Chapter 13

PHASE STABILITY AND EQUILIBRIUM CALCULATIONS IN REACTIVE SYSTEMS USING DIFFERENTIAL EVOLUTION AND TABU SEARCH

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1. Introduction

Reactive separations processes (RSPs), where separation and reaction units are combined, have received considerable interest from chemical engineers and have been used to develop new technologies for the chemical and petrochemical industries. They offer several technological, economic, and operational advantages over conventional systems (Taylor and Krishna, 2000). However, optimal performance of RSPs depends significantly on relevant process design issues, where the basis for most synthesis and analysis is phase equilibrium behavior. In the design of RSPs, it is often necessary to perform numerous phase stability and equilibrium calculations. The goal in phase equilibrium calculations is to determine the number and identity (composition, quantity and type) of phases existing at equilibrium for a mixture under specific conditions, while phase stability analysis helps to confirm if the global minimum of Gibbs free energy has been reached.

There have been many efforts to develop new techniques with the aim of reliably computing phase equilibrium in systems subject to chemical reactions (Seider and Widagdo, 1996). The existing techniques for these calculations can be divided into two main classes: (a) procedures involving minimization of a suitable objective function, and (b) strategies requiring solution of nonlinear equations obtained from the stationary conditions of that objective function. For the case of phase equilibrium calculations, the objective function is generally the Gibbs free energy whereas the stability analysis is performed using the tangent plane distance function. The available strategies can also be classified as either stoichiometric or non-stoichiometric, depending on the formulation of mass balance constraints (Stateva and Wakeham, 1997).

Reactive phase stability and equilibrium problems are non-linear, multivariable and may have multiple solutions. In particular, strong interactions among components, phases and reactions increase the complexity of these thermodynamic calculations (Xiao *et al.*, 1989; Stateva and Wakeham, 1997). Hence, reliable and efficient methods are necessary for solving phase equilibrium problems of reactive systems. Both deterministic and stochastic global solving methods have been proposed for computing chemical and phase equilibrium simultaneously. The former includes homotopy-continuation and interval methods for non-linear equations, and branch-and-bound optimization strategies. Unfortunately, they generally require large computational effort for multi-component mixtures and, in some cases, problem reformulation is needed (Wakeham and Stateva, 2004). On the other hand, stochastic optimization methods are attractive because they do not require continuity and other assumptions about the optimization problem, and are reliable and efficient. However, only a few studies have reported their use for reactive phase equilibrium modeling (e.g. simulated annealing by Reynolds *et al.*, 1997; Bonilla-Petriciolet *et al.*, 2006; and the random search method of Luus and Jaakola by Lee *et al.*, 1999). Results of these studies have shown the potential of stochastic optimization strategies.

In particular, both differential evolution (DE) and tabu search (TS) are capable of solving non-differentiable, non-linear and multi-modal objective functions to find the global minimum. DE is a population based method that mimics biological evolution by performing mutation, crossover and selection steps to find the global optimum. TS is a point-to-point method that uses an adaptive memory to avoid re-visits to the same place in the search region and to identify promising areas for optimization. Both these methods have been used for Chemical Engineering applications (see Chapters 4 and 5). Teh and Rangaiah (2003) have studied phase equilibrium calculations in non-reactive mixtures using TS, and its performance was compared with a genetic algorithm (GA). They concluded that TS has high reliability in locating the global minimum and converges faster than GA. Srinivas and Rangaiah (2007) have compared the performance of TS and DE in phase stability and Gibbs energy minimization problems for non-reactive mixtures; their results show that DE is more reliable compared than TS but the latter is computationally more efficient.

Even though both DE and TS are promising, they have not been applied to and tested for reactive phase equilibrium and stability problems. Therefore, in this chapter, we present the application of TS and DE for these important problems, and compare their performance for benchmark problems in this area. In particular, we have analyzed the reliability and efficiency of these methods using a variable transformation approach for modeling the phase equilibrium behavior of reactive mixtures. The remainder of this chapter is organized as follows. The basic concepts of reactive phase stability and equilibrium problems including available methods for their solution, and their formulation in terms of transformed composition variables are provided in Sec. 2. Section 3 describes the algorithms of DE and TS used in this study. Application and performance comparison of DE and TS for reactive phase equilibrium and stability problems, are presented in Secs. 4 and 5. Finally, conclusions of this study are provided in the last section.

2. Phase Equilibrium and Stability Problems in Reactive Systems

This section introduces the reader to the basic concepts and description of phase stability and equilibrium problems in reactive systems. Mathematically, both the problems can be stated as finding the global minimum, w^* and $f(w^*)$ of a non-linear function, $f(w)$ of n real decision variables, $w = (w_1, w_2, \ldots, w_n)$ subject to $w \in \Omega$ where Ω is the feasible region satisfying the governing constraints and bounds on decision variables.

2.1. Description of phase equilibrium problems

In phase equilibrium problems, given components present, temperature and pressure of a system or stream, the main objectives are to correctly establish the phase number and type, and the distribution of components among the phases at the equilibrium. Classical thermodynamics indicates that minimization of the Gibbs free energy is a natural approach for calculating the equilibrium state of a mixture. Most of the available methods for Gibbs free energy minimization in reactive mixtures have been proposed during the last two decades, and they include a variety of problem formulations and numerical techniques such as local search methods with and without decoupling strategies (Castillo and Grossmann, 1981; Castier *et al.*, 1989; Xiao *et al.*, 1989; Gupta *et al.*, 1991; Perez-Cisneros *et al.*, 1997; Stateva and Wakeham, 1997), branch-and-bound optimization methods (McDonald and Floudas, 1996; McKinnon and Mongeau, 1998), algorithms using homotopy continuation (Jalali and Seader, 1999; Jalali *et al.*, 2008), deterministic methods based on interval mathematics (Burgos-Solorzano *et al.*, 2004) and stochastic optimization methods (Reynolds *et al.*, 1997; Lee *et al.*, 1999; Bonilla-Petriciolet *et al.*, 2006; Bonilla-Petriciolet *et al.*, 2008).

In general, there are several challenges in computing the global minimum of the Gibbs free energy function. First, the number and types of phases, at which this thermodynamic function achieves the global minimum, are usually not known *a priori*. Hence, several equilibrium calculations must be performed using different phase configurations (adding or removing phases) to identify the stable equilibrium state. Moreover, for a fixed number of phases and components, Gibbs free energy function may have a local minimum value very comparable to the global minimum value, which makes it challenging to find the global minimum (Srinivas and Rangaiah, 2007). The poor conditioning of the Hessian matrix of the free energy for mixtures near phase boundaries (such as bubble, dew and critical points) may lead to failure of solving strategies (Seider and Widagdo, 1996). Trivial solutions, which satisfy the necessary equilibrium conditions and the mass constraints in the system, also exist but they are local optima of Gibbs free energy. Consequently, many strategies in the literature are local methods, depend on initialization and may converge to unstable solutions. These limitations have prompted the development of reliable algorithms for the global minimization of Gibbs free energy.

Many available methods for phase equilibrium problems in reactive systems, use conventional composition variables (mole numbers or fractions) as decision variables. A few studies have considered variable transformation approaches with the goal of developing a simpler thermodynamic framework for modeling reactive systems (e.g. Ung and Doherty, 1995b; Perez-Cisneros *et al.*, 1997). These approaches, in combination with appropriate methods such as stochastic optimization strategies, can be used to develop reliable techniques for computing phase equilibrium of reactive systems. Therefore, in this chapter we have used a suitable transformation scheme to formulate phase equilibrium and stability problems involving chemical reactions.

2.1.1. Formulation of the optimization problem

In a reactive mixture with c components and r independent chemical reactions (with $r < c$) that splits into π phases, the Gibbs free energy function can be written as

$$\Delta\hat{g} = \sum_{j=1}^{\pi}\sum_{i=1}^{c-r}\hat{n}_{i,j}\left(\frac{\Delta\mu_{i,j}}{RT}\right), \tag{1}$$

where $\Delta\hat{g}$ is the dimensionless transformed molar Gibbs free energy of mixing (Ung and Doherty, 1995b), $\hat{n}_{i,j}$ is the transformed mole number of component i in phase j and $\frac{\Delta\mu_{i,j}}{RT}$ is the chemical potential of component i in phase j. The transformed mole number and other transformed variables are defined below. Further, the following mass balances must be satisfied:

$$\hat{n}_{i,F} - \sum_{j=1}^{\pi} \hat{n}_{i,j} = 0 \quad \text{for } i = 1, \ldots, c - r, \tag{2}$$

where $\hat{n}_{i,F}$ is the transformed mole number of component i in the feed (or initial system).

The Gibbs free energy minimization problem is to minimize Eq. (1) with respect to $\hat{n}_{i,j}$ (for $i = 1, \ldots, c - r$ and $j = 1, \ldots, \pi$) subject to Eq. (2). Note that the chemical potentials in Eq. (1) are functions of transformed composition variables, which depend on the thermodynamic model used for predicting behavior of each phase.

Transformed mole numbers $\hat{n}_i$, for a system of c components (including both reacting and inert species) subject to r independent chemical reactions, are defined by selecting a set of r reference components (Ung and Doherty, 1995a; 1995b) as:

$$\hat{n}_i = n_i - v_i N^{-1} n_{\text{ref}}, \tag{3}$$

where n_i is the number of moles of component i, n_{ref} is a column vector of dimension r of the moles of each of the reference components, v_i is the row vector of stoichiometric coefficients of component i for each of the r reactions, and N is an invertible and square matrix formed from the stoichiometric coefficients of the reference components in the r reactions. Note that $v_{i,k} < 0$ for reactants, $v_{i,k} > 0$ for products, and $v_{i,k} = 0$ for inert components.

Consequently, the total amount of transformed moles $\hat{n}_T$ is

$$\hat{n}_T = \sum_{i=1}^{c-r} \hat{n}_i = n_T - v_{TOT} N^{-1} n_{\text{ref}}. \tag{4}$$

Here, n_T is the total number of moles present at any instant of time, and v_{TOT} is a row vector where each element corresponds to the sum of stoichiometric coefficients for all components that participate in each of the r reactions.

Dividing $\hat{n}_i$ by $\hat{n}_T$, the transformed mole fractions X_i are obtained:

$$X_i = \frac{\hat{n}_i}{\hat{n}_T} = \frac{x_i - v_i N^{-1} x_{\text{ref}}}{1 - v_{TOT} N^{-1} x_{\text{ref}}} \; i = 1, \ldots, c - r, \tag{5}$$

where x_i is the mole fraction of component i and x_{ref} is the column vector of r reference component mole fractions. Due to mass balance restrictions, the sum of all transformed mole fractions must equal unity, or $\sum_{i=1}^{c-r} X_i = 1$ (Ung and Doherty, 1995a; 1995b).

The transformed composition variables ($\hat{n}_i$ and X_i) depend only on the initial composition of each independent chemical species and take the same value before, during and after reaction (Ung and Doherty, 1995a; 1995b). They also restrict the solution space to the compositions that satisfy stoichiometry requirements and reduce the dimension of the composition space by the number of independent reactions. The transformed variables allow all of the procedures used to compute phase equilibrium/stability of non-reactive mixtures to be extended to systems with chemical reactions (Ung and Doherty, 1995a; 1995b). They ($\hat{n}$ and X) in reactive systems play the same role as the usual composition variables (n and x) in non-reactive mixtures. However, transformed variables can be negative or positive depending on the reference components, number and type of reactions.

In Appendix A, we use a simple reactive mixture to illustrate the correspondence between the transformed composition variables ($\hat{n}$ and X) and the usual composition variables (n and x) at equilibrium, and how to calculate the previous ones by specifying the transformed variables and applying the chemical equilibrium constraints:

$$K_{eq,k} = \prod_{i=1}^{c} a_i^{v_{i,k}}, \quad k = 1, \ldots, r, \tag{6}$$

where $K_{eq,k}$ is the equilibrium constant for reaction k and a_i is the activity of component i. The formulation of phase equilibrium problem for this simple reactive mixture is also shown in this appendix.

For a reactive mixture, minimizing Gibbs free energy with respect to n is equivalent to minimizing the transformed Gibbs free energy with respect to $\hat{n}$ (Ung and Doherty, 1995b). The Gibbs free energy minimization problem has equality constraints (Eq. (2)). To perform an unconstrained minimization of free energy, we can use a set of new variables instead of transformed composition variables as decision variables. The introduction of these variables automatically satisfies the equality constraints (Eq. (2)) and reduces problem dimensionality further. Assuming that all transformed mole fractions have values in the range $X_{i,j} \in (0, 1)$, real variables $\lambda_{i,j} \in [0, 1]$ are defined and employed as decision variables using the following expressions:

$$\hat{n}_{i,1} = \lambda_{i,1}\hat{n}_{i,F} \quad \text{for } i = 1, \ldots, c - r, \tag{7}$$

$$\hat{n}_{i,j} = \lambda_{i,j}\left(\hat{n}_{i,F} - \sum_{\mathrm{m}=1}^{j} \hat{n}_{i,m}\right) \quad \text{for } i = 1, \ldots, c - r \quad \text{and} \quad j = 2, \ldots, \pi - 1, \tag{8}$$

$$\hat{n}_{i,\pi} = \hat{n}_{i,F} - \sum_{m=1}^{\pi-1} \hat{n}_{i,m} \quad \text{for } i = 1, \ldots, c - r, \tag{9}$$

where $\hat{n}_{i,F} = n_{i,F} - v_i N^{-1} n_{\mathrm{ref},F}$, $\hat{n}_{T,F} = n_{T,F} - v_{TOT} N^{-1} n_{\mathrm{ref},F} = \sum_{i=1}^{c-r} \hat{n}_{i,F}$, $n_{T,F} = \sum_{i=1}^{c} n_{i,F}$ and $n_{i,F}$ is the number of moles of component i in the feed. Note that $Z_i = \hat{n}_{i,F}/\hat{n}_{T,F}$.

Using the formulation in Eqs. (7) to (9), all trial compositions will satisfy the mass balances (Eq. (2)), the optimization problem will have only bounds on decision variables and no other constraints, allowing the easy application of stochastic global optimization strategies. Recently, Bonilla-Petriciolet *et al.* (2008) have reported the application of simulated annealing (SA) for the minimization of the transformed Gibbs free energy minimization using the above formulation, and concluded that SA is reliable for this purpose. However, this method required significant computational effort. The study of Bonilla-Petriciolet *et al.* (2008) is the first attempt to apply a stochastic global method to the optimization of Gibbs free energy using transformed composition variables, and it is desirable to test other stochastic methods for this application. Hence, in this chapter, DE and TS are tested and compared for phase equilibrium calculations of reactive systems via Gibbs free energy minimization and transformed composition variables.

2.2. Description of phase stability problem

Phase stability analysis allows identification of the thermodynamic state that corresponds to the global minimum of the Gibbs free energy (i.e. globally stable equilibrium). A phase at a given temperature, pressure and composition, is stable if and only if the Gibbs free energy surface is at no point below the tangent plane to the surface at the given composition (Baker *et al.*, 1982; Michelsen, 1982). This statement is a necessary and sufficient condition for global stability. Generally, stability analysis in reactive systems is performed by the minimization of the distance between the Gibbs free energy surface and the tangent plane to the surface at the given composition (known as the tangent plane distance function, TPDF) with respect to all possible phase compositions, using mole numbers or fractions as decision variables. Non-negativity of the global minimum of this function implies that the given phase is stable. Note that stability calculations in reactive mixtures using TPDF must be performed only for phases that are chemically equilibrated (Michelsen, 1982; Castier *et al.*, 1989). This is because, in reactive systems, the total number of moles (n_T) present at any instant of time may not remain constant as the reactions proceed. Thus, it is not meaningful to directly minimize TPDF to study stability in reactive mixtures, and the proposed methods execute a chemical equilibration procedure before phase stability calculations.

Similar to the phase equilibrium calculations, phase stability analysis in reactive systems is a challenging global optimization problem because the objective function is multivariable, non-convex and highly non-linear. Many optimization methods have been tried for stability calculations in reactive systems using the classical tangent plane criterion (e.g. Gupta *et al.*, 1991; Stateva and Wakeham, 1997; Jalali and Seader, 1999; Jalali *et al.*, 2008). Traditional approaches, which generally utilize different initial estimates and local search methods, may converge to a local or trivial solution based on the initial guess. Several deterministic global optimization methods have also been tested for phase stability analysis in reactive systems; these include branch-and-bound methods (McDonald and Floudas, 1996; McKinnon and Mongeau, 1998), homotopy continuation algorithms (Jalali-Farahani and Seader, 2000) and the interval-Newton/general-bisection approach (Burgos-Solorzano *et al.*, 2004).

Since the tangent plane criterion is also applicable to chemically equilibrated phases, any method proposed for stability calculations in non-reactive systems can be extended to reactive mixtures. Hence, stochastic optimization methods such as SA, GA, TS and DE can be used for this purpose (Rangaiah, 2001; Teh and Rangaiah, 2003; Bonilla-Petriciolet *et al.*, 2006; Srinivas and Rangaiah, 2007). Further, it is possible to reformulate the tangent plane criterion in terms of transformed composition variables. This modified stability criterion, adopted for the present study, and its advantages are described below.

2.2.1. Formulation of the optimization problem

Based on the transformed variables of Ung and Doherty (1995a, 1995b), Wasylkiewicz and Ung (2000) introduced the reactive tangent plane distance function (RTPDF) for multi-component and multi-reaction systems, which is defined as

$$RTPDF = \sum_{i=1}^{c-r} X_i \left(\left.\frac{\Delta\mu_i}{RT}\right|_X - \left.\frac{\Delta\mu_i}{RT}\right|_Z \right), \tag{10}$$

where $\left.\frac{\Delta\mu_i}{RT}\right|_X$ and $\left.\frac{\Delta\mu_i}{RT}\right|_Z$ are the chemical potentials of component i calculated at the transformed mole fractions X and Z, respectively. The RTPDF represents the vertical displacement from the tangent plane at the given composition Z, to the transformed molar Gibbs free energy surface at the composition X.The necessary and sufficient condition for global phase stability is given by RTPDF ≥ 0.0 for any X in the whole transformed composition space. There is at least one solution for RTPDF ($= 0.0$) at the trivial stationary point $X = Z$. For a stable phase, this must be the global minimum of RTPDF.

RTPDF and its stationary points for arbitrary stable and unstable reactive mixtures are illustrated in Fig. 1. In the upper-left plot of this figure, the tangent to the transformed Gibbs free energy at Z lies below this free energy surface throughout the transformed composition space, and, as a consequence, a single phase with the transformed composition Z is stable (i.e. the global minimum of RTPDF is 0.0 at Z, as shown in the lower-left plot). In another case shown in the upper-right plot, the tangent at Z crosses the Gibbs free energy surface at several points; therefore, a phase with this transformed composition is unstable. This unstable mixture shows several stationary points for RTPDF (see the lower-right plot).

The minimization problem for phase stability via tangent plane criterion is to minimize Eq. (10) with respect to X_i (for $i = 1, \ldots, c - r$)

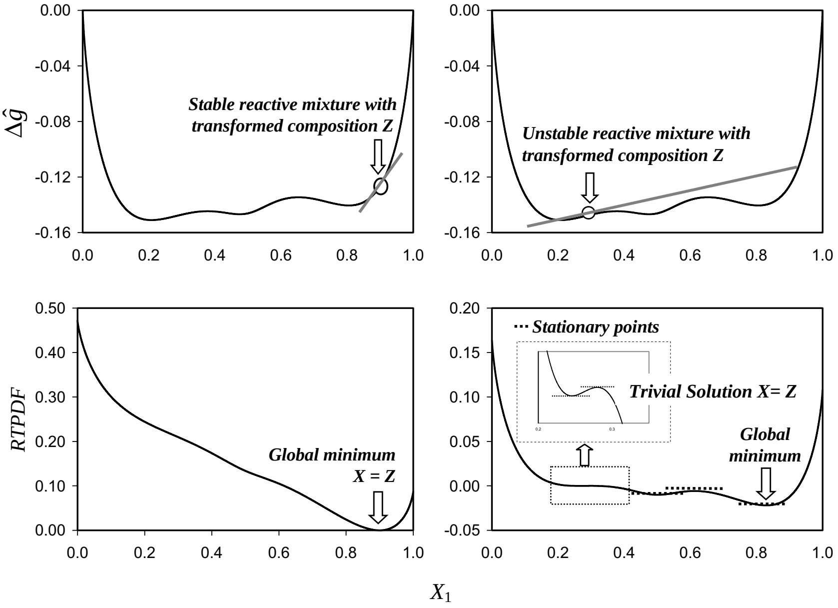

Figure 1. Gibbs free energy of mixing, $\Delta\hat{g}$ and RTPDF for a reactive mixture where $c - r = 2$, illustrating the transformed mole fraction Z of stable and unstable reactive mixtures, and their corresponding stationary points and global minimum of RTPDF. Transformed mole fraction of one component (X_1) is shown on the x-axis and that of the second component is $X_2 = 1.0 - X_1$.

subject to $\sum_{i=1}^{c-r} X_i = 1$. Instead of λ's used as decision variables in phase equilibrium problems to automatically satisfy the equality constraints, an alternate strategy is employed in phase stability problems. Here, $(c - r)$ decision variables, each in the range 0.0 to 1.0, are generated and then normalized so that their sum is equal to unity. The resulting variable values are used for calculating the objective, RTPDF. This strategy will not reduce the number of decision variables but this is not important since number of variables in phase stability problems is less than that in phase equilibrium problems. Note that the chemical potentials in Eq. (10) are functions of X_i, which depend on the thermodynamic model used for predicting the phase behavior. For illustration, phase stability problem for the simple case of an ideal ternary mixture is formulated in Appendix A.

The RTPDF offers two main advantages over the classical TPDF in the stability analysis of reactive systems (Ung and Doherty, 1995b;

Wasylkiewicz and Ung, 2000). First, given the initial composition of the reactive mixture, one can perform the stability test directly using the RTPDF, in contrast to the classical TPDF, where a preliminary chemical equilibration procedure is required. In fact, this equilibration procedure is implicit if the transformed variables are used. Another advantage of this approach is the significant reduction of problem dimensionality for multi-reaction systems.

A few studies have dealt with the global solution of RTPDF. Wasylkiewicz and Ung (2000) applied the homotopy continuation approach to locate all stationary points of RTPDF. Bonilla-Petriciolet *et al.* (2006) reported the application of stochastic optimization methods: SA, very fast SA, modified direct search SA and stochastic differential equations, for the global minimization of RTPDF. Among the methods tested, they found that SA is a reliable strategy for stability calculations in reactive mixtures; but its computational effort is very high for multi-component systems. These studies are the first attempts for the global solution of RTPDF. Hence, efficacy of TS and DE for the global minimization of RTPDF is studied in this chapter.

3. DE and TS, and Parameter Tuning

Introduction to and description of DE and TS are provided in earlier chapters. In the present study, FORTRAN codes developed by Teh and Rangaiah (2003), and Srinivas and Rangaiah (2007) for TS and DE algorithms, respectively, were used. Both methods have been implemented in combination with a local optimization technique for finding the global minimum accurately and efficiently. Figure 2 shows the flowchart of these hybrid algorithms; see Teh and Rangaiah (2003) and Srinivas and Rangaiah (2007) for the description of these algorithms. For local optimization, we have used a fast convergent quasi-Newton method implemented in the subroutine DBCONF from IMSL library. This subroutine calculates the gradient via finite differences and approximates the Hessian matrix (consisting of second derivatives of the objective function) according to BFGS formula. In brief, a quasi-Newton method is a modification of Newton method without the need for second derivatives of the objective function. For more details on this local strategy, see the optimization book by Dennis and Schnabel (1983). The default values of DBCONF parameters in the IMSL library

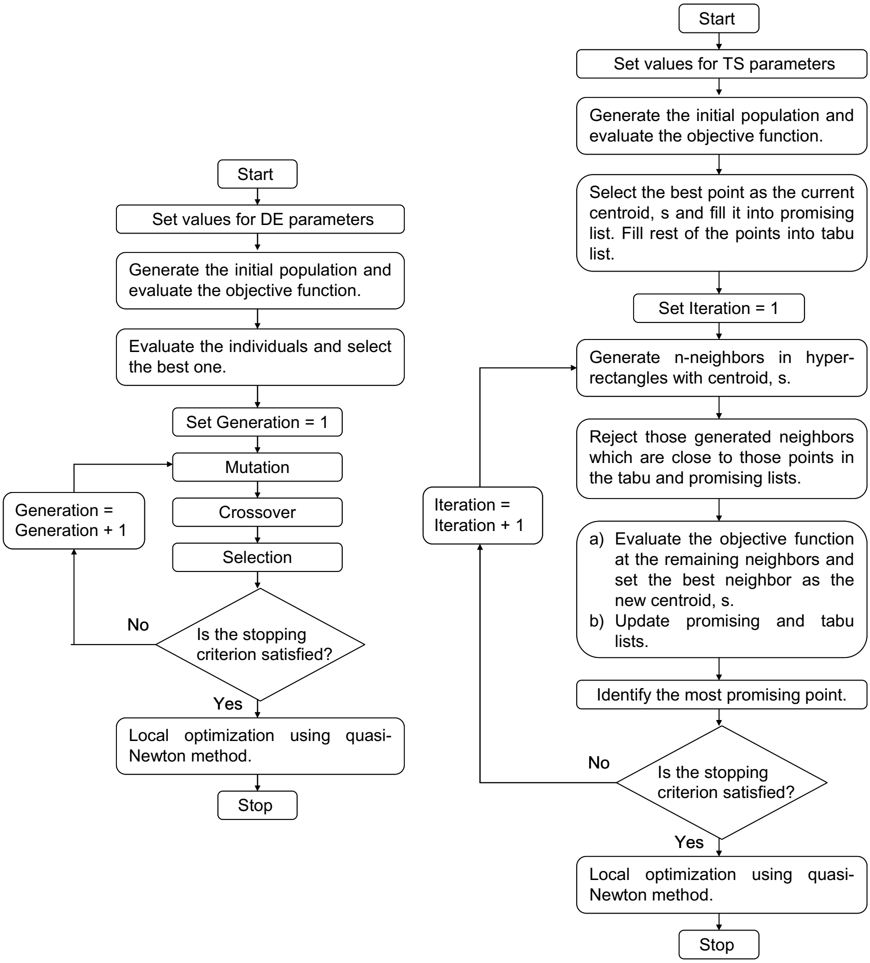

Figure 2. Flowcharts of DE (on the left) and TS (on the right).

were used in our calculations. The procedure used for tuning of DE and TS parameters is described below.

3.1. Tuning of TS and DE parameters using performance profiles

Like any stochastic method, TS and DE have a number of parameters that need to be heuristically tuned for any desired application. This tuning is a key step in the application and evaluation of a stochastic method, where a proper selection of its parameters is essential to achieve the best reliability and efficiency of the method. Parameter tuning is generally performed using benchmark problems and determining the average values of specific performance metrics. However, using this approach, a small number of the most difficult problems may tend to dominate the results for performance metrics and, as a consequence, lead to incorrect conclusions about the algorithm performance (Dolan and More, 2002). To address this shortcoming, we have employed the performance profile (PP) reported by Dolan and More (2002) to tune the parameters of both TS and DE methods.

Dolan and More (2002) introduced PP as an alternative tool for evaluating and comparing the performance of optimization software. In particular, PP has been proposed to compactly and comprehensively represent the data collected from a set of solvers for a specified performance metric. For instance, number of function evaluations (NFE) or computing time (CPUt) can be considered performance metrics for solver comparison. The PP plot allows visualization of the expected performance differences among several solvers and to compare the quality of their solutions by eliminating the bias of failures obtained in a small number of problems.

To introduce PP, consider n_s solvers (i.e. optimization methods) to be tested over a set $\Re$ of n_p problems. For each problem p and solver s, the performance metric t_{ps} must be defined. In our study, reliability of stochastic methods in accurately finding the global optimum of the objective function is considered as the principal goal, and hence the performance metric is defined as

$$t_{ps} = \hat{f}_{\mathrm{calc}} - f^*, \tag{11}$$

where f^* is the known global optimum of the objective function and $\hat{f}_{\mathrm{calc}}$ is the mean value of that objective function calculated by the stochastic method over several runs. In this study, $\hat{f}_{\mathrm{calc}}$ is calculated from 100 runs to solve each test problem by each solver; note that each run is different because of random number seed used and the stochastic nature of the method. So, the focus is on the average performance of stochastic methods, which is desirable (Ali *et al.*, 2005).

For the performance metric of interest, the performance ratio, r_{ps} is used to compare the performance on problem p by solver s with the best performance by any solver on this problem. This performance ratio is given by

$$r_{ps} = \frac{t_{ps}}{\min\{t_{ps} : 1 \leq s \leq n_s\}}. \tag{12}$$

The value of r_{ps} is 1 for the solver s that performs the best on a specific problem p. For example, if $r_{ps} = 2$, the performance metric of solver s on problem p is twice the best value found by another solver on the same problem p.

To obtain an overall assessment of the performance of solver s on n_p problems, the following cumulative function for r_{ps} is used:

$$\rho_s(\varsigma) = \frac{1}{n_p}\, size\, \{p \in \Re : r_{ps} \leq \varsigma\}, \tag{13}$$

where $\rho_s(\varsigma)$ is the fraction of the total number of problems, for which solver s has a performance ratio r_{ps} within a factor $\varsigma \in (1, \infty)$ of the best possible ratio. The PP of a solver is a plot of $\rho_s(\varsigma)$ versus ς; it is a non-decreasing, piece-wise constant function, continuous from the right at each of the breakpoints (Dolan and More, 2002).

Note that $1.0 - \rho_s(\varsigma)$ is the fraction of problems that solver s failed to solve within a factor ς of the best method. This implies that, if the set of n_p problems is reasonably large and representative of circumstances that are likely to occur in the desired application, then solvers with larger $\rho_s(\varsigma)$ are better. If the objective is to identify the best solver, it is only necessary to compare the values of $\rho_s(1)$ for all solvers and to select the highest one, which is the probability that a specific solver will “win” over the rest of solvers used. For the performance metric in Eq. (11), the PP plot compares how accurately the stochastic methods can find the global optimum value relative to one another, and so the term “win” refers to the stochastic method that provides the most accurate value of the global optimum in reactive phase stability and equilibrium problems. We have calculated several PPs, and results are used for tuning TS and DE parameters for reactive phase stability and equilibrium calculations.

Parameters tuned in this study are: (a) DE: amplification factor (A), crossover constant (CR), population size (NP), maximum number of generations ($Gen_{\max}$), and maximum number of generations without improvement in the best function value ($Sc_{\max}$); and (b) TS: tabu list size (N_t), promising list size (N_p), tabu radius (ε_t), promising radius (ε_p), length of the hyper-rectangle (h_n), initial population size (NP_{init}), and maximum number of iterations ($Iter_{\max}$) and $Sc_{\max}$. Note that $Gen_{\max}$, $Iter_{\max}$ and $Sc_{\max}$ are the stopping criteria for DE and TS. The parameter tuning was performed using the stochastic methods without a local search algorithm. This procedure was carried out by varying one parameter at a time, while the remaining parameters were fixed at their nominal values. The tested and nominal values for each strategy are given in Table 1. Some algorithm parameters were associated to n_{var} (i.e. number of decision variables), and

Table 1. Parameters tested for tuning of TS and DE for the global minimization of $\Delta\hat{g}$ and RTPDF.

Method	Parameter	Tested values[a]	Nominal value
DE	Amplification factor A	0.3, 0.5, 0.7	0.5
	Crossover constant CR	0.1, 0.5, 0.9	0.1
	Population size NP	$5n_{var}$, $10n_{var}$, $25n_{var}$, $50n_{var}$	$10n_{var}$
	Maximum number of generations $Gen_{\max}$	50, 100, 200	50
	Maximum number of generations without improvement in the best function value $Sc_{\max}$	$6n_{var}$, $12n_{var}$	$12n_{var}$
TS	Tabu list size N_t	5, 10, 20	10
	Promising list size N_p	5, 10, 20	10
	Tabu radius ε_t	0.005, 0.01, 0.02	0.01
	Promising radius ε_p	0.005, 0.01, 0.02	0.01
	Length of the hyper-rectangle h_n	0.25, 0.5, 0.75	0.5
	Initial population size NP_{init}	$10n_{var}$, $20n_{var}$, $30n_{var}$	$20n_{var}$
	Maximum number of iterations $Iter_{\max}$	$25n_{var}$, $50n_{var}$, $100n_{var}$	$50n_{var}$
	Maximum number of iterations without improvement in the best function value $Sc_{\max}$	$2n_{var}$, $6n_{var}$, $12n_{var}$	$6n_{var}$
	Number of neighbors, N_{neigh} subject to a minimum of 10 and a maximum of 30.	$2n_{var}$	$2n_{var}$

[a] n_{var} is the number of decision variables in the optimization problem.

all values tested were chosen based on the results reported by Teh and Rangaiah (2003) and Srinivas and Rangaiah (2007).

For comparing the algorithm efficiency, NFE and CPUt were used as measures of computational effort. All calculations were performed on the Intel Pentium M 1.73 GHz processor with 504 MB of RAM. This computer performs 254 million floating point operations per second (MFlops) for the LINPACK benchmark program (available at http://www.netlib.org/; accessed in July, 2008) for a matrix of order 500.

4. Phase Equilibrium Calculations in Reactive Systems using DE and TS

4.1. Benchmark problems for parameter tuning

For parameter tuning, we have considered three reactive systems that are benchmarks in the studies on RSPs; they are: (a) the reaction for butyl acetate production at 298.15 K and 1 atm, (b) methyl *tert*-butyl ether (MTBE) reaction system with inert at 10 atm and 373.15 K, and (c) the reactive system for *tert*-amyl methyl ether (TAME) synthesis at 335 K and 1.5 atm. Thermodynamic models, parameters and transformed variables for these reactive systems are reported in Table 2, and Tables B1 - B3 of Appendix B. For variable transformation, the reference components are arbitrarily selected, and we have $c - r = 3$ transformed composition variables for all systems.

In the three problems, the number of phases existing at the equilibrium is assumed to be known *a priori*, but the phase type (vapor or liquid) is *unknown*. Bisection method is used to perform the composition transformation: $X \to x$ (see Appendix A), for objective function evaluation. Note that x obtained from this transformation satisfy the stoichiometry requirements and are chemically equilibrated. Further, the chemical potentials in $\Delta\hat{g}$ and RTPDF (Eqs. 1 and 10) are given by:

$$\frac{\Delta\mu_i}{RT} = \frac{\mu_i - \mu_i^0}{RT} = \ln\left(\frac{x_i\hat{\varphi}_i}{\varphi_i}\right) = \ln(x_i\gamma_i), \tag{14}$$

where μ_i^0 is the chemical potential of pure component i, $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture, φ_i is the fugacity coefficient of pure component, γ_i is the activity coefficient of component i in the mixture, and x_i is the mole fraction of component i in the mixture.

Table 2. Details of the selected reactive mixtures for parameter tuning of TS and DE for reactive phase equilibrium problems.

Mixture	Phases and thermodynamic models (see Appendix B for parameter values)	Transformed mole fractions
$A_1 + A_2 \leftrightarrow A_3 + A_4$ (1) Acetic Acid (2) n-Butanol (3) Water (4) n-Butyl acetate	Liquid-liquid equilibrium, UNIQUAC model. $\ln K_{eq,1} = \frac{450}{T} + 0.8$ where T is in K. Model parameters are taken from Wasylkiewicz and Ung (2000).	$X_1 = x_1 + x_4$ $X_2 = x_2 + x_4$ $X_3 = x_3 - x_4 = 1 - X_1 - X_2$ Reference component: A_4
$A_1 + A_2 \leftrightarrow A_3$, and A_4 as an inert (1) Isobutene (2) Methanol (3) Methyl ter-butyl ether (4) n-Butane	Vapor-liquid equilibrium, Wilson model and ideal gas. $\Delta G^o_{rxs}/R = -4205.05 + 10.0982T - 0.2667T \ln T$ $\ln K_{eq,1} = \frac{-\Delta G^0_{rxs}}{RT}$ where T is in K. Model parameters are taken from Ung and Doherty (1995a).	$X_1 = \frac{x_1+x_3}{1+x_3}$ $X_2 = \frac{x_2+x_3}{1+x_3}$ $X_4 = \frac{x_4}{1+x_3} = 1 - X_1 - X_2$ Reference component: A_3
$A_1 + A_2 + 2A_3 \leftrightarrow 2A_4$ (1) 2-Methyl-1-butene (2) 2-Methyl-2-butene (3) Methanol (4) *Tert*-amyl methyl ether	Vapor-liquid equilibrium, Wilson model and ideal gas. $K_{eq,1} = 1.057 \cdot 10^{-04} e^{4273.5/T}$ where T is in K. Model parameters are taken from Bonilla-Petriciolet *et al.* (2008).	$X_1 = \frac{x_1+0.5x_4}{1+x_4}$ $X_2 = \frac{x_2+0.5x_4}{1+x_4}$ $X_3 = \frac{x_3+x_4}{1+x_4} = 1 - X_1 - X_2$ Reference component: A_4

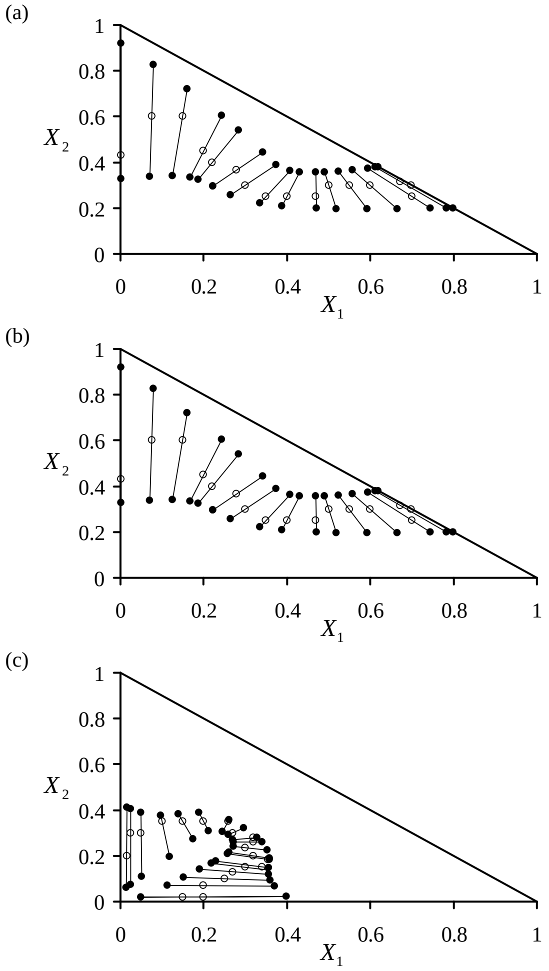

Figure 3. Transformed feed (○) and tie-lines (•) used for parameter tuning of TS and DE in reactive phase equilibrium problems. Reactive systems are: (a) acetic acid + *n*-butanol ↔ water + n-butyl acetate at 298.15 K and 1 atm, (b) isobutene + methanol ↔ methyl *tert*-butyl ether with *n*-butane as an inert at 10 atm and 373.15 K, and (c) 2-methyl-1-butene + 2-methyl-2-butene + 2 methanol ↔ 2 *tert*-amyl methyl ether at 335 K and 1.5 atm.

Feed compositions and tie-lines used to tune the parameters of TS and DE are shown in Fig. 3. We have utilized $n_p = 48$ different feeds, selected from the three reactive mixtures, to calculate PPs. The objective function has at least one local minimum, which corresponds to a trivial solution

($Z_i = X_i$ in phase stability and $Z_i = X_{i,1} = \cdots = X_{i,\pi}$ in equilibrium calculations), for all tested conditions. Note that different models are used in the calculation of thermodynamic properties for different phases (vapor and liquid) of reactive systems (b) and (c). The use of multiple thermodynamic models increases the complexity of phase stability and equilibrium calculations (Xu *et al.*, 2005); since there will be different $\Delta\hat{g}$ functions for different types of phases, evaluation of any trial composition must be done on the surface with the lowest value of transformed Gibbs free energy. Thus, the procedure of variable transformation is performed for each model at specified X and its corresponding $\Delta\hat{g}$ is evaluated. The model having the lowest value of transformed Gibbs free energy is then used for evaluating the objective function. Finally, the selected conditions involve feed compositions near phase boundaries, which are generally challenging for any algorithm. So, the tested conditions are appropriate for tuning the parameters of TS and DE.

In the three reactive systems considered for parameter tuning, $c = 4$ and $r = 1$ (see Table 2). Hence, there are three decision variables, $\lambda_{i,1} \in (0, 1)$ in the Gibbs energy minimization for phase equilibrium calculations. In the problems to test stability of the feed, depending upon the permissible values for X, we have considered different transformed variables and the equality constraint $\sum_{i=1}^{c-r} X_i = 1$. For the reactive system (a), RTPDF is minimized with respect to $X_1, X_2 \in (0, 1)$ only, and $X_3 = 1 - X_1 - X_2$. For phase stability calculations in reactive systems (b) and (c), three transformed fractions $X_i \in (0, 1)$ are used as decision variables, after their normalization to unity: $\bar{X}_i = X_i / \sum_{i=1}^{c-r} X_i$ where $\bar{X}_i$ is the normalized transformed mole fraction of component i.

4.2. Results of parameter tuning

Table 3 shows the performance summary for tuning the parameters of TS and DE; in this table, we report $\rho_s(1)$, NFE and CPUt obtained in the global minimization of RTPDF and $\Delta\hat{g}$. Here, NFE and CPUt are the mean of 100 runs for 48 feeds, and the range given for NFE and CPUt in each row of Table 3 is for the three problems solved. Depending on the parameter values, NFE varied from 390 to 7626 for stability calculations by DE, while it varied from 105 to 801 for stability calculations by TS; this computational

Table 3. Results for parameter tuning of TS and DE for the global minimization of $\Delta\hat{g}$ and RTPDF.

	Parameter tuning		Probability, $\rho_S(1)$ for		NFE for		CPUt (s) for	
Method	Parameter	Value[a]	RTPDF	$\Delta\hat{g}$	RTPDF	$\Delta\hat{g}$	RTPDF	$\Delta\hat{g}$
DE	*A*	0.3	0.542	0.625	769–1528	1471–1524	0.17–0.53	0.43–0.93
		0.5	0.208	0.292	779–1524	1457–1523	0.18–0.53	0.44–0.94
		0.7	0.250	0.083	772–1527	1462–1515	0.17–0.53	0.44–0.94
	CR	0.1	0.0	0.0	779–1524	1457–1523	0.18–0.53	0.44–0.94
		0.5	0.042	0.021	968–1530	1513–1530	0.16–0.53	0.44–0.94
		0.9	0.958	0.979	1020–1530	1511–1530	0.16–0.51	0.45–0.95
	NP	$5n_{var}$	0.0	0.0	396–762	730–758	0.09–0.28	0.21–0.48
		$10n_{var}$	0.0	0.0	779–1524	1457–1523	0.18–0.53	0.44–0.94
		$25n_{var}$	0.0	0.0	1830–3815	3666–3804	0.28–1.28	1.07–2.34
		$50n_{var}$	1.0	1.0	3672–7626	7239–7579	0.69–2.54	2.01–4.69
	$Gen_{\max}$	50	0.021	0.0	779–1524	1457–1523	0.18–0.53	0.44–0.94
		100	0.292	0.396	805–2845	2058–2602	0.22–0.85	0.69–1.58
		200	0.688	0.604	825–5006	2160–3396	0.26–1.17	0.71–1.96
	$Sc_{\max}$	$6n_{var}$	0.0	0.0	390–1291	1015–1220	0.09–0.48	0.42–0.72
		$12n_{var}$	1.0	1.0	779–1524	1457–1523	0.18–0.53	0.44–0.94

(Continued)

Table 3. (*Continued*)

	Parameter tuning		Probability, $\rho_s(1)$ for		NFE for		CPUt (s) for	
Method	Parameter	Value[a]	RTPDF	$\Delta\hat{g}$	RTPDF	$\Delta\hat{g}$	RTPDF	$\Delta\hat{g}$
TS	$N_t = N_p$	5	0.771	0.813	203–636	484–680	0.03–0.16	0.15–0.41
		10	0.083	0.083	194–455	385–521	0.04–0.13	0.11–0.30
		20	0.146	0.104	193–442	393–522	0.03–0.12	0.14–0.25
	$\varepsilon_t = \varepsilon_p$	0.005	0.875	0.938	226–498	408–681	0.03–0.14	0.14–0.35
		0.01	0.125	0.042	194–455	385–521	0.04–0.13	0.11–0.30
		0.02	0.0	0.021	172–418	347–408	0.03–0.12	0.11–0.26
	h_n	0.25	0.229	0.333	182–444	369–511	0.03–0.13	0.10–0.30
		0.5	0.396	0.375	194–455	385–521	0.04–0.13	0.11–0.30
		0.75	0.375	0.292	208–456	390–543	0.02–0.12	0.11–0.29
	NP_{init}	$10n_{var}$	0.250	0.250	183–430	361–519	0.03–0.12	0.09–0.27
		$20n_{var}$	0.438	0.458	194–455	385–521	0.04–0.13	0.11–0.30
		$30n_{var}$	0.313	0.292	214–462	417–541	0.03–0.12	0.11–0.30
	$Iter_{\mathrm{max}}$	$25n_{var}$,	0.333	0.229	192–443	375–487	0.03–0.12	0.08–0.30
		$50n_{var}$	0.396	0.417	194–455	385–521	0.04–0.13	0.11–0.30
		$100n_{var}$	0.271	0.375	196–459	393–532	0.03–0.11	0.12–0.42
	Sc_{max}	$2n_{var}$	0.0	0.0	105–223	177–241	0.01–0.06	0.07–0.11
		$6n_{var}$	0.063	0.0	194–455	385–521	0.04–0.13	0.11–0.30
		$12n_{var}$	0.938	1.0	296–801	656–849	0.05–0.24	0.13–0.53

[a] Remaining parameters were fixed at nominal values, see Table 1.

effort corresponds to 0.09–2.54 s of CPUt for DE, and 0.01–0.24 s for TS (see Table 3). For Gibbs free energy minimization, NFE varied from 730 to 7579 (0.21–4.69 s) for DE, and from 177 to 849 (0.07–0.53 s) for TS, depending on the parameter values.

Since we are only interested in the optimal values of parameters of TS and DE that find the best solution of all tested conditions, only $\rho_S(1)$ is given in Table 3 and not the PPs. However, for illustrative purposes, several PPs obtained for TS and DE are shown in Figs. 4 and 5, which displays the fraction of phase stability and equilibrium problems solved by TS and DE with different parameter values, within a factor ς of the best found solution. These PPs show the effect of a parameter on the relative performance of TS and DE, and enable to find the optimal values of parameters. The results in Table 3 show that algorithm reliability increases with NP, $Gen_{\max}$, $Iter_{\max}$ and $Sc_{\max}$, but at the expense of computational effort. The PPs also show that optimal values of $A = 0.3$ and $CR = 0.9$ for DE agree with those

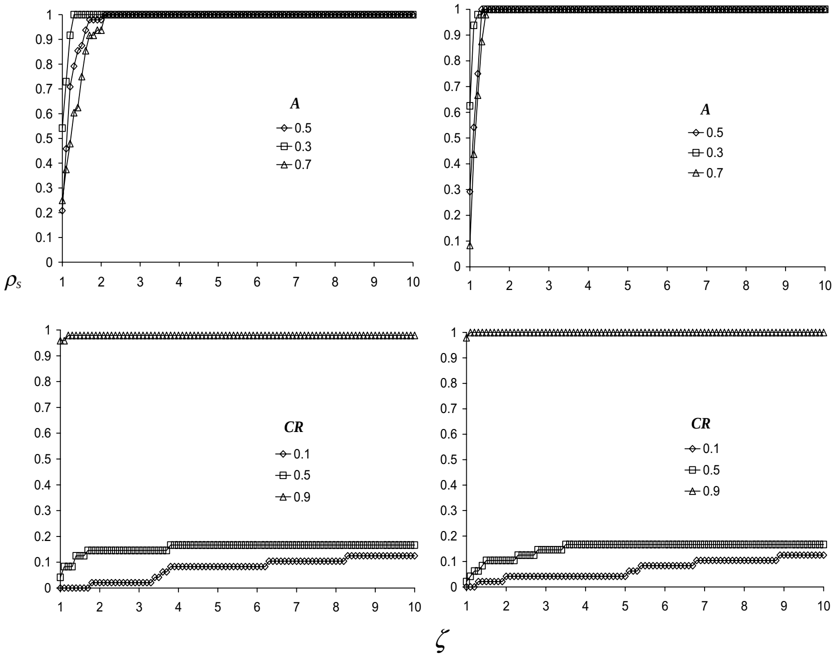

Figure 4. Performance profiles for algorithm parameters of DE in reactive phase stability (RTPDF: plots in the left column) and equilibrium calculations ($\Delta\hat{g}$: plots in the right column).

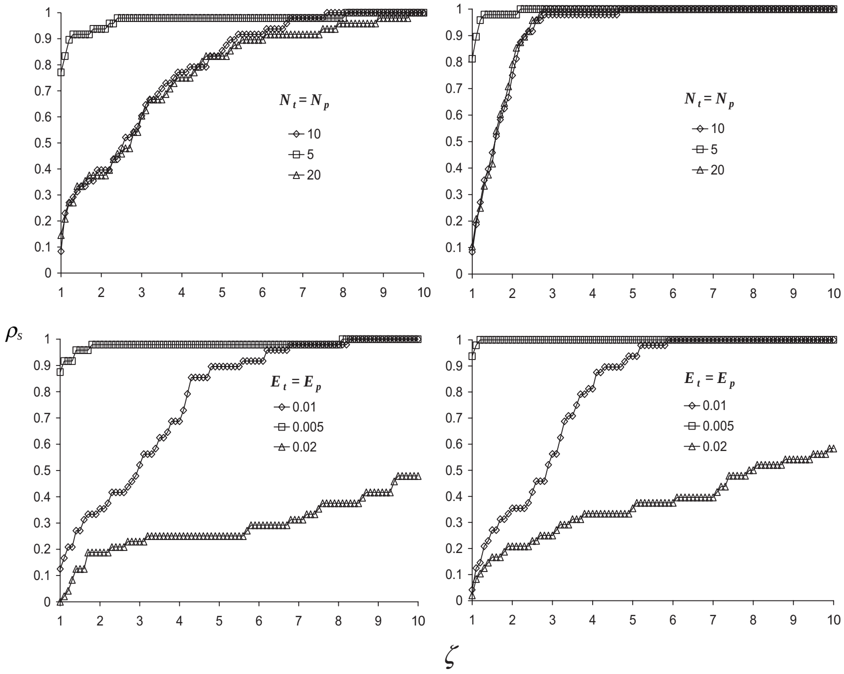

Figure 5. Performance profiles for algorithm parameters of TS in reactive phase stability (RTPDF: plots in the left column) and equilibrium calculations ($\Delta\hat{g}$: plots in the right column).

reported by Srinivas and Rangaiah (2007) for both the stability and equilibrium problems in non-reactive systems. Further, PPs indicate that *CR* is an important parameter to improve the performance of DE (Fig. 4). Finally, results on TS suggest that lower values for $N_t = N_p$ and $\varepsilon_t = \varepsilon_p$ favor the reliability of the method but increase the computational effort (see Table 3 and Fig. 5). The parameters: $h_n = 0.5$ and $NP_{\text{init}} = 20n_{var}$ appear to be optimal for reliability, and are in agreement with those reported by Srinivas and Rangaiah (2007) for the case of non-reactive systems.

5. Applications

Having selected the optimal values of parameters in TS and DE, two reactive systems are analyzed to test and compare their performance for reactive phase stability and equilibrium problems. First system has been selected to reflect different problem difficulties: a challenging objective function with a local minimum value very comparable to the global minimum value, and multi-reaction conditions with the presence of inert components. The second example is a reactive mixture widely used in the literature to test algorithms in the simultaneous calculation of chemical and phase equilibrium (e.g. Xiao *et al.*, 1989; Lee *et al.*, 1999; Jalali *et al.*, 2008).

Note that NP, NP_{init}, $Gen_{\max}$, $Iter_{\max}$, and $Sc_{\max}$ are problem-dependent parameters, significantly affect the performance of DE and TS, and determine the trade-off between efficiency and reliability. The selection of proper values for these is a key step, which depends on the goals of the user for a specific application. Hence, in example 1 we have studied the reliability of TS and DE at different levels of computational effort by changing the values of stopping criteria ($Gen_{\max}$, $Iter_{\max}$, and $Sc_{\max}$). Optimal values identified using PPs for the remaining parameters of both methods were used in these calculations: (a) DE: $A = 0.3$ and $CR = 0.9$; (b) TS: $N_t = N_p = 5$, $\varepsilon_t = \varepsilon_p = 0.005$ and $h_n = 0.5$, respectively. In example 2, all parameters are fixed based on the results on the previous example. Phase stability and equilibrium problems in each example were solved 100 times each, using random initial values via different random number seed. The local search method has been used to refine the solution obtained from the stochastic algorithm. For illustrative purposes, FORTRAN programs developed for example 1 are included in the folder of this chapter on the CD.

5.1. Example 1

Consider a hypothetical multi-component reactive mixture undergoing three reactions:

$$\begin{aligned} A_3 &\Leftrightarrow A_4 \\ A_5 &\Leftrightarrow A_4, \\ A_4 &\Leftrightarrow A_6 \end{aligned} \tag{15}$$

with A_1 and A_2 as inert components. This mixture presents a vapor-liquid equilibrium at $P = 1$ atm and $T = 60°C$, where both phases are ideal (see thermodynamic data and models in Table B4 of Appendix B). For simplicity, equilibrium constants for the three reactions are: $K_{eq,1} = 1.5$, $K_{eq,2} = 0.15$ and $K_{eq,3} = 0.35$. Selecting A_3, A_4 and A_5 as the reference components, transformed mole fractions are defined as:

$$X_1 = x_1, \tag{16}$$

$$X_2 = x_2, \tag{17}$$

$$X_6 = x_3 + x_4 + x_5 + x_6, \tag{18}$$

where all $X_i \in (0, 1)$.

Due to the ideal phases assumed for modeling this system, the transformation procedure for $X \rightarrow x$ is straightforward. The chemical equilibrium constants for this mixture are given by

$$\begin{aligned} K_{eq,1} &= \frac{a_4}{a_3} \\ K_{eq,2} &= \frac{a_4}{a_5}, \\ K_{eq,3} &= \frac{a_6}{a_4} \end{aligned} \tag{19}$$

where the activity of component i is given by: $a_i = x_i \gamma_i$ for the liquid phase or $a_i = x_i P / P_i^{sat}$ for the ideal vapor phase, and P_i^{sat} is the saturation pressure of the pure component i. Expressing the mole fractions in terms of x_4 using Eqs. (16)–(18), and substituting into the chemical equilibrium constraints (Eq. (19)), mole fraction of this reference component for the set of specified transformed variables can be obtained from:

$$x_4 = \frac{X_6}{1 + \frac{\theta_{43}}{K_{eq,1}} + \frac{\theta_{45}}{K_{eq,2}} + \frac{K_{eq,3}}{\theta_{64}}}, \tag{20}$$

where $\theta_{ij} = \gamma_i / \gamma_j = 1$ for the ideal liquid phase or $\theta_{ij} = P_j^{sat} / P_i^{sat}$ for the ideal vapor phase. Remaining components come from Eqs. (16) and (17) for x_1 and x_2; while x_3, x_5 and x_6 are obtained using

$$x_3 = \frac{x_4 \theta_{43}}{K_{eq,1}}, \tag{21}$$

$$x_5 = \frac{x_4 \theta_{45}}{K_{eq,2}}, \tag{22}$$

$$x_6 = 1 - \sum_{i=1}^{5} x_i. \tag{23}$$

Based on preliminary trials, we have chosen a challenging condition to test and compare the stochastic methods in the global minimization of RTPDF and $\Delta\hat{g}$. Specifically, we have determined the equilibrium compositions for a feed that corresponds to a liquid phase with initial composition $n_{i,F} = (0.6305, 0.00355, 0.1, 0.1, 0.1, 0.06595)$ and $n_{T,F} = \sum_{i=1}^{c} n_{i,F} = 1$. In transformed variables, we have $Z_i = (0.6305, 0.00355, 0.36595)$ and $\hat{n}_{T,F} = 1$. This feed is near a phase boundary and, as consequence, the objective function of both phase stability and equilibrium problems has a local minimum that is comparable to the global minimum (i.e. function values at the local and global minima are close to each other).

The global minimum of RTPDF is -0.001591 at $X_i = (0.708954, 0.004042, 0.287004)$ versus 0.0 at Z; and the global minimum of $\Delta\hat{g} = -1.853908$ is at vapor-liquid equilibrium with transformed compositions of $X_{i,1} = (0.625858, 0.003521, 0.370621)$ and $X_{i,2} = (0.704855, 0.004015, 0.291130)$, versus the local minimum of $\Delta\hat{g} = -1.853861$ at $Z_i = X_{i,1} = X_{i,2}$. When the objective function value of a local minimum is very close to that at the global minimum, premature convergence of an optimization method is likely. As a consequence, low reliability may be obtained under these conditions.

For this reactive mixture, the reactive tangent plane for stability criterion is defined as:

$$RTPDF = X_1\left(\left.\frac{\Delta\mu_1}{RT}\right|_X - \ln(z_1\gamma_1)\right) + X_2\left(\left.\frac{\Delta\mu_2}{RT}\right|_X - \ln(z_2\gamma_2)\right) + X_6\left(\left.\frac{\Delta\mu_6}{RT}\right|_X - \ln(z_6\gamma_6)\right), \tag{24}$$

where z_i is obtained from $Z \rightarrow z$ using Eqs. (20)–(23). The expression for the chemical potential at X should be for the phase with lower Gibbs free energy of mixing, and is:

$$\left.\frac{\Delta\mu_i}{RT}\right|_X = \ln\left(\frac{x_i P}{P_i^{sat}}\right) \quad \text{if } \Delta\hat{g}_2 < \Delta\hat{g}_1 \quad \text{else } \left.\frac{\Delta\mu_i}{RT}\right|_X = \ln\left(x_i\gamma_i\right). \tag{25}$$

Here, the transformed Gibbs free energy expressions for liquid ($\Delta\hat{g}_1$) and vapor ($\Delta\hat{g}_2$) are:

$$\Delta\hat{g}_1 = \sum_{\substack{i=1 \\ i \neq 3,4,5}}^{6} X_i \ln(x_i \gamma_i), \tag{26}$$

$$\Delta\hat{g}_2 = \sum_{\substack{i=1 \\ i \neq 3,4,5}}^{6} X_i \ln\left(\frac{x_i P}{P_i^{sat}}\right), \tag{27}$$

where x_i is the mole fraction of component i that satisfy the chemical equilibrium, which is obtained from $X \rightarrow x$ using Eqs. (20)–(23). Three decision variables X_1, X_2 and X_6 are used, after their normalization to unity, $\bar{X}_i = X_i/(X_1 + X_2 + X_6)$, in the global optimization of RTPDF. Thus, the unconstrained minimization problem that must be solved for phase stability can be expressed as:

$$\begin{aligned} &\min_X RTPDF(X) \\ &X_1, X_2, X_6 \in (0, 1). \end{aligned} \tag{28}$$

For phase equilibrium calculations, the transformed Gibbs free energy function is:

$$\begin{aligned} \Delta\hat{g} = {} & \hat{n}_{1,1}\frac{\Delta\mu_{1,1}}{RT} + \hat{n}_{2,1}\frac{\Delta\mu_{2,1}}{RT} + \hat{n}_{6,1}\frac{\Delta\mu_{6,1}}{RT} + \hat{n}_{1,2}\frac{\Delta\mu_{1,2}}{RT} \\ & + \hat{n}_{2,2}\frac{\Delta\mu_{2,2}}{RT} + \hat{n}_{6,2}\frac{\Delta\mu_{6,2}}{RT}, \end{aligned} \tag{29}$$

where the chemical potentials of phases 1 and 2 are also given by Eqs. (25)–(27). Using Eq. (7) gives the following expressions for the decision variables:

$$\begin{aligned} \hat{n}_{1,1} &= 0.6305\lambda_{1,1} \\ \hat{n}_{2,1} &= 0.00355\lambda_{2,1}, \\ \hat{n}_{3,1} &= 0.36595\lambda_{3,1} \end{aligned} \tag{30}$$

where $\hat{n}_{i,2}$ is obtained from Eq. (9). Thus, the unconstrained minimization problem that must be solved for phase equilibrium calculations is:

$$\begin{array}{l} \min\limits_{\lambda_{i,1}} \Delta\hat{g} \\ \lambda_{1,1}, \lambda_{2,1}, \lambda_{3,1} \in (0,1) \end{array} . \tag{31}$$

Phase stability test and equilibrium calculations have been carried out using different values for NP, NP_{init}, iterations (*Iter*) and generations (*Gen*). To assess the quality of solutions obtained as the search progresses and to capture the improvement in the objective function values and their variation in each run performed, individual quartile sequential plots (Ali *et al.*, 2005) are prepared. A quartile is any of the three values which divide the sorted data set into four equal parts, so that each part represents 1/4th of the sampled population. In our case, this population is the set of objective values obtained by the stochastic method over 100 independent runs. Then, a quartile sequential plot displays the progress of the 25th, 50th and 75th percentiles of the objective values calculated by the stochastic method versus *Iter* or *Gen*. Here, quartile sequential plots were obtained using the best objective function values, without using the local search method, recorded at different values of *Iter* or *Gen*. To complement the quartile results, we also present the plots of success ratio (SR) versus *Iter* or *Gen*, where SR is defined as the number of runs out of 100 that satisfy the condition $|f_{\text{calc}} - f^*| \leq 10^{-06}$ but using both DE and TS in combination with the quasi-Newton method. For the case of SR plots, the switch to the local method takes place once stochastic method has performed the specified number of *Iter* or *Gen*. In these calculations, *Iter* or *Gen* are used alone as a stopping criterion (i.e. without $Sc_{\max}$).

Figures 6 and 7 show the quartile sequential and SR plots for TS and DE for phase stability and equilibrium calculations in this example. In the quartile plots, the vertical bar at the k-th *Iter* or *Gen* represents a range of objective function values between the 25th and the 75th percentiles, while the symbol ($\times$, $\diamond$ or Δ) corresponds to the 50th percentile (i.e. the median of the objective function values which are calculated by the stochastic method over 100 trials). As expected, these results indicate that the algorithm performance is highly dependent on the maximum number of *Gen* or *Iter*. For the case of stability calculations, TS and DE improve the solution quality as

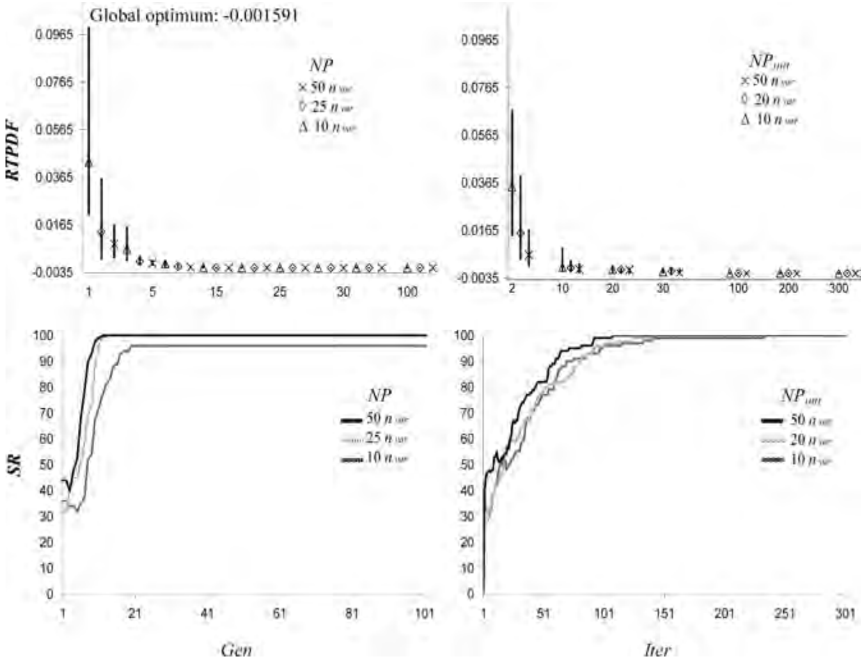

Figure 6. Quartile sequential and success rate plots of DE (in the left column) and TS (in the right column) in the global minimization of RTPDF for example 1.

Gen or *Iter* increases, irrespective of the values used for *NP* and NP_{init}. The variance of solutions obtained for the two stochastic methods is relatively large at the small values of *Iter* or *Gen*, and also for low values of *NP* and NP_{init} (see the broad percentile ranges in Fig. 6). As a consequence, both TS and DE, in combination with the local method, show low reliability (SR) in these conditions. However, with proper values for the maximum number of *Iter* or *Gen*, the global optimum of RTPDF can be found with a 100% SR.

Note that DE can reach a high SR (> 90%) at *Gen* > 15, unlike TS where more than 60 *Iter* are required to obtain an acceptable performance. Nevertheless, there are significant differences between the NFE of the two strategies because one generation in DE involves many more NFE compared to that in one iteration of TS (see Fig. 8). Comparing the reliability of both DE and TS followed by the quasi-Newton method in this stability problem at the same level of computational effort using NFE as reference

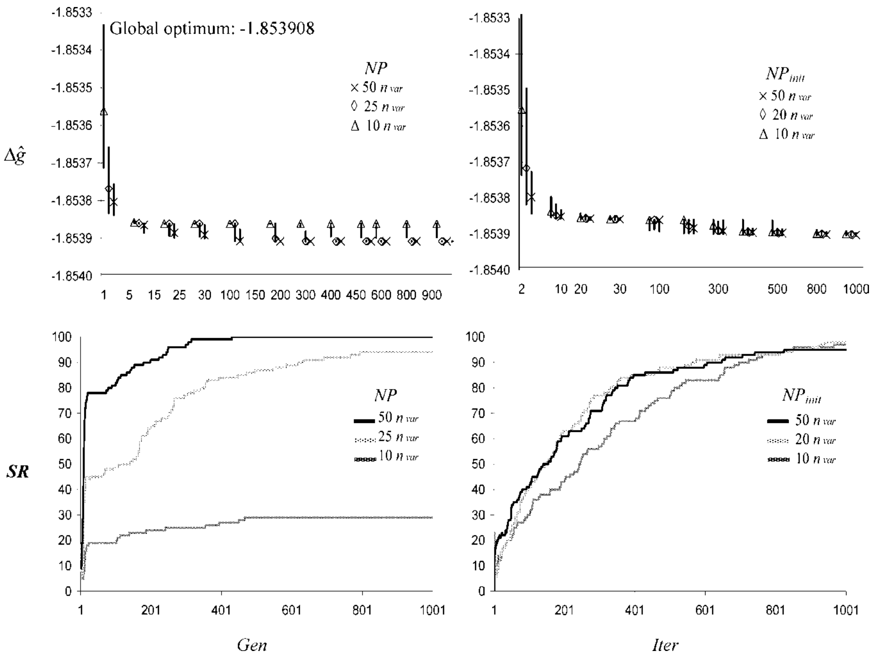

Figure 7. Quartile sequential and success rate plots of DE (in the left column) and TS (in the right column) in the global minimization of $\Delta\hat{g}$ for example 1.

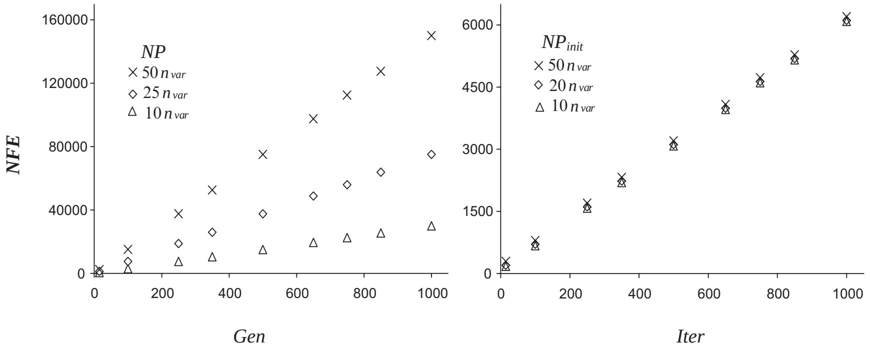

Figure 8. Mean computational effort of DE (right column) and TS (left column), each followed by the local method, in the global minimization of RTPDF and $\Delta\hat{g}$ for example 1.

(which includes the computational effort of both stochastic and local methods), reliability of TS is better than DE when NFE $< 1{,}000$, and vice versa for larger NFE. For the case of the stopping criterion $Sc_{\max}$, DE needs a mean value of 55, 119, and 156 generations to satisfy $Sc_{\max} = 2n_{var}$, $6n_{var}$ and $12n_{var}$, respectively. For the case of TS, these stopping conditions are reached in, on average, 18, 42 and 77 iterations. It is evident from Fig. 6 that the reliability of DE is better compared to TS if $Sc_{\max}$ is used alone as the convergence criterion.

Results for the minimization of $\Delta\hat{g}$ indicate that both DE and TS may be trapped at a local optimum depending on the algorithm parameters (see Fig. 7). In fact, this problem is very challenging due to the presence of trivial solution ($Z_i = X_{i,1} = X_{i,2}$) which has an objective value very near to the global minimum (-1.853861 and -1.853908, respectively). As before, the variance of solutions obtained from TS and DE is higher at low values of *NP*, NP_{init}, *Gen* and *Iter* and improves with increased values of these parameters. Quartile plots show that the objective function values are not improving throughout a significant amount of generations/iterations performed by TS and DE (Fig. 7). For the case of DE, combined with the local method, 100% SR is reached only for $NP = 50n_{var}$ and $Gen > 400$. In fact, this method can show improvement in the function values after getting stuck at a local optimum in early iterations. However, good performance is obtained at a significant computational cost: NFE $> 60{,}000$ (see Fig. 8). In this problem, *NP* plays an important role to determine the reliability of DE.

On the other hand, results show that TS followed by the quasi-Newton method gives poor performance at smaller values of *Iter* because it failed many times to locate the global minimum of the transformed Gibbs free energy (Fig. 7). The TS algorithm improves over further iterations and performs relatively well at $Iter > 600$ (NFE > 3700). However, it can only reach a maximum of 98% SR at 1,000 iterations and $NP_{\text{init}} = 20n_{var}$ (NFE $\approx 6{,}000$). There is no clear effect of NP_{init} on the reliability of TS, although it appears a large value for this parameter is better. Results show that DE requires an average of 38, 127, and 255 generations to fulfill $Sc_{\max} = 2n_{var}$, $6n_{var}$, and $12n_{var}$, while TS needs an average of 14, 37, and 70 iterations to satisfy these stopping conditions. As for phase stability problems, DE is more reliable than TS if $Sc_{\max}$ is used alone as the convergence criterion in phase equilibrium problems.

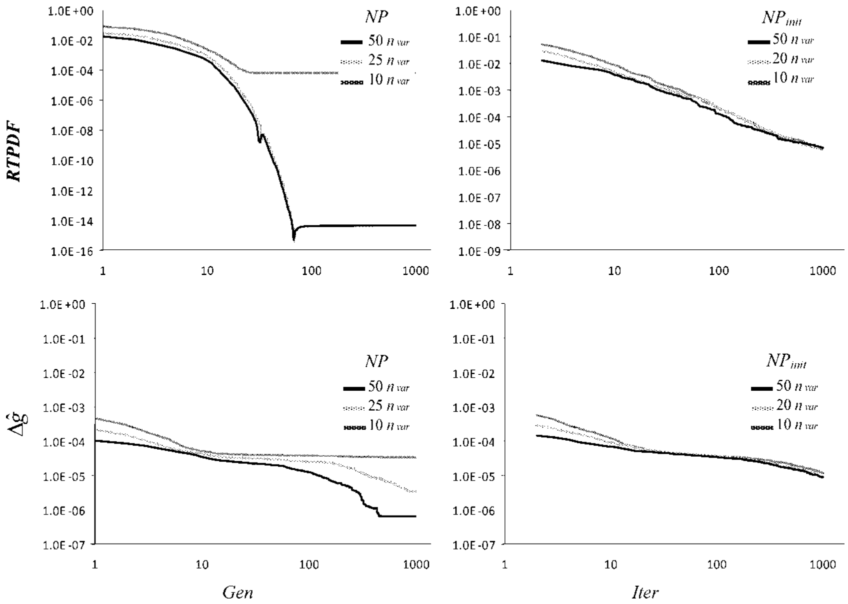

Figure 9. Convergence histories of the norm $|\hat{f}_{\text{calc}} - f^*|$ of DE (in the left column) and TS (in the right column) in the global minimization of RTPDF and $\Delta\hat{g}$ for example 1.

Figure 9 provides the convergence histories of the norm of $|\hat{f}_{\text{calc}} - f^*|$ for both TS and DE, *without* the local search method, in the global minimization of RTPDF and $\Delta\hat{g}$. This norm is based on the average (over 100 runs) of the best objective function $\hat{f}_{\text{calc}}$ recorded at each *Gen* and *Iter*. In general, the mean value of best solution obtained by TS and DE is nearer to the global minimum as the *Gen* and *Iter* increases. However, the norm reached by DE is lower than that achieved by TS in both stability and equilibrium calculations but at the expense of a significant computational effort (see Figs. 6–8).

For both TS and DE, the accuracy of final solutions is improved after the switch to the local optimization method. However, this accuracy is problem-specific because the objective function may be flat near the global minimum region, affecting the quality of solutions obtained by gradient-based methods combined with numerical derivatives (Srinivas and Rangaiah, 2007). In this reactive mixture, both TS and DE in combination with the local method can find very accurate solutions with an absolute error (i.e. $f_{\text{calc}} - f^*$) lower than 10^{-10} for phase stability calculations; in Gibbs free energy minimization, this absolute error is around 10^{-10} for DE and is slightly lower than 10^{-7} for TS. The use of direct search methods (e.g. Nelder–Mead simplex method) for local optimization at the end of TS and DE is a suitable option for handling objective functions that are flat near the global minimum. However, these local search strategies are known to be less efficient than the gradient-based methods. With respect to algorithm efficiency, CPUt ranged from 0.01 to 2.09 seconds for DE, and from 0.01 to 0.08 seconds for TS in all stability and equilibrium calculations performed.

Finally, we have solved the phase stability and equilibrium problems in this example using the quasi-Newton method alone with random initial values (100 runs for each problem). This local solver generally converged to trivial solutions, with only 42% SR for phase stability and 16% SR for equilibrium calculations. When the method converged to the global solution, it required an average of 351 NFE for phase stability and 156 NFE for equilibrium calculations (CPUt < 0.001 s). As expected, the quasi-Newton method is more efficient than DE and TS but less reliable for finding the global minimum and dependent on the initial values. Therefore, this and other local methods are not suitable for phase stability and equilibrium calculations in reactive systems.

5.2. Example 2

This example refers to the esterification reaction of ethanol and acetic acid to form ethyl acetate and water:

$$\text{ethanol (1)} + \text{acetic acid (2)} \leftrightarrow \text{ethyl acetate (3)} + \text{water (4)}. \tag{32}$$

This system is a benchmark problem for testing algorithms in phase equilibrium calculations for reactive systems (e.g. Castillo and Grossmann, 1981; Xiao *et al.*, 1989; McDonald and Floudas, 1996; Lee *et al.*, 1999; Jalali *et al.*, 2008). In this study, water is selected as the reference component for composition transformation, and transformed variables are given by:

$$X_1 = x_1 + x_4, \tag{33}$$

$$X_2 = x_2 + x_4, \tag{34}$$

$$X_3 = x_3 - x_4, \tag{35}$$

where $X_1, X_2 \in (0, 1)$ and $X_3 \in (-1, 1)$. We use the NRTL model for calculating the thermodynamic properties of the liquid phase, while the vapor phase is assumed to be ideal where the dimerization of acetic acid is not considered (see thermodynamic data in Table B5 of Appendix B).

Three feeds are analyzed at different temperatures and 1 atm. First, we consider an equi-molar feed of ethanol and acetic acid, $n_{i,F} = (0.5, 0.5, 0.0, 0.0)$ at 358 K. So, the transformed composition $Z_i = (0.5, 0.5, 0.0)$, where $\hat{n}_{i,F} = (0.5, 0.5, 0.0)$ and $\hat{n}_{T,F} = 1.0$, is tested for phase stability. In these conditions, the chemical equilibrium constant for this reaction is $K_{eq,1} = 18.154056$, which was calculated using the thermodynamic data reported by Lee *et al.* (1999), and this feed corresponds to a vapor phase (McDonald and Floudas, 1996; Lee *et al.*, 1999). Thus, RTPDF is defined as:

$$RTPDF = X_1\left(\left.\frac{\Delta\mu_1}{RT}\right|_X - \ln\left(\frac{z_1 P}{P_1^{sat}}\right)\right) + X_2\left(\left.\frac{\Delta\mu_2}{RT}\right|_X - \ln\left(\frac{z_2 P}{P_2^{sat}}\right)\right), + X_3\left(\left.\frac{\Delta\mu_3}{RT}\right|_X - \ln\left(\frac{z_3 P}{P_3^{sat}}\right)\right), \tag{36}$$

where the chemical potential at X is obtained from Eq. (25) with $\Delta\hat{g}_1$ and $\Delta\hat{g}_2$ given by

$$\Delta\hat{g}_1 = \sum_{i=1}^{3} X_i \ln(x_i\gamma_i), \tag{37}$$

$$\Delta\hat{g}_2 = \sum_{i=1}^{3} X_i \ln\left(\frac{x_i P}{P_i^{sat}}\right), \tag{38}$$

for liquid and vapor phases respectively. Note that z in Eq. 36 are the chemically equilibrated mole fractions, and are obtained from variable transformation $Z \rightarrow z$ (see Appendix A).

Phase stability analysis is performed using Eq. (36) and two decision variables: X_1, $X_2(0, 1)$; and X_3 is calculated using $X_3 = 1 - X_1 - X_2$. In these calculations, we use the following parameters for stochastic methods: (a) DE: $A = 0.3$, $CR = 0.9$, $NP = 50n_{var}$, $Gen_{\max} = 50$ and $Sc_{\max} = 6n_{var}$; and (b) TS: $N_t = N_p = 5$, $\varepsilon_t = \varepsilon_p = 0.005$, $NP_{\text{init}} = 20n_{var}$, $Iter_{\max} = 50n_{var}$, $h_n = 0.5$ and $Sc_{\max} = 12n_{var}$, where $n_{var} = 2$. Results of stability calculations are reported in Table 4. Since the global minimum of RTPDF is 0.0 at the trivial solution $Z_i = X_i$, this feed is stable. This result is consistent with that reported by Xiao *et al.* (1989), McDonald and

Floudas (1997) and Lee *et al.* (1999). Both TS and DE in combination with the local method, find the global solution of this stability problem with 100% SR, and TS is more efficient than DE (see Table 4).

Now, the same feed, $n_{i,F} = (0.5, 0.5, 0.0, 0.0)$ is analyzed at 355 K with $K_{eq,1} = 18.670951$ where both the liquid and vapor exists (Xiao *et al.*, 1989; McDonald and Floudas, 1996; Lee *et al.*, 1999). Again, $K_{eq,1}$ is determined from thermodynamic data reported by Lee *et al.* (1999). Stability calculations are performed using Eqs. (36) to (38) and the same decision variables; the results of stability analysis are reported in Table 4. Again, both TS and DE are reliable to determine that this mixture is unstable, and TS is more efficient than DE.

Considering the results of stability criterion, we have performed the minimization of transformed Gibbs free energy for calculating the phase equilibrium:

$$\Delta\hat{g} = \hat{n}_{1,1}\frac{\Delta\mu_{1,1}}{RT} + \hat{n}_{2,1}\frac{\Delta\mu_{2,1}}{RT} + \hat{n}_{3,1}\frac{\Delta\mu_{3,1}}{RT} + \hat{n}_{1,2}\frac{\Delta\mu_{1,2}}{RT} + \hat{n}_{2,2}\frac{\Delta\mu_{2,2}}{RT} + \hat{n}_{3,2}\frac{\Delta\mu_{3,2}}{RT}, \tag{39}$$

where the chemical potentials are defined by Eqs. (25), (37) and (38). For this feed, recall that $\hat{n}_{i,F} = (0.5, 0.5, 0.0)$ and $\hat{n}_{T,F} = 1.0$, and as a consequence $\hat{n}_{3,2} = -\hat{n}_{3,1}$. We can define the transformed moles of phase 1 as a fraction of total transformed moles in the feed (i.e. $\hat{n}_{T,1} = \hat{n}_{T,F}\lambda_F$ where $\lambda_F \in (0, 1)$). So, the global optimization of $\Delta\hat{g}$ is performed with respect to three decision variables: $\lambda_{1,1}, \lambda_{2,1} \in (0, 1)$ and $\lambda_F \in (0, 1)$. The transformed mole numbers are given by:

$$\begin{aligned}\hat{n}_{1,1} &= 0.5\lambda_{1,1}\\ \hat{n}_{2,1} &= 0.5\lambda_{2,1},\\ \hat{n}_{3,1} &= \hat{n}_{T,F}\lambda_F - (\hat{n}_{1,1} + \hat{n}_{2,1})\end{aligned} \tag{40}$$

and Eq. (9) is used to determine $\hat{n}_{i,2}$.

In these calculations, the parameters of DE and TS are the same as those for phase stability calculations except $Gen_{\max} = 75$, $Iter_{\max} = 100n_{var}$, and $Sc_{\max} = 12n_{var}$ where $n_{var} = 3$. These parameter values have been

Table 4. Results of phase stability and equilibrium calculations for example 2 using TS and DE.

Feed			SR (%) for		NFE(CPUt, s) for	
Z	T, K	Global optimum	DE	TS	DE	TS
(0.5, 0.5, 0)	358	RTPDF = 0.0 at $X_i = (0.5, 0.5, 0)$ or $x = (0.075325, 0.075325, 0.424675, 0.424675)$	100	100	5112 (1.4)	536 (0.14)
	355	RTPDF = −0.032057 at $X_i = (0.727391, 0.892842, -0.620233)$ or $x = (0.035139, 0.200590, 0.072019, 0.692252)$	100	99	5178 (1.3)	550 (0.14)
		$\Delta\hat{g} = -2.058125$ at $X_{i,1} = (0.716726, 0.878827, -0.595553)$ and $X_{i,2} = (0.488798, 0.480420, 0.030782)$; or $x_{i,1} = (0.078272, 0.069894, 0.441308, 0.410526)$ and $x_{i,2} = (0.039748, 0.201849, 0.081425, 0.676978)$	24	0	10623 (5.9)	—
(0.2, 0.4, 0.4)	355	RTPDF = −0.223934 at $X_i = (0.146452, 0.732001, 0.121547)$ or $x = (0.010354, 0.595904, 0.257644, 0.136098)$	100	100	5178 (1.3)	524 (0.13)
		$\Delta\hat{g} = -1.302752$ at $X_{i,1} = (0.163826, 0.575748, 0.260426)$ and $X_{i,2} = (0.217557, 0.314700, 0.467743)$; or $x_{i,1} = (0.023539, 0.435461, 0.400713, 0.140287)$ and $x_{i,2} = (0.029435, 0.126577, 0.655865, 0.188123)$	100	74	11592 (6.1)	780 (0.41)

modified because phase equilibrium problems are generally more difficult to solve compared to stability ones (Srinivas and Rangaiah, 2007). Results for these calculations are also reported in Table 4. In this case, both DE and TS face difficulties in finding the global minimum of $\Delta\hat{g}$; SR of DE is 24% whereas TS fails to find the global minimum. This problem is challenging due to the presence of a trivial solution ($Z_i = X_{i,1} = X_{i,2}$) which has an objective value (−2.057331) very comparable to the global minimum (−2.058125). Phase equilibrium compositions given in Table 4 are consistent with those reported by McDonald and Floudas (1996) and Lee *et al.* (1999). Note that there are differences between the objective function values in Table 4 and those given in these references because the previous works incorporated the Gibbs free energies of formation into the objective function (i.e. the total Gibbs free energy) while we have used the transformed Gibbs free energy of mixing as the objective. Both approaches are equivalent and can be used for phase equilibrium calculations in reactive systems.

Finally, consider a vapor mixture of ethanol, acid acetic, and ethyl acetate with initial composition of $n_{i,F} = (0.2, 0.4, 0.4, 0.0)$ at 355 K and 1 atm. At these conditions, $Z_i = (0.2, 0.4, 0.4)$, $\hat{n}_{i,F} = (0.2, 0.4, 0.4)$ and $\hat{n}_{T,F} = 1$, and this mixture also shows a vapor-liquid equilibrium with $K_{eq,1} = 18.670951$. Stability test is performed using Eqs. (36)–(38) and the same decision variables as in the previous feeds. Both TS and DE are capable of finding the global optimum of RTPDF without any difficulty (Table 4). Based on stability result, we have performed the minimization of transformed Gibbs free energy using Eqs. (25), (37)–(39). The global optimization of $\Delta\hat{g}$ is performed with respect to three decision variables $\lambda_{i,1} \in (0, 1)$. The transformed mole numbers are given by:

$$\begin{aligned} \hat{n}_{1,1} &= 0.2\lambda_{1,1} \\ \hat{n}_{2,1} &= 0.4\lambda_{2,1}, \\ \hat{n}_{3,1} &= 0.4\lambda_{3,1} \end{aligned} \tag{41}$$

and Eq. (9) is used to determine $\hat{n}_{i,2}$. The results of Gibbs energy minimization are summarized in Table 4. DE is 100% reliable, but it requires significant computational effort; although TS is very efficient, it may fail to find the equilibrium compositions as shown in Table 4.

5.3. Discussion

In this study, relative performance of TS and DE is in accordance with that reported for equilibrium calculations of non-reactive mixtures (Srinivas and Rangaiah, 2007). The differences between the performance of TS and DE may be associated with the efficacy of their escaping strategies. DE applies mutation and crossover strategies on a specific population to diversify the search and to escape from the local optimum. In this algorithm, the best solution that has been identified over all generations is reported after satisfying the convergence criterion. On the contrary, TS uses the best point in each iteration to create the new test points and to escape from the local solution, even though the current best solution may be worse than the best solutions found in the earlier iterations.

For comparison purposes, we have solved examples 1 and 2 using the SA method (Bonilla-Petriciolet *et al.*, 2006) with the following cooling schedule: initial annealing temperature = 10, number of iterations before reduction of annealing temperature = 5, and temperature reduction factor = 0.85. Each example was solved using 100 trials with random initial values via random number seed. Results of these calculations are summarized in Table 5. It appears that DE and TS are better than SA in terms of both NFE and CPUt but the order of reliability of these methods is: SA $>$ DE $>$ TS in both reactive phase stability and equilibrium calculations.

Table 5. Performance comparison of SA, DE and TS for reactive phase stability and equilibrium calculations for examples 1 and 2.

		SA			DE[a]			TS[a]		
Objective function		SR,%	NFE	CPUt	SR,%	NFE	CPUt	SR,%	NFE	CPUt
Example 1	*RTPDF*	100	23869	0.33	100	7677	0.07	86	595	0.004
	$\Delta\hat{g}$	92	22201	0.53	74	10841	0.15	26	578	0.008
Example 2	*RTPDF*[b]	100	18163	6.1	100	5112	1.4	100	536	0.14
	RTPDF[c]	100	17305	5.6	100	5178	1.3	99	550	0.14
	$\Delta\hat{g}$[c]	44	26319	17.5	24	10623	5.9	0	—	—
	RTPDF[d]	100	17005	5.7	100	5178	1.3	100	524	0.13
	$\Delta\hat{g}$[d]	100	27106	17.7	100	11592	6.1	74	780	0.41

[a] Parameters of TS and DE are those described in Example 2;
[b] Results for feed $Z_i = (0.5, 0.5, 0.0)$ at 358 K and 1 atm;
[c] Results for feed $Z_i = (0.5, 0.5, 0.0)$ at 355 K and 1 atm;
[d] Results for feed $Z_i = (0.2, 0.4, 0.4)$ at 355 K and 1 atm.

6. Conclusions

This study shows, for the first time, that both TS and DE can be successful, if they are properly implemented, for solving phase stability and equilibrium calculations in multi-component and multi-reactive systems using transformed composition variables. Also, we demonstrate that performance profiles can be used to systematically tune the algorithm parameters of these methods. In general, the performance of DE is better than TS, but requires more NFE and CPUt. For both stability and equilibrium calculations, the maximum number of generations/iterations significantly affects the performance of these stochastic methods. Depending on problem characteristics, proper value for the termination criterion: $Sc_{\max}$ and the maximum number of generations/iterations should be selected to improve the performance of these stochastic methods.

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7. Exercises

(1) Consider a hypothetical reacting ternary mixture $A_1 + A_2 \Leftrightarrow A_3$ with liquid-liquid equilibrium (Iglesias-Silva *et al.*, 2006), where reaction equilibrium constant is independent of temperature, and thermodynamic properties are calculated using the Margules solution model $\frac{G^{ex}}{RT} = 3.6x_1x_2 + 2.4x_1x_3 + 2.3x_2x_3$. This system shows complex equilibrium behavior for some values of the reaction equilibrium constant. The third component is selected as the reference substance. For a transformed feed $Z_i = (0.6, 0.4)$, $\hat{n}_{T,F} = 1.0$ and $K_{eq,1} = 0.9825$, determine if this mixture is stable; if it is not stable, calculate the corresponding equilibrium compositions. Use both TS and DE, and compare their performance for different values of NP, NP_{init}, $Iter_{\max}$ and $Gen_{\max}$. [*Solution:* RTPDF $= -0.020055$ at $X_i = (0.83575, 0.16425)$; $\Delta\hat{g} = -0.144508$ at $X_{i,1} = (0.484538, 0.515462)$ and $X_{i,2} = (0.815044, 0.184956)$].

(2) Consider a six-component mixture with only one chemical reaction $2A_5 \Leftrightarrow A_6$ but with four inert components: A_1, A_2, A_3 and A_4. This mixture shows vapor-liquid equilibrium at 75°C and 1.5 atm where the reaction equilibrium constant is 5.0. Assume that the vapor and liquid phases behave as an ideal gas and ideal solution, thermodynamic data are given in Table B4, and choose component A_6 as the reference for calculating the transformed mole fractions. Establish the equilibrium compositions for a transformed feed $Z_i = (0.00497, 0.605, 0.0324, 0.31, 0.04763)$ and $\hat{n}_{T,F} = 1.0$ using both TS and DE. Construct the quartile sequential plots for different values of *NP* and NP_{init}. Perform at least 25 runs with random initial values for this purpose. Compare and discuss the results obtained from these trials. Which of the two methods is better, and why? [*Solution:* RTPDF = −0.004072 at $X_i = (0.005931, 0.736912, 0.033105, 0.180695, 0.043356)$; $\Delta\hat{g} = -0.144508$ at $X_{i,1} = (0.004923, 0.598568, 0.032360, 0.316323, 0.047827)$ and $X_{i,2} = (0.005899, 0.732032, 0.033198, 0.185129, 0.043742)$].

Appendix A

To illustrate the application of the transformation procedure of Ung and Doherty (1995a, 1995b), consider a ternary mixture that follows the reaction: $A_1 + A_2 \leftrightarrow A_3$. For this system, we have $c = 3$, $r = 1$ and $c - r = 2$ transformed composition variables. For variable transformation, it is necessary to select a set of r reference components such that N is an invertible matrix. This requires that all the reactions must involve at least one of the reference components, an inert component can not be a reference component and no two reference components can have identical stoichiometric coefficients in each reaction (Ung and Doherty, 1995a).

If A_3 is selected as the reference component, N is invertible and equal to unity. In this case, $v_1 = -1$, $v_2 = -1$, and $v_{TOT} = -1$, and so the transformed mole numbers and fractions are given by:

$$\hat{n}_1 = n_1 + n_3, \tag{A1}$$

$$\hat{n}_2 = n_2 + n_3, \tag{A2}$$

$$X_1 = \frac{\hat{n}_1}{\hat{n}_T} = \frac{n_1 + n_3}{n_T + n_3} = \frac{x_1 + x_3}{1 + x_3}, \tag{A3}$$

$$X_2 = \frac{\hat{n}_2}{\hat{n}_T} = \frac{n_2 + n_3}{n_T + n_3} = \frac{x_2 + x_3}{1 + x_3} = 1 - X_1, \tag{A4}$$

where $n_T = n_1 + n_2 + n_3$, $\hat{n}_T = \hat{n}_1 + \hat{n}_2$ and $X_1, X_2 \in [0, 1]$. Note that, for this mixture, any of the three components can be used as the reference component to define the transformed composition variables ($\hat{n}$ and X).

If the initial composition (mole numbers or fractions) of the reactive mixture is available, the corresponding transformed variables can be obtained by using the above equations. For example, consider a mixture with initial composition: $n_{i,F} = (0.3, 0.2, 0.5)$. Using Eqs. (A1)–(A4), transformed mole numbers are: $\hat{n}_{1,F} = 0.3 + 0.5 = 0.8$, $\hat{n}_{2,F} = 0.2 + 0.5 = 0.7$, and $\hat{n}_{T,F} = 0.8 + 0.7 = 1.5$; while transformed mole fractions are: $Z_1 = 0.8/1.5 \cong 0.5333$ and $Z_2 = 0.7/1.5 = 1 - Z_1 \cong 0.4667$.

The transformed composition variables take the same value before, during and after reaction (Ung and Doherty, 1995a) but depend on the initial composition. Therefore, the mole fractions that are chemically equilibrated, satisfy the stoichiometry requirements and corresponding to Z must be obtained. To do this, we need to find the composition of reference components that satisfy the chemical equilibrium constraints. In the general case, for a set of $c - r$ specified transformed variables X_i, the reference mole fractions x_{ref} are calculated using Eq. (5) and the equilibrium constants for each reaction $K_{eq,k}$; this requires solution of r nonlinear equations given by Eq. (6) because $K_{eq,k}$ are non-linear functions of x. After knowing x_{ref}, the corresponding mole fractions of $c - r$ non-reference components are calculated using Eq. (5) again. For this transformation procedure $X \rightarrow x$, any solver such as the bisection method (for systems with only one reaction) or the Newton method (for multi-reaction systems) can be used to find x_{ref}. Figure A1 presents the steps in the variable transformation between X and x. Note that if different models are used in the calculation of thermodynamic properties for the different phases, the procedure of variable transformation must be performed for each model at specified X. In these cases, the mole fraction x that corresponds to the lower value of transformed Gibbs free energy is selected.

For illustrative purposes, let us consider that this ternary mixture is an ideal liquid phase (i.e. $\gamma_i = 1.0$). The chemical equilibrium constant is

1. Start with the specified components, composition (mole numbers or fractions) of reactive mixture, T, P and the thermodynamic models.
2. Select r reference components, and determine $\boldsymbol{N}$ and $\boldsymbol{N}^{-1}$. Calculate the equilibrium constant, $K_{eq,k}$ of each of all reactions at the given T using relevant thermodynamic equations (e.g. see Table 2).
3. Calculate X using Eqs. (3)−(5), and choose initial values for $\boldsymbol{x}_{\text{ref}}$.
4. Using $\boldsymbol{x}_{\text{ref}}$, $c - r$ values of X_i obtained in step 3, and rearranged Eq. (5): $x_i = X_i\,(1 - \boldsymbol{v}_{TOT}\boldsymbol{N}^{-1}\boldsymbol{x}_{\text{ref}}) + \boldsymbol{v}_i\,\boldsymbol{N}^{-1}\boldsymbol{x}_{\text{ref}}$, determine mole fractions of non-reference components.
5. Calculate the activity, a_i of each of all components using the specified thermodynamic model for the phase and x_i found in Step 4.
6. Substitute values of equilibrium constants and activities in the r non-linear equations (Eq. 6). If these equations are not satisfied, use any solver such as the bisection method (for situations with only one reaction) or the Newton method (for multi-reaction systems) to find new values of $\boldsymbol{x}_{\text{ref}}$, and then go to step 4. Note that the gradient for the Newton method can be calculated via finite differences.
7. If the r non-linear equations are satisfied to the desired tolerance level, current values of $\boldsymbol{x}$ are chemically equilibrated and satisfy the stoichiometry and equilibrium requirements.

Figure A1. Steps in the composition transformation procedure $X \rightarrow x$.

defined as

$$K_{eq,1} = \frac{a_3}{a_1 a_2} = \frac{x_3\gamma_3}{x_1\gamma_1 x_2\gamma_2}. \tag{A5}$$

We can rearrange Eqs. (A3) and (A4) to obtain

$$x_i = X_i(1 + x_3) - x_3 \quad \text{for } i = 1, 2. \tag{A6}$$

Substituting Eq. (A6) into Eq. (A5), we find

$$f(x_3) = K_{eq}[X_1(1 + x_3) - x_3][X_2(1 + x_3) - x_3]\gamma_1\gamma_2 - x_3\gamma_3 = 0. \tag{A7}$$

Therefore, if we specify X, mole fractions x that simultaneously satisfy the chemical equilibrium equation and map onto the specified values of the transformed composition variables are determined by solving Eq. (A7) for the reference component x_3. For our example, if $K_{eq,1} = 1.0$, $\gamma_i = 1.0$ and $Z_i = (0.5333, 0.4667)$, solving $f(x_3)$ we find *chemically equilibrated* mole fractions in the given feed as $z_i = (0.4537, 0.3758, 0.1705)$. Note that these are not the given mole fractions in the feed but are chemically equilibrated mole fractions.

Now, consider this mixture but with the presence of liquid-liquid equilibrium while the reaction occurs at 323.15 K and $K_{eq,1} = 3.5$. In these conditions, we calculate the activity coefficient γ_i using the Margules solution equation:

$$T \ln \gamma_k = \frac{1}{2} \sum_{i=1}^{c} \sum_{j=1}^{c} (A_{ik} + A_{jk} - A_{ij}) x_i x_j, \tag{A8}$$

with $A_{ij} = A_{ji}$, $A_{ii} = 0.0$, $A_{12} = 478.6$, $A_{13} = 1074.484$ and $A_{23} = 626.9$. Note that Margules model is used to represent the liquid-phase non-idealities because there is no phase split (i.e. liquid-liquid phase equilibrium) for an ideal liquid (i.e. $\gamma_i = 1.0$). The chemical potential of each component and the transformed Gibbs free energy of mixing are respectively

$$\frac{\Delta \mu_i}{RT} = \ln(x_i \gamma_i), \tag{A9}$$

$$\Delta \hat{g}_1 = X_1 \ln(x_1 \gamma_1) + X_2 \ln(x_2 \gamma_2), \tag{A10}$$

where x_i results from $X \to x$ using Eqs. (A5)–(A7). Note that $f(x_3)$ is a non-linear function with x_3 as unknown and has to be solved for given X.

Figure A2 shows the plot of $\Delta \hat{g}_1$ versus X_1 for this mixture. This plot is obtained by varying X_1 from 0.0 to 1.0, calculating the associated mole fractions x for each X_1 (using Algorithm of Fig. A1), and evaluating $\Delta \hat{g}_1$ (Eq. A10). As shown in this figure, this reactive mixture exhibits a phase split for Z_1 between 0.497527 and 0.840050. Any trial composition inside this range will show phase equilibrium. For our analysis, we have selected the same feed $Z_i = (0.5333, 0.4667)$ and $\hat{n}_{T,F} = 1.0$. To evaluate phase stability, we need to minimize the reactive plane distance function, obtained from Eqs. (10) and (A9):

$$RTPDF = X_1(\ln(x_1 \gamma_1) - \ln(z_1 \gamma_1)) + X_2(\ln(x_2 \gamma_2) - \ln(z_2 \gamma_2)). \tag{A11}$$

Note that RTPDF can be optimized with respect to $X_1 \in (0, 1)$ because X_2 is obtained from the equality constraint: $X_2 = 1 - X_1$. The global optimum for this feed is -0.406606 at $X_i = (0.9527, 0.0473)$. As expected, the given feed is unstable.

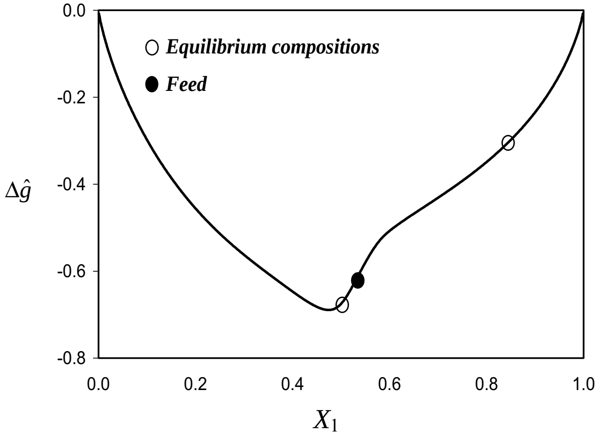

Figure A2. Transformed molar Gibbs free energy of mixing versus X_1 for reactive mixture: $A_1 + A_2 \leftrightarrow A_3$ at 323.15 K and $K_{eq,1} = 3.5$.

For performing phase equilibrium calculations, the Gibbs free energy function is obtained from Eqs. (1) and (A9) as:

$$\begin{aligned}\Delta\hat{g} &= \hat{n}_{1,1}\ln(x_{1,1}\gamma_{1,1}) + \hat{n}_{2,1}\ln(x_{2,1}\gamma_{2,1}) \\ &\quad + \hat{n}_{1,2}\ln(x_{1,2}\gamma_{1,2}) + \hat{n}_{2,2}\ln(x_{2,2}\gamma_{2,2}),\end{aligned} \qquad \text{(A12)}$$

where $\hat{n}_{i,j}$ is the transformed mole number of component i in liquid phase j. Note that the transformation procedure $X \rightarrow x$ is performed for each liquid phase, taking into account its corresponding transformed composition $\hat{n}_{i,j}$. We have two decision variables: $\lambda_{1,1}$ and $\lambda_{2,1}$ for this example. They are used to calculate $\hat{n}_{1,1} = 0.5333\lambda_{1,1}$ and $\hat{n}_{2,1} = 0.4667\lambda_{2,1}$ as well as the transformed composition of the second liquid phase by $\hat{n}_{1,2} = 0.5333 - 0.5333\lambda_{1,1}$ and $\hat{n}_{2,2} = 0.4667 - 0.4667\lambda_{1,1}$ (Eqs. 7 and 9). The global optimum of $\Delta\hat{g}$ is -0.639429 at $X_{i,1} = (0.497527, 0.502473)$ and $X_{i,2} = (0.840050, 0.15995)$, which are the transformed mole fractions at liquid-liquid equilibrium; the equilibrium compositions in conventional mole fractions are: $x_{i,1} = (0.056907, 0.066186, 0.876907)$ and $x_{i,2} = (0.829728, 0.105473, 0.064529)$.

Appendix B

Thermodynamic data and model parameters for all reactive systems used in this chapter are given in Tables B1–B5.

Table B1. Thermodynamic data for the methyl *tert*-butyl ether (MTBE) reaction system with inert at 10 atm and 373.15 K.

	Parameters of pure component				u_{ij} in the Wilson model (cal/mol)			
Component[1]	A_i	B_i	C_i	V_i	1	2	3	4
1	6.84132	923.201	239.99	93.33	—	169.9953	−60.1022	—
2	8.07372	1578.23	239.382	44.44	2576.8532	—	1483.2478	2283.8726
3	6.87201	1116.825	224.744	118.8	271.5669	−406.3902	—	—
4	6.80896	935.86	238.73	100.39	—	382.3429	—	—

$\log_{10} P_i^{sat} = A_i - \frac{B_i}{T+C_i}$ where P_i^{sat} in mmHg and T in °C.

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

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(\frac{-u_{ij}}{RT}\right)$$

$K_{eq,1} = \frac{a_3}{a_1 a_2}$ where $a_i = x_i \gamma_i$ for liquid phase and $a_i = x_i P / P_i^{sat}$ for vapor phase.

[1] 1: Isobutene, 2: Methanol, 3: MTBE, and 4: Butane.

Table B2. Thermodynamic data for the reactive system for *tert*-amyl methyl ether (TAME) synthesis at 335 K and 1.5 atm.

	Parameters of pure component					u_{ij} in the Wilson model (cal/mol)			
Component[1]	A_i	B_i	C_i	D_i	V_i	1	2	3	4
1	74.527	−5232.2	−8.1482	8.474E-06	0.10868	—	478.8	1376.5	−611.75
2	82.614	−5586.1	−9.4429	1.0858E-05	0.10671	−477.94	—	968.81	−386.04
3	23.5347	−3661.468	−32.77		0.04069	9772.3	10147	—	4826.3
4	20.9441	−2936.223	−47.70385		0.13345	951.33	712.33	−177	—

$$\ln P_i^{sat} = A_i + \frac{B_i}{T} + C_i \ln T + D_i T^2 \text{ for } i = 1, 2$$

$$\ln P_i^{sat} = A_i + \frac{B_i}{T + C_i} \text{ for } i = 3, 4$$

where P_i^{sat} in Pa and T in Kelvin.

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{c} x_j \Lambda_{ij}\right) - \sum_{k=1}^{c}\left(x_k \Lambda_{ki} \Big/ \sum_{j=1}^{c} x_j \Lambda_{kj}\right)$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(\frac{-u_{ij}}{RT}\right)$$

$$K_{eq,1} = \frac{a_4^2}{a_1 a_2 a_3^2} \text{ where } a_i = x_i \gamma_i \text{ for liquid phase and } a_i = x_i P / P_i^{sat} \text{ for vapor phase.}$$

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[1] 1: 2-Methyl-1-butene, 2: 2-Methyl-2-butene, 3: Methanol, and 4: TAME.

Table B3. Thermodynamic data for the reaction for butyl acetate production at 298.15 K and 1 atm.

			u_{ij} in the UNIQUAC model (cal/mol)			
Component[1]	Q	R_u	1	2	3	4
1	2.072	2.2024	—	−131.7686	−343.593	−298.4344
2	3.052	3.4543	148.2833	—	68.0083	82.5336
3	1.4	0.92	527.9269	581.1471	—	394.2396
4	4.196	4.8724	712.2349	24.6386	756.4163	—

$$\ln \gamma_i = \ln \gamma_i^E + \ln \gamma_i^R$$

$$\ln \gamma_i^E = \ln \frac{\phi_i}{x_i} + 5Q_i \ln \frac{\phi_i}{x_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{c} x_j l_j$$

$$\ln \gamma_i^R = Q_i \left(1 - \ln\left(\sum_{j=1}^{c} \theta_j \tau_{ji}\right) - \sum_{j=1}^{c} \left(\frac{\theta_j \tau_{ji}}{\sum_{l=1}^{c} \theta_l \tau_{li}}\right)\right)$$

$$\theta_i = \frac{Q_i x_i}{\sum_{j=1}^{c} Q_j x_j} \quad \phi_i = \frac{R_{u,i} x_i}{\sum_{j=1}^{c} R_{u,j} x_j}$$

$$l_i = 5(R_{u,i} - Q_i) - (R_{u,i} - 1) \quad K_{eq,1} = \frac{a_3 a_4}{a_1 a_2} \text{ where } a_i = x_i \gamma_i.$$

[1] 1: Acetic acid, 2: n-Butanol, 3: Water, and 4: n-Butyl acetate.

Table B4. Thermodynamic data for Example 1.

Component	A_i	B_i	C_i	γ_i
1	7.6313	1566.69	273.419	1.0
2	7.11714	1210.595	229.664	1.0
3	7.44777	1488.99	264.915	1.0
4	8.1122	1592.864	226.184	1.0
5	7.9701	1521.23	233.97	1.0
6	6.8664	1188.05	226.276	1.0

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

where P_i^{sat} in mmHg and T in °C.

$$K_{eq,1} = \frac{a_4}{a_3} \quad K_{eq,2} = \frac{a_4}{a_5} \quad K_{eq,3} = \frac{a_6}{a_4}$$

where $a_i = x_i \gamma_i$ for liquid phase and $a_i = x_i P / P_i^{sat}$ for vapor phase.

Table B5. Thermodynamic data for Example 2.

	Parameters of pure component			τ_{ij} in the NRTL model			
Component[1]	A_i	B_i	C_i	1	2	3	4
1	9.95614	1440.52	−60.44	0.0	1.3941	0.6731	−0.2019
2	9.6845	1644.05	−39.63	−1.0182	0.0	0.007	−0.4735
3	9.22298	1238.71	−56.15	0.1652	0.5817	0.0	1.7002
4	10.09171	1668.21	−45.14	2.1715	1.6363	1.9257	0.0
	$\log_{10} P_i^{sat} = A_i - \frac{B_i}{T+C_i}$ where P_i^{sat} in N/m^2 and T in K.			$\alpha_{ij} = 0.3$ $\ln \gamma_i = \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{j=1}^{c} G_{ji} x_j} + \sum_{j=1}^{c} \frac{G_{ij} x_j}{\sum_{l=1}^{c} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{l=1}^{c} \tau_{lj} G_{lj} x_l}{\sum_{l=1}^{c} G_{lj} x_l} \right)$ $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$			
	$K_{eq,1} = \frac{a_3 a_4}{a_1 a_2}$ where $a_i = x_i \gamma_i$ for liquid phase and $a_i = x_i P / P_i^{sat}$ for vapor phase.						

[1] 1: Ethanol, 2: Acetic acid, 3: Ethyl acetate, and 4: Water.