Reliable Computation of Homogeneous Azeotropes

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It is important to determine the existence and composition of homogeneous azeotropes in the analysis of phase behavior and in the synthesis and design of separation systems, from both theoretical and practical standpoints. A new method for reliably locating any and all homogeneous azeotropes for multicomponent mixtures is presented. The method also verifies the nonexistence of homogeneous azeotropes if none are present. The method is based on interval analysis, in particular an interval-Newton/generalized-bisection-algorithm providing a mathematical and computational guarantee that all azeotropes are located. This general-purpose technique can be applied in connection with any thermodynamic models. The technique is illustrated in several example problems using the Wilson, NRTL, and UNIQUAC activity-coefficient models.

Introduction

The determination of the existence and composition of homogeneous azeotropes is important both from theoretical and practical standpoints. Two important tests of thermodynamic models are whether or not known azeotropes are predicted and whether or not they are predicted accurately. Model parameters can be fine-tuned by comparing the model predictions with known azeotropic data. The determination of azeotropes strictly from experiment alone can be expensive. Predicting azeotropes computationally is one method of reducing this cost, as the computational results can be used to narrow the experimental search space. Of course, knowledge of azeotropes is important, since they often present limitations in separation operations that must be known. Furthermore, this knowledge can be used in the construction of residue curve maps for the synthesis and design of separation operations.

The problem of computing homogeneous azeotropes from models of phase behavior has attracted significant attention (e.g., Aristovich and Stepanova, 1970; Teja and Rowlinson, 1973; Wang and Whiting, 1986; Chapman and Goodwin, 1993), and has been reviewed recently by Widagdo and Seider (1996). The highly nonlinear form of the thermodynamic equations for phase equilibrium makes the computation of azeotropes a particularly difficult problem. 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 of the difficulties in providing such guarantees, there has been considerable recent interest in developing more reliable techniques for the computation of homogeneous azeotropes. For example, Fidkowski et al. (1993) and Westerberg and Wahnschafft (1996) have presented continuation methods for this purpose, and Okasinski and Doherty (1997) have used a similar approach for finding reactive azeotropes. While these methods are very reliable, a drawback is that they cannot completely guarantee that all azeotropes have been enclosed. More recently, Maranas et al. (1996) and Harding et al. (1997) 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 azeotropes may occur is narrowed. This technique does provide a mathematical guarantee that all azeotropes have been enclosed. Harding et al. (1997) have developed appropriate convex underestimating functions for several specific thermodynamic models. While global optimization methods based on branch and bound can provide mathematical guarantees, in principle this guarantee can be lost computationally if the technique is implemented in floating-point arithmetic, due to rounding error. In practice, however, if variables are well scaled, as is the case here, this is unlikely to cause problems.

We describe here a new approach for reliably enclosing *all* homogeneous azeotropes of multicomponent mixtures, and for verifying when none exist. 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

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and all homogeneous azeotropes, automatically dealing with rounding error and requiring no initial starting point. 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 as ideal, and the Wilson, NRTL, and UNIQUAC activity coefficient models are used to describe the liquid phase.

In this article, we present the mathematical formulation of the problem, the interval-Newton/generalized-bisection (IN/GB) method, and the results for several test problems.

Mathematical Formulation

At a homogeneous azeotrope, vapor and liquid phases of the same composition are in equilibrium. For a mixture of N components, the equilibrium condition can be written in terms of the equality of fugacities,

$$\hat{f}_i^V = \hat{f}_i^L, \qquad \forall i \in \mathcal{C},$$

where $\hat{f}_i^V$ refers to the fugacity of component i in the vapor phase; $\hat{f}_i^L$ refers to the fugacity of component i in the liquid solution; and $\mathcal{C}$ is the set of components in question. These solution fugacities can in turn be written as

$$y_i \hat{\phi}_i^V P = x_i \gamma_i^L f_i^L, \qquad \forall i \in \mathcal{C},$$

where P is the system pressure; $\hat{\phi}_i^V$ is the mixture fugacity coefficient of component i in the vapor phase; γ_i^L is the activity coefficient of component i in the liquid phase; f_i^L is the pure-component fugacity of component i in the liquid phase; y_i is the mole fraction of component i in the vapor phase; and x_i is the mole fraction of component i in the liquid phase. Assuming ideal vapor behavior and Poynting correction factors of one, this becomes

$$y_i P = x_i \gamma_i^L P_i^{\text{sat}}, \qquad \forall i \in \mathcal{C},$$

where P_i^{sat} is the vapor pressure of component i. Using the homogeneous azeotropy condition $x_i = y_i$, $\forall i \in \mathcal{C}$, now yields

$$x_i (P - \gamma_i^L P_i^{\text{sat}}) = 0, \qquad \forall i \in \mathcal{C}. \tag{1}$$

This has the solution $x_i = 0$ or $P = \gamma_i^L P_i^{\text{sat}}$. It is convenient to rewrite the latter as $\ln P - \ln P_i^{\text{sat}} - \ln \gamma_i^L = 0$, since the vapor pressure and activity coefficient relationships are typically expressed in terms of their logarithms. Equation 1 can now be expressed as

$$x_i [\ln P - \ln P_i^{\text{sat}}(T) - \ln \gamma_i^L(T)] = 0, \qquad \forall i \in \mathcal{C}, \tag{2}$$

where we have emphasized the temperature dependence of P_i^{sat} and γ_i^L. This equation, and the constraint that the mole fractions sum to one

$$\sum_{i=1}^{N} x_i - 1 = 0, \tag{3}$$

constitute an $(N+1) \times (N+1)$ set of nonlinear equations that can be solved for the azeotropic composition(s) and temperature(s). We refer to Eqs. 2 and 3 as the *simultaneous* formulation. This is the formulation used by Fidkowski et al. (1993), and is one of the formulations used by Harding et al. (1997). Solving Eqs. 2 and 3, we will simultaneously obtain all k-ary azeotropes ($k \leq N$) in the system, as well as trivial roots representing the pure components. Clearly, this equation system may have many roots, and a solution method guaranteed to enclose all the roots is required.

If we assume that there is a set of k components $\mathcal{C}_{nz}$ for which $x_i \neq 0$, then for this set of k nonzero components, Eq. 2 can be rewritten

$$\ln P - \ln P_i^{\text{sat}}(T) - \ln \gamma_i^L(T) = 0, \qquad \forall i \in \mathcal{C}_{nz}. \tag{4}$$

We refer to Eqs. 3 and 4 as the *sequential* formulation. This is one of the formulations used by Harding et al. (1997), and is similar to the approach used by Westerberg and Wahnschafft (1996). Solving this $(k+1) \times (k+1)$ system, we obtain all k-ary azeotropes for the chosen component set, $\mathcal{C}_{nz}$. To find all the azeotropes in the original N-component system, a sequence (unordered) of such systems must be solved, one for each combination of k components, $k = 2, \ldots, N$. These equation systems may have multiple roots or no roots at all. A solution method is required that is guaranteed to enclose all roots and that is also capable of verifying when none exist. Both the simultaneous and sequential formulations are considered here, and their relative efficiency compared.

To model the temperature dependence of $P_i^{\text{sat}}(T)$ we use the Antoine equation

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

This is a dimensional equation with P_i^{sat} in mm Hg and T in °C. Values used for the constants A_i, B_i, and C_i in the example problems below were taken from Gmehling et al. (1977–1990), and are listed in Table 1.

In many cases, the temperature dependence of $P_i^{\text{sat}}(T)$ is significantly stronger than the temperature dependence of

Table 1. Antoine Equation Parameters

Component i	A_i	B_i (°C)	C_i (°C)
Acetone (Problems 4 and 5)	7.63130	1,566.690	273.419
Acetone (Problem 8)	7.11714	1,210.595	229.664
Benzene	6.87987	1,196.760	219.161
Chloroform	7.44777	1,488.990	264.915
Ethanol	8.11220	1,592.864	226.184
Ethyl formate	7.00902	1,123.943	218.247
Hexafluorobenzene	7.03295	1,227.984	215.491
Hexane	6.91058	1,189.640	226.280
Methanol (Problems 1 and 5)	8.08097	1,582.271	239.726
Methanol (Problem 4)	7.97010	1,521.230	233.970
Methyl acetate	7.06524	1,157.630	219.726
Methylcyclopentane	6.86640	1,188.050	226.276
Methyl ethyl ketone	7.06356	1,261.340	221.969
i-Propanol	8.87829	2,010.330	252.636
n-Propanol	7.74416	1,437.686	198.463
Water	8.07131	1,730.630	233.426

Data from Gmehling et al. (1977–1990).

$\gamma_i^L(T)$, which arises only in the temperature dependence of the binary interaction parameters in the activity coefficient model used. Thus, as done by Harding et al. (1997), it is not unreasonable to evaluate $\gamma_i^L(T)$ at some reference temperature T_{REF} and then treat it as independent of temperature, instead of using a fully temperature-dependent $\gamma_i^L(T)$ model. Assuming a good guess of T_{REF} is made, this approach may provide good estimates for the azeotropes in the fully temperature-dependent model. There is no guarantee of this, however, and it is possible that the number of azeotropes found in the T_{REF}-based model will not be the same as the number of azeotropes that exist in the fully temperature-dependent model, even if a relatively good guess of T_{REF} has been made. This is demonstrated in Problem 5 below.

The method described here is model-independent and can be applied in connection with any models of phase behavior. For the first five example problems below, one of the activity-coefficient models used is the Wilson equation. In this model, the nonsymmetric binary interaction parameters $\Lambda_{ij} = (V_j/V_i)\exp(-A_{ij}/RT)$ are based on energy parameters A_{ij}, values of which are reported as constants or as linear functions of temperature. For the problems below, we use the constants reported in Gmehling et al. (1977–1990), as listed in Table 2. For the saturated liquid molar volumes V_i, Gmehling et al. (1977–1990) use temperature-independent constants. To be consistent with Harding et al. (1997), however, we use a modified Rackett equation (Yamada and Gunn, 1973),

$$V_i = V_{scr_i} Z_{cr_i}^{(1-T_{R_i})^{2/7}},$$

where T_{R_i} is the reduced temperature of component i. The other quantities are V_{scr_i}, the scaling volume for component i, and Z_{cr_i}, the critical compressibility of component i for the Rackett equation, and are given by

$$V_{scr_i} = V_i' Z_{cr_i}^{-(1-T'_{R_i})^{2/7}}$$

and

$$Z_{cr_i} = 0.29056 - 0.08775\,\omega_i,$$

where V_i' is the molar volume for component i at T'_{R_i}, a reference reduced temperature for which the molar volume of component i is accurately known, and ω_i is the acentric factor for component i. The values used for these three parameters are given in Table 3, and were taken from Reid et al. (1987) and Lide (1995).

Table 2. Wilson Equation Parameters

Component 1	Component 2	A_{12} (cal/mol)	A_{21} (cal/mol)
Acetone	Benzene	543.9352	−182.5230
Acetone	Chloroform	28.8819	−484.3856
Acetone	Ethanol	180.4365	252.2864
Acetone	Methanol	−161.8813	583.1054
Benzene	Hexafluorobenzene	−406.6544	922.6229
Benzene	*i*-Propanol	392.7020	813.9198
Benzene	*n*-Propanol	312.1615	996.2753
Chloroform	Benzene	−161.8065	49.6010
Chloroform	Ethanol	−315.6205	1,434.1695
Chloroform	Methanol	−351.1964	1,760.6741
Ethanol	Benzene	1,399.9279	207.3433
Ethanol	Methyl ethyl ketone	694.0825	−149.7978
Ethanol	Water	393.1971	926.2630
Methanol	Benzene	1,734.4181	183.0383
Methanol	Ethanol	−65.7022	143.6658
Methanol	*i*-Propanol	−38.4124	176.3185
Methanol	*n*-Propanol	150.2057	−33.8819
Methyl ethyl ketone	Water	6,811.3433	1,888.8509
i-Propanol	*n*-Propanol	818.3291	−481.0590

Data from Gmehling et al. (1977–1990).

Table 3. Rackett Equation Parameters

Component i	ω_i	V_i' (cm^3/mol)	T_i' (K)
Acetone	0.304	73.52	293.0
Benzene	0.212	88.26	289.0
Chloroform	0.218	80.17	293.0
Ethanol	0.644	58.39	293.0
Hexafluorobenzene	0.396	114.96	293.2
Methanol	0.556	40.51	293.0
Methyl ethyl ketone	0.320	89.57	293.0
i-Propanol	0.665	76.46	293.0
n-Propanol	0.665	74.75	293.0
Water	0.344	18.05	293.0

Data from Reid et al. (1987), except V_i' and T_i' values for hexafluorobenzene are from Lide (1995).

For the first five example problems below, a second activity-coefficient model used is the NRTL equation. In this model, the binary interaction parameters $\tau_{ij} = A_{ij}/RT$ and $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ are based on constants $\alpha_{ij} = \alpha_{ji}$ and energy parameters A_{ij}, values of which are reported as constants or functions of temperature. For the problems below, we use the constant A_{ij} and α_{ij} values reported in Gmehling et al. (1977–1990), as listed in Table 4.

In the last three example problems, the activity-coefficient model used is the UNIQUAC equation as modified by Anderson and Prausnitz (1978), with coordination number $z =$

Table 4. NRTL Equation Parameters

Component 1	Component 2	A_{12} (cal/mol)	A_{21} (cal/mol)	$\alpha_{12} = \alpha_{21}$
Acetone	Benzene	−193.3405	569.9314	0.3007
Acetone	Chloroform	−643.2770	228.4574	0.3043
Acetone	Ethanol	45.3706	375.3497	0.3006
Acetone	Methanol	184.7013	222.6450	0.3084
Benzene	Hexafluorobenzene	1,251.4578	−794.4003	0.2978
Benzene	*i*-Propanol	728.6353	366.6632	0.2910
Benzene	*n*-Propanol	874.2419	285.7774	0.2899
Chloroform	Benzene	176.8791	−288.2136	0.3061
Chloroform	Ethanol	1,438.3602	−327.5518	0.3023
Chloroform	Methanol	2,736.8604	−1,244.0315	0.0950
Ethanol	Benzene	516.1410	1,065.9086	0.4774
Ethanol	Methyl ethyl ketone	64.4957	463.1931	0.3010
Ethanol	Water	−175.0164	1,440.3479	0.2959
Methanol	Benzene	730.0904	1,175.4126	0.4743
Methanol	Ethanol	−25.9969	12.7341	0.3356
Methanol	*i*-Propanol	−137.8776	66.8301	0.3028
Methanol	*n*-Propanol	24.9003	9.5349	0.3011
Methyl ethyl ketone	Water	674.4614	1,809.8868	0.3536
i-Propanol	*n*-Propanol	−673.7647	991.7833	0.2978

Data from Gmehling et al. (1977–1990).

Table 5. UNIQUAC Equation Unary Parameters

Component i	r_i	q_i	q'_i
Acetone	2.5735	2.3360	2.3360
Benzene	3.1878	2.4000	2.4000
Ethanol (Problem 6)	2.1055	1.9720	1.9720
Ethanol (Problem 7)	2.1055	1.9720	0.9200
Ethyl formate	2.8042	2.5760	2.5760
Hexane	4.4998	3.8560	3.8560
Methyl acetate	2.8042	2.5760	2.5760
Methylcyclopentane	4.0456	3.2360	3.2360
Water	0.9200	1.4000	1.4000

Data from Gmehling et al. (1977–1990), except for the q'_i value for ethanol (Problem 7), which is from Prausnitz et al. (1986).

10. The binary interaction parameters $\tau_{ij} = \exp(-A_{ij}/RT)$ are computed from energy parameters A_{ij}, values of which are reported as constants or as functions of temperature. For the problems below, we use the A_{ij} constants, as well as the pure-component r_i, q_i, and q'_i constants, reported in Gmehling et al. (1977–1990) and Prausnitz et al. (1986), as listed in Tables 5 and 6.

Finally, it should be noted that because solutions of the equifugacity equations may not be stable phases (the liquid may split), any solutions enclosed using either of the formulations just described should next be checked for phase stability. This can be reliably done using either an interval approach (Stadtherr et al., 1995) or a branch-and-bound global optimization approach (McDonald and Floudas, 1995).

Solution Method

We apply here interval mathematics, in particular an interval-Newton/generalized-bisection (IN/GB) technique, to find enclosures for all homogeneous azeotropes. Recent monographs that introduce interval computations include those of Neumaier (1990), Hansen (1992), and Kearfott (1996). The IN/GB algorithm used here 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), provided only that initial upper and lower bounds are available for all variables. This is made possible through the use of the existence and uniqueness test provided by the interval-Newton method. Our implementation of the IN/GB method for the homogeneous azeotrope problem is based on appropriately modified FORTRAN-77 routines from the packages INTBIS (Kearfott and Novoa, 1990) and INTLIB (Kearfott et al., 1994).

Table 6. UNIQUAC Equation Energy Parameters

Component 1	Component 2	A_{12} (cal/mol)	A_{21} (cal/mol)
Acetone	Ethyl formate	−130.2025	137.5744
Acetone	Methyl acetate	188.9707	−135.3474
Benzene	Ethanol (Problem 6)	766.4564	−105.3291
Benzene	Hexane	−26.1184	125.3113
Benzene	Water	1,072.790	428.452
Ethanol	Benzene (Problem 7)	−276.02347	1,882.2853
Ethanol	Hexane	−216.46679	2,864.7023
Ethanol	Methylcyclopentane	−235.02733	2,750.1595
Ethanol	Water	9.5115	307.7309
Methyl acetate	Ethyl formate	−63.2528	65.5118
Methylcyclopentane	Benzene	160.3455	−65.2945
Methylcyclopentane	Hexane	−221.7560	272.9120

Data from Gmehling et al. (1977–1990).

In the past, interval techniques were not widely used. One reason for this was that the theoretical guarantees on solution enclosures often came at a very large cost in additional computing time relative to faster, but not guaranteed, local methods. However, with continuing improvements in methodology (e.g., Kearfott, 1996) and continuing advances in computation speed and parallel computing, both the premium paid to obtain the guarantee, as well as the absolute execution time required, have shrunk dramatically.

One method for improving the computational efficiency of the interval approach is to develop *interval extensions* that are computationally inexpensive and that more tightly enclose the range of a function than the *natural* interval extension. For an arbitrary function $f(\boldsymbol{x})$ over an interval $\boldsymbol{X} = (X_1, X_2, \ldots, X_n)^T$, with n real interval components X_i, the interval extension $\boldsymbol{F}(\boldsymbol{X})$ encloses all values of $f(\boldsymbol{x})$ for $\boldsymbol{x} \in \boldsymbol{X}$; that is, it encloses the range of $f(\boldsymbol{x})$ over $\boldsymbol{X}$. Often, the natural interval extension, that is, the enclosure $\boldsymbol{F}(\boldsymbol{X})$ computed using interval arithmetic, is wider than the actual range of $f(\boldsymbol{x})$ over $\boldsymbol{X}$. Because of the complexity of the functions to be solved here, the use of interval arithmetic may lead to significant overestimation of the true range of the functions. One simple way to alleviate this difficulty in solving the azeotrope problem is to focus on tightening the enclosure when computing interval extensions of mole-fraction weighted averages, such as $\bar{s} = \sum_{i=1}^{n} x_i s_i$, where the s_i are constants, since such expressions occur frequently in activity-coefficient models. The natural interval extension of $\bar{s}$ will yield the true range of the expression in the space in which all the mole-fraction variables x_i are independent. The range can be tightened, however, by considering the constraint that the mole fractions must sum to one. Thus we use a *constrained-space interval extension* of $\bar{s}$. One approach for doing this is simply to eliminate one of the mole-fraction variables, say x_n. Then an enclosure for the range of $\bar{s}$ in the constrained space can be determined by computing the natural interval extension of $s_n + \sum_{i=1}^{n-1}(s_i - s_n)x_i$. As noted by Hua et al. (1998) and Tessier (1997), however, this may not yield the sharpest possible bounds on $\bar{s}$ in the constrained space. For determining the *exact* (within roundout) bounds on $\bar{s}$ in the constrained space, Tessier (1997) and Hua et al. (1998) have presented a very simple method, and that method was used in obtaining the results presented here. A comparison of computation times with and without use of these constrained-space interval extensions for mole-fraction weighted averages is given below using Problems 6–8.

Results

The computational results for several example problems are given below. In Problems 1–5, both the Wilson and NRTL equations are used to model the liquid-phase activity coefficients, and in Problems 6–8 the UNIQUAC equation is used. For each problem solved we present the azeotrope(s) found, as well as the CPU time required. The CPU times are given in seconds on a Sun Ultra 1/140 workstation. Each problem was solved using a fully temperature-dependent activity-coefficient model, and also solved using the approach in which the activity coefficients are evaluated at some reference temperature T_{REF} and then treated as temperature-independent (e.g., Harding et al., 1997). Unless otherwise noted, the reference temperatures used are those used by Harding et al. (1997). Since these reference temperatures are very close approximations to the actual azeotropic temperatures, the azeotropic compositions and temperatures found using the T_{REF}-based approach are not significantly different from the results of the fully temperature-dependent approach. Thus, in the tables of results, only the latter results are given, though computation times for both approaches are provided. However, there are dangers in using the T_{REF}-based approach, even when the reference temperature is quite close to the azeotropic temperature, as emphasized in Problem 5.

The values of the energy parameters A_{ij} used in each model were taken from Gmehling et al. (1977–1990) and are listed in Tables 2, 4, and 6. For many binaries, Gmehling et al. (1977–1990) present multiple data sets, and thus a choice of parameter values. In some cases, as noted below, our computed results do not match those of Harding et al. (1997). This is presumably due to their use of a different set of parameter values.

It should be noted that, although 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 a very narrow interval known to contain a *unique* root, based on the interval-Newton uniqueness test. The initial interval used for all mole-fraction variables was [0, 1]. The initial interval used for temperature was [10, 100] °C, except for Problem 4, in which it was [100, 200]°C. These are the same initial temperature ranges used by Harding et al. (1997). Note that no initial starting points are required. Unless noted otherwise, the ranges of all mole-fraction weighted averages were determined using the constrained-space interval extension previously discussed. Detailed results for each problem are given in Tables 8–17 for the Wilson and NRTL equation problems, and in Tables 20–22 for the UNIQUAC equation problems. Table 23 gives a summary of the total computation time required for each problem.

In addition to presenting the azeotropes and computation times, in this section we also consider (1) the relative computational expense of the sequential and simultaneous formulations; (2) the difficulties that may arise in using the T_{REF}-based approach for the temperature dependence of the activity coefficients; and (3) the effect on computation time of using constrained-space interval extensions to tighten the evaluation of function ranges involving mole-fraction weighted averages.

Table 7. Comparison of Sequential and Simultaneous Problem Formulations Using the Wilson Equation with Reference Temperatures

	CPU Time (s)		Number of Leaves	
Problem	Sequential	Simultaneous	Sequential	Simultaneous
1	0.71	3.72	371	1,600
2	0.029	0.10	23	99
3	0.25	1.05	164	642
4	0.084	0.73	41	465
5	14.1	157.3	3,991	39,805

Wilson and NRTL equations

The first five example problems were solved using both the Wilson equation and the NRTL equation as liquid-phase activity-coefficient models. These problems were previously solved by Fidkowski et al. (1993) using the Wilson equation, and by Harding et al. (1997) using both the Wilson and NRTL equations. Harding et al. (1997) used the reference temperature approach in their calculations; Fidkowski et al. (1993) do not state whether or not they considered the binary interaction parameters to be constants at a reference temperature or functions of temperature.

Before proceeding to the detailed results on individual problems, we first consider the relative computational efficiency of the sequential (Eqs. 3 and 4) and simultaneous (Eqs. 2 and 3) problem formulations. For this comparison we used the Wilson equation with the reference-temperature case for each of the five examples. Results of this comparison are summarized in Table 7, which gives the total time required for each problem and formulation, as well as the number of leaves that occur in the binary tree generated in the bisection process. The results clearly indicate that use of the sequential formulation is much more efficient. This same conclusion was also reached by Harding et al. (1997) when they performed a

Table 8. Problem 1: Methanol(M)/Benzene(B)/*i*-Propanol(I)/*n*-Propanol(N); 1 atm; Wilson Equation

Components	Mole Fraction (MBIN)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 71.05°C CPU Time (s)
MB	0.615 0.385 0.000 0.000	58.16	0.067	0.011
MI	No Azeotrope		0.043	0.006
MN	No Azeotrope		0.028	0.004
BI	0.000 0.590 0.410 0.000	71.98	0.054	0.009
BN	0.000 0.773 0.000 0.227	76.75	0.056	0.009
IN	No Azeotrope		0.049	0.009
MBI	No Azeotrope		0.66	0.077
MBN	No Azeotrope		0.50	0.047
MIN	No Azeotrope		0.44	0.032
BIN	No Azeotrope		0.73	0.077
MBIN	No Azeotrope		4.67	0.43
Total			7.30	0.71

Table 9. Problem 1: Methanol(M)/Benzene(B)/*i*-Propanol(I)/*n*-Propanol(N); 1 atm; NRTL Equation

Components	Mole Fraction (MBIN)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 89.91°C CPU Time (s)
MB	0.611 0.389 0.000 0.000	58.13	0.048	0.033
MI	No Azeotrope		0.037	0.031
MN	No Azeotrope		0.037	0.031
BI	0.000 0.588 0.412 0.000	71.83	0.045	0.034
BN	0.000 0.764 0.000 0.236	76.83	0.044	0.036
IN	No Azeotrope		0.064	0.047
MBI	No Azeotrope		0.73	0.46
MBN	No Azeotrope		0.65	0.43
MIN	No Azeotrope		1.05	0.82
BIN	No Azeotrope		1.18	0.76
MBIN	No Azeotrope		10.4	6.12
Total			14.3	8.80

similar comparison using their solution method. As suggested by Harding et al. (1997), one reason for this may be the increased complexity introduced by the additional factor of x_i in Eq. 2 in comparison to Eq. 4. It is also likely that another reason for this is that, when the simultaneous formulation is used, there are also trivial roots, corresponding to each pure component at its boiling temperature, that are found using the interval approach, since this approach finds enclosures of *all* roots of the equation system. In obtaining all of the results (Tables 8–23), the sequential approach was used. In all cases, however, the same azeotropic compositions and temperature were also found using the simultaneous approach. In reporting the results for the sequential approach, the CPU time required to solve each problem in the sequence is reported, along with the total time.

Problem 1. The first example problem is a four-component system consisting of methanol, benzene, *i*-propanol, and *n*-propanol at 1 atm. Table 8 shows the computational results for this system when the Wilson equation is used, and Table 9 shows them for when the NRTL equation is used. In all cases, three binary azeotropes were found, corresponding to each of the binary pairs that include benzene, and no higher-order azeotropes were located. These results correspond closely to experimental data (Gmehling et al., 1994). While comparisons to experimental results are interesting, it should be emphasized that such comparisons serve only as a measure of the accuracy of the model solved and not of the effectiveness of the solution method used. The results are also in agreement with both Fidkowski et al. (1993) and Harding et al. (1997) for the Wilson equation cases. For the NRTL equation, the computed methanol/benzene binary azeotrope differs significantly from the result obtained by Harding et al. (1997), presumably because they used a different set of model parameters. As might be expected, the use of a fully temperature-dependent activity-coefficient model increased computation times, most dramatically in the case of the Wilson equation. In general, the use of the NRTL equation was more expensive than the Wilson equation, especially in the reference-temperature case. The computation times for finding the binary azeotropes in the reference-temperature cases are significantly less than those reported by Harding et al. (1997), even after adjusting for the difference in the machines used. However, no meaningful comparisons along these lines can be made, since Harding et al. (1997) implemented their solution technique using GAMS, which adds significant computational overhead. Furthermore, Harding et al. (1997) do not report the computation time required to confirm that there are no ternary or quaternary azeotropes or binary azeotropes for three of the binary pairs. As can clearly be seen, the expense of verifying the nonexistence of azeotropes makes up the bulk of computation time for solving this problem.

Problem 2. The second problem is the binary system of benzene and hexafluorobenzene at 0.2 atm. Table 10 shows the computational results for this system when the Wilson equation is used, and Table 11 shows them for when the NRTL equation is used. Although only a two-component system, it contains two distinct azeotropes. The results shown here for the Wilson equation are in good agreement with those of Fidkowski et al. (1993) and Harding et al. (1997). Neither group reported results for the NRTL equation. This example demonstrates the ability of the interval method to easily find multiple azeotropes when they exist for a given set of nonzero components.

Problem 3. The third example problem is the ternary system consisting of ethanol, methyl ethyl ketone, and water at 1

Table 10. Problem 2: Benzene(B)/Hexafluorobenzene(H); 0.2 atm; Wilson Equation

Components	Mole Fraction (BH)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 36.00°C CPU Time (s)
BH	0.955 0.045 0.034 0.966	35.50 37.65	0.145	0.029
Total			0.145	0.029

Table 11. Problem 2: Benzene(B)/Hexafluorobenzene(H); 0.2 atm; NRTL Equation

Components	Mole Fraction (BH)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 36.56°C CPU Time (s)
BH	0.975 0.025 0.169 0.831	35.56 37.82	0.215	0.134
Total			0.215	0.134

Table 12. Problem 3: Ethanol(E)/Methyl Ethyl Ketone(M)/Water(W); 1.0 atm; Wilson Equation

Components	Mole Fraction (EMW)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 73.65°C CPU Time (s)
EM	0.485 0.515 0.000	74.10	0.061	0.009
EW	0.910 0.000 0.090	78.17	0.058	0.010
MW	0.000 0.681 0.319	73.70	0.14	0.033
EMW	0.231 0.544 0.225	72.75	1.42	0.20
Total			1.68	0.25

atm. Table 12 shows the computational results for this system when the Wilson equation is used, and Table 13 shows them for when the NRTL equation is used. Experimentally, this system contains one binary azeotrope for each pair of components and one ternary azeotrope (Gmehling et al., 1994). The results for the binary azeotropes are fairly consistent with experimental data while the results for the ternary azeotrope are less accurate in this regard, indicating some shortcomings in the models solved. Our computed results are consistent in all respects with the results of Fidkowski et al. (1993) and Harding et al. (1997).

Problem 4. The fourth problem is a ternary system of acetone, chloroform, and methanol at 15.8 atm. Tables 14 and 15 show the computational results for this system for the Wilson and NRTL models, respectively. This ternary system was found to contain one azeotrope for each of the binary pairs and no ternary azeotropes. These results are consistent with those obtained by Harding et al. (1997) using their branch-and-bound technique, and also with the results obtained by Fidkowski et al. (1993) for the Wilson equation. In the temperature-dependent case, this was the only example problem in which use of the NRTL model was faster than using the Wilson model.

Problem 5. The fifth problem is a quinary system consisting of acetone, chloroform, methanol, ethanol, and benzene at 1 atm. Tables 16 and 17 show the computational results for this example for the Wilson and NRTL models, respectively. Experimentally, this quinary system is reported to have six binary azeotropes, three ternary azeotropes, and one quaternary azeotrope (Gmehling et al., 1994). In each set of computed results, all of these azeotropes were found except for a ternary azeotrope involving chloroform, methanol, and benzene. Thus neither model appears to provide a completely accurate picture of this system. The computed results given here again match closely those of Fidkowski et al. (1993) and Harding et al. (1997). It is well worth noting again that the bulk of the computation time is spent in verifying the nonexistence of azeotropes.

Table 13. Problem 3: Ethanol(E)/Methyl Ethyl Ketone(M)/Water(W); 1.0 atm; NRTL Equation

Components	Mole Fraction (EMW)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 73.39°C CPU Time (s)
EM	0.486 0.514 0.000	74.08	0.051	0.037
EW	0.952 0.000 0.048	78.28	0.085	0.055
MW	0.000 0.657 0.343	73.39	0.053	0.034
EMW	0.187 0.560 0.252	72.96	2.53	1.52
Total			2.72	1.65

Table 14. Problem 4: Acetone(A)/Chloroform(C)/Methanol(M); 15.8 atm; Wilson Equation

Components	Mole Fraction (ACM)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 150.80°C CPU Time (s)
AC	0.324 0.676 0.000	181.46	0.25	0.008
AM	0.275 0.000 0.725	155.32	0.21	0.009
CM	0.000 0.392 0.608	151.44	0.17	0.010
ACM	No Azeotrope		3.09	0.057
Total			3.72	0.084

In the results presented so far, there has been little significant difference in azeotrope locations obtained using the reference-temperature approach and using the fully temperature-dependent approach, and thus only locations obtained with the latter were given in Tables 8–17. Essentially, the T_{REF} values used proved to be good approximations of the azeotropic temperatures. However, as noted earlier, even with a relatively good guess of the T_{REF} value to use, there is no guarantee that the number of azeotropes found in the T_{REF}-based model will be the same as the number of azeotropes that exist in the fully temperature-dependent model. This can be seen in the case of the quaternary azeotrope (acetone/chloroform/methanol/benzene) in Problem 5. Table 18 shows the effect of using different values of T_{REF} on the location of this azeotrope when the NRTL equation is used. For this case, the azeotrope in the fully temperature-dependent model is found to be at 57.05°C. As expected, setting T_{REF} = 57.05°C and using the reference-temperature approach to compute the azeotrope yields the same result, as shown in the first row of Table 18. As T_{REF} is increased beyond 57.05°C, however, the mole fraction of benzene decreases to zero, at which point no quaternary azeotrope is found. This shows that, although the use of a reference temperature is faster, it is possible to miss azeotropes when this approach is used. In this case, just a 20°C change in the reference temperature results in loss of an azeotrope. In attempting to use the reference-temperature approach, one can imagine using an algorithm in which an initial value of T_{REF} is chosen to compute an azeotrope, after which the computed azeotropic temperature is then used as T_{REF} and the azeotrope computed again, and so on. However, such an approach will fail if at the initial reference temperature the azeotrope sought does not exist. One cannot tell how close T_{REF} must be to the azeotrope in order to ensure that it will be found. Therefore, there is no guarantee using the reference-temperature approach that the azeotropes existing in the fully temperature-dependent model will be found.

Table 15. Problem 4: Acetone(A)/Chloroform(C)/Methanol(M); 15.8 atm; NRTL Equation

Components	Mole Fraction (ACM)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 150.40°C CPU Time (s)
AC	0.318 0.682 0.000	181.16	0.062	0.038
AM	0.286 0.000 0.714	155.37	0.039	0.031
CM	0.000 0.406 0.594	151.57	0.095	0.055
ACM	No Azeotrope		2.59	1.49
Total			2.79	1.61

Table 16. Problem 5: Acetone (A)/Chloroform(C)/Methanol(M)/Ethanol(E)/Benzene(B); 1 atm; Wilson Equation

Components	Mole Fraction (ACMEB)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 65.09°C CPU Time (s)
AC	0.365 0.635 0.000 0.000 0.000	65.27	0.068	0.008
AM	0.785 0.000 0.215 0.000 0.000	55.56	0.068	0.009
AE	No Azeotrope		0.041	0.004
AB	No Azeotrope		0.042	0.005
CM	0.000 0.659 0.341 0.000 0.000	53.52	0.088	0.012
CE	0.000 0.862 0.000 0.138 0.000	59.41	0.076	0.010
CB	No Azeotrope		0.038	0.004
ME	No Azeotrope		0.048	0.006
MB	0.000 0.000 0.615 0.000 0.385	58.16	0.072	0.012
EB	0.000 0.000 0.000 0.450 0.550	67.87	0.069	0.010
ACM	0.341 0.212 0.447 0.000 0.000	57.56	1.08	0.082
ACE	0.358 0.451 0.000 0.191 0.000	63.80	0.97	0.091
ACB	No Azeotrope		0.59	0.037
AME	No Azeotrope		0.60	0.037
AMB	No Azeotrope		1.30	0.18
AEB	No Azeotrope		0.83	0.082
CME	No Azeotrope		0.87	0.077
CMB	No Azeotrope		0.95	0.078
CEB	No Azeotrope		0.89	0.071
MEB	No Azeotrope		0.87	0.093
ACME	No Azeotrope		6.82	0.68
ACMB	0.251 0.154 0.477 0.000 0.117	57.48	12.6	2.12
ACEB	No Azeotrope		9.95	1.16
AMEB	No Azeotrope		7.12	0.87
CMEB	No Azeotrope		8.17	1.12
ACMEB	No Azeotrope		51.5	7.28
Total			105.7	14.1

Table 17. Problem 5: Acetone(A)/Chloroform(C)/Methanol(M)/Ethanol(E)/Benzene(B); 1 atm; NRTL Equation

Components	Mole Fraction (ACMEB)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 67.79°C CPU Time (s)
AC	0.361 0.639 0.000 0.000 0.000	65.26	0.059	0.038
AM	0.784 0.000 0.216 0.000 0.000	55.56	0.038	0.025
AE	No Azeotrope		0.039	0.028
AB	No Azeotrope		0.036	0.026
CM	0.000 0.656 0.344 0.000 0.000	53.29	0.10	0.045
CE	0.000 0.847 0.000 0.153 0.000	59.26	0.060	0.034
CB	No Azeotrope		0.040	0.028
ME	No Azeotrope		0.037	0.027
MB	0.000 0.000 0.611 0.000 0.389	58.13	0.049	0.029
EB	0.000 0.000 0.000 0.447 0.553	67.79	0.046	0.029
ACM	0.377 0.202 0.421 0.000 0.000	57.07	2.23	1.07
ACE	0.360 0.445 0.000 0.195 0.000	63.63	1.68	0.95
ACB	No Azeotrope		1.20	0.72
AME	No Azeotrope		0.58	0.38
AMB	No Azeotrope		2.02	1.05
AEB	No Azeotrope		1.33	0.72
CME	No Azeotrope		1.31	0.57
CMB	No Azeotrope		2.14	0.87
CEB	No Azeotrope		1.24	0.61
MEB	No Azeotrope		0.91	0.47
ACME	No Azeotrope		19.7	9.05
ACMB	0.357 0.166 0.427 0.000 0.050	57.05	98.9	52.2
ACEB	No Azeotrope		40.8	21.1
AMEB	No Azeotrope		16.5	8.33
CMEB	No Azeotrope		28.2	10.9
ACMEB	No Azeotrope		389.5	163.7
Total			608.7	273.0

Table 18. Problem 5: Effect of T_{REF} Value Used in Finding the Acetone(A)/Chloroform(C)/Methanol(M)/Benzene(B) Azeotrope, Using NRTL Equation*

T_{REF} (°C)	Mole Fraction (ACMB)	T (°C)
57.05	0.357 0.166 0.427 0.050	57.05
67.79	0.373 0.183 0.420 0.024	57.12
72.75	0.380 0.191 0.417 0.011	57.14
77.75	No Azeotrope	
87.75	No Azeotrope	
107.75	No Azeotrope	

*See text for discussion.

Table 19. Effect of Using Constrained-Space Interval Extensions Instead of Natural Interval Extensions to Determine Ranges of Mole Fraction Weighted Averages in Using the UNIQUAC Equation with Reference Temperature

	CPU Time (s)		No. of Leaves	
Problem	Constrained Space	Natural	Constrained Space	Natural
6	0.73	4.23	373	4,023
7	37.5	579.0	10,210	294,752
8	1.81	40.7	692	32,896

Table 20. Problem 6: Benzene(B)/Ethanol(E)/Water(W); 1.0 atm; UNIQUAC Equation

Components	Mole Fraction (BEW)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 60.00°C CPU Time (s)
BE	0.552 0.448 0.000	67.66	0.036	0.023
BW	0.572 0.000 0.428	61.98	0.037	0.022
EW	0.000 0.886 0.114	78.11	0.041	0.029
BEW	No Azeotrope		1.21	0.66
Total			1.32	0.73

UNIQUAC equation

The final three example problems were solved using the UNIQUAC equation as the activity-coefficient model, with both the reference-temperature and temperature-dependent approaches. These problems were also considered by Harding et al. (1997), who used the reference-temperature approach.

Before proceeding to the detailed results on individual problems, we first consider the effect of using constrained-space interval extensions instead of natural interval extensions for determining the range of the mole-fraction weighted averages occurring in the model. As noted earlier, this appears to be a simple way of improving the computational efficiency of the method used here. For this comparison, we used the reference-temperature case for each of the three UNIQUAC examples. Results of this comparison are summarized in Table 19, which gives the total time required for each problem and interval extension, as well as the number of leaves that occur in the binary tree generated in the bisection process. The results clearly indicate that use of the constrained-space interval extensions for mole-fraction weighted averages results in a dramatic increase in computational efficiency. The results in all other tables are for the case in which the constrained-space interval extensions are used.

Problem 6. The first UNIQUAC problem is a ternary system consisting of benzene, ethanol, and water at 1 atm. Table 20 shows the computational results for this example. Experimentally, this ternary system is known to have one binary azeotrope for each binary pair, but no homogeneous ternary azeotrope (Gmehling et al., 1994). The computed results for this system match the experimental data well in all respects. Our computed results differ significantly from those of Harding et al. (1997), however, in that those authors compute a ternary azeotrope, while we do not. Presumably, this is due to some difference in the model parameters used. As in the previous examples, use of the temperature-dependent approach is more expensive computationally than using the reference-temperature approach. As in the case of the NRTL equation, the increased expense is less dramatic (about a factor of 2) than in the problems using the Wilson equation.

Problem 7. This problem is a quaternary system consisting of ethanol, methylcyclopentane, benzene, and hexane at 1 atm. Table 21 shows the computational results for this problem. Experimentally, this quaternary system is reported to have five binary azeotropes and none of higher order (Gmehling et al., 1994). The computed results for this system match these experimental results quite well. Again, however, there

Table 21. Problem 7: Ethanol(E)/Methylcyclopentane(M)/Benzene(B)/Hexane(H); 1 atm; UNIQUAC Equation

Components	Mole Fraction (EMBH)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 60.00°C CPU Time (s)
EM	0.355 0.645 0.000 0.000	60.70	0.062	0.034
EB	0.446 0.000 0.554 0.000	67.82	0.051	0.023
EH	0.339 0.000 0.000 0.661	58.58	0.074	0.038
MB	0.000 0.902 0.098 0.000	71.72	0.076	0.041
MH	No Azeotrope		0.10	0.049
BH	0.000 0.000 0.077 0.923	68.88	0.092	0.054
EMB	No Azeotrope		1.60	0.75
EMH	No Azeotrope		3.78	1.88
EBH	No Azeotrope		2.01	1.01
MBH	No Azeotrope		4.40	2.07
EMBH	No Azeotrope		64.9	31.6
Total			77.1	37.5

Table 22. Problem 8: Acetone(A)/Methyl Acetate (M)/ Ethyl Formate(E); 1.0 atm; UNIQUAC Equation*

Components	Mole Fraction (AME)	T (°C)	T-Dependent CPU Time (s)	T_{REF} = 60.00°C CPU Time (s)
AM	0.661 0.339 0.000	55.55	0.081	0.054
AE	No Azeotrope		0.047	0.031
ME	No Azeotrope		0.017	0.013
AME	0.591 0.284 0.125	55.60	2.57	1.71
Total			2.72	1.81

*Harding et al. (1997) used T_{REF} = 55°C on this problem.

are significant deviations between our computed results and those of Harding et al. (1997), as they compute azeotropes for all of the six cases in which we find none, presumably due to differences in model parameters used.

Problem 8. The final example is a ternary system containing acetone, methyl acetate, and ethyl formate at 1 atm. Table 22 shows the computational results for this problem. Experimentally, this ternary system is known to have one binary azeotrope (acetone/methyl acetate) and one ternary azeotrope (Gmehling et al., 1994). The computed results for this system match the experimental data closely in all respects. As in the previous problems using the UNIQUAC model, our results and those of Harding et al. (1997) differ, as they compute an azeotrope for the acetone/ethyl formate pair and we do not. Again, this is presumably due to differences in model parameters used.

Concluding Remarks

We have described here a new method for reliably locating *all* homogeneous azeotropes in multicomponent mixtures, and for verifying their nonexistence if none are present. The method is based on interval analysis, in particular an IN/GB algorithm, which provides a mathematical and computational guarantee that all azeotropes are enclosed. We applied the technique here to several problems in which the Wilson, NRTL, and UNIQUAC activity-coefficient models were used. However, the technique is general-purpose and can be applied in connection with any thermodynamic models.

Both a sequential and simultaneous formulation of the problem were considered, with the sequential proving to be the most efficient computationally (Table 7), as was also noted by Harding et al. (1997). The use of a constrained-space interval extension for finding exact (within roundout) bounds on mole-fraction weighted averages greatly improves the computational efficiency of the method, as shown on Problems 6–8 (Table 19). We also considered two approaches for handling the temperature dependence of the activity coefficients, one in which the activity coefficient is evaluated at a reference temperature and then treated as independent of temperature, and the other in which a fully temperature-dependent activity-coefficient model is used. A summary of the total computation times for each problem, given in Table 23, shows that use of the fully temperature-dependent model increases computation times moderately when the NRTL or UNIQUAC equations are used, but dramatically when the Wilson equation is used. The strong effect on the Wilson equation problems is probably due to the increased complexity of the temperature dependence arising from the use of the modified Rackett equation. This additional layer of complexity does not occur in the other models. The reason for use of the temperature-dependent approach was demonstrated in Problem 5, in which it was seen how, even using a reference temperature that is within 20°C of the azeotropic temperature, the use of the reference-temperature approach could lead to the failure to find an azeotrope predicted by the fully temperature-dependent model. Thus, if a reference-temperature approach is used, one cannot guarantee that all azeotropes have been located. The ability of the solution method described here to easily handle the fully temperature-dependent case shows the flexibility and generality of the approach.

Table 23. Summary of Total CPU Time Required to Solve Each Problem

	Total CPU Time (s)					
	Wilson Equation		NRTL Equation		UNIQUAC Equation	
Problem	T_{REF}	T-Dependent	T_{REF}	T-Dependent	T_{REF}	T-Dependent
1	0.71	7.30	8.80	14.3		
2	0.029	0.145	0.134	0.215		
3	0.25	1.68	1.65	2.72		
4	0.084	3.72	1.61	2.79		
5	14.1	105.7	273.0	608.7		
6					0.73	1.32
7					37.5	77.1
8					1.81	2.72

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