Reliable Computation of Reactive Azeotropes

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Abstract

The determination of the existence and composition of reactive azeotropes is important from both theoretical and practical standpoints in the analysis of combined reaction and phase equilibrium and in the synthesis and design of reactive separation systems. We present here a new method for reliably locating, from given thermodynamic models, any and all reactive azeotropes for multicomponent mixtures. The method also verifies the nonexistence of reactive azeotropes if none are present. The method is based on interval analysis, in particular an interval-Newton/generalized-bisection algorithm that provides a mathematical and computational guarantee that all reactive azeotropes are located. The technique is general purpose and can be applied in connection with any thermodynamic models. We illustrate the technique here using several example problems. In two cases, the liquid phase is modeled as ideal; in the other cases, liquid phase nonideality is modeled using either the Wilson or NRTL equation. In one problem, self-association of a component in the vapor phase is also included.

1 Introduction

Today there is increasing interest in the use of reactive distillation in chemical process engineering. Reasons for this interest include the need to separate close-boiling compounds, to save on equipment and operating costs, and to reduce environmental emissions (e.g., Barbosa and Doherty, 1988; Venimadhavan et al., 1994). In some cases, compounds that are very expensive to separate using conventional techniques can be purified more cheaply, cleanly and efficiently using reactive distillation processes. Thus, determining the existence and composition of reactive azeotropes is important both from theoretical and practical standpoints. Of course, knowledge of azeotropes is important since they often present limitations in separation operations which must be known. In the case of reactive systems, azeotropes may also prove to be beneficial, for example by preventing an adverse back reaction (Ung and Doherty, 1995b). Furthermore, the location of reactive azetropes is needed in the construction of residue curve maps for the synthesis and design of reactive separation operations.

An additional use of azeotrope calculations is in the modeling of phase behavior. An important test of thermodynamic models is whether or not known nonreactive azeotropes are predicted, and whether or not they are predicted accurately. These models must also be able to accurately predict reactive azeotropes in order to model reactive systems effectively. Model parameters can be fine tuned by comparing the model predictions with known reactive azeotropic data as such data becomes available. The determination of reactive azeotropes strictly from experiment alone can be expensive. Predicting reactive azeotropes computationally is one method of reducing this cost, as the computational results can be used to narrow the experimental search space.

The problem of computing reactive phase equilibrium, including the presence of reactive azeotropes, has attracted significant attention (e.g., Barbosa and Doherty, 1988; Venimadhavan et al., 1994; Ung and Doherty, 1995a,b; Seider and Widagdo, 1996; Nisoli et al., 1997; Song et al., 1997). The difficult nonlinear form of the thermodynamic models for chemical and phase equilibrium makes these computations particularly difficult, especially since there is generally no knowledge *a priori* concerning the number of reactive azeotropes, or if there are any. In order to be most useful, a computational method for locating azeotropes must be completely reliable, capable of finding (or, more precisely, *enclosing* within a very narrow interval) *all* azeotropes when one or more exists, and capable of verifying (within limits of machine precision) when none exist. Because such guarantees cannot be provided when using standard local solvers, even with multiple initial guesses, there has been considerable recent interest in developing more reliable techniques for the computation of reactive azeotropes. For example, Okasinski and Doherty (1997) used arc-length continuation to track the location of reactive azeotropes as a function of the reaction equilibrium constant. This is a very reliable approach, but offers no theoretical guarantee that all reactive azeotropes will be found. Harding and Floudas (1998) have used a powerful global optimization procedure; it is based on branch and bound with convex underestimating functions that are continuously refined as the domain in which reactive azeotropes may occur is narrowed. This technique does provide a theoretical guarantee that all azeotropes have been enclosed. Harding et al. (1997) have developed appropriate convex underestimating functions for several specific thermodynamic models. However, one difficulty with this approach is that in general it may be necessary to perform problem reformulations and develop convex underestimators specific to each new model. Also, branch and bound methods implemented in floating point arithmetic may be vulnerable to rounding error problems, and thus lose their theoretical guarantees.

We describe here a new approach for reliably enclosing *all* reactive azeotropes of multicomponent mixtures, and for verifying when none exist. Like the method of Maier et al. (1998) for finding nonreactive homogeneous azeotropes, the technique is based on interval analysis, in particular the use of an interval-Newton/generalized-bisection algorithm. The method is mathematically *and* computationally guaranteed to enclose any and all reactive azeotropes, automatically dealing with rounding error. It does not require the construction of model-specific convex underestimating functions, is general purpose and can be applied in connection with any thermodynamic model. In the work presented here, the vapor phase is modeled either as ideal, or with the association (dimerization) of one component, and the liquid phase is modeled either as ideal or as nonideal using the Wilson or NRTL activity coefficient model.

In the next section, we present the mathematical formulation of the problem. In Section 3, we describe the problem solving methodology. Then, in Section 4 we present the results for several test problems, and in Section 5 provide some concluding remarks concerning this study.

2 Problem Formulation

At a reactive homogeneous azeotrope, the change in composition of the liquid phase due to reaction is compensated by the change in composition due to phase equilibrium, and so a constant boiling mixture is achieved. For a mixture of C components involving R independent reactions, a convenient way to represent the reactive azeotropy condition is (Ung and Doherty, 1995b)

$$X_i = Y_i, \quad i = 1, \ldots, C - R, \tag{1}$$

where X_i and Y_i are a set of *transformed* mole fraction variables in the liquid phase and vapor phase respectively. The $C - R$ transformed mole fractions are defined in terms of a set of R reference components. Here we number the nonreference components from 1 to $C - R$, and the reference components from $C - R + 1$ to C. The transformed mole fractions are then given as

$$X_i = \frac{x_i - \mathbf{s}_i \mathbf{x}_{\text{ref}}}{1 - \mathbf{s}_{\text{T}} \mathbf{x}_{\text{ref}}}, \quad i = 1, \ldots, C - R \tag{2}$$

$$Y_i = \frac{y_i - \mathbf{s}_i \mathbf{y}_{\text{ref}}}{1 - \mathbf{s}_{\text{T}} \mathbf{y}_{\text{ref}}}, \quad i = 1, \ldots, C - R, \tag{3}$$

where x_i and y_i are the actual (nontransformed) mole fractions of component i in the liquid and vapor phases, $\mathbf{x}_{\text{ref}} = (x_{C-R+1}, \ldots, x_C)^{\text{T}}$ and $\mathbf{y}_{\text{ref}} = (y_{C-R+1}, \ldots, y_C)^{\text{T}}$ are the column vectors of the reference component mole fractions in the liquid and vapor phases, and $\mathbf{s}_i$ and $\mathbf{s}_{\text{T}}$ are row vectors defined in terms of the reaction stoichiometry. These row vectors are defined by

$$\mathbf{s}_i = \boldsymbol{\nu}_i^{\text{T}} \mathcal{V}^{-1}, \quad i = 1, \ldots, C - R \tag{4}$$

$$\mathbf{s}_{\mathrm{T}} = \boldsymbol{\nu}_{\mathrm{tot}}^{\mathrm{T}} \mathcal{V}^{-1}, \tag{5}$$

where the matrix $\mathcal{V}$ and the row vectors $\boldsymbol{\nu}_i^{\mathrm{T}}$ are related to the stoichiometric coefficient ν_{ir} of component i in reaction r by $\boldsymbol{\nu}_i^{\mathrm{T}} = (\nu_{i1}, \ldots, \nu_{iR}), i = 1, \ldots, C - R$, and

$$\mathcal{V} = \begin{pmatrix} \nu_{(C-R+1)1} & \cdots & \nu_{(C-R+1)R} \\ \vdots & \nu_{ir} & \vdots \\ \nu_{c1} & \cdots & \nu_{cR} \end{pmatrix}, \tag{6}$$

and $\boldsymbol{\nu}_{\mathrm{tot}}^{\mathrm{T}} = (\nu_{\mathrm{T}1}, \ldots, \nu_{\mathrm{T}R})$ is a row vector comprising the total mole number changes in each reaction; that is $\nu_{\mathrm{T}r} = \sum_{i=1}^{C} \nu_{ir}, r = 1, \ldots, R$.

At a reactive azeotrope, both phase (vapor-liquid) and reaction equilibrium conditions must be satisfied. The vapor-liquid equilibrium relationship is given by

$$y_i = \frac{x_i \gamma_i P_i^s}{\zeta_i P}, \quad i = 1, \ldots, C. \tag{7}$$

Here, P is the system pressure, $P_i^s = P_i^s(T)$ is the vapor pressure of pure component i and is a function of the temperature T, $\gamma_i = \gamma_i(\mathbf{x}, T)$ is the activity coefficient of component i and is a function of T and of the liquid phase composition $\mathbf{x} = (x_1, \ldots, x_C)^{\mathrm{T}}$, and $\zeta_i = \zeta_i(y_{\mathrm{A}}, T)$ is a correction factor which is introduced when we consider the vapor phase association of one component $\mathrm{A} \in \{1, \ldots, C\}$, as in the last example presented in this paper. If no associating components are present, then $\zeta_i = 1$. Otherwise, following Manning (1999) and Venimadhavan et al. (1999), we use the method of Marek and Standart (1954) to calculate this correction factor as

$$\zeta_A = \frac{1 + (1 + 4k_A P_A^{sat})^{\frac{1}{2}}}{1 + [1 + 4kPy_A(2 - y_A)]^{\frac{1}{2}}} \tag{8}$$

$$\zeta_N = \frac{2\left\{1 - y_A + \left[1 + 4kPy_A\left(2 - y_A\right)\right]^{\frac{1}{2}}\right\}}{\left(2 - y_A\right)\left\{1 + \left[1 + 4kPy_A\left(2 - y_A\right)\right]^{\frac{1}{2}}\right\}}, \tag{9}$$

where ζ_A is used for the associating component, and ζ_N for the non-associating components. Here $k = k(T)$ is the dimerization equilibrium constant for component A in the mixture, and $k_{\mathrm{A}} = k_{\mathrm{A}}(T)$ is the dimerization equilibrium constant for pure A, both of which are functions of temperature. Here we use the approximation $k \approx k_{\mathrm{A}}$, as in Marek (1955) and Manning (1999). This dimerization reaction is treated in this way, instead of being included in the set of R independent reactions, because the dimer is assumed not be present in the liquid phase. Eq. (7) for y_i can be now substituted into the reactive azeotropy condition yielding

$$\frac{x_i - \mathbf{s}_i\mathbf{x}_{\mathrm{ref}}}{1 - \mathbf{s}_{\mathrm{T}}\mathbf{x}_{\mathrm{ref}}} = \frac{\left(x_i\gamma_i P_i^s/\zeta_i\right) - \mathbf{s}_i\hat{\mathbf{y}}_{\mathrm{ref}}}{P - \mathbf{s}_{\mathrm{T}}\hat{\mathbf{y}}_{\mathrm{ref}}}, \quad i = 1, \ldots, C - R, \tag{10}$$

where

$$\hat{\mathbf{y}}_{\mathrm{ref}} = \hat{\mathbf{y}}_{\mathrm{ref}}(\mathbf{x}, T, y_{\mathrm{A}}) = P\mathbf{y}_{\mathrm{ref}} = \left(\frac{x_{C-R+1}\gamma_{C-R+1}P^s_{C-R+1}}{\zeta_{C-R+1}}, \ldots, \frac{x_C\gamma_C P^s_C}{\zeta_C}\right)^{\mathrm{T}}, \tag{11}$$

thus eliminating all y_i, $i \neq \mathrm{A}$. Note that for an ideal vapor phase $\zeta_i = 1, i = 1, \ldots, C$ and $\hat{\mathbf{y}}_{\mathrm{ref}} = \hat{\mathbf{y}}_{\mathrm{ref}}(\mathbf{x}, T)$, thus all the y_i are eliminated. In order to avoid potential division by zero, we rearrange Eq. (10) to obtain

$$x_i\left(P - \mathbf{s}_{\mathrm{T}}\hat{\mathbf{y}}_{\mathrm{ref}} + \frac{\gamma_i P_i^s}{\zeta_i}\left[\mathbf{s}_{\mathrm{T}}\mathbf{x}_{\mathrm{ref}} - 1\right]\right) + \mathbf{s}_i\mathbf{x}_{\mathrm{ref}}\left(\mathbf{s}_{\mathrm{T}}\hat{\mathbf{y}}_{\mathrm{ref}} - P\right) + \mathbf{s}_{\mathrm{i}}\hat{\mathbf{y}}_{\mathrm{ref}}\left(1 - \mathbf{s}_{\mathrm{T}}\mathbf{x}_{\mathrm{ref}}\right) = 0, \tag{12}$$

$$i = 1, \ldots, C - R.$$

The equations for chemical equilibrium are

$$K_r\left(T\right) = \prod_{i=1}^{C} a_i^{\nu_{ri}}, \quad r = 1, \ldots, R \tag{13}$$

where $a_i = x_i \gamma_i$ is the activity of component i in the liquid phase. The reaction equilibrium constant $K_r(T)$ is determined from $\ln K_r(T) = -\Delta G_r^o / RT$, where ΔG_r^o is the standard Gibbs free energy of reaction for reaction r, and R is the gas constant. For an ideal vapor phase, Eqs. (12) and (13), together with the requirement that the sum of the liquid phase mole fractions sum to one

$$\sum_{i=1}^{C} x_i = 1, \tag{14}$$

make up a system of $C + 1$ equations in $C + 1$ unknowns, namely the C liquid phase mole fractions x_i and the temperature T. For a vapor phase in which one component associates, there is an additional variable, namely y_{A}, the vapor phase mole fraction of the associating component, and an additional equation, namely the phase equilibrium relationship

$$y_{\mathrm{A}} \zeta_{\mathrm{A}} P = x_{\mathrm{A}} \gamma_{\mathrm{A}} P_{\mathrm{A}}^s, \tag{15}$$

for the associating component, which yields a system of $C+2$ equations in $C+2$ unknowns. In either case, whether the vapor phase is modeled as ideal, or with one associating component, the system of equations to be solved for reactive azeotropes may have one solution, multiple solutions, or no solution, and the number of solutions is not known *a priori*. The interval method used here can provide both mathematical and computational guarantees that all solutions will be enclosed, and can also determine with certainty if there are no solutions.

In the examples considered below, the pure component vapor pressures $P_i^s(T)$ are modeled using the Antoine equation. The liquid phase activity coefficients $\gamma_i(\mathbf{x}, T)$ are modeled using either the Wilson or NRTL equation, or are treated as ideal ($\gamma_i = 1$). The model equations and parameters used are listed in the Appendix.

3 Methodology

We apply here interval mathematics, in particular an interval-Newton/generalized-bisection (IN/GB) technique, to find enclosures for all reactive azeotropes or demonstrate that there are none. Recent monographs that introduce interval computations include those of Neumaier (1990), Hansen (1992) and Kearfott (1996). The algorithm used here is a modification of the method that was used by Maier et al. (1998) for the nonreactive homogeneous azeotrope problem, and that has been summarized by Hua et al. (1998) and given in more detail by Schnepper and Stadtherr (1996). Properly implemented, this technique provides the power to find, with mathematical and computational certainty, enclosures of *all* solutions of a system of nonlinear equations (Neumaier, 1990; Kearfott and Novoa, 1990), or to determine with certainty that there are none, provided that initial upper and lower bounds are available for all variables. This is made possible through the use of the powerful existence and uniqueness test provided by the interval-Newton method. Our implementation of the IN/GB method for the reactive azeotrope problem is based on appropriately modified routines from the FORTRAN-77 packages INTBIS (Kearfott and Novoa, 1990) and INTLIB (Kearfott et al., 1994). The methodology used is summarized very briefly here, with emphasis on the modification to the previously used method (Maier et al., 1998; Hua et al., 1998; Schnepper and Stadtherr, 1996).

Consider the solution of a nonlinear equation system $\mathbf{f}(\mathbf{z}) = \mathbf{0}$ where $\mathbf{z} \in \mathbf{Z}^{(0)}$. The solution algorithm is applied to a sequence of intervals, beginning with the initial interval vector (box) $\mathbf{Z}^{(0)}$ specified by the user. This initial interval can be chosen to be sufficiently large to enclose all physically feasible behavior. For an interval $\mathbf{Z}^{(k)}$ in the sequence, the first step in the solution algorithm is the *function range test*. Here an *interval extension* $\mathbf{F}(\mathbf{Z}^{(k)})$ of the function $\mathbf{f}(\mathbf{z})$ is calculated. An interval extension provides upper and lower bounds on the range of values that a function may have in a given interval. It is often computed by substituting the given interval into the function and then evaluating the function using interval arithmetic. The interval extension so determined is often wider than the actual range of function values, but it always includes the actual range. If there is any component of the interval extension $\mathbf{F}(\mathbf{Z}^{(k)})$ that does not contain zero, then we may discard the current interval $\mathbf{Z}^{(k)}$, since the range of the function does not include zero anywhere in this interval, and thus no solution of $\mathbf{f}(\mathbf{z}) = \mathbf{0}$ exists in this interval. Otherwise, if $\mathbf{0} \in \mathbf{F}(\mathbf{Z}^{(k)})$, then the processing of $\mathbf{Z}^{(k)}$ continues.

The next step is a simple *domain reduction* technique in which we attempt to reduce the size of $\mathbf{Z}^{(k)}$. This step was not used by Maier et al. (1998) and so its addition represents a modification of the previously applied procedure. The method used in this step is sometimes referred to as constraint propagation, especially in the context of optimization problems. The basic idea is to rewrite one or more of the equations in the system in the form $z_i = g_i(\mathbf{z})$. For example, we can rewrite Eq. (12) as

$$x_i = -\frac{\mathbf{s}_i \mathbf{x}_{\mathrm{ref}} \left(\mathbf{s}_{\mathrm{T}} \hat{\mathbf{y}}_{\mathrm{ref}} - P\right) + \mathbf{s}_{\mathrm{i}} \hat{\mathbf{y}}_{\mathrm{ref}} \left(1 - \mathbf{s}_{\mathrm{T}} \mathbf{x}_{\mathrm{ref}}\right)}{\left(P - \mathbf{s}_{\mathrm{T}} \hat{\mathbf{y}}_{\mathrm{ref}} + \frac{\gamma_i P_i^s}{\zeta_i} \left[\mathbf{s}_{\mathrm{T}} \mathbf{x}_{\mathrm{ref}} - 1\right]\right)}, \quad i = 1, \ldots, C - R, \tag{16}$$

and can do similar rearrangements with the other equations. Once the rearrangement to $z_i = g_i(\mathbf{z})$ has been done, we can then calculate a new range for z_i by substituting the current interval $\mathbf{Z}^{(k)}$ into the expression for g_i, thus obtaining $Z_{i,\mathrm{calc}}^{(k)} = G_i(\mathbf{Z}^{(k)})$. The range for z_i can now be reduced in many cases by using the intersection of the original range $Z_i^{(k)}$ and the calculated range $Z_{i,\text{calc}}^{(k)}$; that is $Z_i^{(k)} \leftarrow Z_i^{(k)} \cap Z_{i,\text{calc}}^{(k)}$. If desired, this domain reduction step can be iterated until there is no further reduction in $\mathbf{Z}^{(k)}$; however, for the problems solved here, our tests indicate that, in terms of CPU time, a single application of this step is most effective.

The next step is to apply the *interval-Newton test* to the current interval $\mathbf{Z}^{(k)}$. This involves setting up and solving a system of linear interval equations for a new interval, the *image* $\mathbf{N}^{(k)}$. Comparison of the current interval and the image provides a powerful existence and uniqueness test (Kearfott, 1996; Neumaier, 1990). If $\mathbf{N}^{(k)} \cap \mathbf{Z}^{(k)} = \emptyset$, this is mathematical proof that there is no solution of $\mathbf{f}(\mathbf{z}) = \mathbf{0}$ in $\mathbf{Z}^{(k)}$. If $\mathbf{N}^{(k)} \subset \mathbf{Z}^{(k)}$, then this is mathematical proof that there is a *unique* solution of $\mathbf{f}(\mathbf{z}) = \mathbf{0}$ in $\mathbf{Z}^{(k)}$. If $\mathbf{N}^{(k)} \cap \mathbf{Z}^{(k)} \neq \emptyset$ and $\mathbf{N}^{(k)} \not\subset \mathbf{Z}^{(k)}$, then no conclusions can be made about the number of solutions in the current interval. However, it is known (e.g., Moore, 1966) that any solutions that do exist must lie in the intersection $\mathbf{N}^{(k)} \cap \mathbf{Z}^{(k)}$. If the intersection is sufficiently smaller than the current interval, one can proceed by reapplying the interval-Newton test to the intersection. Otherwise, the intersection is bisected, and the resulting two intervals added to the sequence of intervals to be tested. These are the basic ideas of an interval-Newton/generalized-bisection (IN/GB) method.

It should be emphasized that, when machine computations with interval arithmetic operations are done, as in the procedures outlined above, the endpoints of an interval are computed with a directed outward rounding. That is, the lower endpoint is rounded down to the next machine-representable number and the upper endpoint is rounded up to the next machine-representable number. In this way, through the use of interval, as opposed to floating point arithmetic, any potential rounding error problems are eliminated. Overall, the IN/GB method described above provides a procedure that is mathematically *and* computationally guaranteed to enclose all reactive azeotropes, or to determine with certainty that there are none.

4 Results

The computational results for five example problems are given below. In each case, problems previously presented elsewhere are used; thus, we are able to verify the ability of the technique described here to reliably enclose all solutions. The model parameters used are summarized in the Appendix. For each problem solved we present the reactive azeotrope(s) found, as well as the CPU time required. The CPU times are given in seconds on a Sun Ultra 2/1300 workstation. It should be noted that, while point approximations of the azeotropic compositions and temperature are reported in the tables here, we have actually determined verified enclosures of each root. Each such enclosure is an extremely narrow interval known to contain a *unique* root, based on the interval-Newton uniqueness test described above. The initial interval used for mole fraction variables was $[10^{-10}, 1]$ for reactive species, and $[0, 1]$ for inerts (reactive species must be present in nonzero amounts, since otherwise one or more reaction equilibrium condition cannot be satisfied). The initial interval used for temperature was $[10, 200]$ °C.

4.1 Problem 1

The first example problem is a hypothetical three component system at $P = 1$ atmosphere with one equilibrium reaction, $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$. For this problem, the liquid phase was assumed to be ideal ($\gamma_i = 1, i, \ldots, C$). This problem was originally solved by Barbosa and Doherty (1988). The reaction equilibrium constant $K_r(T)$ was determined using $\Delta G_r^o = -8314$ J/mol. The chosen reference component was C, and from the reaction stoichiometry, $s_{\mathrm{A}} = -1$, $s_{\mathrm{B}} = -1$ and $s_{\mathrm{T}} = -1$. Table 1 shows the computational results for this system, including the results for the independent variables T and $x_i, i = 1, \ldots, C$, and the corresponding values of the dependent variables $y_i, i = 1, \ldots, C$ and, for the nonreference components, of the transformed mole fractions $X_i = Y_i$. Although the liquid phase is ideal, meaning there can be no nonreactive azeotropes, this system does exhibit a reactive azeotrope at the conditions indicated. The solution found is the same as that reported by Barbosa and Doherty (1988).

4.2 Problem 2

The second example problem is a hypothetical four component system at $P = 1$ atmosphere undergoing one equilibrium reaction, $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$. Again the liquid phase was assumed to be ideal. This problem was also originally solved by Barbosa and Doherty (1988). The reaction equilibrium constant $K_r(T)$ was determined using $\Delta G_r^o = 831.4$ J/mol. The chosen reference component was D, and from the reaction stoichiometry, $s_{\mathrm{A}} = -1$, $s_{\mathrm{B}} = -1$, $s_{\mathrm{C}} = 1$ and $s_{\mathrm{T}} = 0$. Table 2 shows the computational results for this system. This is another example of an ideal system which exhibits a reactive azeotrope. The solution presented in Table 2 is the same as that found by Barbosa and Doherty (1988).

4.3 Problem 3

The third example problem is the three component system of isobutene (IB), methanol (M), and methyl *tert*-butyl ether (MTBE) at 8 atmospheres. The one independent equilibrium reaction is IB + M $\rightleftharpoons$ MTBE. The Wilson equation was used to model the liquid phase activity coefficients. This problem was originally set up and solved by Okasinski and Doherty (1997). They assumed the reaction equilibrium constant K_r to be independent of temperature, and then solved a series of problems with different values of K_r (covering a range reported experimentally) to examine its effect on the reactive phase equilibrium. The chosen reference component was MTBE, and from the reaction stoichiometry, $s_{\mathrm{IB}} = -1$, $s_{\mathrm{M}} = -1$ and $s_{\mathrm{T}} = -1$. The computational results for this system are given in Table 3. This shows that when $K_r = 0.04$, there is a single reactive azeotrope, but that at higher K_r there is no reactive azeotrope, and that at still higher K_r there are two reactive azeotropes. These results match those of Okasinski and Doherty (1997). This example demonstrates the difficulty of knowing *a priori* how many reactive azeotropes there may be, if indeed there are any.

4.4 Problem 4

The fourth example problem is the four component system of isobutene (IB), methanol

(M), methyl *tert*-butyl ether (MTBE), and *n*-butane (NB). The problem is solved at pressures of 10, 20 and 40 atmospheres. The Wilson equation was used to model the liquid phase. Here *n*-butane is an inert component, the only reaction being formation of MTBE, as in the previous example problem. This problem was originally solved by Ung and Doherty (1995a,b) at a pressure of 10 atmospheres. The reaction equilibrium constant was determined from $\Delta G_r^o/R = -4205.05 + 10.0982T - 0.2667T \ln T$, where T is in K, and R is the gas constant. The chosen reference component was MTBE, and from the reaction stoichiometry, $s_{\mathrm{IB}} = -1$, $s_{\mathrm{M}} = -1$, $s_{\mathrm{NB}} = 0$ and $s_{\mathrm{T}} = -1$. Table 4 shows the computed results for this system. At 10 atmospheres, there is a single reactive azeotrope at almost pure *n*-butane, as also found by Ung and Doherty (1995a). At the higher pressures, the reactive azeotrope occurs at decreasing mole fraction of *n*-butane, as shown in Table 4. Of course, for any of the pressures used here, the assumption of an ideal vapor phase may not be realistic.

4.5 Problem 5

The fifth example problem is the four component system of acetic acid (AA), isopropanol (IPOH), isopropyl acetate (IPAC) and water. The system pressure is 1 atmosphere, and there is one reaction, $\mathrm{AA} + \mathrm{IPOH} \rightleftharpoons \mathrm{IPAC} + \mathrm{H_2O}$. A reactive azeotrope in this system was originally discovered experimentally by Song et al. (1997), and later modeled by Manning (1999) and Venimadhavan et al. (1999). The liquid phase activity coefficients were modeled using the NRTL equation. The reaction equilibrium constant was taken as $K_r = 8.7$ and was assumed independent of T. While in the previous examples, the vapor phase was modeled as an ideal gas, here the association (dimerization) of acetic acid in the vapor phase is taken into account, using the model discussed above in Section 2. The dimerization constant was determined from $\log_{10} k = \log_{10} k_\mathrm{A} = -12.5454 + (3166.0/T)$, with T in K and k and k_A in Pa^{-1}. The chosen reference component was IPA, and from the reaction stoichiometry, $s_\mathrm{AA} = -1$, $s_\mathrm{IPOH} = -1$, $s_{\mathrm{H_2O}} = 1$ and $s_\mathrm{T} = 0$. Computational results are shown in Table 5. One reactive azeotrope is found, which agrees with that found by Huss et al. (1999) using this model. The substantial increase in computation time, compared to the other example problems, is due to the increased problem complexity resulting from modeling the vapor phase association of acetic acid.

5 Concluding Remarks

We have described here a new method for reliably locating, from given thermodynamic models, *all* reactive azeotropes in multicomponent mixtures, and for verifying their nonexistence if none are present. The method is based on interval analysis, in particular an interval-Newton/generalized-bisection algorithm, which provides a mathematical and computational guarantee that all reactive azeotropes are enclosed. In the work presented here, the liquid phase was modeled either as ideal or as nonideal using the Wilson or NRTL activity coefficient model, and the vapor phase was modeled either as ideal, or with the association (dimerization) of one component. However, the technique is general purpose and can be applied in connection with any thermodynamic models. In addition to the solution of reactive azeotrope problems, the methodology used here can also be applied to a wide variety of other problems in the modeling of phase behavior (e.g., Stadtherr et al., 1995; Hua et al., 1998; Maier et al., 1998; Tessier et al., 2000; Gau and Stadtherr, 1999, 2000; Xu et al., 2000), and in the solution of process modeling problems (Schnepper and Stadtherr, 1996).

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Appendix. Models and Parameters

A.1 Antoine Equation

To model the temperature dependence of $P_i^s(T)$ we use the Antoine equation

$$\log_{10} P_i^s = A_i - \frac{B_i}{T + C_i}.$$

This is a dimensional equation with P_i^s in mmHg and T in °C. The values of the parameters A_i, B_i and C_i used in the example problems are given in Table A1.

A.2 Wilson Equation

For the problems that use the Wilson activity coefficient model, the equation used is

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{C} x_j \Lambda_{ij} \right) - \sum_{k=1}^{C} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{C} x_j \Lambda_{kj}},$$

where the non-symmetric binary interaction parameter, Λ_{ij} is given by

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left[-\frac{A_{ij}}{RT} \right].$$

The values of the energy parameters A_{ij} and the volumes V_i used in the example problems are given in Table A2. R is the gas constant.

A.3 NRTL Equation

For the problems that use the NRTL activity coefficient model, the equation is

$$\ln \gamma_i^L = \frac{d_i}{c_i} + \sum_{j=1}^{C} \left[\frac{x_j G_{ij}}{c_j} \left(\tau_{ij} - \frac{d_j}{c_j} \right) \right],$$

where

$$c_j = \sum_{k=1}^{C} G_{kj} x_k,$$

$$d_j = \sum_{k=1}^{C} \tau_{kj} G_{kj} x_k,$$

and the interaction parameters are given by

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right),$$

$$\tau_{ij} = \frac{A_{ij}}{RT}.$$

Values of the parameters A_{ij} and $\alpha_{ij} = \alpha_{ji}$ used in the example problems are given in Table A3. R is the gas constant.

Table 1: Reactive azeotrope computed in Problem 1.

Component i	x_i	y_i	$X_i = Y_i$
A	0.07	0.17	0.35
B	0.50	0.55	0.65
C	0.43	0.28	
$T = 121.7$ °C			
CPU time = 0.17 s			

Table 2: Reactive azeotrope computed in Problem 2.

Component i	x_i	y_i	$X_i = Y_i$
A	0.19	0.07	0.43
B	0.36	0.24	0.60
C	0.22	0.33	-0.03
D	0.24	0.36	
$T = 89.5$ °C			
CPU time = 2.14 s			

Table 3: Reactive azeotropes computed in Problem 3.

	$K_r = 0.04$			$K_r = 20.0$	$K_r = 49.0$					
Component i	x_i	y_i	$X_i = Y_i$	no azeotrope	x_i	y_i	$X_i = Y_i$	x_i	y_i	$X_i = Y_i$
Isobutene	0.93	0.94	0.93		0.01	0.07	0.38	0.04	0.17	0.48
Methanol	0.05	0.06	0.07		0.40	0.44	0.62	0.12	0.24	0.52
MTBE	0.02	0.00			0.58	0.49		0.84	0.59	
	$T = 60.9$ °C				$T = 118.0$ °C			$T = 119.1$ °C		
	CPU time = 0.33 s			CPU time = 0.97 s	CPU time = 0.86 s					

Table 4: Reactive azeotropes computed in Problem 4.

	$P = 10$ atm			$P = 20$ atm			$P = 40$ atm		
Component i	x_i	y_i	$X_i = Y_i$	x_i	y_i	$X_i = Y_i$	x_i	y_i	$X_i = Y_i$
Isobutene	0.0055	0.0066	0.0069	0.0287	0.0342	0.0364	0.1478	0.1708	0.1887
Methanol	0.0003	0.0015	0.0018	0.0014	0.0070	0.0090	0.0066	0.0334	0.0475
MTBE	0.0015	0.0003		0.0077	0.0020		0.0409	0.0128	
n-Butane	0.9927	0.9916	0.9913	0.9622	0.9568	0.9545	0.8047	0.7830	0.7638
	$T = 80.8$ °C			$T = 115.2$ °C			$T = 161.6$ °C		
	CPU time = 18.6 s			CPU time = 19.5 s			CPU time = 24.4 s		

Table 5: Reactive azeotrope computed in Problem 5.

Component i	x_i	y_i	$X_i = Y_i$
Acetic Acid	0.048	0.003	0.231
Isopropanol	0.565	0.520	0.748
Isopropyl Acetate	0.183	0.228	
Water	0.204	0.249	0.021
$T = 79.7$ °C			
CPU time = 150.6 s			

Table A1. Antoine equation parameters used in example problems.

Problem(s)	Component i	A_i	B_i (°C)	C_i (°C)
1	A	11.187	4068.457	392.722
	B	8.02099	1936.010	258.441
	C	7.68849	1669.898	211.8
2	A	7.38781	1533.313	222.299
	B	8.11219	1592.864	226.174
	C	7.10178	1244.951	217.871
	D	8.0713	1730.630	233.416
3–4	Isobutene	6.84132	923.201	239.99
	Methanol	8.07372	1578.230	239.382
	MTBE	6.87201	1116.825	224.744
	n-Butane	6.80896	935.860	238.73
5	Acetic Acid	8.02100	1936.011	258.451
	Water	8.07129	1730.629	233.426
	Isopropanol	8.87830	2010.332	252.636
	Isopropyl Acetate	7.33394	1436.529	233.665

Table A2. Wilson equation parameters[1] used in Problems 3 and 4.

Component i	Component j	A_{ij} (cal/mol)	A_{ji} (cal/mol)	V_i(cm^3/mol)	V_j(cm^3/mol)
Isobutene	Methanol	169.9953	2576.8532	93.33	44.44
Isobutene	MTBE	-60.1022	271.5669	93.33	118.8
Methanol	MTBE	1483.2478	-406.3902	44.44	118.8
Methanol	*n*-Butane	2283.8726	382.3429	44.44	100.39

[1] For the isobutene/*n*-butane and MTBE/*n*-butane binaries, $\Lambda_{ij} = \Lambda_{ji} = 1$.

Table A3. NRTL equation parameters used in Problem 5.

Component i	Component j	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$\alpha_{ij} = \alpha_{ji}$
Acetic Acid	Water	-219.7238	842.6081	0.2997
Acetic Acid	Isopropanol	-281.4482	81.3926	0.3048
Acetic Acid	Isopropyl Acetate	141.0082	154.7885	0.3014
Water	Isopropanol	1655.255	39.8541	0.3255
Water	Isopropyl Acetate	1270.2036	1165.709	0.33
Isopropanol	Isopropyl Acetate	269.9606	140.0972	0.3009