Locating All Homogeneous Azeotropes In Multicomponent Mixtures

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Abstract

A novel approach for enclosing *all* homogeneous azeotropes in multicomponent mixtures is presented. The thermodynamic criteria for azeotropy are outlined, and mathematical equations for each criterion are developed. The global optimization approach is based on developing convex underestimators which are coupled with a branch and bound framework in which upper and lower bounds on the solution are refined by successively partitioning the target region into small disjoint rectangles. The objective of such an approach is to enclose all global minima since each global minimum corresponds to an homogeneous azeotrope. Because of the nature of the thermodynamic equations which describe the behavior of the liquid phase, the constraint equations are highly nonlinear and nonconvex. The success of this approach depends upon constructing valid convex lower bounds for each nonconvex function in the constraints. Four different thermodynamic models are studied, the Wilson, NRTL, UNIQUAC, and UNIFAC equations. Tight convex lower bounding functions are found for the nonconvex terms in each model. The unique element of the proposed approach is that it offers a theoretical guarantee of enclosing all homogeneous azeotropes. The effectiveness of the proposed approach is illustrated in several example problems.

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1 Introduction

The ability to predict whether a given mixture will form one or more azeotropes and to calculate the conditions and compositions of each azeotrope is essential if one wants to model separation processes. Similarly, it is necessary to calculate the effects of temperature and pressure on the composition of an azeotrope for process design applications.

Many thermodynamic models have been proposed which can predict the phase behavior of nonideal mixtures. Unfortunately, the accuracy of these models is not uniform over a wide range of mixtures. One useful way of testing the accuracy of a model for a given mixture is to compare the compositions of the azeotropes predicted by the model with those determined by experiment. In order to be most useful, a method for calculating the azeotropes of a mixture must be robust, and must be able to guarantee that all possible azeotropes can be found.

Despite the considerable interest in the area of predicting phase equilibria for chemical mixtures, relatively few methods for prediction of azeotropes have been reported. This is because the task of finding the pressure, temperature, and composition of *all* azeotropes is an especially difficult one, due to the highly nonlinear form of the equations which constitute the thermodynamic models.

Most of the previous work reported in the literature has been limited to calculating homogeneous azeotropes. Aristovich and Stepanova (1970) calculated ternary homogeneous azeotropes using the Wilson model under isothermal conditions. Teja and Rowlinson (1973) calculated homogeneous azeotropes of binary mixtures using an equation of state as the thermodynamic model. Their approach was to fix temperature and vary composition and volume until thermodynamic equilibrium conditions were satisfied. Wang and Whiting (1986) also used an equation of state to calculate homogeneous azeotropes for binary mixtures. Fidkowski *et al.* (1993) have presented an interesting homotopy continuation method for finding homogeneous azeotropes.

Chapman and Goodwin (1993) presented a search method for finding homogeneous and heterogeneous azeotropes which uses a Levenberg-Marquardt algorithm to find homogeneous azeotropes and then checks the stability of each solution with the tangent plane criterion described by Michelsen (1981). A solution which is found to be unstable is then used as the starting point for a new search for an heterogeneous azeotrope. This method is limited by the fact that heterogeneous azeotropes do not necessarily correspond to an unstable homogeneous azeotrope solution and vice versa. This method cannot find azeotropes for which one or more components have a vapor phase mole fraction of zero. An excellent review on nonideal distillation, including a discussion on the computation of azeotropes has recently been published by Widagdo and Seider (1996).

The purpose of this paper is to propose a new method for determining all homogeneous azeotropes of a non-reacting mixture for several different thermodynamic models. This method models the vapor phase as an ideal gas at low pressure, and uses activity coefficient models for the liquid phase. The activity coefficient models examined are: the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation. The problem is formulated as a global optimization problem in which each global minimum solution corresponds to an homogeneous azeotrope. Examples demonstrating the performance of this method will be shown for each model.

In the Section 2, the mathematical formulation of the problem will be developed. In Section 3, the specific activity coefficient models will be examined, and convex lower bounding functions developed for each nonconvex term. The approach based on global optimization will be explained in Section 4, and extensive computational results for each activity coefficient model will be presented in Section 5.

2 Problem Description and Formulation

In this section, the fundamentals of azeotropy will be summarized and the thermodynamic equations which determine the existence of azeotropes will be presented. Finally, the problem of enclosing all homogeneous azeotropes will be formulated as a global optimization problem in which the objective is to enclose all global solutions.

2.1 Azeotropy

In order to develop a method for finding all azeotropes of a mixture, it is essential to first determine the thermodynamic conditions for azeotropy. Azeotropes occur in a boiling mixture of one or more liquid phases when the composition of the vapor phase is the same as the overall composition of the liquid phase(s).

Azeotropes can be classified by two categories: order and type. The order of the azeotrope describes the number of species that participate in the azeotrope. For example, a mixture of compounds A, B, and C may have a ternary azeotrope ABC in which all three components participate, and three binary azeotropes, AB, AC, and BC. The type of azeotrope reflects the number of phases present at the point of azeotropy. When a vapor phase and only one liquid phase are present, the azeotrope is termed an homogeneous azeotrope. In the case of homogeneous azeotropy, application of the condition that the overall composition of the phases are identical produces the familiar equation:

$$x_i = y_i \qquad \forall\ i \in N \tag{1}$$

where x_i is the mole fraction of component i in the liquid phase, y_i is the mole fraction of component i in the vapor phase, and N is the set of components.

The second type of azeotrope is an heterogeneous azeotrope. Heterogeneous azeotropes occur when a vapor phase and two or more liquid phases are present at the point of azeotropy. In this case, the composition of the vapor phase must be equal to the *overall* composition of the liquid phases. In general, a mixture of N components and M phases may have both homogeneous and heterogeneous azeotropes. This paper will not deal with calculation of heterogeneous azeotropes.

2.2 Thermodynamic Conditions for Azeotropy

There are three thermodynamic conditions which a system must meet in order for an azeotrope to exist. These conditions are: 1) equilibrium, 2) the composition of vapor phase must be identical to the overall composition of the liquid phase(s), and 3) the mole fractions of the components in each phase must sum to unity and must be non-negative.

The equilibrium condition requires that the chemical potential of each component must be the same in all phases. Since an homogeneous azeotropic system contains a vapor phase (V), and only one liquid phase (L), this condition can be written:

$$\mu_i^V = \mu_i^L \qquad \forall\ i \in N \tag{2}$$

where μ_i^V and μ_i^L represent the chemical potential of component i in the vapor and liquid phases. From the definition of the fugacity of component i in a mixture, $\hat{f}_i$,

$$\hat{f}_i^V = \hat{f}_i^L \qquad \forall\ i \in N \tag{3}$$

hence,

$$y_i \hat{\phi}_i^V P = x_i \gamma_i^L f_i^L \tag{4}$$

The symbol $\hat{\phi}_i^V$ represents the mixture fugacity coefficient of component i in the vapor phase. For the liquid phase, γ_i^L is the activity coefficient, and f_i^L is the fugacity of component i in the liquid phase. Rearranging equation (4) gives,

$$\frac{y_i}{x_i} = \frac{\gamma_i^L f_i^L}{\hat{\phi}_i^V P} \qquad \forall\ i \in N \tag{5}$$

At low pressure, the vapor phase can be modeled as an ideal gas, for which $\hat{\phi}_i^V = 1$, and for the liquid phase the fugacity is equal to $f_i^L = \phi_i^{sat} P_i^{sat} (PF)_i$. But, for an ideal gas, $\phi_i^{sat} = 1$, and $(PF)_i = 1$. Therefore

$$\frac{y_i}{x_i} = \frac{\gamma_i^L P_i^{sat}}{P} \tag{6}$$

Now all of the nonidealities of the system are confined to the activity coefficient term. For binary homogeneous azeotropes, negative deviations from Raoult's law ($\gamma_i^L < 1$) result in a maximum-boiling azeotrope, also called a minimum-pressure azeotrope. Positive deviations result in a minimum-boiling (maximum-pressure) azeotrope. Ternary and higher order azeotropes may also occur at saddle points in the temperature (or pressure) vs. composition surface.

Conversely, an heterogeneous azeotrope only occurs when positive deviations from Raoult's law are very large ($\gamma_i^{L_j} \gg 1$) where j represents each liquid phase $j \in M$, and the vapor-liquid equilibrium surface overlaps the liquid-liquid equilibrium surface.

Note that for an homogeneous azeotrope, the vapor and liquid phases all have the same composition, unlike the heterogeneous case. The azeotropy condition requires that the composition of the vapor phase is identical to the overall composition of the liquid phase(s). In the case of an homogeneous azeotrope, this condition simplifies to:

$$y_i = x_i \qquad \forall\ i \in N \tag{7}$$

The third condition requires that the mole fractions in each phase sum to unity and have values between 0 and 1.

$$\begin{aligned} \sum_{i \in N} y_i = \sum_{i \in N} x_i = 1 \\ 0 \leq y_i, x_i \leq 1 \qquad \forall\, i \in N \end{aligned} \tag{8}$$

2.3 Mathematical Formulation

In order to find all azeotropes, one must find all solutions to the system of nonlinear equations (6), (7), and (8) listed in the previous section. This paper uses the approach outlined in Maranas and Floudas (1995), which reformulates the problem of enclosing all solutions of nonlinear systems of constrained equations into a global optimization problem in which the task is to enclose all global solutions. In this approach, each nonlinear equality is replaced by two inequalities and a single slack variable is introduced. For the location of all homogeneous azeotropes, this corresponds to employing equations (6), (7), and (8) and reformulating them as the following global optimization problem:

$$\begin{array}{lll} \min\limits_{\mathbf{x},\mathbf{y},T,s} & s & \\ \text{subject to} & Py_i - P_i^{sat}\gamma_i x_i - s \ \leq \ 0 & \forall\, i \in N \\ & -Py_i + P_i^{sat}\gamma_i x_i - s \ \leq \ 0 & \forall\, i \in N \\ & y_i - x_i \ = \ 0 & \forall\, i \in N \\ & \sum\limits_{i \in N} y_i \ = \ 1 & \\ & \sum\limits_{i \in N} x_i \ = \ 1 & \\ & s \geq 0 & \\ & 0 \leq y_i \leq 1 & \forall\, i \in N \\ & 0 \leq x_i \leq 1 & \forall\, i \in N \end{array} \tag{9}$$

Problem (9) may have multiple global minima. Each global minimum of Problem (9) (where the solution $s^* = 0$) corresponds to an homogeneous azeotrope since when $s = 0$ the constraints (6), (7), and (8) are satisfied. Note that the first two sets of constraints of (9) correspond to the nonlinear equations (6) of the equilibrium constraint written as two inequalities. In addition, note that the nonlinear term $P_i^{sat}\gamma_i x_i$ appears as both a positive and a negative term. Thus, this term must be nonconvex in at least one of the two constraints. This means that if a local optimization approach is used to solve Problem (9), some or all of the global solutions may be missed. This problem will be considered in Section 3.

Because $x_i = y_i$ for every i, the system of equations can be simplified by replacing each y_i by x_i. Therefore, the equilibrium condition becomes,

$$x_i(P - P_i^{sat}\gamma_i) = 0 \qquad \forall\, i \in N \tag{10}$$

In order to satisfy this condition, either $x_i = 0$, or $(P - P_i^{sat}\gamma_i) = 0$ for each $i \in N$. If we wish to search only for azeotropes in which *all* components participate (an N-ary azeotrope), the condition can be further simplified to $(P - P_i^{sat}\gamma_i) = 0$ for each $i \in N$.

Because P_i^{sat} and γ_i are usually given as $\ln P_i^{sat}$ and $\ln \gamma_i$, it is convenient to take the natural log of the simplified equilibrium constraint, resulting in:

$$\ln P - \ln P_i^{sat} - \ln \gamma_i = 0 \qquad \forall\, i \in N \tag{11}$$

Then the formulation becomes:

$$\begin{array}{ll} \min\limits_{\mathbf{x},T,s} & s \\ \text{subject to} & \ln P - \ln P_i^{sat} - \ln \gamma_i - s \;\leq\; 0 \quad \forall\, i \in N \\ & -\ln P + \ln P_i^{sat} + \ln \gamma_i - s \;\leq\; 0 \quad \forall\, i \in N \\ & \sum\limits_{i \in N} x_i \;=\; 1 \\ & 0 < \mathbf{x} < 1 \\ & s \geq 0 \end{array} \tag{12}$$

Note that the first two sets of constraints in (12) represent the nonlinear equation (10) for $x_i \neq 0, \forall\, i \in N$ in the form of two inequalities. For azeotropes in which less than N of the components participate (a k-ary azeotrope where $k \leq N$), the case where $x_i = 0$ for one or more component must be accounted for. This can be done by multiplying the equilibrium constraints used in (11) by x_i. The general search for all k-ary homogeneous azeotropes is formulated as:

$$\begin{array}{ll} \min\limits_{\mathbf{x},T,s} & s \\ \text{subject to} & x_i(\ln P - \ln P_i^{sat} - \ln \gamma_i) - s \;\leq\; 0 \quad \forall\, i \in N \\ & x_i(-\ln P + \ln P_i^{sat} + \ln \gamma_i) - s \;\leq\; 0 \quad \forall\, i \in N \\ & \sum\limits_{i \in N} x_i \;=\; 1 \\ & 0 \leq \mathbf{x} \leq 1 \\ & s \geq 0 \end{array} \tag{13}$$

In the following section, this general formulation will be applied to four different activity coefficient models: the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation. For each model, the nonconvex terms are identified and convex lower bounding functions are developed.

3 Activity Coefficient Models

The problem formulations, (12), and (13) contain several nonconvex functions. If a local optimization approach is used to solve these problems, it is likely that some of the multiple global minima will be missed, or even that none will be found. Therefore, in order to guarantee that *all* global minima are enclosed, it is necessary to develop a convex relaxation of the problem. In the approach used in this paper, a lower bound on the solution of (12) and (13) is obtained by replacing each nonconvex constraint with a tight convex underestimator and then using a commercially available nonlinear solver such as MINOS5.4 as described in Maranas and Floudas (1993) and Maranas and Floudas (1994a). The upper and lower bounds on the solutions are then refined using a branch and bound approach.

A convex relaxation is developed by partitioning each nonlinear function in the constraint equations into convex and nonconvex terms. Tight convex lower bounding functions are then developed and replace each nonconvex term in the constraints.

This section analyzes the equations in the azeotropy problem formulation which contain nonconvex terms. In each case, the form of the equation is introduced, and the nonconvex terms are identified. For each nonconvex term, a convex lower bounding function is calculated. The saturated vapor pressure equation is examined first, then the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation will each be discussed.

3.1 Saturated Vapor Pressure Equation

In this work, the saturated vapor pressure is calculated using the Antoine equation:

$$\ln P_i^{sat} = a_i - \frac{b_i}{T + c_i} \tag{14}$$

where a_i, b_i, and c_i are constants. The parameters a_i and b_i are always positive, while c_i may be positive or negative but $\mid c_i \mid < T$. In the problem of finding all N-ary azeotropes, denoted as Problem (12), this term appears in the constraints as both $(-\ln P_i^{sat})$ and $(+\ln P_i^{sat})$. It can be easily shown that the term:

$$-\frac{b_i}{T + c_i} \tag{15}$$

is concave in T. As a result, in the first set of constraints of (12) which have $(-\ln P_i^{sat})$, this term is convex and no underestimation is needed. In the second set of constraints however, this term is concave and a convex underestimator is required. A convex underestimator for this concave term is simply a line segment between the values of the term at each limit. That is,

$$-\frac{b_i}{T + c_i} \geq -\frac{b_i}{T^L + c_i} + \frac{-\frac{b_i}{T^U + c_i} + \frac{b_i}{T^L + c_i}}{T^U - T^L}(T - T^L) \tag{16}$$

where T^L, T^U are the lower and upper bounds on the temperature in the current region.

In the formulation for finding all k-ary azeotropes (13), the Antoine equation is multiplied by the liquid mole fraction, x_i. In this case, both the positive and negative terms $(-x_i \ln P_i^{sat})$ and $(+x_i \ln P_i^{sat})$ are nonconvex. These terms have the form:

$$x_i \ln P_i^{sat} = f(x_i) \cdot \frac{1}{g(T)} \tag{17}$$

where $f(x_i)$ and $g(T)$ are univariate functions. Maranas and Floudas (1995) extended the work of Al-Khayyal and Falk (1983) on the convex lower bound of the bilinear product xy to products and quotients of arbitrary univariate functions, i.e., $f(x)g(y)$ and $\frac{f(x)}{g(y)}$. For a term of the form $\frac{f(x)}{g(y)}$, where $x^L \geq 0$ and $x^U \geq 0$, the convex lower bound is given by:

$$\begin{aligned}\frac{f(x)}{g(y)} \geq \max & \left\{ \frac{f^L(x)}{g(y)} + \frac{f(x)}{g^U(y)} - \frac{f^L(x)}{g^U(y)}, \right. \\ & \left. \frac{f^U(x)}{g(y)} + \frac{f(x)}{g^L(y)} - \frac{f^U(x)}{g^L(y)} \right\}.\end{aligned}$$

where $f^L(x)$ refers to the minimum of f over the domain $x^L \leq x \leq x^U$ and $f^U(x)$ is the maximum of f. The same notation is true for $g(y)$ also. When applied to the current problem, the convex lower bound becomes:

$$\begin{aligned}\frac{b_i x_i}{T + c_i} \geq \max & \left\{ \frac{b_i x_i^L}{T + c_i} + \frac{b_i x_i}{T^U + c_i} - \frac{b_i x_i^L}{T^U + c_i}, \right. \\ & \left. \frac{b_i x_i^U}{T + c_i} + \frac{b_i x_i}{T^L + c_i} - \frac{b_i x_i^U}{T^L + c_i} \right\}.\end{aligned}$$

For the case when a convex underestimator for a term of the form $-\frac{f(x)}{g(y)}$ is needed a different formula must be used, Maranas and Floudas (1995).

$$\begin{aligned}-\frac{f(x)}{g(y)} \geq \max & \left\{ -\frac{f(x)}{g^L(y)} + \frac{f^L(x)g(y)}{g^L(y)g^U(y)} - \frac{f^L(x)}{g^U(y)}, \right. \\ & \left. -\frac{f(x)}{g^U(y)} + \frac{f^U(x)g(y)}{g^L(y)g^U(y)} - \frac{f^U(x)}{g^L(y)} \right\}.\end{aligned}$$

So the convex lower bounding function for the term of this form is:

$$
-\frac{b_i x_i}{T+c_i} \;\geq\; \max\left\{-\frac{b_i x_i}{T^L+c_i} + \frac{b_i x_i^L}{(T^L+c_i)(T^U+c_i)}T - \frac{b_i x_i^L}{T^U+c_i},\right.
$$
$$
\left. -\frac{b_i x_i}{T^U+c_i} + \frac{b_i x_i^U}{(T^L+c_i)(T^U+c_i)}T - \frac{b_i x_i^U}{T^L+c_i}\right\}.
$$

3.2 Wilson Equation

Wilson (1964) developed an equation to model the fluid phase excess Gibbs free energy for vapor-liquid systems. The Wilson equation is often used to model solutions containing polar and nonpolar components. The Wilson activity coefficient equation is:

$$
\ln \gamma_i = 1 - \ln\left(\sum_{j\in N} x_j \Lambda_{ij}\right) - \sum_{j\in N} \frac{x_j \Lambda_{ji}}{\sum\limits_{k\in N} x_k \Lambda_{jk}} \tag{18}
$$

where Λ_{ij} is the nonsymmetric binary interaction parameter between components i and j with $\Lambda_{ii} = 1$. When the Wilson equation is used, the problem of finding all N-ary homogeneous azeotropes is formulated as:

$$
\begin{aligned}
\min_{\mathbf{x},s} \quad & s \\
\text{subject to} \quad & \ln\left(\sum_{j\in N} x_j\Lambda_{ij}\right) + \sum_{j\in N} s_j^1 \Lambda_{ji} + \tfrac{b_i}{T+c_i} + \ln P - a_i - 1 - s \;\leq\; 0 \qquad \forall\, i \in N \\
& -\ln\left(\sum_{j\in N} x_j\Lambda_{ij}\right) + \sum_{j\in N} s_j^2 \Lambda_{ji} - \tfrac{b_i}{T+c_i} - \ln P + a_i + 1 - s \;\leq\; 0 \quad \forall\, i \in N \\
& \sum_{i\in N} x_i \;=\; 1 \\
& 0 < \mathbf{x} < 1 \\
& s \geq 0
\end{aligned} \tag{19}
$$

where,

$$
s_j^1 = \frac{x_j}{\sum\limits_{k\in N} x_k \Lambda_{jk}} \tag{20}
$$

and,

$$
s_j^2 = -\frac{x_j}{\sum\limits_{k\in N} x_k \Lambda_{jk}} \tag{21}
$$

The s_j^1 and s_j^2 equations are used to isolate the nonconvex terms in the complicated summation expression. The Wilson expression for the activity coefficients contains three different nonconvex terms. The first nonconvex term is $(\ln \sum_{j \in N} x_j \Lambda_{ij})$. The second and third nonconvex terms are s_j^1 and s_j^2. As was described in the preceding section on the Antoine equation, multiplication of the equilibrium constraints by x_i in the problem of finding all k-ary azeotropes further complicates the nonconvex expressions. For the k-ary azeotrope problem (13), the Wilson equation now contains nonconvex terms:

$$x_i \ln(\sum_{j \in N} x_j \Lambda_{ij}) \qquad -x_i \ln(\sum_{j \in N} x_j \Lambda_{ij}) \qquad x_i \sum_{j \in N} s_j^1 \Lambda_{ji} \quad \text{and} \quad x_i \sum_{j \in N} s_j^2 \Lambda_{ji} \tag{22}$$

A convex lower bounding function must be developed for each of these nonconvex terms. The procedure for constructing the underestimating functions for the Wilson equation is presented in Appendix A. Using the convex underestimating functions, we have developed a method for finding all homogeneous azeotropes with the Wilson activity coefficient equation. The algorithm for the method will be presented in Section 4. Example calculations using the Wilson model are shown in Section 5.

3.3 NRTL Equation

The NRTL equation was derived by Renon and Prausnitz (1968) for fluid phase activity coefficients using the Non-Randomness assumption and Scott's Two-Liquid theory. The NRTL formula for the activity coefficient is:

$$\ln \gamma_i = \frac{\sum_{j \in N} \tau_{ji} G_{ji} x_j}{\sum_{j \in N} G_{ji} x_j} + \sum_{j \in N} \frac{G_{ij} x_j}{\sum_{k \in N} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{k \in N} \tau_{kj} G_{kj} x_k}{\sum_{k \in N} G_{kj} x_k}\right) \tag{23}$$

Substituting this expression into formulation (12) yields:

$$\begin{array}{ll} \min\limits_{\mathbf{x},s} & s \\ \text{subject to} & -\sum_{j \in N} \tau_{ij} \frac{G_{ij} x_j}{y_j} + \sum_{j \in N} \frac{G_{ij} x_j}{y_j} \frac{w_j}{y_j} - \frac{w_i}{y_i} + \frac{b_i}{T + c_i} + \ln P - a_i - s \ \leq \ 0 \quad \forall\, i \in N \\ & \sum_{j \in N} \tau_{ij} \frac{G_{ij} x_j}{y_j} - \sum_{j \in N} \frac{G_{ij} x_j}{y_j} \frac{w_j}{y_j} + \frac{w_i}{y_i} - \frac{b_i}{T + c_i} - \ln P + a_i - s \ \leq \ 0 \quad \forall\, i \in N \\ & \sum_{i \in N} x_i \ = \ 1 \\ & 0 < \mathbf{x} < 1 \\ & s \geq 0 \end{array} \tag{24}$$

where $\mathbf{x}$ denotes the vector of compositions, and

$$\begin{aligned} y_i &= \sum_{j \in N} G_{ji} x_j \\ w_i &= \sum_{j \in N} \tau_{ji} G_{ji} x_j \end{aligned} \tag{25}$$

The interaction parameters, τ_{ij} and G_{ij}, are functions of temperature. However, for most systems, the temperature dependence of the Antoine equation for the vapor pressure outweighs the temperature dependence of the activity coefficient equation. Therefore, in this analysis, the interaction parameters are considered to be constants, and are calculated using a reference temperature located between the upper and lower bounds for the system being modeled. Taking this into account, formulation (24) contains nonconvex terms of the form:

$$u_i = \frac{f_i}{g_i}$$

and,

$$v_i = \frac{f_i^1 f_i^2}{g_i^1 g_i^2}$$

The task of constructing convex underestimators for nonconvex terms of the second form is a difficult one. In the work of Maranas and Floudas (1995), products of N univariate functions can be underestimated by successively convex lower bounding pairs of univariate functions in a recursive manner until no pairs are left. A proof is given that there are $\frac{(N!)^2}{N 2^{N-1}}$ ways of combining the N univariate function in pairs of two. In Appendix B, the procedure of Maranas and Floudas (1995) is applied to the above nonconvex terms and convex underestimators are derived explicitly.

3.4 UNIQUAC Equation

The UNIQUAC equation was originally developed by Abrams and Prausnitz (1975). They postulated that the excess Gibbs energy depended on two effects: a combinatorial contribution due to the differences in the sizes and shapes of the components, and a residual contribution due to the energetic interactions between the components. The original equation was modified by Anderson and Prausnitz (1978) in order to improve predictions for systems containing polar molecules such as water and alcohols. The activity coefficient for the UNIQUAC equation is given as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{26}$$

where,

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j \in N} l_j x_j \tag{27}$$

and,

$$\ln \gamma_i^R = q_i'(1 - \ln(\sum_{j \in N} \tau_{ji} \theta_j') - \sum_{j \in N} \frac{\tau_{ij} \theta_j'}{\sum_{k \in N} \theta_k' \tau_{kj}}) \tag{28}$$

The combinatorial and residual contributions to the activity coefficient are represented by γ_i^C and γ_i^R respectively. The τ_{ij} are non-symmetric binary interaction parameters, q_i, q_i', and r_i are structural parameters of the pure components, and z is a lattice coordination number. The values l_i, θ_i, θ_i', and ϕ_i are defined in terms of the parameters described above and are given by:

$$\begin{array}{rll} l_i = & \frac{z}{2}(r_i - q_i) - (r_i - 1) & \forall\ i \in N \\ \theta_i = & \frac{q_i x_i}{\sum_{j \in N} q_j x_j} & \forall\ i \in N \\ \theta_i' = & \frac{q_i' x_i}{\sum_{j \in N} q_j' x_j} & \forall\ i \in N \\ \phi_i = & \frac{r_i x_i}{\sum_{j \in N} r_j x_j} & \forall\ i \in N \end{array} \tag{29}$$

When the definitions of these parameters are substituted into the $\ln \gamma_i^C$ and $\ln \gamma_i^R$ expressions, and these two are added together to form the complete $\ln \gamma_i$ equation some simplifications can be made. The final expression is:

$$\begin{aligned} \ln \gamma_i \quad = \quad & (\frac{z}{2} q_i - 1) \ln(\sum_{j \in N} r_j x_j) - \frac{z}{2} q_i \ln(\sum_{j \in N} q_j x_j) - r_i \frac{\sum_{j \in N} l_j x_j}{\sum_{j \in N} r_j x_j} \\ & - q_i' \ln(\sum_{j \in N} \tau_{ji} q_j' x_j) + q_i' \ln(\sum_{j \in N} q_j' x_j) - q_i' \sum_{j \in N} \frac{\tau_{ij} q_j' x_j}{\sum_{k \in N} \tau_{kj} q_k' x_k} \\ & + \left(\ln r_i + \frac{z}{2} q_i \ln(\frac{q_i}{r_i}) + l_i + q_i' \right) \end{aligned}$$

As is evident, this expression contains many nonconvex terms. The first four nonconvex terms are log terms:

$$\ln\left(\sum_{j\in N} r_j x_j\right), \quad \ln\left(\sum_{j\in N} q_j x_j\right), \quad \ln\left(\sum_{j\in N} q'_j x_j\right), \quad \text{and} \quad \ln\left(\sum_{j\in N} \tau_{ji} q'_j x_j\right) \tag{30}$$

The last four nonconvex term are fractional terms:

$$+\frac{\sum\limits_{j\in N} l_j x_j}{\sum\limits_{l\in N} r_l x_l}, \quad -\frac{\sum\limits_{j\in N} l_j x_j}{\sum\limits_{l\in N} r_l x_l}, \quad +\frac{\sum\limits_{j\in N} \tau_{ij} q'_j x_j}{\sum\limits_{l\in N} \tau_{lj} q'_l x_l}, \quad \text{and} \quad -\frac{\sum\limits_{j\in N} \tau_{ij} q'_j x_j}{\sum\limits_{l\in N} \tau_{lj} q'_l x_l} \tag{31}$$

Note that the binary interaction parameter, τ_{ij}, is considered to be a constant in this analysis, as described in Section 3.3. Convex underestimating functions are derived for each term in Appendix C. The global optimization problem of finding all N-ary homogeneous azeotropes using the UNIQUAC model is formulated as follows:

$$\begin{aligned}
\min_{\mathbf{x},s} \quad & s \\
\text{subject to} \quad & (\tfrac{z}{2}q_i - 1)\ln(\sum_{j\in N} r_j x_j) - \tfrac{z}{2}q_i \ln(\sum_{j\in N} q_j x_j) - r_i \frac{\sum_{j\in N} l_j x_j}{\sum_{j\in N} r_j x_j} \\
& -q'_i \ln(\sum_{j\in N} \tau_{ji} q'_j x_j) + q'_i \ln(\sum_{j\in N} q'_j x_j) - q'_i \sum_{j\in N} \frac{\tau_{ij} q'_j x_j}{\sum_{k\in N} \tau_{kj} q'_k x_k} \\
& + \left(\ln r_i + \tfrac{z}{2} q_i \ln(\tfrac{q_i}{r_i}) + l_i + q'_i\right) + \tfrac{b_i}{T+c_i} + \ln P - a_i - s \ \leq \ 0 \quad \forall\, i \in N \\
& -(\tfrac{z}{2}q_i - 1)\ln(\sum_{j\in N} r_j x_j) + \tfrac{z}{2}q_i \ln(\sum_{j\in N} q_j x_j) + r_i \frac{\sum_{j\in N} l_j x_j}{\sum_{j\in N} r_j x_j} \\
& +q'_i \ln(\sum_{j\in N} \tau_{ji} q'_j x_j) - q'_i \ln(\sum_{j\in N} q'_j x_j) + q'_i \sum_{j\in N} \frac{\tau_{ij} q'_j x_j}{\sum_{k\in N} \tau_{kj} q'_k x_k} \\
& - \left(\ln r_i + \tfrac{z}{2} q_i \ln(\tfrac{q_i}{r_i}) + l_i + q'_i\right) - \tfrac{b_i}{T+c_i} - \ln P + a_i - s \ \leq \ 0 \quad \forall\, i \in N \\
& \sum_{i\in N} x_i \ = \ 1 \\
& 0 < \mathbf{x} < 1 \\
& s \geq 0
\end{aligned} \tag{32}$$

3.5 UNIFAC Equation

In some cases, one would like to predict the azeotropes for a system where there is insufficient equilibrium data to obtain accurate binary interaction parameter values. As a result, several solution-of-groups methods have been developed to allow equilibrium predictions in these systems. Solution-of-groups methods consider the molecules in the chemical system as groupings of elements. For example, 1-propanol contains one CH_3 group, one CH_2 group, and one CH_2OH group. The interactions between the molecules can then be approximated by determining the interactions between the groups that make up the molecules.

The most widely used solution-of-groups method is the UNIFAC equation, originally developed by Fredenslund *et al.* (1975), primarily because the group-interaction parameters for many pairs of groups have been calculated and compiled and are updated periodically, Gmehling *et al.* (1990). As its name indicates, the UNIFAC (UNIQUAC Functional Group Activity Coefficients) method is based on the UNIQUAC equation. Like the UNIQUAC equation, the natural logarithm of the UNIFAC activity coefficient is the sum of a combinatorial contribution and a residual contribution:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{33}$$

The combinatorial part, $\ln \gamma_i^C$, uses only pure-component data, and therefore no modifications of the UNIQUAC combinatorial part, Equation (27), are needed. However, in the UNIFAC method, the residual part is calculated as the sum of the energetic interactions of the *groups*, rather than the molecules themselves.

First, the pure component parameters, q_i and r_i, are defined as:

$$q_i \;=\; \sum_{g \in G} v_{gi} Q_g \qquad \text{and} \qquad r_i \;=\; \sum_{g \in G} v_{gi} R_g \tag{34}$$

where G is the set of all groups in the system; v_{gi} is the number of groups g contained in component i; Q_g is the group area parameter; and R_g is the group volume parameter.

The residual part of the UNIFAC equation is given by the following expression:

$$\begin{aligned}
\ln \gamma_i^R \;=\; \sum_{g \in G} Q_g v_{gi} \quad \Bigg\{ & - \sum_{m \in G} \frac{\Psi_{gm} \sum_{j \in N} Q_m v_{mj} x_j}{\sum_{l \in G} \Psi_{lm} \sum_{k \in N} Q_l v_{lk} x_k} \\
& - \ln \left(\sum_{m \in G} \Psi_{mg} \sum_{j \in N} Q_m v_{mj} x_j \right) \\
& + \ln \left(\sum_{j \in N} q_j x_j \right) \\
& + \ln \left(\sum_{m \in G} \Psi_{mg} Q_m v_{mi} \right) \\
& - \ln q_i \\
& + \sum_{m \in G} \frac{\Psi_{gm} Q_m v_{mi}}{\sum_{l \in G} \Psi_{lm} Q_l v_{li}} \Bigg\}
\end{aligned} \tag{35}$$

where the temperature-dependent group-interaction parameter, Ψ_{gm}, is given by

$$\Psi_{gm} \;=\; \exp\left(-\frac{a_{gm}}{T}\right) \tag{36}$$

and the group-interaction parameter, a_{gm}, is determined from experimental phase equilibrium data. Similar to the NRTL and UNIQUAC equations, the group interaction parameters are treated as constants with respect to temperature in this paper. By introducing a few substitutions, the residual contribution can be simplified to

$$\begin{aligned}
\ln \gamma_i^R = \; & -\sum_{g \in G} \kappa_{gi} \ln \left(\sum_{j \in N} \alpha_{gj} x_j \right) \\
& + \sum_{g \in G} \kappa_{gi} \ln \left(\sum_{j \in N} q_j x_j \right) \\
& - \sum_{g \in G} \frac{\sum_{j \in N} \beta_{gij} x_j}{\sum_{k \in N} \alpha_{gk} x_k} \\
& + \delta_i
\end{aligned} \tag{37}$$

where the constants $\kappa_{gi}, \alpha_{gj}, \beta_{gij},$ and δ_i are given by

$$\begin{aligned}
\kappa_{gi} &= Q_g v_{gi} \\
\alpha_{gj} &= \sum_{m \in G} \kappa_{mj} \Psi_{mg} \\
\beta_{gij} &= \sum_{m \in G} \kappa_{mi} \kappa_{gj} \Psi_{mg} \\
\delta_i &= \sum_{g \in G} \kappa_{gi} \cdot \ln \left(\frac{\sum_{m \in G} \kappa_{mi} \Psi_{mg}}{q_i} \right) \\
& \quad + \sum_{g \in G} \kappa_{gi} \sum_{m \in G} \frac{\kappa_{mi} \Psi_{gm}}{\sum_{l \in G} \kappa_{li} \Psi_{lm}}
\end{aligned}$$

Using the simplified expression for the residual contribution, the N-ary formulation using the UNIFAC equation is written

$$
\begin{aligned}
\min_{\mathbf{x},s} \quad & s \\
\text{subject to} \quad & (\tfrac{z}{2}q_i - 1)\ln(\sum_{j\in N} r_j x_j) - \tfrac{z}{2}q_i \ln(\sum_{j\in N} q_j x_j) - r_i \frac{\sum_{j\in N} l_j x_j}{\sum_{j\in N} r_j x_j} \\
& - \sum_{g\in G} \kappa_{gi} \ln\left(\sum_{j\in N} \alpha_{gj} x_j\right) + \sum_{g\in G} \kappa_{gi} \ln\left(\sum_{j\in N} q_j x_j\right) - \sum_{g\in G} \frac{\sum_{j\in N} \beta_{gij} x_j}{\sum_{k\in N} \alpha_{gk} x_k} \\
& + \left(\ln r_i + \tfrac{z}{2} q_i \ln(\tfrac{q_i}{r_i}) + l_i + \delta_i\right) + \tfrac{b_i}{T+c_i} + \ln P - a_i - s \ \le \ 0 \qquad \forall\, i \in N \\
& -(\tfrac{z}{2}q_i - 1)\ln(\sum_{j\in N} r_j x_j) + \tfrac{z}{2}q_i \ln(\sum_{j\in N} q_j x_j) + r_i \frac{\sum_{j\in N} l_j x_j}{\sum_{j\in N} r_j x_j} \\
& + \sum_{g\in G} \kappa_{gi} \ln\left(\sum_{j\in N} \alpha_{gj} x_j\right) - \sum_{g\in G} \kappa_{gi} \ln\left(\sum_{j\in N} q_j x_j\right) + \sum_{g\in G} \frac{\sum_{j\in N} \beta_{gij} x_j}{\sum_{k\in N} \alpha_{gk} x_k} \\
& - \left(\ln r_i + \tfrac{z}{2} q_i \ln(\tfrac{q_i}{r_i}) + l_i + \delta_i\right) - \tfrac{b_i}{T+c_i} - \ln P + a_i - s \ \le \ 0 \qquad \forall\, i \in N \\
& \sum_{i\in N} x_i \ = \ 1 \\
& 0 < \mathbf{x} < 1 \\
& s \ge 0
\end{aligned} \tag{38}
$$

Formulation (38) contains several nonconvex terms. As was the case for the UNIQUAC equation, these terms fall into two categories: logarithmic terms, and fractional terms. In addition, since the combinatorial part of the UNIFAC equation is identical to the UNIQUAC equation, the nonconvex terms that arise from this part are also identical. These equations are the first two expressions in (30), and the first two expressions in (31). The convex lower bounding functions for these terms are given in Appendix C. The nonconvex terms from the residual part are the following:

$$
\ln\left(\sum_{j\in N} \alpha_{gj} x_j\right), \quad \text{and} \quad \ln\left(\sum_{j\in N} q_j x_j\right) \tag{39}
$$

and

$$
+\frac{\beta_{gij} x_j}{\sum_{k\in N} \alpha_{gk} x_k}, \quad \text{and} \quad -\frac{\beta_{gij} x_j}{\sum_{k\in N} \alpha_{gk} x_k} \tag{40}
$$

Note that the second logarithmic nonconvex term is identical to one of the nonconvex terms from the combinatorial part, for which we have already derived a convex lower bounding function. Convex underestimators for the remaining terms are derived in Appendix D.

4 Procedure for Locating All Azeotropes

4.1 Description

The method presented in this paper for locating all homogeneous azeotropes is based on the work of Maranas and Floudas (1995). In this section, the global optimization procedure will be summarized. The problem is formulated by introducing a slack variable to the equilibrium constraint of the initial problem. This transforms the initial problem into a global optimization problem (9). The problem is simplified by using the homogeneous azeotropy condition to replace y_i by x_i. Each feasible solution to the original system of equations corresponds to a zero objective function value and denotes the existence of an azeotrope.

The multiple global minima of Formulation (9) are enclosed based on a branch and bound procedure. This procedure creates a convex relaxation of the problem by constructing tight convex lower bounding functions for each nonconvex term in the constraints. Then, the global minimum of the convex relaxed problem within some box constraints can be found using any commercially available local optimization algorithm.

When the convex relaxed problem is solved, there are two possibilities. If the solution of the relaxed problem is strictly positive inside some rectangular region, then because it is an underestimator, the solution of the original problem must also be strictly positive inside the region. This allows us to fathom (eliminate) parts of the total region which do not contain any solutions. The second outcome is that the solution is zero or negative. In this case, the original problem may or may not have a solution in the current region and thus the region cannot be fathomed. Instead, the current region is partitioned into smaller regions and the procedure is repeated until all regions are fathomed, or a feasible solution is found.

It is critical to note that as the size of the current region decreases, the maximum separation between the original constraint functions and the convex relaxed functions also decreases. Therefore, any feasible point of the relaxed problem can become at least ϵ-feasible for the original problem by tightening the bounds around the point.

In this work, each region which has a non-positive solution of the convex relaxed problem is partitioned into two smaller regions by bisecting the longest side of the initial region. At each iteration in the branch and bound procedure, the lower bound of the original problem is calculated by finding the infimum over all minima of the relaxed problem in each region which has not been fathomed. Thus, a simple way of improving the lower bound is to halve only the subrectangle responsible for the infimum of the minima of the relaxed problem at each iteration. Convergence is reached when none of the subrectangles inside the total region have a negative lower bound in which case there are no solutions, or when all of the remaining subrectangles with negative lower bounds have been refined to a prespecified size tolerance. In the following section, the basic steps of the algorithm are outlined.

4.2 Algorithmic Steps

STEP 0 - *Initialization*

A size tolerance ϵ_r and feasibility tolerance ϵ_f are selected and the iteration counter is set to one. Global bounds are set for temperature T, and the local bounds are set equal to the global bounds. In addition, an initial point is selected.

STEP 1 - *Feasibility and Convergence Check*

If the maximum violation of all nonconvex constraints of the original problem calculated at the current point for solution $s = 0$ is less than the feasibility tolerance ϵ_f, then the current point is an ϵ_f-solution of the original problem. The current rectangle is fathomed if it has been refined to the point where its diagonal is less than ϵ_r.

STEP 2 - *Partitioning of Current Rectangle*

The current rectangle is partitioned into two smaller rectangles by bisecting the longest side in the current rectangle.

STEP 3 - *Solution of Convex Problems Inside Subrectangles*

Solve the convexified optimization problem in both subrectangles by using any convex nonlinear solver (e.g. MINOS 5.4 (Murtagh and Saunders, 1988)). If the solution $s_{sol}^{r,Iter}$, where r denotes a rectangle, is negative then it is stored along with the value of the variables $(\mathbf{x}, T)$ at the solution point. If $s_{sol}^{r,Iter}$ is strictly positive then the element $(r, Iter)$ is fathomed and the corresponding rectangle is no longer considered to contain a possible solution. Note that the global solution of the original nonconvex problem is known to be zero, thus no upper bounding problem needs to be solved.

STEP 4 - *Update Iteration Counter and Lower Bound*

The iteration counter is increased by one, and the lower bound of the solution is updated to be the minimum solution over the stored ones from previous iterations. Furthermore, the solution selected as the new lower bound is erased from the stored set.

STEP 5 - *Update Current Point and Current Bounds*

The current point is selected to be the solution point of the previously found minimum solution in **STEP 4**, and the current rectangle becomes the subrectangle containing the previously found solution,

STEP 7 - *Check for Convergence*

If the lower bound of the solution is less than or equal to zero, then return to **STEP 1**. Otherwise, terminate.

A proof that this procedure is guaranteed to converge is given in Maranas and Floudas (1995).

5 Computational Results

The algorithm for finding all homogeneous azeotropes in a multicomponent mixture is written in GAMS and was run on a Hewlett Packard 9000/730 machine. The solver MINOS5.4 is used as a subroutine (Murtagh and Saunders, 1988). All times reported are the total cpu time in seconds needed to obtain all azeotropes in the system. A convergence tolerance of 10^{-5} was used for all examples.

In Section 5.1, several example problems are solved using both the Wilson and NRTL equations. In Example 1, both the N-ary and k-ary formulations are used to find the azeotropes for a ternary system. In the rest of the examples, only the N-ary formulation is used, due to the large advantage in computational requirements it has over the k-ary formulation. In Section 5.2, the application for the UNIQUAC equation is demonstrated with three examples. Finally, in Section 5.3, the UNIFAC equation is used to locate all azeotropes in three systems.

In each example, the N-ary azeotrope formulation was used to locate all azeotropes for all combinations of the components. To illustrate, in the first example, a ternary system containing acetone, methyl acetate, and methanol is studied. All N-ary azeotropes for the binary systems acetone-methyl acetate, acetone-methanol, and methyl acetate-methanol, and the full ternary system are located. Only the combinations that contained azeotropes are reported in the tables. For each system experimental data reported in Gmehling *et al.* (1994) are listed for *all* combinations, whether they contained azeotropes or not.

In comparing the computational results for the examples with the experimental data, it is noted that in some cases the equations will fail to predict a known azeotrope, or will predict azeotropes where none exist. This demonstrates the importance of obtaining reliable estimates of the pure-component and binary-interaction parameters for the system being studied. In addition, it is well known that no single thermodynamic model provides superior results for every system. The purpose of the following examples is to demonstrate the performance of the global optimization based approach for several different activity coefficient equations. No attempt is made to determine the most accurate model or set of parameters for the systems presented.

The binary interaction parameters used in this work are taken from the DECHEMA Vapor-Liquid Equilibria Data Collection, Gmehling and Onken (1977). In the examples where the Wilson equation is used, the liquid molar volumes were calculated by a modified Rackett equation, Yamada and Gunn (1973). For the UNIFAC equation, the group interaction parameters were obtained from Gmehling *et al.* (1982) and Hansen *et al.* (1991).

5.1 Application to the Wilson and NRTL Models

Example 1: Acetone/Methyl Acetate/Methanol

A common system encountered in the literature of phase equilibria is the Acetone/Methyl Acetate/Methanol system, Fidkowski *et al.* (1993). Experimental data show that this system contains three binary azeotropes and one ternary azeotrope, Table 1. In this example, the Wilson and NRTL equations are used to model the liquid phase activity coefficients. As can be seen in Table 2, the Wilson equation predicted all four azeotropes. The Acetone-Methanol and Methyl Acetate-Methanol binary azeotrope predictions are close to the experimental results. On the other hand, the prediction for the Acetone-Methyl Acetate azeotrope and the ternary azeotrope are significantly different than the experimental results. Note, hoewever, that our results with the Wilson equation are virtually identical to the results of Fidkowski *et al.* (1993).

This verifies that the global optimization method will find all homogeneous azeotropes that can be predicted by a given activity coefficient equation and set of parameters. In general, the NRTL equation gave better results for the prediction of the binary azeotropes, but the NRTL equation does not predict a ternary azeotrope.

The computational requirements for calculating the binary azeotropes were under one cpu second for both activity coefficient models. In Table 2, the column *NLP Subs.* refers to the number of nonlinear subproblems that were solved in order to converge to the global solution. For the binary systems in this example, about forty nonlinear subproblems were solved per CPU second. In the ternary system, about thirty subproblems were solved per CPU second, due to the larger size of the problem. For the ternary azeotrope with the Wilson model, the cpu requirement was 7.39 seconds.

In the the second part of this example, the k-ary azeotrope problem defined in formulation (13) was used with the Wilson activity coefficient equation to locate all binary and ternary azeotropes in the system. The results for this example are listed in Table 3.

While this method successfully located all of the azeotropes, it was much slower than the N-ary formulation (278.75 cpu seconds). A total of 272 NLP subproblems were solved in order to find all of the azeotropes using the N-ary formulation. However, the k-ary formulation required 1763 subproblems, and only six subproblems per CPU second could be solved. This is due to the more complicated nonconvex expressions in the k-ary azeotrope problem, see Appendix A. The convex underestimators in this case are not as tight as for the N-ary azeotrope problem. As a result, it is more efficient to formulate a *series* of N-ary azeotrope problems to find all azeotropes in a multicomponent mixture, rather than solve a single k-ary azeotrope problem.

Example 2: Methanol/Benzene/i-Propanol/n-Propanol

In this quaternary example, three binary azeotropes have been reported in the literature, as shown in Table 4. No experimental data was found for the ternary and quaternary systems.

Both the Wilson and NRTL equations predicted only the three reported azeotropes. The results for the Wilson equation are very close to the reported compositions and temperatures of the azeotropes. The results for the NRTL equation are also close to the reported values, with the exception of the Methanol-Benzene azeotrope. As in Example 1, the binary azeotropes were identified using the N-ary azeotrope problem formulation which required less than one cpu second to converge. Both the Wilson and NRTL models showed similar cpu times.

Example 3: Benzene/Hexafluorobenzene

This is an interesting example in which there are *two* azeotropes in a single binary system. This example demonstrates the ability of the global optimization method to find multiple azeotropes in a single system. The system examined is benzene/hexafluorobenzene, which has two binary azeotropes one of which is minimum boiling and benzene rich and the other is maximum boiling and benzene poor. For this example, only the Wilson equation was used. No experimental data were available for a pressure of 0.2 atmospheres. However, by comparison with the experimentally observed azeotropes at 30° C and at 40° C, in Table 5, it can be seen that the predicted azeotropes are very close to the actual azeotropes. The cpu requirement for finding both azeotropes was 2.16 cpu seconds.

Example 4: Ethanol/Methyl Ethyl Ketone/Water

This example is the ternary system of ethanol/methyl ethyl ketone/water. This system contains three binary azeotropes and a ternary azeotrope. Using the N-ary formulation, both the Wilson and NRTL models were able to locate all azeotropes, and the results are shown in Table 6. In this case, the Wilson and NRTL results are very similar, and are reasonable close to the experimental data. The CPU requirements are similar to those in the previous examples.

Example 5: Acetone/Chloroform/Methanol

In this example, a ternary system at higher pressure is studied. No experimental data was found for this system, but Fidkowski *et al.* (1993) report that the system contains three binary azeotropes. All of the binary azeotropes were located by both the Wilson and NRTL models. The higher pressure had no effect on the computational requirements. The results are shown in Table 7.

Example 6: Acetone/Chloroform/Methanol/Ethanol/Benzene

A quinary system containing a large number of azeotropes is studied in this example. The experimental data in Table 8 show only the systems for which azeotropes have been reported. For the remaining ternary systems, it has been reported in Gmehling *et al.* (1994) that no azeotropes exist for these systems. With the exception of the single quaternary azeotrope, no experimental data was found for the other quaternary or for the full quinary system.

The Wilson and NRTL models using the N-ary formulation were both able to locate all six binary azeotropes, two of the three ternary azeotropes, and the quaternary azeotrope. As expected, computational requirements increased as the number of components participating in the azeotrope increased, and the results are reported in Table 9. Note that the Wilson equation was able to find the quaternary azeotrope in 7.58 seconds, while the NRTL equation took 35.19 seconds. These CPU times are very reasonable, given the size of the system.

5.2 Application to the UNIQUAC Model

Example 7: Benzene/Ethanol/Water

In this example, the UNIQUAC formulation is used to find all azeotropes in the benzene/ethanol/water system. This example has been widely examined due to the importance of the azeotropic distillation process used to separate ethanol and water using benzene as an entrainer. The N-ary azeotrope method located all three binary azeotropes. The benzene-ethanol and ethanol-water predictions are close to the experimental values. The benzene-water binary azeotrope prediction is not as accurate. It has been reported in the experimental literature that this system contains a ternary heterogeneous azeotropes, but no ternary homogeneous azeotropes. However, the UNIQUAC equation did predict a ternary homogeneous azeotrope. The results are included in Table 10. The computational requirements were similar to the Wilson and NRTL examples. Between thirty and forty NLP subproblems per CPU second were solved for the binary examples, and around sixteen NLP subproblems per second for the ternary system. This is slightly slower than Example 1 for the Wilson and NRTL examples.

Example 8: Ethanol/Methyl-Cyclopentane/Benzene/Hexane

In this example, the UNIQUAC formulation is used to find all N-ary azeotropes in a quaternary system. For this system, only four binary azeotropes have been reported in the literature, Table 11. The UNIQUAC equation predicts all of the binary azeotropes fairly well, as shown in Table 12. The exceptions are the methyl cyclopentane-benzene azeotrope and the benzene-hexane azeotrope for which the predictions deviate significantly from the experimental results. In addition, the UNIQUAC equation predicts azeotropes in all four ternary systems and in the quaternary system. For three of these systems, it has been determined experimentally that no azeotropes exist. The computational requirements were similar to the previous examples and increased as the number of components in the system increased.

Example 9: Acetone/Methyl Acetate/Ethyl Formate

This ternary system contains a ternary azeotrope, but only one binary azeotrope, as shown in Table 13. The UNIQUAC equation locates a ternary azeotrope, but the temperature and composition are quite different from the experimental results. The acetone-methyl acetate azeotrope is also located along with an additional binary azeotrope, acetone-ethyl formate.

5.3 Application to the UNIFAC Model

Example 10: Ethanol/Methyl-Cyclopentane/Benzene/Hexane

In this example, the same quaternary system as Example 8 is studied, this time using the UNIFAC equation. The experimental azeotrope data were shown previously in Table 12. Surprisingly, the UNIFAC equation gives better results, shown in Table 14, than the UNIQUAC equation. The UNIFAC equation locates all of the binary azeotropes reported in the Gmehling *et al.* (1994), and is does not predict the non-existant ternary and quaternary azeotropes that the UNIQUAC equation did. The CPU times are of the same order of magnitude as the other thermodynamic models.

Example 11: Acetone/Methyl Acetate/Ethyl Formate

This example is the same ternary system that was discussed in Example 9. The experimental data are shown in Table 13. The UNIFAC predictions, Table 15 are similar to the UNIQUAC equation. It is interesting to not that the UNIFAC equation also predicts an acetone-ethyl formate azeotrope at almost the identical position as the UNIQUAC equation, even though it has been reported that no azeotrope exists for this binary system. In fact, the UNIFAC equation also predicts a second acetone-ethyl formate azeotrope.

Between twenty and thirty NLP subproblems per CPU second were solved for the binary systems in this example, slightly slower than the UNIQUAC equation. For the ternary system, around eight subproblems per second were solved.

Example 12: Acetone/Methyl Ethyl Ketone/Cyclohexane

In the final example, a ternary system containing two binary azeotropes is studied. The azeotropes are acetone-cyclohexane and methyl ethyl ketone-cyclohexane. For this system, the UNIFAC equation predicts both binary azeotropes, and did not locate any extra azeotropes, as shown in Table 16. Again, the CPU times are in the same range as previous examples.

6 Conclusions

This work has presented a deterministic global optimization method for computing all N-ary and k-ary ($k \leq N$) homogeneous azeotropes in mixtures containing N components. This method is based on a branch and bound algorithm to iteratively solve a formulation of the original problem in which the nonconvex constraints are replaced by valid convex underestimating functions. Nonconvex terms for the saturated vapor pressure equation $\ln P_i^{sat}$, the Wilson equation, the NRTL equation, the UNIQUAC equation, and the UNIFAC equation were identified and convex underestimating terms derived for each. While only four thermodynamic models were used, this method can be extended to include the modified Wilson, and ASOG activity coefficient models.

The novel contribution of this approach is that it offers a theoretical guarantee of enclosing all azeotropes, while at the same time the computational effort is modest. The effectiveness of this method was demonstrated for several chemical systems and three different thermodynamic models of the liquid phase activity coefficients. In all examples, the method found all azeotropes for the systems studied.

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A Convex Underestimators for the Wilson Equation

The first nonconvex term in the problem of finding all N-ary azeotropes using the Wilson formulation that will be examined is $\ln\left\{\sum_{j\in N} x_j\Lambda_{ij}\right\}$, which is concave in x_i, for $i = 1, 2, ..., N$. Therefore, this term can be underestimated by the following expression:

$$\ln \sum_{j\in N} x_j\Lambda_{ij} \geq \ln m_i^L + \frac{\ln \frac{m_i^U}{m_i^L}}{(m_i^U - m_i^L)}\left(\sum_{j\in N} x_j\Lambda_{ij} - m_i^L\right) \tag{41}$$

where,

$$\begin{aligned} m_i^L \; = \; \min \quad & \sum_{j\in N} x_j\Lambda_{ij} \\ \text{s.t.} \quad & \sum_{j\in N} x_j = 1 \\ & x_j^L \leq x_j \leq x_j^U \end{aligned} \tag{42}$$

and,

$$\begin{aligned} m_i^U \; = \; \max \quad & \sum_{j\in N} x_j\Lambda_{ij} \\ \text{s.t.} \quad & \sum_{j\in N} x_j = 1 \\ & x_j^L \leq x_j \leq x_j^U \end{aligned} \tag{43}$$

The second type of nonconvex terms found in the Wilson formulation have the form:

$$\left(s_j^1 = +\frac{x_j}{\sum_{k\in N} x_k\Lambda_{jk}}\right) \text{ and } \left(s_j^2 = -\frac{x_j}{\sum_{k\in N} x_k\Lambda_{jk}}\right)$$

Following the method presented in Maranas and Floudas (1995) for products of univariate functions, the convex underestimators for these terms are:

$$\begin{aligned} s_j^1 \;\geq\; \max \; & \left\{ \frac{x_j^L}{\sum_{k\in N} x_k\Lambda_{jk}} + \frac{x_j}{m_j^U} - \frac{x_j^L}{m_j^U}, \right. \\ & \left. \frac{x_j^U}{\sum_{k\in N} x_k\Lambda_{jk}} + \frac{x_j}{m_j^L} - \frac{x_j^U}{m_j^L} \right\}. \\ s_j^2 \;\geq\; \max \; & \left\{ -\frac{x_j}{m_j^L} + \frac{x_j^L \sum_{k\in N} x_k\Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^L}{m_j^U}, \right. \\ & \left. -\frac{x_j}{m_j^U} + \frac{x_j^U \sum_{k\in N} x_k\Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^U}{m_j^L} \right\}. \end{aligned}$$

For the k-ary azeotrope problem (13) the nonconvex terms are:

$$\left(x_i \ln(\sum_{j\in N} x_j\Lambda_{ij})\right), \left(-x_i \ln(\sum_{j\in N} x_j\Lambda_{ij})\right), \left(x_i \sum_{j\in N} s_j^1\Lambda_{ji}\right), \text{and} \left(-x_i \sum_{j\in N} s_j^1\Lambda_{ji}\right) \tag{44}$$

The first nonconvex term above can be considered as the product of two univariate functions, $x_i u_i$, where u_i is the log term in the equation. The convex underestimator for this product is, Al-Khayyal and Falk (1983):

$$\begin{aligned} x_i u_i \quad \geq \quad \max \ & \left\{ x_i^L u_i + x_i u_i^L - x_i^L u_i^L, \right. \\ & \left. x_i^U u_i + x_i u_i^U - x_i^U u_i^U \right\}. \end{aligned}$$

where,

$$u_i = \ln(\sum_{j\in N} x_j\Lambda_{ij})$$

and,

$$\begin{aligned} u_i^L \ = \ & \ln(\min \ \textstyle\sum_{j\in N} x_j\Lambda_{ij}) \\ & \text{s.t.} \ \textstyle\sum_{j\in N} x_j = 1 \\ & \qquad x_j^L \leq x_j \leq x_j^U \\ \\ u_i^U \ = \ & \ln(\max \ \textstyle\sum_{j\in N}) x_j\Lambda_{ij}) \\ & \text{s.t.} \ \textstyle\sum_{j\in N} x_j = 1 \\ & \qquad x_j^L \leq x_j \leq x_j^U \end{aligned} \tag{45}$$

Note that $x_i^L u_i$ and $x_i^U u_i$ are nonconvex, so the convex underestimator developed in Equation (41) should be used in place of u_i.

Similarly, the second nonconvex term is of the form $x_i(-u_i)$. The convex underestimator for this product is:

$$\begin{aligned} -x_i u_i \quad \geq \quad \max \ & \left\{ -x_i^U u_i - x_i u_i^L + x_i^U u_i^L, \right. \\ & \left. -x_i^L u_i - x_i u_i^U + x_i^L u_i^U \right\}. \end{aligned}$$

and again, the u_i term in nonconvex and must be replaced by the convex underestimator developed in Equation (41). Consider the third and fourth nonconvex terms in Equation (44) to be of the form:

$$t_i = x_i(\sum_{j \in N} u_j)$$

which is a sum of products of univariate functions. As shown by Al-Khayyal and Falk (1983), each term can be underestimated by:

$$\begin{aligned} x_i u_j \quad \geq \quad \max \; & \left\{ x_i^L u_j + x_i u_j^L - x_i^L u_j^L, \right. \\ & \left. x_i^U u_j + x_i u_j^U - x_i^U u_j^U \right\}. \end{aligned}$$

Now when these terms are summed over each j in the set of components N, the following formula results:

$$\begin{aligned} \sum_{j \in N} x_i u_j \quad \geq \quad \max \; & \left\{ x_i^L \sum_{j \in N} u_j + x_i \sum_{j \in N} u_j^L - x_i^L \sum_{j \in N} u_j^L, \right. \\ & \left. x_i^U \sum_{j \in N} u_j + x_i \sum_{j \in N} u_j^U - x_i^U \sum_{j \in N} u_j^U \right\}. \end{aligned}$$

However, the term u_j is nonconvex, so it must be replaced by a valid convex underestimator. Recall $u_j = s_j^1 \Lambda_{ij}$ and a convex underestimator for this term was constructed at the beginning of Appendix A.

The upper and lower bounds for the summation terms can be obtained essentially by minimizing the numerator of each term while maximizing the denominator. Substituting in for s_j^1 gives:

$$\begin{aligned} \sum_{j \in N} u_j^L \quad &= \quad \sum_{j \in N} \Lambda_{ji} \frac{\min_{j \in N} x_j}{\max_{k \in N} x_k \Lambda_{jk}} \\ &= \quad \sum_{j \in N} \frac{x_j^L \Lambda_{ji}}{m_j^U} \end{aligned}$$

The term m_j^U was defined in Section 3 by Equation (43). The term $\sum_{j \in N} u_i^U$ is determined in a similar manner and is:

$$\sum_{j \in N} u_j^U \quad = \quad \sum_{j \in N} \frac{x_j^U \Lambda_{ji}}{m_j^L}$$

Therefore, the nonconvex term:

$$t_i^1 = x_i \sum_{j\in N} s_j^1 \Lambda_{ji}$$

is underestimated by:

$$\begin{aligned} t_i^1 \;\; \geq \;\; \max \;\; & \left\{ x_i^L \sum_{j\in N} u_j + x_i \sum_{j\in N} \frac{x_j^L \Lambda_{ji}}{m_j^U} - x_i^L \sum_{j\in N} \frac{x_j^L \Lambda_{ji}}{m_j^U}, \right. \\ & \left. x_i^U \sum_{j\in N} u_j + x_i \sum_{j\in N} \frac{x_j^U \Lambda_{ji}}{m_j^L} - x_i^U \sum_{j\in N} \frac{x_j^U \Lambda_{ji}}{m_j^L} \right\}. \end{aligned}$$

where

$$\begin{aligned} u_j \;\; \geq \;\; \max \;\; & \left\{ \frac{x_j^L \Lambda_{ji}}{\sum_{k\in N} x_k \Lambda_{jk}} + \frac{x_j \Lambda_{ji}}{m_j^U} - \frac{x_j^L \Lambda_{ji}}{m_j^U}, \right. \\ & \left. \frac{x_j^U \Lambda_{ji}}{\sum_{k\in N} x_k \Lambda_{jk}} + \frac{x_j \Lambda_{ji}}{m_j^L} - \frac{x_j^U \Lambda_{ji}}{m_j^L} \right\}. \end{aligned}$$

Through a similar analysis, the term:

$$t_i^2 = -x_i \sum_{j\in N} s_j^1 \Lambda_{ji}$$

can be underestimated by:

$$\begin{aligned} t_i^2 \;\; \geq \;\; \max \;\; & \left\{ x_i^L \sum_{j\in N} v_j - x_i \sum_{j\in N} \frac{x_j^L \Lambda_{ji}}{m_j^U} + x_i^L \sum_{j\in N} \frac{x_j^L \Lambda_{ji}}{m_j^U}, \right. \\ & \left. x_i^U \sum_{j\in N} v_j - x_i \sum_{j\in N} \frac{x_j^U \Lambda_{ji}}{m_j^L} + x_i^U \sum_{j\in N} \frac{x_j^U \Lambda_{ji}}{m_j^L} \right\}. \end{aligned}$$

where

$$\begin{aligned} v_j \;\; \geq \;\; \max \;\; & \left\{ -\frac{x_j}{m_j^L} + \frac{x_j^L \sum_{k\in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^L}{m_j^U}, \right. \\ & \left. -\frac{x_j}{m_j^U} + \frac{x_j^U \sum_{k\in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \frac{x_j^U}{m_j^L} \right\}. \end{aligned}$$

B Convex Underestimating Functions for the NRTL Equation

In the NRTL equation formulation of the problem of finding all N-ary azeotropes, Equation (24), three different types of nonconvex terms are encountered:

$$
\begin{aligned}
+p_i &= \frac{w_i}{y_i} \\
-p_i &= -\frac{w_i}{y_i} \\
+q_i &= \sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} \\
-q_i &= -\sum_{j \in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} \\
+r_i &= \sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j} \\
-r_i &= -\sum_{j \in N} G_{ij} \frac{x_j w_j}{y_j y_j}
\end{aligned}
$$

where

$$
\begin{aligned}
y_i &= \sum_{j \in N} G_{ji} x_j \\
w_i &= \sum_{j \in N} \tau_{ji} G_{ji} x_j
\end{aligned}
$$

so $x_i, y_i \geq 0$, but w_i can be positive or negative.

Following the method of Maranas and Floudas (1995) for fractional terms, the first two types of nonconvex term can be underestimated by:

$$
\begin{aligned}
\frac{w_i}{y_i} &\geq \max \left\{ \begin{bmatrix} \frac{w_i^L}{y_i} + \frac{w_i}{y_i^U} - \frac{w_i^L}{y_i^U} & \text{if } w_i^L \geq 0 \\ \frac{w_i}{y_i^U} - \frac{w_i^L y_i}{y_i^L y_i^U} + \frac{w_i^L}{y_i^L} & \text{if } w_i^L < 0 \end{bmatrix} \right. \\
&\qquad\quad \left. \begin{bmatrix} \frac{w_i^U}{y_i} + \frac{w_i}{y_i^L} - \frac{w_i^U}{y_i^L} & \text{if } w_i^U \geq 0 \\ \frac{w_i}{y_i^L} - \frac{w_i^U y_i}{y_i^L y_i^U} + \frac{w_i^U}{y_i^U} & \text{if } w_i^U < 0 \end{bmatrix} \right\} \\
-\frac{w_i}{y_i} &\geq \max \left\{ \begin{bmatrix} -\frac{w_i^L}{y_i} - \frac{w_i}{y_i^L} + \frac{w_i^L}{y_i^L} & \text{if } w_i^L \leq 0 \\ -\frac{w_i}{y_i^L} + \frac{w_i^L y_i}{y_i^L y_i^U} - \frac{w_i^L}{y_i^U} & \text{if } w_i^L > 0 \end{bmatrix} \right. \\
&\qquad\quad \left. \begin{bmatrix} -\frac{w_i^U}{y_i} - \frac{w_i}{y_i^U} + \frac{w_i^U}{y_i^U} & \text{if } w_i^U \leq 0 \\ -\frac{w_i}{y_i^U} + \frac{w_i^U y_i}{y_i^L y_i^U} - \frac{w_i^U}{y_i^L} & \text{if } w_i^U > 0 \end{bmatrix} \right\}
\end{aligned}
$$

where

$$
\begin{aligned}
w_j^L &= \min_{k\in N} \tau_{kj} G_{kj} x_k \\
w_j^L &= \max_{k\in N} \tau_{kj} G_{kj} x_k \\
y_j^L &= \min_{k\in N} G_{kj} x_k \\
y_j^U &= \max_{k\in N} G_{kj} x_k
\end{aligned}
$$

and in the second type of nonconvex term, each fractional term in the summation can be underestimated by:

$$
\begin{aligned}
\frac{x_j}{y_j} &\geq \max \left\{ \frac{x_j^L}{y_j} + \frac{x_j}{y_j^U} - \frac{x_j^L}{y_j^U}, \right. \\
&\qquad\qquad \left. \frac{x_j^U}{y_j} + \frac{x_j}{y_j^L} - \frac{x_j^U}{y_j^L} \right\} \\
-\frac{x_j}{y_j} &\geq \max \left\{ -\frac{x_j}{y_j^L} + \frac{x_j^L y_j}{y_j^L y_j^U} - \frac{x_j^L}{y_j^U}, \right. \\
&\qquad\qquad \left. -\frac{x_j}{y_j^U} + \frac{x_j^U y_j}{y_j^L y_j^U} - \frac{x_j^U}{y_j^L} \right\}
\end{aligned}
$$

Therefore, since $\sum_j (\max x_j) = \max\left(\sum_j x_j\right)$, the convex underestimator for the second term is:

$$
\begin{aligned}
\sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} &\geq \max \left\{ \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j} + \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^U} - \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j^U}, \right. \\
&\qquad \left. \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j} + \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^L} - \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j^L} \right\} \\
-\sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j} &\geq \max \left\{ -\sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^L} + \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^L y_j}{y_j^L y_j^U} - \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^L}{y_j^U}, \right. \\
&\qquad \left. -\sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j}{y_j^U} + \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^U y_j}{y_j^L y_j^U} - \sum_{j\in N} \tau_{ij} G_{ij} \frac{x_j^U}{y_j^L} \right\}
\end{aligned}
$$

The third term is more difficult to underestimate, but a convex underestimator can be constructed by successively finding the convex lower bounding function for pairs of univariate functions in a recursive manner until no pairs are left. The recursive procedure for constructing convex underestimators from pairs of univariate functions, as shown by Maranas and Floudas

(1995), can be used for the third nonconvex term from the NRTL equation as illustrated below.

First, the fractional term $\left(\frac{x_j}{y_j}\right)$ is considered. Since x_j^L and x_j^U are both always greater than zero, this term can be underestimated by:

$$\begin{aligned}\frac{x_j}{y_j} \geq \lambda_j^2 &= \max \left\{\frac{x_j^L}{y_j} + \frac{x_j}{y_j^U} - \frac{x_j^L}{y_j^U},\right.\\ &\left.\frac{x_j^U}{y_j} + \frac{x_j}{y_j^L} - \frac{x_j^U}{y_j^L}\right\}\end{aligned}$$

and since $(x_j - x_j^L)$ is always positive, λ_j^2 is always positive. Next, a convex underestimating function is constructed for the term $\left(\frac{\lambda_j^2}{y_j}\right)$:

$$\begin{aligned}\frac{\lambda_j^2}{y_j} \geq \lambda_j^1 &= \max \left\{\frac{\lambda_j^{2,L}}{y_j} + \frac{\lambda_j^2}{y_j^U} - \frac{\lambda_j^{2,L}}{y_j^U},\right.\\ &\left.\frac{\lambda_j^{2,U}}{y_j} + \frac{\lambda_j^2}{y_j^L} - \frac{\lambda_j^{2,U}}{y_j^L}\right\}\end{aligned}$$

where $\left(\lambda_j^{2,L} = \frac{x_j^L}{y_j^U}\right)$ and $\left(\lambda_j^{2,U} = \frac{x_j^U}{y_j^L}\right)$.

Finally, convex underestimating functions for the terms $(\lambda_j^1 w_j)$ and $(\lambda_j^1(-w_j))$ are constructed:

$$\begin{aligned}\lambda_j^1 w_j &\geq \max \left\{w_j^L\lambda_j^1 + w_j\lambda_j^{1,L} - w_j^L\lambda_j^{1,L},\right.\\ &\left.w_j^U\lambda_j^1 + w_j\lambda_j^{1,U} - w_j^U\lambda_j^{1,U}\right\}\\ \lambda_j^1(-w_j) &\geq \max \left\{-w_j^U\lambda_j^1 - w_j\lambda_j^{1,L} + w_j^U\lambda_j^{1,L},\right.\\ &\left.-w_j^L\lambda_j^1 - w_j\lambda_j^{1,U} + w_j^L\lambda_j^{1,U}\right\}\end{aligned}$$

where $\left(\lambda_j^{1,L} = \frac{\lambda_j^{2,L}}{y_j^U} = \frac{x_j^L}{y_j^U y_j^U}\right)$ and $\left(\lambda_j^{1,U} = \frac{\lambda_j^{2,U}}{y_j^L} = \frac{x_j^U}{y_j^L y_j^L}\right)$. Combining these terms gives a convex underestimating function for the each fractional term in the summation.

$$\begin{aligned}\frac{x_j w_j}{y_j y_j} &\geq \max \left\{w_j^L\lambda_j^1 + \frac{w_j x_j^L}{y_j^U y_j^U} - \frac{w_j^L x_j^L}{y_j^U y_j^U},\right.\\ &\left.w_j^U\lambda_j^1 + \frac{w_j x_j^U}{y_j^L y_j^L} - \frac{w_j^U x_j^U}{y_j^L y_j^L}\right\}\\ -\frac{x_j w_j}{y_j y_j} &\geq \max \left\{-w_j^U\lambda_j^1 - \frac{w_j x_j^L}{y_j^U y_j^U} + \frac{w_j^U x_j^L}{y_j^U y_j^U},\right.\\ &\left.-w_j^L\lambda_j^1 - \frac{w_j x_j^U}{y_j^L y_j^L} + \frac{w_j^L x_j^U}{y_j^L y_j^L}\right\}\end{aligned}$$

and λ_j^1, λ_j^2, y_j^L, y_j^U, w_j^L, and w_j^U are as defined above. Now, by the same argument as was given for the second type of nonconvex term, the convex underestimator for the third type of term is:

$$\begin{aligned}
\sum_{j\in N} G_{ij}\frac{x_j w_j}{y_j y_j} \;\; &\geq \;\; \max \left\{ \sum_{j\in N} G_{ij} w_j^L \lambda_j^1 + \sum_{j\in N} G_{ij}\frac{w_j x_j^L}{y_j^U y_j^U} - \sum_{j\in N} G_{ij}\frac{w_j^L x_j^L}{y_j^U y_j^U}, \right. \\
&\qquad \left. \sum_{j\in N} G_{ij} w_j^U \lambda_j^1 + \sum_{j\in N} G_{ij}\frac{w_j x_j^U}{y_j^L y_j^L} - \sum_{j\in N} G_{ij}\frac{w_j^U x_j^U}{y_j^L y_j^L} \right\} \\
-\sum_{j\in N} G_{ij}\frac{x_j w_j}{y_j y_j} \;\; &\geq \;\; \max \left\{ -\sum_{j\in N} G_{ij} w_j^U \lambda_j^1 - \sum_{j\in N} G_{ij}\frac{w_j x_j^L}{y_j^U y_j^U} + \sum_{j\in N} G_{ij}\frac{w_j^U x_j^L}{y_j^U y_j^U}, \right. \\
&\qquad \left. -\sum_{j\in N} G_{ij} w_j^L \lambda_j^1 - \sum_{j\in N} G_{ij}\frac{w_j x_j^U}{y_j^L y_j^L} + \sum_{j\in N} G_{ij}\frac{w_j^L x_j^U}{y_j^L y_j^L} \right\}
\end{aligned}$$

C Convex Underestimating Functions for the UNIQUAC Equation

The N-ary azeotrope problem using the UNIQUAC equation contains many nonlinear terms. The nonconvex terms can be grouped into two basic categories. The first group has the form:

$$\ln\left(\sum_{j\in N} c_j x_j\right)$$

The nonconvex terms in this group are:

$$\ln\left(\sum_{j\in N} r_j x_j\right), \quad \ln\left(\sum_{j\in N} q_j x_j\right), \quad \ln\left(\sum_{j\in N} q'_j x_j\right), \quad \text{and} \quad \ln\left(\sum_{j\in N} \tau_{ji} q'_j x_j\right)$$

These are all concave terms, thus convex underestimating functions can easily be constructed. When terms of this form appear as $(-\ln \sum_{j\in N} c_j x_j)$ they are convex and do not need underestimators. The convex underestimators for the first three terms above are written:

$$\ln\left(\sum_{j\in N} c_j x_j\right) \;\geq\; \ln m^L \;+\; \frac{\ln\left\{\frac{m^U}{m^L}\right\}}{(m^U - m^L)}\left(\sum_{j\in N} c_j x_j \;-\; m^L\right)$$

for $c_j \;=\; r_j, q_j,$ or q'_j and where,

$$
\begin{aligned}
m^U \ = \ \max \quad & \sum_{j \in N} c_j x_j \\
\text{s.t.} \quad & \sum_{j \in N} x_j \ = \ 1 \\
& x_j^L \leq x_j \leq x_j^U
\end{aligned}
$$

and,

$$
\begin{aligned}
m^L \ = \ \min \quad & \sum_{j \in N} c_j x_j \\
\text{s.t.} \quad & \sum_{j \in N} x_j \ = \ 1 \\
& x_j^L \leq x_j \leq x_j^U
\end{aligned}
$$

The convex underestimator for the fourth term is very similar:

$$
\ln\left(\sum_{j \in N} c_{ij} x_j\right) \ \geq \ \ln m_i^L \ + \ \frac{\ln\left\{\frac{m_i^U}{m_i^L}\right\}}{(m_i^U - m_i^L)} \left(\sum_{j \in N} c_{ij} x_j \ - \ m_i^L\right)
$$

for $c_{ij} \ = \ \tau_{ji} q_j'$ and where,

$$
\begin{aligned}
m_i^U \ = \ \max \quad & \sum_{j \in N} \tau_{ji} q_j' x_j \\
\text{s.t.} \quad & \sum_{j \in N} x_j \ = \ 1 \\
& x_j^L \leq x_j \leq x_j^U
\end{aligned}
$$

and,

$$
\begin{aligned}
m_i^L \ = \ \min \quad & \sum_{j \in N} \tau_{ji} q_j' x_j \\
\text{s.t.} \quad & \sum_{j \in N} x_j \ = \ 1 \\
& x_j^L \leq x_j \leq x_j^U
\end{aligned}
$$

The second group of nonconvex terms are fractional terms of the form:

$$
c \cdot \frac{x_j}{\sum_{l \in N} d_l x_l} \tag{46}
$$

This group includes the terms:

$$
+\frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad -\frac{\sum_{j \in N} l_j x_j}{\sum_{l \in N} r_l x_l}, \quad +\frac{\sum_{j \in N} \tau_{ij} q_j' x_j}{\sum_{l \in N} \tau_{lj} q_l' x_l}, \quad \text{and} \quad -\frac{\sum_{j \in N} \tau_{ij} q_j' x_j}{\sum_{l \in N} \tau_{lj} q_l' x_l}
$$

For terms of this type, the sign of the constant in the numerator determines the formula that is used for the underestimating function. For the UNIQUAC equation, the parameters q_j, q'_j, r_j, and τ_{ij} are always positive, while l_j may be either positive or negative. Therefore the constant $c = +\tau_{ij} q'_j$ will always be positive and $c = -\tau_{ij} q'_j$ will always be negative. However, the sign of the constant for the first two terms, $c = +l_j$ and $c = -l_j$ must be determined before the underestimating function is constructed. When c is positive, the underestimating function for a linear fractional term is given by:

$$\begin{aligned} \frac{c x_j}{\sum\limits_{j \in N} d_j x_j} \geq \max & \left\{ \frac{c x_j^L}{\sum\limits_{l \in N} d_l x_l} + \frac{c x_j}{m^U} - \frac{c x_j^L}{m^U}, \right. \\ & \left. \frac{c x_j^U}{\sum\limits_{l \in N} d_l x_l} + \frac{c x_j}{m^L} - \frac{c x_j^U}{m^L} \right\} \end{aligned}$$

When c is negative, the underestimating function is given by:

$$\begin{aligned} \frac{c x_j}{\sum\limits_{j \in N} d_j x_j} \geq \max & \left\{ -\frac{c x_j}{m^L} + \frac{c x_j^L \cdot \sum\limits_{l \in N} d_l x_l}{m^L m^U} - \frac{c x_j^L}{m^U}, \right. \\ & \left. -\frac{c x_j}{m^U} + \frac{c x_j^U \sum\limits_{l \in N} d_l x_l}{m^L m^U} - \frac{c x_j^U}{m^L} \right\} \end{aligned}$$

where,

$$\begin{aligned} m^U = \max \ & \sum_{l \in N} d_l x_l \\ \text{s.t.} \ & \sum_{l \in N} x_l = 1 \\ & x_l^L \leq x_l \leq x_l^U \end{aligned}$$

and,

$$\begin{aligned} m^L = \min \ & \sum_{l \in N} d_l x_l \\ \text{s.t.} \ & \sum_{l \in N} x_l = 1 \\ & x_l^L \leq x_l \leq x_l^U \end{aligned}$$

D Convex Underestimating Functions for the UNIFAC Equation

The N-ary azeotrope problem using the UNIFAC equation contains several nonconvex terms. Most of the terms are identical to the nonconvex terms from the UNIQUAC equation, as discussed in Section 5.3. Convex lower bounding functions for these terms are derived in Appendix C. Of the remaining nonconvex terms, the first term has the same logarithmic form as discussed for the UNIQUAC equation.

$$\ln\left(\sum_{j\in N}\alpha_{gj}x_j\right)$$

This is a concave term, thus the convex lower bounding function is given by the following equation:

$$\ln\left(\sum_{j\in N}\alpha_{gj}x_j\right) \;\geq\; \ln m_g^L \;+\; \frac{\ln\left\{\frac{m_g^U}{m_g^L}\right\}}{\left(m_g^U - m_g^L\right)}\left(\sum_{j\in N}\alpha_{gj}x_j \;-\; m_g^L\right)$$

where

$$\begin{aligned} m_g^U \;=\; \max \quad & \sum_{j\in N}\alpha_{gj}x_j \\ \text{s.t.} \quad & \sum_{j\in N} x_j \;=\; 1 \\ & x_j^L \leq x_j \leq x_j^U \end{aligned}$$

and,

$$\begin{aligned} m_g^L \;=\; \min \quad & \sum_{j\in N}\alpha_{gj}x_j \\ \text{s.t.} \quad & \sum_{j\in N} x_j \;=\; 1 \\ & x_j^L \leq x_j \leq x_j^U \end{aligned}$$

The last two nonconvex terms for the UNIFAC equation are fractional terms.

$$+\frac{\beta_{gij}x_j}{\sum_{k\in N}\alpha_{gk}x_k}, \qquad \text{and} \qquad -\frac{\beta_{gij}x_j}{\sum_{k\in N}\alpha_{gk}x_k}$$

For the UNIFAC equation, the parameter β_{gij} is always positive. Therefore, for the positive fractional term, the underestimating function is given by:

$$\begin{aligned} +\frac{\beta_{gij}x_j}{\sum_{k\in N}\alpha_{gk}x_k} \;\geq\; \max \;& \left\{\frac{\beta_{gij}x_j^L}{\sum_{k\in N}\alpha_{gk}x_k} + \frac{\beta_{gij}x_j}{m_g^U} - \frac{\beta_{gij}x_j^L}{m_g^U},\right. \\ & \left.\frac{\beta_{gij}x_j^U}{\sum_{k\in N}\alpha_{gk}x_k} + \frac{\beta_{gij}x_j}{m_g^L} - \frac{\beta_{gij}x_j^U}{m_g^L}\right\} \end{aligned}$$

For the negative fractional term, the underestimating function is given by:

$$-\frac{\beta_{gij}x_j}{\sum\limits_{k\in N}\alpha_{gk}x_k} \;\geq\; \max\left\{-\frac{\beta_{gij}x_j}{m_g^L}+\frac{\beta_{gij}x_j^L\cdot\sum\limits_{k\in N}\alpha_{gk}x_k}{m_g^L m_g^U}-\frac{\beta_{gij}x_j^L}{m_g^U},\right.$$
$$\left.-\frac{\beta_{gij}x_j}{m_g^U}+\frac{\beta_{gij}x_j^U\sum\limits_{k\in N}\alpha_{gk}x_k}{m_g^L m_g^U}-\frac{\beta_{gij}x_j^U}{m_g^L}\right\}$$

where,

$$\begin{aligned} m_g^U \;=\; \max \quad & \sum_{k\in N}\alpha_{gk}x_k \\ \text{s.t.} \quad & \sum_{k\in N}x_k \;=\; 1 \\ & x_k^L \leq x_k \leq x_k^U \end{aligned}$$

and,

$$\begin{aligned} m_g^L \;=\; \min \quad & \sum_{k\in N}\alpha_{gk}x_k \\ \text{s.t.} \quad & \sum_{k\in N}x_k \;=\; 1 \\ & x_k^L \leq x_k \leq x_k^U \end{aligned}$$

Experimental Data for Acetone (1) – Methyl Acetate (2) – Methanol (3) $P = 1.0$ atm				
Azeotrope	x_1	x_2	x_3	T (deg C)
Data from Gmehling *et al.* (1994)				
1-2	0.610	0.390	—–	56.10
1-3	0.785	—–	0.215	55.20
2-3	—–	0.680	0.320	54.00
1-2-3 †	0.048	0.620	0.332	55.10

Table 1: Experimental Data for Example 1

† : This azeotrope was reported at a pressure of 1.05 atm.

Results for Acetone (1) – Methyl Acetate (2) – Methanol (3) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)	NLP Subs.
Wilson Equation						
1-2	0.532	0.468	—–	55.675	0.47	21
1-3	0.747	—–	0.253	54.505	0.37	17
2-3	—–	0.677	0.323	54.356	0.43	17
1-2-3	0.272	0.465	0.253	54.254	7.39	217
NRTL Equation						
1-2	0.655	0.345	—–	55.557	0.94	29
1-3	0.777	—–	0.223	55.117	0.57	19
2-3	—–	0.663	0.337	53.545	0.52	19
1-2-3	No ternary azeotrope was found using the NRTL Equation					
Wilson Equation solution from Fidkowski *et al.* (1993)						
AMa	0.5396	0.4606	——	55.66		
AM	0.7480	——	0.2520	54.48		
MaM	——	0.6764	0.3236	54.36		
AMaM	0.2852	0.4538	0.2610	54.25		

Table 2: N-ary Solutions for Example 1

Solution for Acetone (1) – Methyl Acetate (2) – Methanol (3) Find all k-ary Azeotropes: Wilson Equation $P = 1.0$ atm CPU = 278.75 sec NLP Subproblems Solved = 1763				
Azeotropes	x_1	x_2	x_3	T (deg C)
1-2	0.532	0.468	—–	55.675
1-3	0.747	—–	0.253	54.505
2-3	—–	0.677	0.323	54.356
1-2-3	0.272	0.465	0.263	54.254

Table 3: k-ary Solutions for Example 1

Solution for Methanol (1) – Benzene (2) – i-Propanol (3) – n-Propanol (4) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	x_4	T (deg C)	CPU (sec)
Experimental Data from Gmehling *et al.* (1994)						
1-2	0.605	0.395	—–	—–	58.08	
1-3	No Azeotrope					
1-4	No Azeotrope					
2-3	—–	0.600	0.400	—–	71.80	
2-4	—–	0.791	—–	0.209	77.10	
3-4	No Azeotrope					
Wilson Equation						
1-2	0.624	0.376	—–	—–	58.129	0.72
2-3	—–	0.586	0.414	—–	71.951	0.62
2-4	—–	0.780	—–	0.220	76.946	0.63
NRTL Equation						
1-2	0.063	0.937	—–	—–	80.166	0.99
2-3	—–	0.588	0.412	—–	71.832	0.68
2-4	—–	0.776	—–	0.224	77.131	0.80

Table 4: Solutions for Example 2

Solution for Benzene (1) – Hexafluorobenzene (2) Find all N-ary Azeotropes				
Azeotrope	x_1	x_2	T (deg C)	P (atm)
Experimental Data from Gmehling *et al.* (1994)				
1-2	0.150	0.850	30.00	0.14
1-2	0.950	0.050	30.00	0.16
1-2	0.160	0.840	40.00	0.22
1-2	0.930	0.070	40.00	0.24
Wilson Equation CPU = 2.16				
1-2	0.051	0.949	37.650	0.2
1-2	0.956	0.044	35.508	0.2

Table 5: Solutions for Example 3

Solution for Ethanol (1) – Methyl Ethyl Ketone (2) – Water (3) Find all N-ary Azeotropes: $P = 1.0$ atm					
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)
Experimental Data from Gmehling *et al.* (1994)					
1-2	0.501	0.499	—–	74.00	
1-3	0.895	—–	0.105	78.10	
2-3	—–	0.661	0.339	73.50	
1-2-3	0.126	0.580	0.294	73.30	
Wilson Equation					
1-2	0.489	0.511	—–	74.059	0.62
1-3	0.924	—–	0.076	78.211	0.62
2-3	—–	0.682	0.318	74.035	2.52
1-2-3	0.253	0.536	0.211	73.006	3.22
NRTL Equation					
1-2	0.486	0.514	—–	74.076	0.51
1-3	0.952	—–	0.048	78.275	0.70
2-3	—–	0.657	0.343	73.388	0.85
1-2-3	0.187	0.560	0.253	72.957	7.19

Table 6: Solutions for Example 4

Solution for Acetone (1) – Chloroform (2) – Methanol (3) Find all N-ary Azeotropes: $P = 15.8$ atm					
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)
Experimental Data					
No experimental data was found for this system					
Wilson Equation					
1-2	0.312	0.688	—–	184.914	0.53
1-3	0.239	—–	0.761	154.379	0.28
2-3	—–	0.358	0.642	150.268	0.67
NRTL Equation					
1-2	0.289	0.711	—–	184.627	0.79
1-3	0.266	—–	0.734	154.267	0.61
2-3	—–	0.349	0.651	152.401	0.65

Table 7: Solutions for Example 5

Experimental Data for Acetone (1) – Chloroform (2) – Methanol (3) – Ethanol (4) – Benzene (5) $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	x_4	x_5	T (deg C)
Data from Gmehling *et al.* (1994)						
1-2	0.360	0.640	—–	—–	—–	64.50
1-3	0.800	—–	0.200	—–	—–	55.70
2-3	—–	0.653	0.347	—–	—–	53.35
2-4	—–	0.840	—–	0.160	—–	59.30
3-5	—–	—–	0.610	—–	0.390	58.15
4-5	—–	—–	—–	0.431	0.569	64.80
1-2-3	0.318	0.241	0.441	—–	—–	57.67
1-2-4	0.350	0.460	—–	0.190	—–	63.20
2-3-5	No composition given					60.90
1-2-3-5	0.182	0.120	0.500	—–	0.198	57.90

Table 8: Experimental Data for Example 6

Solution for Acetone (1) – Chloroform (2) – Methanol (3) – Ethanol (4) – Benzene (5) Find all N-ary Azeotropes: $P = 1.0$ atm							
Azeotrope	x_1	x_2	x_3	x_4	x_5	T (deg C)	CPU (sec)
Wilson Equation							
1-2	0.371	0.629	—–	—–	—–	64.656	0.78
1-3	0.802	—–	0.198	—–	—–	55.457	0.48
2-3	—–	0.631	0.369	—–	—–	53.070	0.81
2-4	—–	0.842	—–	0.158	—–	59.250	0.95
3-5	—–	—–	0.624	—–	0.376	58.015	0.43
4-5	—–	—–	—–	0.454	0.546	67.700	0.84
1-2-3	0.375	0.189	0.436	—–	—–	57.218	2.03
1-2-4	0.374	0.438	—–	0.188	—–	63.180	2.11
1-2-3-5	0.295	0.148	0.463	—–	0.094	57.154	7.58
NRTL Equation							
1-2	0.351	0.649	—–	—–	—–	65.109	0.83
1-3	0.777	—–	0.223	—–	—–	55.117	0.55
2-3	—–	0.661	0.339	—–	—–	53.675	1.07
2-4	—–	0.846	—–	0.154	—–	59.344	0.69
3-5	—–	—–	0.618	—–	0.382	58.013	0.64
4-5	—–	—–	—–	0.447	0.553	67.795	0.98
1-2-3	0.329	0.237	0.434	—–	—–	57.205	3.88
1-2-4	0.352	0.454	—–	0.194	—–	63.498	3.93
1-2-3-5	0.313	0.222	0.440	—–	0.025	57.201	35.19

Table 9: Solutions for Example 6

Solution for Benzene (1) – Ethanol (2) – Water (3) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)	NLP Subs.
Experimental Data from Gmehling *et al.* (1994)						
1-2	0.570	0.430	—–	64.80		
1-3	0.704	—–	0.296	69.30		
2-3	—–	0.895	0.105	78.10		
1-2-3	No Homogeneous Azeotropes					
UNIQUAC Equation						
1-2	0.572	0.428	—–	67.331	0.94	31
1-3	0.608	—–	0.392	61.317	0.84	31
2-3	—–	0.886	0.114	78.153	0.84	29
1-2-3	0.604	0.013	0.383	61.583	6.48	107

Table 10: Solutions for Example 7

Experimental Data for Ethanol (1) – Methyl-Cyclopentane (2) – Benzene (3) – Hexane (4) $P = 1.0$ atm					
Azeotrope	x_1	x_2	x_3	x_4	T
Data from Gmehling *et al.* (1994)					
1-2	0.378	0.622	—–	—–	60.30
1-3	0.440	—–	0.560	—–	64.70
1-4	0.332	—–	—–	0.668	58.70
2-3	—–	0.875	0.125	—–	71.65
2-4	No Azeotrope				
3-4	—–	—–	0.052	0.948	68.50
1-2-3	No Azeotrope				
1-2-4	No Experimental Data				
1-3-4	No Azeotrope				
2-3-4	No Azeotrope				
1-2-3-4	No Experimental Data				

Table 11: Experimental Data for Example 8

Solution for Ethanol (1) – Methyl-Cyclopentane (2) – Benzene (3) – Hexane (4) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	x_4	T	CPU
UNIQUAC Equation						
1-2	0.316	0.684	—–	—–	63.489	1.56
1-3	0.441	—–	0.559	—–	67.292	0.94
1-4	0.334	—–	—–	0.666	61.265	1.37
2-3	—–	0.738	0.262	—–	70.367	0.77
2-4	—–	0.654	—–	0.346	72.892	0.78
3-4	—–	—–	0.307	0.693	66.919	1.04
1-2-3	0.301	0.545	0.154	—–	63.029	3.49
1-2-4	0.344	0.418	—–	0.238	64.401	7.94
1-3-4	0.300	—–	0.172	0.528	60.669	6.86
2-3-4	—–	0.458	0.333	0.209	71.235	5.53
1-2-3-4	0.322	0.322	0.222	0.133	63.558	27.31

Table 12: Solutions for Example 8

Solution for Acetone (1) – Methyl Acetate (2) – Ethyl Formate (3) Find all N-ary Azeotropes: $P = 1.0$ atm					
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)
Experimental Data from Gmehling *et al.* (1994)					
1-2	0.610	0.390	—–	56.10	
1-3	No Azeotrope				
2-3	No Azeotrope				
1-2-3	0.548	0.407	0.045	55.61	
UNIQUAC Equation					
1-2	0.774	0.226	—–	55.877	0.78
1-3	0.684	—–	0.316	56.860	1.08
1-2-3	0.359	0.456	0.185	56.299	12.28

Table 13: Solutions for Example 9

Solution for Ethanol (1) – Methyl-Cyclopentane (2) – Benzene (3) – Hexane (4) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	x_4	T (deg C)	CPU (sec)
UNIFAC Equation						
1-2	0.371	0.629	—	—	60.632	1.86
1-3	0.450	—	0.550	—	67.841	1.16
1-4	0.357	—	—	0.643	59.054	2.04
2-3	—	0.865	0.135	—	71.651	1.60
3-4	—	—	0.065	0.935	68.900	1.48

Table 14: Solutions for Example 10

Solution for Acetone (1) – Methyl Acetate (2) – Ethyl Formate (3) Find all N-ary Azeotropes: $P = 1.0$ atm						
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)	NLP Subs.
UNIFAC Equation						
1-2	0.443	0.557	—–	55.490	1.82	47
1-3	0.683	—–	0.317	54.658	1.62	53
1-3	0.443	—–	0.557	54.718	4.32	89
1-2-3	0.605	0.354	0.041	55.596	18.28	141

Table 15: Solutions for Example 11

Solution for Acetone (1) – Methyl Ethyl Ketone (2) – Cyclohexane (3) Find all N-ary Azeotropes: $P = 1.0$ atm					
Azeotrope	x_1	x_2	x_3	T (deg C)	CPU (sec)
Experimental Data from Gmehling *et al.* (1994)					
1-2	No Azeotrope				
1-3	0.750	—–	0.250	53.10	
2-3	—–	0.500	0.500	71.00	
1-2-3	No Azeotrope				
UNIFAC Equation					
1-3	0.878	—–	0.122	55.726	1.60
2-3	—–	0.424	0.576	71.822	1.56

Table 16: Solutions for Example 12