td></td>
<td>-1.67523</td>
<td>0.00372</td>
<td>0.68841</td>
<td>(—)</td>
</tr>
<tr>
<td>(\phi^k)</td>
<td></td>
<td>0.34820</td>
<td>0.65180</td>
<td>(—)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ((G^*))</th>
<th>(\mu_i^0(z))</th>
<th>Liquid I (x_i^L)</th>
<th>Liquid II (x_i^{II})</th>
<th>Vapor (y_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_2H_5OH) (1)</td>
<td>Global LLV</td>
<td>-1.59634</td>
<td>0.27208</td>
<td>0.00565</td>
<td>0.20264</td>
</tr>
<tr>
<td>(C_6H_6) (2)</td>
<td>((-1.23589))</td>
<td>-0.50349</td>
<td>0.00663</td>
<td>0.99054</td>
<td>0.60442</td>
</tr>
<tr>
<td>(H_2O) (3)</td>
<td></td>
<td>-1.64535</td>
<td>0.72129</td>
<td>0.00381</td>
<td>0.19294</td>
</tr>
<tr>
<td>(\phi^k)</td>
<td></td>
<td>0.56228</td>
<td>0.21160</td>
<td>0.22612</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Solutions for Example 3

### Ethanol (1) – Acetic Acid (2) – Ethyl Acetate (3) – Water (4)

<table>
<thead>
<tr>
<th>(A_{ij})</th>
<th>(EtOH)</th>
<th>(HAc)</th>
<th>(EtAc)</th>
<th>(H_2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(EtOH)</td>
<td>1.0</td>
<td>2.28180</td>
<td>0.76670</td>
<td>0.15347</td>
</tr>
<tr>
<td>(HAc)</td>
<td>0.27558</td>
<td>1.0</td>
<td>0.61790</td>
<td>0.26838</td>
</tr>
<tr>
<td>(EtAc)</td>
<td>0.55046</td>
<td>0.89277</td>
<td>1.0</td>
<td>0.12353</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>0.92038</td>
<td>1.22642</td>
<td>0.14907</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 7: Binary data for Example 4
Data for the elemental mass constraints

<table>
<thead>
<tr>
<th>$a_a$</th>
<th>$EtOH$</th>
<th>$HAc$</th>
<th>$EtAc$</th>
<th>$H_2O$</th>
<th>$b_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>$H$</td>
<td>6</td>
<td>4</td>
<td>8</td>
<td>2</td>
<td>5.0</td>
</tr>
<tr>
<td>$O$</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 8: Elemental abundance parameters for Example 4

Ethanol (1) – Acetic Acid (2) – Ethyl Acetate (3) – Water (4)

Solution: $G^* = -90.7816$ with $T = 355K$, $P = 1$ atm.

<table>
<thead>
<tr>
<th>Component</th>
<th>Liquid (mol fraction)</th>
<th>Vapor (mol fraction)</th>
<th>$\Delta G_i^{V/L}$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$EtOH$ (1)</td>
<td>0.04898</td>
<td>0.08289</td>
<td>-37.0918</td>
</tr>
<tr>
<td>$HAc$ (2)</td>
<td>0.20419</td>
<td>0.06570</td>
<td>-87.3031</td>
</tr>
<tr>
<td>$EtAc$ (3)</td>
<td>0.11719</td>
<td>0.45408</td>
<td>-72.8406</td>
</tr>
<tr>
<td>$H_2O$ (4)</td>
<td>0.62965</td>
<td>0.39733</td>
<td>-54.0234</td>
</tr>
<tr>
<td>Total mols</td>
<td>0.09970</td>
<td>0.90030</td>
<td>(—)</td>
</tr>
</tbody>
</table>

Table 9: Global solution for Example 4 at $T=355K$
Ethanol (1) – Acetic Acid (2) – Ethyl Acetate (3) – Water (4)

Solution: \( G^* = -89.8003 \) with \( T = 358K, P = 1 \) atm.

<table>
<thead>
<tr>
<th>Component</th>
<th>Liquid (mol fraction)</th>
<th>Vapor (mol fraction)</th>
<th>( \Delta G_{i,j}^{v,l} ) (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH (1)</td>
<td>(—)</td>
<td>0.075313</td>
<td>-36.9228</td>
</tr>
<tr>
<td>HAc (2)</td>
<td>(—)</td>
<td>0.075313</td>
<td>-87.1561</td>
</tr>
<tr>
<td>EtAc (3)</td>
<td>(—)</td>
<td>0.424687</td>
<td>-72.5494</td>
</tr>
<tr>
<td>H2O (4)</td>
<td>(—)</td>
<td>0.424687</td>
<td>-53.9903</td>
</tr>
<tr>
<td>Total mols</td>
<td>0.0</td>
<td>1.0</td>
<td>(—)</td>
</tr>
</tbody>
</table>

Table 10: Global solution for Example 4 at \( T = 358K \)

Solution for Methanol (1) – Cyclohexane (2)

\( G^* = -0.07439 \), \( T = 298K, P = 1.0 \) atm

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (mols)</th>
<th>Liquid I ( x_i^I )</th>
<th>Liquid II ( x_i^{II} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3OH ) (1)</td>
<td>0.50</td>
<td>0.12496</td>
<td>0.82760</td>
</tr>
<tr>
<td>( C_6H_{12} ) (2)</td>
<td>0.50</td>
<td>0.87504</td>
<td>0.17240</td>
</tr>
<tr>
<td>( \phi^k )</td>
<td></td>
<td>0.46624</td>
<td>0.53376</td>
</tr>
</tbody>
</table>

Table 11: Global Solution for Example 5

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### ASOG data for Toluene (1) – n-Heptane (2) – Acetonitrile (3)

<table>
<thead>
<tr>
<th>Component</th>
<th>$q_i$</th>
<th>$v^{(i)}$</th>
<th>$\hat{\nu}_k$ ($\nu_k$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$CH_2$</td>
</tr>
<tr>
<td>$C_7H_9$ (1)</td>
<td>7</td>
<td>0.08258</td>
<td>5.53812 (1)</td>
</tr>
<tr>
<td>$C_7H_{14}$ (2)</td>
<td>7</td>
<td>0</td>
<td>7.00000 (7)</td>
</tr>
<tr>
<td>$CH_3N$ (3)</td>
<td>3</td>
<td>0.60779</td>
<td>3.14273 (1)</td>
</tr>
</tbody>
</table>

Table 12: Data for Example 6

### Solution for Toluene (1) – n-Heptane (2) – Acetonitrile (3)

$n_i^T = \{0.10, 0.45, 0.45\}, T = 313K, P = 1.0$ atm

<table>
<thead>
<tr>
<th>Components</th>
<th>Solution ($G^*$)</th>
<th>Liquid I $x_i^I$</th>
<th>Liquid II $x_i^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_9$ (1)</td>
<td>Global LL</td>
<td>0.12298</td>
<td>0.06115</td>
</tr>
<tr>
<td>$C_7H_{14}$ (2)</td>
<td>$(-0.36916)$</td>
<td>0.64165</td>
<td>0.12603</td>
</tr>
<tr>
<td>$C_6H_{14}$ (3)</td>
<td></td>
<td>0.23537</td>
<td>0.81282</td>
</tr>
<tr>
<td>$\phi^k$</td>
<td></td>
<td>0.62831</td>
<td>0.37169</td>
</tr>
</tbody>
</table>

Table 13: Solutions for Example 6