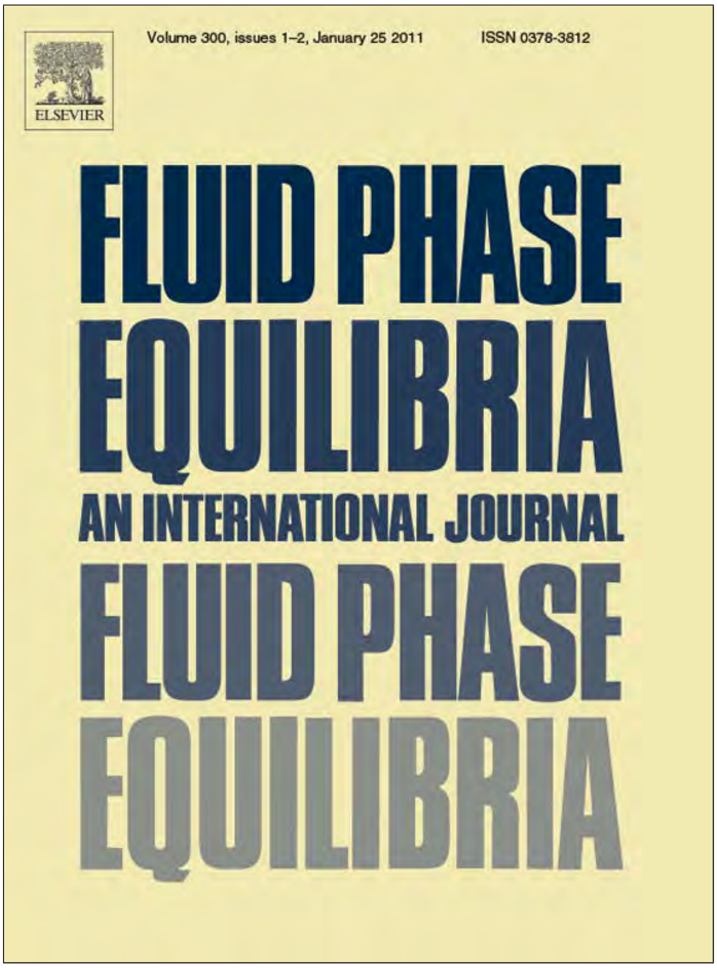

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Constrained and unconstrained Gibbs free energy minimization in reactive systems using genetic algorithm and differential evolution with tabu list

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ABSTRACT

Phase equilibrium modeling plays an important role in design, optimization and control of separation processes. The global optimization problem involved in phase equilibrium calculations is very challenging due to the high non-linearity of thermodynamic models especially for multi-component systems subject to chemical reactions. To date, a few attempts have been made in the application of stochastic methods for reactive phase equilibrium calculations compared to those reported for non-reactive systems. In particular, the population-based stochastic methods are known for their good exploration abilities and, when optimal balance between the exploration and exploitation is found, they can be reliable and efficient global optimizers. Genetic algorithms (GAs) and differential evolution with tabu list (DETL) have been very successful for performing phase equilibrium calculations in non-reactive systems. However, there are no previous studies on the performance of both these strategies to solve the Gibbs free energy minimization problem for systems subject to chemical equilibrium. In this study, the constrained and unconstrained Gibbs free energy minimization in reactive systems have been analyzed and used to assess the performance of GA and DETL. Specifically, the numerical performance of these stochastic methods have been tested using both conventional and transformed composition variables as the decision vector for free energy minimization in reactive systems, and their relative strengths are discussed. The results of these strategies are compared with those obtained using SA, which has shown competitive performance in reactive phase equilibrium calculations. To the best of our knowledge, there are no studies in the literature on the comparison of reactive phase equilibrium using both the formulations with stochastic global optimization methods. Our results show that the effectiveness of the stochastic methods tested depends on the stopping criterion, the type of decision variables, and the use of local optimization for intensification stage. Overall, unconstrained Gibbs free energy minimization involving transformed composition variables requires more computational time compared to constrained minimization, and DETL has better performance for both constrained and unconstrained Gibbs free energy minimization in reactive systems.

1. Introduction

The accurate modeling of phase equilibrium plays a major role in the design, development, operation, optimization and control of chemical processes. For example, phase behavior has significant impact on equipment and energy costs of separation and purification processes in chemical industry. Further, solving phase equilibrium problems is a dominant task in the process simulation software. The development of reliable methods has long been a challenge and is still a research topic of continual interest [1]. The determination of the number of phases, their identity, and composition at equilibrium of multi-component systems is a complex issue and presents several numerical difficulties [1]. Chemical reactions, if present, increase the complexity and dimensionality of phase equilibrium problems, and so phase split calculations in reactive systems are more challenging due to non-linear interactions among phases and reactions [2]. This fact has prompted growing interest in reliable and efficient methods for the simultaneous computation of physical and chemical equilibrium.

The phase distribution and composition at equilibrium of a reactive mixture are determined by the global minimization of Gibbs free energy (G) subject to mass balance and chemical equilibrium constraints [3]. Specifically, the global optimization problem for reactive phase equilibrium calculations follows the form: minimize $F_{obj}(\boldsymbol{u})$ subject to $h_j(\boldsymbol{u}) = 0$ for $j = 1, 2, \ldots, m$ and $\boldsymbol{u} \in \Omega$ where $\boldsymbol{u}$ is a vector of continuous variables in the domain $\Omega \in \Re^n$, m is

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the number of equality constraints related to material balances and chemical equilibrium, and $F_{obj}(\boldsymbol{u}) = G: \Omega \Rightarrow \Re$ is a real-valued function. The domain Ω is defined by the upper and lower limits of each decision variable, which are composition variables. This optimization problem can be formulated using either conventional composition variables (i.e., mole fractions or numbers), or transformed composition variables [3–5]. Based on the problem formulation and the numerical strategy used for this minimization, the methods can be grouped into two main categories: equation-solving methods and direct optimization strategies. In addition, depending on the handling of material balance constraints, these strategies can also be classified as either stoichiometric or non-stoichiometric [3,6].

In general, classical strategies for determining the phase equilibrium of non-reactive systems have been extended and applied to systems subject to chemical reactions [3]. Equation-solving methods are based on the solution of non-linear equations obtained from the stationary conditions of the optimization criterion. Local search methods with and without decoupling strategies are frequently used to solve these equations in conjunction with the mass balance and chemical equilibrium restrictions [7]. However, they are prone to severe computational difficulties and may fail to converge to the correct solution when initial estimates are not suitable, especially for non-ideal multi-component and multi-reactive systems [1,3,6]. Note that the minimization of G in reactive systems involves many complexities because it is generally non-convex, constrained, highly non-linear with many decision variables, and often has unfavorable attributes such as discontinuity and non-differentiability (e.g., when cubic equations of state or asymmetric models are used for modeling thermodynamic properties). Additional complexities arise near the phase boundaries, in the vicinity of critical points or saturation conditions, and when the same model is used for determining the thermodynamic properties of the mixture [1,3]. As consequence, G may have several local minima including trivial and non-physical solutions. In these conditions, conventional numerical methods are not suitable for performing reactive phase equilibrium calculations.

On the other hand, a number of optimization strategies for performing the minimization of G in reactive systems have been proposed, and they comprise local and global methods (e.g., [2,3,5,6,8–23]). The use of Lagrange multipliers is usually the preferred approach for G minimization but its performance is highly dependent on initial estimates of Lagrange multipliers [17]. There has been significant and increasing interest in the development of deterministic and stochastic global strategies for reliably solving reactive phase equilibrium problems. Studies on deterministic reactive phase equilibrium calculations have been focused on the application of the linear programming [9,21], branch and bound global optimization [11], homotopy continuation methods [13,15,20], and interval analysis using an interval-Newton/generalized bisection algorithm [16]. Although these methods have proven to be promising, some of them are model-dependent, may require problem reformulation or significant computational time for multi-component systems [1,24].

Alternatively, stochastic optimization techniques have often been found to be as reliable and effective as deterministic methods. Further, they offer more advantages for the global optimization of G. These methods are robust, require a reasonable computational effort for the optimization of multivariable functions (generally less time than deterministic approaches), applicable to ill-structure or unknown structure problems, require only objective function calculations and can be used with all thermodynamic models. In fact, it appears that they may fulfill the requirements of an ideal algorithm: reliability, generality and efficiency. To date, a few attempts have been made in the application of stochastic methods for reactive phase equilibrium calculations, compared to those reported for non-reactive systems [14,19,22,23,25]. Specifically, Lee et al. [14] introduced the application of the random search method of Luus and Jaakola for the global minimization of G using a non-stoichiometric formulation. On the other hand, Bonilla-Petriciolet et al. [19] formulated the unconstrained optimization problem for G minimization using simulated annealing (SA) and transformed composition variables. In another study, particle swarm optimization (PSO) and several of its variants have been applied for reactive phase equilibrium calculations using transformed composition variables [22]. Recently, our group [23] has tested and compared the performance of differential evolution (DE) and tabu search (TS) for the global minimization of G using reaction-invariant composition variables. Finally, Reynolds et al. [25] outlined a general procedure for the global optimization of G in reactive systems using SA and a non-stoichiometric approach. Results of these studies have shown the potential of stochastic optimization solvers for phase equilibrium calculations subject to chemical reactions.

In particular, the population-based stochastic methods are known for their good exploration abilities; when optimal balance between the exploration and exploitation is found, they can be reliable and efficient global optimizers. This is because at each generation/iteration a whole population of potential solutions is improved rather than a single solution. A variety of population-based stochastic methods have been proposed for chemical engineering applications including the modeling of phase equilibrium, e.g. [26–29]. Specifically, genetic algorithms (GAs) and differential evolution with tabu list (DETL) have been very successful for performing phase equilibrium calculations in non-reactive systems [26,28]. However, to the best of our knowledge, there are no studies on the performance of both these strategies for G minimization in systems subject to chemical equilibrium. These methods are suitable and promising for overcoming the numerical difficulties of this global optimization problem.

In this study, the constrained and unconstrained Gibbs free energy minimization in reactive systems have been analyzed and used to assess the performance of GA and DETL. Specifically, the numerical performance of these stochastic methods have been tested using both conventional and transformed composition variables as the decision vector for G minimization, and their relative strengths are discussed. The results of GA and DETL are compared with those obtained using SA, which has shown a competitive performance in reactive phase equilibrium calculations [19]. Our results on a variety of reactive systems indicate that DETL is superior to SA and GA for both the constrained and unconstrained Gibbs free energy minimization in reactive systems.

2. Formulation of the Gibbs free energy minimization in reactive systems

2.1. Gibbs free energy function

Classical thermodynamics indicates that, at constant temperature T and pressure P, the equilibrium for a c multi-component and π multi-phase system is achieved when the G function is at the global minimum [1]. This thermodynamic function is expressed as a linear combination of the chemical potential of each component in each phase, then

$$G = \sum_{j=1}^{\pi} \sum_{i=1}^{c} n_{ij} \mu_{ij} \tag{1}$$

where n_{ij} is the number of moles of component i present in phase j and μ_{ij} is the chemical potential of component i in phase j, respectively.

For reactive phase equilibrium, the mass balance restrictions and non-negativity requirements are usually formulated using the conservation of chemical elements in the components [3,14]

$$\sum_{i=1}^{c}\sum_{j=1}^{\pi} d_{li} n_{ij} = b_l \quad l = 1, \ldots, m_e \tag{2}$$

where d_{li} represents the number of gram-atoms of element l in component i, b_l is the total number of gram-atoms of element l in the system, and m_e is the number of elements, respectively. So, the bounds on n_{ij} are given by

$$0 \le d_{li} n_{ij} \le b_l \quad i = 1, \ldots, c; \quad j = 1, \ldots, \pi; \quad l = 1, \ldots, m_e \tag{3}$$

Therefore, to determine the phase equilibrium compositions in reactive systems, it is necessary to find the global minimum of Eq. (1) with respect to n_{ij} subject to constraints given by Eq. (2) and in the region bounded by Eq. (3). The expressions for G and its mathematical properties depend completely on the structure of the thermodynamic equation(s) chosen to model each of the phases that may exist at equilibrium [26].

Alternatively, the G function in reactive systems can be expressed in terms of transformed composition variables that have been introduced by different research groups [4,5] to provide a simpler framework for treating reactive systems. As stated by Ung and Doherty [4], mole numbers are not the natural composition variables to use in the modeling of reactive systems because they do not have the same dimensionality as the number of degrees of freedom (i.e., they are inconsistent with respect to the Gibbs phase rule). Therefore, in this study, we have applied the reaction-invariant composition variables proposed by Ung and Doherty [4]. These variables are based on the transformation of physical compositions, restrict the solution space to the compositions that satisfy stoichiometry requirements, and also reduce the dimension of the composition space by the number of independent reactions satisfying the Gibbs phase rule. These features allow all the procedures and algorithms used to model non-reactive mixtures to be easily modified and extended to systems subject to chemical reactions [4].

For a system of c components that undergo r independent chemical reactions, the transformed mole numbers $\hat{n}_i$ are defined by selecting r reference components

$$\hat{n}_i = n_i - \boldsymbol{\upsilon}_i \boldsymbol{N}^{-1} \boldsymbol{n}_{ref} \quad \text{for} \quad i = 1, \ldots, c - r \tag{4}$$

where n_i is the number of moles of component i, $\boldsymbol{\upsilon}_i$ is the row vector (of dimension r) of stoichiometric coefficients of component i in r reactions, $\boldsymbol{N}$ is an invertible, square matrix formed from the stoichiometric coefficients of r reference components in r reactions, and $\boldsymbol{n}_{ref}$ is a column vector (of dimension r) of moles of each of the reference components. The transformed mole fractions X_i are given by

$$X_i = \frac{\hat{n}_i}{\hat{n}_T} = \frac{x_i - \boldsymbol{\upsilon}_i \boldsymbol{N}^{-1} \boldsymbol{x}_{ref}}{1 - \boldsymbol{\upsilon}_{TOT} \boldsymbol{N}^{-1} \boldsymbol{x}_{ref}} \quad \text{for} \quad i = 1, \ldots, c - r \tag{5}$$

where x_i is the mole fraction of component i, $\boldsymbol{x}_{ref}$ is a column vector of mole fractions of r reference components, $\hat{n}_T = \sum_{i=1}^{c-r} \hat{n}_i$, and $\boldsymbol{\upsilon}_{TOT}$ is a row vector (of dimension r) where each element corresponds to the sum of stoichiometric coefficients of all components in each of the r reactions.

The transformed mole fractions (X) in reactive systems are similar to the mole fractions (x) in non-reactive mixtures, and the sum of all transformed mole fractions is equal to unity (i.e., $\sum_{i=1}^{c-r} X_i = 1$), but a transformed mole fraction can be negative or positive depending on the reference components, number and type of reactions. It is important to note that the set of X and $\hat{n}$ has the desirable property of taking the same numerical values before and after the reactions. This is in contrast to conventional mole variables x and n, which have different values for the components in the unmixed and mixed (i.e., reacting) states [4].

The transformed variables X are related to x via the reaction equilibrium constants $K_{eq,k}$:

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

where υ_{ik} is the stoichiometric coefficient of component i in reaction k, and a_i is the activity of component i. To evaluate thermodynamic properties in reactive systems using this approach, mole fractions are obtained from the transformation procedure $X \rightarrow x$ using Eqs. (5) and (6), which requires solution of one or more nonlinear equations. The resulting mole fraction values (x) satisfy the stoichiometry requirements and are chemically equilibrated [4]. In our study, bisection method is used to perform the composition transformation. Note that multiple solutions are not possible for x_{ref} during variable transformation $X \rightarrow x$ because only one solution set of x simultaneously satisfies the chemical equilibrium equations and corresponds to the specified values of the transformed composition variables [4]. For more details on this transformation procedure, see our recent work [23].

For a reactive mixture, minimizing the Gibbs free energy with respect to n_{ij} is equivalent to minimizing the transformed Gibbs free energy ($\hat{G}$) with respect to $\hat{n}_{ij}$ [4]. For a multi-phase reactive system, $\hat{G}$ is defined as

$$\hat{G} = \sum_{j=1}^{\pi}\sum_{i=1}^{c-r} \hat{n}_{ij} \mu_{ij} \tag{7}$$

where $\hat{n}_{ij}$ is the transformed mole numbers of component i in phase j. In transformed composition space, the material balances are given by

$$\sum_{j=1}^{\pi} \hat{n}_{ij} = Z_i \hat{n}_F \quad i = 1, \ldots, c - r \tag{8}$$

$$0 \le \hat{n}_{ij} \le Z_i \hat{n}_F \quad i = 1, \ldots, c - r; \quad j = 1, \ldots, \pi \tag{9}$$

where $\hat{n}_F$ is the total amount of transformed moles in the feed, and Z_i is the corresponding transformed mole fraction of component i. So, the transformed phase compositions at equilibrium are determined by the global minimization of Eq. (7) subject to constraints imposed by Eq. (8) in the feasible region defined by Eq. (9). Note that this formulation requires the transformation procedure $X \rightarrow x$ for evaluating the objective function value.

The global minimization of G and $\hat{G}$ is difficult and requires robust numerical methods since these functions are multivariable, non-convex and highly non-linear. In this study, two different optimization approaches (i.e., constrained and unconstrained), using the conventional and transformed composition variables, are adopted for global optimization of Gibbs free energy. To the best of our knowledge, there are no studies in the literature on the comparison and modeling of phase equilibrium in reactive systems using both formulations with either deterministic or stochastic global optimization methods. In the following section, formulations for both constrained and unconstrained optimization problems are described.

2.2. Constrained minimization approach

For modeling reactive systems, the chemical equilibrium condition can be evaluated from either Gibbs free-energy data or chemical equilibrium constants determined experimentally [30]. In such cases, we can use different objective functions for the constrained minimization of Gibbs energy function. In practice, Gibbs free-energy data are not available at tested conditions and the use of chemical equilibrium constants obtained from experimental measurements is more convenient. Based on this and to perform a direct comparison of results obtained employing both conventional and transformed variables as the decision vector, we have used a G function defined in terms of chemical equilibrium constants ($K_{eq,k}$). This objective function is derived from the relationship between G and $\hat{G}$ [31]. However, in our analysis, Gibbs free energy of mixing is used to avoid the calculation of pure component free energies, which do not influence the equilibrium and stability results [4].

For a multi-phase and multi-component reactive system, the transformed Gibbs free energy of mixing is defined as [4,15,31]

$$\Delta\hat{g} = \sum_{j=1}^{\pi}\sum_{i=1}^{c-r}\hat{n}_{ij}\ln(x_{ij}\gamma_{ij}) \tag{10}$$

where γ_{ij} and x_{ij} are respectively the activity coefficient and mole fraction of component i in phase j. Using the definition of transformed composition variables (Eq. (4)), $\Delta\hat{g}$ can be written as [31]:

$$\begin{aligned}\Delta\hat{g} &= \sum_{j=1}^{\pi}\sum_{i=1}^{c-r}(n_{ij} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j})\ln(x_{ij}\gamma_{ij}) \\ &= \sum_{j=1}^{\pi}\left[\sum_{i=1}^{c}n_{ij}\ln(x_{ij}\gamma_{ij}) - \sum_{i=1}^{c}\boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}\ln(x_{ij}\gamma_{ij})\right. \\ &\quad \left. - \sum_{i=c-r+1}^{c}(n_{ij} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j})\ln(x_{ij}\gamma_{ij})\right]\end{aligned} \tag{11}$$

Define an unit, row vector $\boldsymbol{e}_i = (0, \ldots, 1, \ldots, 0)$ of length r with all elements zeros except one in the ith position. For all components selected as reference for the transformed composition variables, the vector $\boldsymbol{v}_i$ can be calculated as follows

$$\boldsymbol{v}_i = \boldsymbol{e}_i\boldsymbol{N} \quad i = c-r+1, \ldots, c \tag{12}$$

This expression is applied to the matrix product

$$\boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j} = \boldsymbol{e}_i\boldsymbol{N}\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j} = n_{ij} \quad i = c-r+1, \ldots, c; \quad j = 1, \ldots, \pi \tag{13}$$

This result gives

$$\sum_{i=c-r+1}^{c}[(n_{ij} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j})\ln(x_{ij}\gamma_{ij})] = 0 \quad j = 1, \ldots, \pi \tag{14}$$

Since $\ln(\gamma_{ij}x_{ij})$ is a scalar quantity, we have

$$\begin{aligned}\sum_{i=1}^{c}\boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}\ln(x_{ij}\gamma_{ij}) &= \sum_{i=1}^{c}\boldsymbol{v}_i\ln(x_{ij}\gamma_{ij})\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j} \\ &= \left[\sum_{i=1}^{c}\boldsymbol{v}_i\ln(x_{ij}\gamma_{ij})\right]\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}\end{aligned} \tag{15}$$

Recall that $\boldsymbol{v}_i$ is the row vector (of dimension r) of stoichiometric coefficients of component i in r reactions. So, element k of the row vector $\sum_{i=1}^{c}\boldsymbol{v}_i\ln(x_{ij}\gamma_{ij})$ can be re-written as

$$\sum_{i=1}^{c}v_{ik}\ln(x_{ij}\gamma_{ij}) = \sum_{i=1}^{c}\ln(x_{ij}\gamma_{ij})^{v_{ik}} = \ln\left(\prod_{i=1}^{c}(x_{ij}\gamma_{ij})^{v_{ik}}\right) = \ln K_{eq,k} \tag{16}$$

Substituting Eq. (16) into Eq. (15), yields

$$\sum_{i=1}^{c}\boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}\ln(x_{ij}\gamma_{ij}) = \ln\boldsymbol{K}_{eq}\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j} \tag{17}$$

where $\ln\boldsymbol{K}_{eq}$ is a row vector of logarithms of chemical equilibrium constants for all r independent chemical reactions. Then, $\Delta\hat{g}$ (Eqs. (10) and (11)) becomes

$$F_G = \Delta\hat{g} = \Delta g - \sum_{j=1}^{\pi}\ln\boldsymbol{K}_{eq}\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j} \tag{18}$$

where $\Delta g = \sum_{j=1}^{\pi}\sum_{i=1}^{c}n_{ij}\ln(x_{ij}\gamma_{ij})$ is the Gibbs free energy of mixing.

Eq. (18) is an alternative objective function involving reaction equilibrium constants, for performing phase equilibrium calculations in reactive systems. This objective function must be globally minimized subject to mass balance restrictions. In this context, mass balance equations can be rearranged to reduce the number of decision variables of the optimization problem [14] and to eliminate equality constraints which are challenging for stochastic algorithms. The change in the number of moles of each reacting component, while the set of reactions is proceeding, is given by $\sum_{j=1}^{\pi}n_{ij} = n_{iF} + v_i\boldsymbol{\varepsilon}$ for $i = 1, \ldots, c$ where $n_{i,F}$ is the initial moles of component i in the feed and $\boldsymbol{\varepsilon}$ is the vector of the r extents of reactions for each of the r reactions. Under these conditions, a set of r reference components can be chosen to find the r extents of reaction in the following way [4]:

$$\boldsymbol{\varepsilon} = \boldsymbol{N}^{-1}(\boldsymbol{n}_{ref} - \boldsymbol{n}_{ref,F}) \tag{19}$$

Recall that $\boldsymbol{N}$ is an invertible, square matrix formed from the stoichiometric coefficients of the reference components in the r reactions, and $\boldsymbol{n}_{ref}$ is a column vector of moles of each of the reference components. Therefore, we can establish that

$$\sum_{j=1}^{\pi}(n_{ij} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}) = n_{iF} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,F} \quad i = 1, \ldots, c-r \tag{20}$$

Thus, the mass balance restrictions can be used as follows to reduce the number of decision variables.

$$n_{i\pi} = n_{iF} - \boldsymbol{v}_i\boldsymbol{N}^{-1}(\boldsymbol{n}_{ref,F} - \boldsymbol{n}_{ref,\pi}) - \sum_{j=1}^{\pi-1}(n_{ij} - \boldsymbol{v}_i\boldsymbol{N}^{-1}\boldsymbol{n}_{ref,j}) \quad i = 1, \ldots, c-r \tag{21}$$

Using Eq. (21), the decision variables are $c(\pi-1)+r$ mole numbers (n_{ij}). Then, the global optimization problem can be solved by minimizing F_G with respect to $c(\pi-1)+r$ decision variables n_{ij} and the remaining $c-r$ mole numbers ($n_{i\pi}$) are determined from Eq. (21) and subject to the inequality constraints $n_{i\pi} > 0$. Note that the bounds on decision variables are given by Eq. (3).

The global minimization of F_G is a constrained optimization problem. The search space in constrained optimization problems consists of both feasible and infeasible points. In reactive phase equilibrium calculations, feasible points satisfy all the mass balance constraints, Eq. (21) and bounds, Eq. (3), while infeasible points violate at least one of them (i.e., $n_{i\pi} < 0$ where $i = 1, \ldots, c-r$). In this study, the penalty function approach [32,33] is used to solve the constrained Gibbs free energy minimization in reactive systems. It is one of the popular techniques for handling constraints in the stochastic methods. This method is easy to implement and is considered efficient. It transforms the constrained problem into an unconstrained problem by penalizing infeasible solutions. In our calculations, an absolute value of constraint violation is multiplied with a high penalty weight and then added to the corresponding Gibbs free energy function. In case of more than one constraint violation, all constraint violations are first multiplied with the penalty weight, and all of them are added to the objective function value.

Specifically, the penalty function is given by

$$F_1 = \begin{cases} F_G & \text{if } \forall n_{ij} > 0 \quad i = 1, \ldots, c; \quad j = 1, \ldots, \pi, \\ F_G + p & \text{otherwise,} \end{cases} \tag{22}$$

where p is the penalty term whose value is positive. For phase equilibrium calculations, infeasible solutions (i.e., $n_{i\pi} < 0$) imply that the Gibbs free energy function of phase π cannot be determined due to the logarithmic terms of the activity or fugacity coefficients. Taking into account the inequality constraints $n_{i\pi} > 0$, the penalty term is defined as

$$p = 10 \cdot \sum_{i=1}^{n_{unf}} |n_{i\pi}| \tag{23}$$

where $n_{i\pi}$ is obtained from Eq. (21) and n_{unf} is the number of infeasible mole fractions (i.e., $n_{i\pi} < 0$ where $i = 1, \ldots, c - r$). This penalty term is straightforward and preliminary calculations indicate that its value is appropriate for handling infeasible solutions in the constrained Gibbs free energy minimization in systems subject to chemical reactions.

2.3. Unconstrained minimization approach

Alternatively, Gibbs free energy function can be written in terms of reaction-invariant composition variables $\hat{n}_{ij}$ to transform the problem into an unconstrained form. Specifically, to perform an unconstrained minimization of $F_2 = \Delta\hat{g}$ (Eq. (10)), we can use a set of new variables, namely, β_{ij} as decision variables. The introduction of these variables eliminates the restrictions imposed by material balances, reduces problem dimensionality, and the optimization problem is transformed into an unconstrained one [19,26–28]. However, this will require the solution of nonlinear equations for evaluating the objective function due to the transformation procedure $X \rightarrow x$ using Eqs. (5) and (6).

For multi-phase reactive systems, real variables $\beta_{ij} \in (0, 1)$ are defined and employed as decision variables by using the following expressions

$$\hat{n}_{i1} = \beta_{i1} Z_i \hat{n}_F \quad i = 1, \ldots, c - r \tag{24}$$

$$\hat{n}_{ij} = \beta_{ij} \left(Z_i \hat{n}_F - \sum_{m=1}^{j-1} \hat{n}_{im} \right) \quad i = 1, \ldots, c - r; \quad j = 2, \ldots, \pi - 1 \tag{25}$$

$$\hat{n}_{i\pi} = Z_i \hat{n}_F - \sum_{j=1}^{\pi-1} \hat{n}_{ij} \quad i = 1, \ldots, c - r \tag{26}$$

Using this formulation, equality constraints, Eqs. (8) and (9) are eliminated and all trial transformed compositions satisfy the material balances allowing the easy application of optimization strategies. For the unconstrained minimization of $\Delta\hat{g}$, Eq. (10), the overall number of decision variables (i.e., β_{ij}) is $(c - r)(\pi - 1)$. Finally, it is important to note that the global optima of F_1 and F_2 are equal but their decision variables are different (n_{ij} and β_{ij}, respectively).

3. Description of stochastic optimization methods

In this study, we used three methods: SA, GA and DETL for the global minimization of constrained and unconstrained Gibbs free energy functions using both conventional (i.e., constrained minimization approach) and transformed composition variables (i.e., unconstrained minimization approach). SA has recently been used for reactive systems in [19,25], whereas DETL and GA have not yet been tried for phase equilibrium calculations in reactive systems. SA is a point-to-point method while GA and DETL are population-based methods. These algorithms are described briefly in the following subsections, and their detailed description and flowcharts is available in the cited References

3.1. Simulated annealing

SA is a stochastic method that mimics the thermodynamic process of cooling molten metals to attain the lowest free energy state [34]. In the minimization problems, this algorithm performs a stochastic search of the space defined for decision variables where uphill moves may be accepted with a probability controlled by the parameter called annealing temperature: T_{SA}. The probability of acceptance of uphill moves decreases as T_{SA} decreases. At high T_{SA}, the search is almost random, while at low T_{SA} the search becomes selective where good moves are favored. The core of SA algorithm is the Metropolis criterion [35] used to accept or reject uphill movements with the acceptance probability given by

$$M(T_{SA}) = \min \left\{ 1, \exp\left(\frac{-\Delta f}{T_{SA}} \right) \right\} \tag{27}$$

where Δf is the change in objective function value from the current point to new/trial point.

In this study, the SA algorithm proposed by Corana et al. [36] has been used because of its good performance in thermodynamic calculations, e.g., [19,26,37]. In this algorithm, a trial point is randomly chosen within the step length VM (which is a vector of length n_{var}) from the current point. The objective function is evaluated at this trial point, and its value is compared to the objective value at the current point. Eq. (27) is used to accept or reject the trial point. If this trial point is accepted, the algorithm continues the search using that point; otherwise, another trial point is generated within the neighborhood of the current point. Each element of VM is periodically adjusted so that half of all function evaluations in that direction are accepted. A fall in T_{SA}, after $NT \times NS \times n_{var}$ function evaluations, is imposed upon the system using the cooling schedule. Note that NT is the number of iterations before T_{SA} reduction and NS is the number of cycles for updating the decision variables.

In our calculations, cooling schedule for decreasing T_{SA} is defined as

$$T_{SA,k} = 0.5(T_{SA,0} - T_{SA,F}) \left(1 - \tanh\left(\frac{17k}{Iter_{\max}} - 5 \right) \right) + T_{SA,F} \tag{28}$$

where $Iter_{max}$ is the maximum number of iterations for SA, $T_{SA,k}$ is the annealing temperature at iteration k, and $T_{SA,0}$ and $T_{SA,F}$ are respectively the initial and final values of the annealing temperature. Thus, as T_{SA} declines, downhill moves are less likely to be accepted and SA focuses on the most promising area for optimization. The iterative steps are performed until the specified stopping criterion: either the maximum number of successive iterations (Sc_{max}) without improvement in the best function value, or until the maximum number of iterations ($Iter_{max}$), is satisfied. The main parameters of SA are $T_{SA,0}$, $T_{SA,F}$, NS, NT, Sc_{max} and $Iter_{max}$. Detailed description of this algorithm can be found in Corana et al. [36]. We have used, after suitable modifications, the subroutine developed by Goffe et al. [38], for the present study.

3.2. Genetic algorithm

GA is a stochastic technique that simulates natural evolution on the solution space of the optimization problem. It operates on a population of potential solutions (individuals) in each iteration (i.e., generation). Specifically, the first step of GA is to create randomly an initial population of NP solutions in the feasible region. GA works on this population, and combines (crossover) and modifies (mutation) some chromosomes according to specified genetic operations, to generate a new population with better characteristics. Individuals for reproduction are selected based on their objective function values and the Darwinian principle of the survival of the fittest [39].

Genetic operators are used to create new individuals for the next population from the selected individuals of the current population, and they serve as the searching mechanisms in GA. In particular, crossover forms two new individuals by first choosing two individuals from the mating pool (containing the selected individuals) and then swapping different parts of genetic information between them. This combining (crossover) operation takes place with a user-defined crossover probability (P_{cros}) so that some parents remain unchanged even if they are chosen for reproduction. Mutation is an unary operator that creates a new solution by a random change in an individual with a probability P_{mut}. It ensures that the probability of searching any given string will never be zero and acting as a safety net to recover good genetic material which may be lost through the action of selection and crossover.

Selection, crossover and mutation procedures are recursively used to improve the population and to identify promising areas for optimization. GA terminates when the user-specified criterion is satisfied. For comparison purposes, the stopping conditions described for SA have been implemented in all stochastic methods tested in this work. Specifically, GA stops after evolving for the specified number of generations (Gen_{max}), or until performing the maximum number of successive generations (Sc_{max}) without improvement in the best objective value. We have used GA with floating-point encoding, selection via stochastic universal sampling, modified arithmetic crossover and non-uniform mutation. Details of this algorithm are available in Rangaiah [26]. The key parameters of GA are NP, P_{cros}, P_{mut}, Gen_{max} and Sc_{max}.

3.3. Differential evolution with tabu list

This recent stochastic method developed by Srinivas and Rangaiah [28] is a hybrid strategy obtained from differential evolution (DE) and tabu search (TS). DETL begins with the selection of values for parameters: population size (NP), amplification factor (A), crossover constant (CR), tabu radius (tr), tabu list size (tls), Gen_{max} and Sc_{max}. The algorithm generates the initial population of size NP using uniformly distributed random numbers to cover the entire feasible region. The objective function is evaluated at each individual/point, and the best one is selected. The tabu concept of TS is implemented in the generation step of DE (i.e., after crossover and mutation) to improve the diversity among the individuals and consequently the computational efficiency. It employs a tabu list with the parameters: tr and tls, to keep track of the evaluated points for avoiding revisits to them during the subsequent search.

The three main steps: mutation, crossover and selection of DE along with tabu checking are performed on the population during each generation. For this, a mutant individual is generated for each randomly chosen target individual ($X_{i,j}$) in the population by

$$V_{i,G+1} = X_{R1,G} + A(X_{R2,G} - X_{R3,G}) \quad i = 1, 2, 3, \ldots, NP \tag{29}$$

where random numbers R_1, R_2 and R_3 are distinct and belong to the set {1, 2, 3, ..., NP}, and $X_{R1,G}$, $X_{R2,G}$ and $X_{R3,G}$ represent the three random individuals chosen from the current generation, to produce the mutant vector for the next generation, $V_{i,G+1}$. The random numbers should be different from the running index, i, and hence NP should be ≥ 4 to allow mutation. Parameter A is a real value between 0 and 2, and it controls the amplification of the differential variation between the two random individuals.

In the crossover step, a trial individual/vector is generated by copying some elements of the mutant individual to the target individual with a probability of CR. A boundary violation check is performed to check the feasibility of the resulting trial individual; if any bound is violated, the trial individual is replaced by generating a new individual. The trial individual is then compared to the already evaluated points in the tabu list in terms of the Euclidean distance. If the Euclidean distance is smaller than the tabu radius, which indicates that the objective function value at the trial vector and at one of the points in the tabu list are comparable, the trial individual is rejected as it may not give new information about the objective function except increasing the number of function evaluations. The rejected point is replaced by generating another trial point by mutation and crossover operations, until the Euclidean distance between the new point and each of the points in the tabu list is greater than the tabu radius. Whenever a trial individual is rejected, the number of rejected individuals (N_{fail}) at the current generation is updated.

The objective function is evaluated at the trial individual only if it is away from all the points in the tabu list and if $N_{fail} < 15n_{var}$. In this algorithm, the parameter N_{fail} is used to avoid indefinite cycling in the generation step. After each evaluation, the tabu list is updated dynamically to keep the latest point(s) in the list by replacing the earliest entered point(s). In the selection step, objective function value is used to select the better one between the trial and target individuals. If the trial individual is selected, it replaces the target individual in the population immediately and may participate in the subsequent mutation and crossover operations. If the target individual is better, then it remains in the population and may participate in the subsequent mutation and crossover operations. The algorithm runs until the stopping criterion (Gen_{max} or Sc_{max}) is satisfied, and gives the best point obtained over all the generations. More details on DETL algorithm can be found in Srinivas and Rangaiah [28].

3.4. Implementation of the methods

In the present study, FORTRAN codes developed for the three stochastic algorithms were used. All codes are available to interested readers upon request to the corresponding author. Each method has been implemented in combination with a local optimization technique at the end of global search. Specifically, the best point identified by the stochastic algorithm is used as the initial guess for local optimization. This is because stochastic optimization methods may require a significant computational effort to improve the accuracy of the solution since they explore the search space by creating random movements instead of using a logical optimization trajectory. Therefore, intensification step using a local optimizer is needed for rapid convergence and for improving accuracy of the best solution obtained with a stochastic method.

In this study, performance of SA, DETL and GA is tested for constrained and unconstrained Gibbs free energy minimization with and without local optimization. The quasi-Newton method implemented in the subroutine DBCONF of IMSL library was used for local optimization. This subroutine calculates the gradient via finite differences and approximates the Hessian matrix according to BFGS formula. For more details on this local strategy, see the book by Dennis and Schnabel [40]. The default values of DBCONF parameters in the IMSL library were employed. Preliminary calculations indicate that these parameter settings are a reasonable compromise between numerical effort and reliability for intensification stage. All calculations were performed on a HP Workstation with Dual-Core AMD Opteron 2.19 GHz processor with 1.87 GB of RAM. This computer performs 254 million floating point operations per second for the LINPACK benchmark program (available at http://www.netlib.org/) for a matrix of order 500.

Table 1
Examples selected for the constrained and unconstrained Gibbs free energy minimization in reactive systems.

No.	System	Feed conditions	Thermodynamic models	Ref.
1	$A_1 + A_2 \leftrightarrow A_3 + A_4$ (1) Ethanol (2) Acetic acid (3) Ethyl acetate (4) Water	$n_F = (0.5, 0.5, 0.0, 0.0)$ at 355 K and 101.325 kPa	NRTL model and ideal gas. $K_{eq,1} = 18.670951$	[2,11,14]
2	$A_1 + A_2 \leftrightarrow A_3$, and A_4 as an inert component (1) Isobutene (2) Methanol (3) Methyl ter-butyl ether (4) n-Butane	$n_F = (0.3, 0.3, 0.0, 0.4)$ at 373.15 K and 1013.25 kPa	Wilson model and ideal gas. $\frac{\Delta G^0_{rxs}}{R} = -4205.05 + 10.0982T - 0.2667T \ln T$ $\ln K_{eq,1} = \frac{-\Delta G^0_{rxs}}{RT}$ where T is in K.	[41]
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	$n_F = (0.354, 0.183, 0.463, 0.0)$ at 335 K and 151.95 kPa	Wilson model and ideal gas. $K_{eq,1} = 1.057 \cdot 10^{-04} e^{4273.5/T}$ where T is in K.	[19]
4	$A_1 + A_2 \leftrightarrow A_3 + A_4$ (1) Acetic acid (2) n-Butanol (3) Water (4) n-Butyl acetate	$n_F = (0.3, 0.4, 0.3, 0.0)$ at 298.15 K and 101.325 kPa	UNIQUAC model. $\ln K_{eq,1} = \frac{450}{T} + 0.8$ where T is in K.	[15,43]
5	$A_1 + A_2 \leftrightarrow A_3$	$n_F = (0.6, 0.4, 0.0)$	Margules solution model. $\frac{g^E}{R_g T} = 3.6x_1x_2 + 2.4x_1x_3 + 2.3x_2x_3$ $K_{eq,1} = 0.9825$	[42]
6	$A_1 + A_2 + 2A_3 \leftrightarrow 2A_4$ with A_5 as inert component (1) 2-Methyl-1-butene (2) 2-Methyl-2-butene (3) Methanol (4) *Tert*-amyl methyl ether (5) n-Pentane	$n_F = (0.1, 0.15, 0.7, 0.0, 0.05)$ at 335 K and 151.9875 kPa	Wilson model and ideal gas. $K_{eq,1} = 1.057 \cdot 10^{-04} e^{4273.5/T}$ where T is in K.	[19]
7	$A_1 + A_2 \leftrightarrow A_3$	$n_F = (0.52, 0.48, 0.0)$ at 323.15 K and 101.325 kPa	Margules solution model. $K_{eq,1} = 3.5$	[4]
8	$A_1 + A_2 \leftrightarrow A_3 + A_4$	$n_F = (0.048, 0.5, 0.452, 0.0)$ at 360 K and 101.325 kPa	NRTL model. $K_{eq,1} = 4.0$	[43]

Table 2
Problem formulation for the constrained and unconstrained Gibbs free energy minimization in selected reactive systems.

No.	Constrained optimization			Unconstrained optimization			
	F_1[a]	n_{var}	Decision variables	F_2[b]	Reference component	n_{var}	Decision variables
1, 4, 8	$\Delta g - (n_{4,1} + n_{4,2}) \ln K_{eq,1}$	5	$n_{i,1}$ for $i = 1, \ldots, 4$ and $n_{4,2}$	$\Delta \hat{g}$	A_4	3	$\beta_{i,1}$ for $i = 1, 2, 3$
2	$\Delta g - (n_{3,1} + n_{3,2}) \ln K_{eq,1}$	5	$n_{i,1}$ for $i = 1, \ldots, 4$ and $n_{3,2}$	$\Delta \hat{g}$	A_3	3	$\beta_{i,1}$ for $i = 1, 2, 4$
3	$\Delta g - 0.5(n_{4,1} + n_{4,2}) \ln K_{eq,1}$	5	$n_{i,1}$ for $i = 1, \ldots, 4$ and $n_{4,2}$	$\Delta \hat{g}$	A_4	3	$\beta_{i,1}$ for $i = 1, 2, 3$
5, 7	$\Delta g - (n_{3,1} + n_{3,2}) \ln K_{eq,1}$	4	$n_{i,1}$ for $i = 1, \ldots, 3$ and $n_{3,2}$	$\Delta \hat{g}$	A_3	2	$\beta_{i,1}$ for $i = 1, 2$
6	$\Delta g - 0.5(n_{4,1} + n_{4,2}) \ln K_{eq,1}$	6	$n_{i,1}$ for $i = 1, \ldots, 5$ and $n_{4,2}$	$\Delta \hat{g}$	A_4	4	$\beta_{i,1}$ for $i = 1, 2, 3, 5$

[a] Where $\Delta g = \sum_{i=1}^{c} (n_{i,1} \ln(x_{i,1}\gamma_{i,1}) + n_{i,2} \ln(x_{i,2}P/P_{i,sat}))$ for VLE and $\Delta g = \sum_{i=1}^{c} (n_{i,1} \ln(x_{i,1}\gamma_{i.1}) + n_{i,2} \ln(x_{i,2}\gamma_{i,2}))$ for LLE.

[b] Where $\Delta \hat{g} = \sum_{i=1}^{c-r} (\hat{n}_{i,1} \ln(x_{i,1}\gamma_{i,1}) + \hat{n}_{i,2} \ln(x_{i,2}P/P_{i,sat}))$ for VLE and $\Delta \hat{g} = \sum_{i=1}^{c-r} (\hat{n}_{i,1} \ln(x_{i,1}\gamma_{i.1}) + \hat{n}_{i,2} \ln(x_{i,2}\gamma_{i,2}))$ for LLE.

4. Results and discussion

4.1. Description of reactive phase equilibrium problems

We have tested and compared the performance of SA, GA and DETL using a number of reactive systems and different thermodynamic models. The test problems include systems with vapor–liquid (VL) and liquid–liquid (LL) equilibrium. Details (i.e., feed conditions, thermodynamic models, objective function, decision variables and global optimum) of all examples are reported in Tables 1–3. Parameters of thermodynamic models for these reactive systems are given in Appendix A. Most of the selected reactive systems have been used for testing other deterministic and stochastic optimization strategies, e.g., [2,4,11,14,15,18–20,22,23,41–43]. In all examples, the number of phases existing at the equilibrium is assumed to be known *a priori*. In general, the selected reactive phase equilibrium problems have different dimensionality and inherent difficulties (e.g., discontinuities in objective function for VL equilibrium problems, or feed composition near phase boundaries which are generally challenging for any algorithm). Therefore, we consider that the number and features of the test problems are sufficient to demonstrate and compare the performance of SA, GA and DETL for solving reactive phase equilibriums problems via unconstrained and constrained approaches.

Table 3
Global minimum of the reactive examples studied.

No.	Equilibrium	Global minimum of F_1 and F_2
1	Vapor–Liquid	−2.058125
2	Vapor–Liquid	−1.434267
3	Vapor–Liquid	−1.226367
4	Liquid–Liquid	−1.106296
5	Liquid–Liquid	−0.144508
6	Vapor–Liquid	−0.872577
7	Liquid–Liquid	−0.653756
8	Liquid–Liquid	−0.311918

Note: Global solutions of all problems can be found in Refs. [2,11,14,15,18,19,23].

The performance of all stochastic methods is evaluated based on both reliability (measured in terms of number of times the algorithm located the global minimum out of 100 trials with random initial values, refereed to as success rate SR) and computational efficiency (measured in terms of average number of function evaluations NFE and CPU time). Note that NFE includes both the function calls for evaluating the objective function using the stochastic method (NFE_{stc}) and the function calls for the local optimization (NFE_{qN}). The average NFE and CPU time are evaluated using successful trials only. A trial is considered successful if the global optimum is obtained with an absolute error of 10^{-5} or less in the objective function value. To compare the performance of stochastic algorithms and to analyze their relative merits for reactive phase equilibrium calculations, we have considered Eqs. (10) and (22) as the objective function for unconstrained and constrained Gibbs free energy minimization, respectively.

4.2. Parameter tuning of SA, GA and DETL

Reactive examples 1 and 4 have been used to establish the most suitable parameter values for solving the constrained and unconstrained Gibbs free energy minimization problems efficiently and reliably. Parameter tuning was carried out by varying one parameter at a time with the remaining parameters fixed at nominal values, which were established using the reported results in the literature [19,26,28]. The tested and suggested values for parameters of each stochastic method are summarized in Table 4. Our preliminary calculations suggest that these parameter values are a reasonable compromise between numerical effort and reliability of tested stochastic methods.

4.3. Performance of SA, GA and DETL

The three stochastic methods were studied using two stopping criteria: (a) maximum number of iterations/generations $Iter_{max}$ or Gen_{max} (referred to as stopping criterion 1, SC1) and (b) maximum number of iterations/generations without improvement in the best function value Sc_{max} (referred to as stopping criterion 2, SC2). The methods are compared in terms of SR and NFE by examining different levels of algorithm efficiency, which are obtained by changing the values of $Iter_{max}/Gen_{max}$ and Sc_{max}. Note that optimal values of these parameters may be problem dependent, and they also determine the trade-off between efficiency and reliability. As a consequence, selection of proper values for them is important for the comparison. For all calculations performed in this study, $NS \times NT$ (=NP) = $10n_{var}$ where n_{var} is the number of decision variables used in reactive phase equilibrium calculations.

Table 4
Tested and suggested values of parameters in the stochastic optimization methods for the constrained and unconstrained Gibbs free energy minimization in reactive systems.

Method	Parameter[a]	Tested values	Suggested values
SA	$T_{SA,0}$	0.1–1000	10
	$T_{SA,F}$	10^{-9}–10^{-3}	10^{-6}
GA	P_{cros}	0.5–0.9	0.9
	P_{mut}	0.001–0.5	0.1
DETL	CR	0.1–0.9	0.9
	A	0.1–0.9	0.3
	tr	$0.001n_{var}$–$0.01n_{var}$	$0.001n_{var}$
	tls	50–75	50

[a] $NS \times NT$ (=NP) = $10n_{var}$ where n_{var} is the number of decision variables for the Gibbs free energy minimization problems.

The performance of SA, DETL and GA implemented with and without the local optimization method is given in Figs. 1 and 2. For the sake of brevity, algorithm reliability results are summarized as the global success rate (GSR), defined as the average successes rate on the collection of reactive phase equilibrium problems tested:

$$GSR = \frac{1}{N_{prob}} \sum_{i=1}^{N_{prob}} SR_i \tag{30}$$

where SR_i is the success rate on the ith problem.

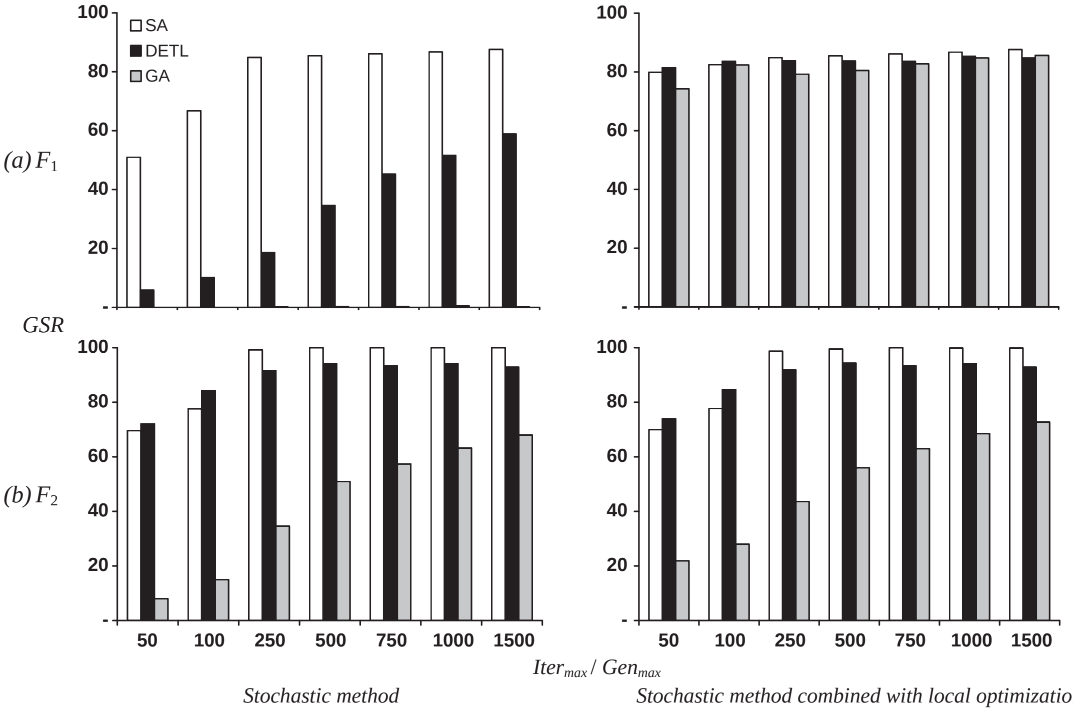

Fig. 1. Global success rate (GSR) versus $Iter_{max}/Gen_{max}$ (without using Sc_{max}) of SA, DETL and GA for the (a) constrained and (b) unconstrained Gibbs free energy minimization in reactive systems. Algorithm parameters: $NS \times NT = NP = 10n_{var}$.

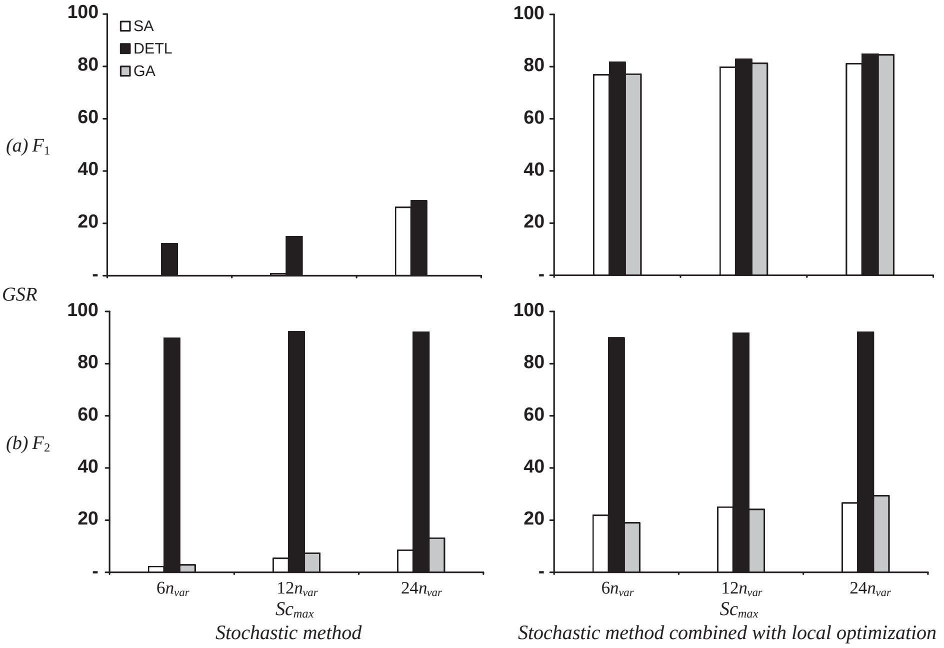

Fig. 2. Global success rate (*GSR*) versus Sc_{max} of SA, DETL and GA for the (a) constrained and (b) unconstrained Gibbs free energy minimization in reactive systems. Algorithm parameters: $NS \times NT = NP = 10n_{var}$.

Our results indicate that the reliability of SA, DETL and GA for Gibbs free energy minimization varies significantly with the stopping condition, the problem formulation (i.e., constrained and unconstrained), and the use of local optimization method (see Figs. 1 and 2). In general, DETL and SA can achieve high *GSR* values, and their performance is usually better than or comparable to that of GA using either SC1 or SC2 as the stopping condition, with and without the quasi-Newton method, in both constrained and unconstrained minimization approaches. The stochastic methods may fail to find the global minimum of Gibbs free energy function using both conventional and transformed composition variables (see Figs. 1 and 2). These failures may be due to the presence of local optima and/or flat objective function near the global solution in some reactive problems.

As expected, the reliability and computational effort of the stochastic methods increase with $Iter_{max}/Gen_{max}$ and Sc_{max} (see Figs. 1, 2 and 4 and Tables 5 and 6). Even though the stopping criterion used for all stochastic methods is the same, NFE required by DETL is generally less than that of both SA and GA because the tabu checking and the parameter N_{fail} are implemented in the generation step of DETL. SR of the methods is affected when the stopping conditions are limited to low values (i.e., early iterations) especially for constrained function F_1 and without using quasi-Newton method. Application of local optimization method for the intensification stage is important to improve *GSR* especially in constrained Gibbs free energy minimization using either SC1 or SC2 as the stopping condition. Without local optimization, SA outperformed the DETL and GA in solving reactive phase equilibrium problems espe-

Table 5

Percentage reduction in NFE of DETL with local optimization for solving the constrained (F_1) and unconstrained (F_2) Gibbs free energy problems in reactive systems with SC1 alone as the stopping criterion.

Problem	F_{obj}	Percentage reduction in NFE for $Iter_{max}$ or Gen_{max}[a]						
		50	100	250	500	750	1000	1500
1	F_1	−1.35	−12.59	−33.15	−50.54	−58.54	−61.98	−67.75
	F_2	64.38	45.66	11.41	−17.56	−30.90	−36.63	−46.24
2	F_1	−6.06	−28.73	−53.68	−65.78	−68.79	−72.06	−74.55
	F_2	56.52	18.77	−22.81	−42.97	−47.99	−53.43	−57.59
3	F_1	−4.86	−18.69	−38.34	−50.62	−56.71	−60.01	−62.94
	F_2	58.52	35.49	2.75	−17.70	−27.86	−33.36	−38.24
4	F_1	1.26	−1.95	−18.14	−35.62	−42.21	−46.39	−52.46
	F_2	68.73	63.40	36.42	7.30	−3.68	−10.65	−20.77
5	F_1	−14.91	−43.33	−65.05	−74.23	−76.96	−80.13	−81.87
	F_2	70.09	13.30	−30.11	−48.46	−53.92	−60.27	−63.75
6	F_1	−1.19	−31.51	−55.39	−67.48	−71.36	−73.70	−76.43
	F_2	48.18	2.73	−33.09	−51.22	−57.03	−60.55	−64.65
7	F_1	−7.05	−28.44	−50.10	−59.73	−65.75	−70.17	−71.24
	F_2	85.81	43.09	−0.21	−19.46	−31.51	−40.35	−42.48
8	F_1	−3.49	−32.84	−56.54	−67.94	−72.49	−74.32	−77.67
	F_2	60.81	11.92	−27.56	−46.56	−54.15	−56.78	−62.41

[a] % reduction = 100(NFE of DETL – mean NFE of SA and GA)/(mean NFE of SA and GA). Note that the NFE of SA and GA is comparable.

Table 6
NFE and SR of SA, DETL and GA with local optimization for solving the constrained (F_1) and unconstrained (F_2) Gibbs energy minimization problems in reactive systems using SC2 alone as the stopping criterion.

Problem	Sc_{max}	NFE (with SR in brackets) for[a]					
		Constrained (F_1)			Unconstrained (F_s)		
		SA	DETL	GA	SA	DETL	GA
1	$6n_{var}$	5544 (93)	7791 (100)	4650 (89)	1509 (2)	3007 (98)	1396 (1)
	$12n_{var}$	10,818 (99)	9787 (100)	7866 (98)	2769 (4)	3213 (100)	2470 (2)
	$24n_{var}$	44,083 (100)	11,548 (100)	13,228 (99)	5760 (2)	3570 (100)	4948 (2)
2	$6n_{var}$	4703 (98)	4237 (100)	4465 (99)	1215 (9)	1235 (99)	1295 (6)
	$12n_{var}$	10,159 (100)	5708 (100)	7363 (100)	2381 (11)	1472 (100)	2224 (14)
	$24n_{var}$	35,837 (100)	6665 (100)	12,464 (100)	4900 (14)	1833 (100)	4569 (16)
3	$6n_{var}$	4740 (95)	6366 (100)	4670 (98)	1530 (7)	2814 (100)	1476 (5)
	$12n_{var}$	9299 (100)	8017 (100)	7484 (100)	2720 (11)	3181 (100)	2535 (12)
	$24n_{var}$	32,630 (100)	10,893 (100)	12,680 (100)	4935 (12)	3723 (100)	5041 (13)
4	$6n_{var}$	4460 (11)	10,621 (1)	4234 (15)	1266 (7)	2132 (29)	1257 (6)
	$12n_{var}$	8396 (10)	15,420 (1)	7065 (11)	2354 (12)	2848 (44)	2451 (10)
	$24n_{var}$	29,589 (11)	22,043 (2)	12,136 (17)	4937 (13)	4330 (40)	4256 (21)
5	$6n_{var}$	2401 (71)	2235 (88)	2403 (63)	569 (97)	612 (98)	611 (90)
	$12n_{var}$	4725 (76)	2705 (86)	4223 (73)	1041 (100)	713 (97)	1078 (95)
	$24n_{var}$	9508 (79)	3205 (92)	8292 (70)	1947 (100)	869 (98)	1998 (99)
6	$6n_{var}$	8038 (99)	4859 (100)	6420 (100)	2368 (3)	1893 (100)	2398 (4)
	$12n_{var}$	18,759 (100)	5994 (100)	10,708 (100)	4602 (4)	2450 (100)	4320 (4)
	$24n_{var}$	66,336 (100)	8532 (100)	17,623 (100)	9507 (4)	3084 (100)	7874 (7)
7	$6n_{var}$	2690 (56)	3955 (65)	2913 (58)	593 (46)	555 (97)	645 (36)
	$12n_{var}$	5389 (55)	4985 (77)	4584 (70)	1058 (46)	700 (95)	1142 (51)
	$24n_{var}$	13,599 (61)	5713 (85)	8257 (90)	1946 (55)	802 (99)	2250 (58)
8	$6n_{var}$	5733 (92)	4057 (100)	4906 (95)	1477 (4)	1161 (98)	1515 (4)
	$12n_{var}$	11,096 (98)	5036 (100)	7777 (98)	2856 (12)	1393 (98)	2548 (5)
	$24n_{var}$	31,887 (98)	6124 (100)	12,420 (100)	5507 (13)	1852 (100)	4738 (19)
Total NFE		380,416	176,498	188,834	69,749	49,443	65,036

[a] $Iter_{max}/Gen_{max}$ is restricted to a maximum of 1500; however, this condition was not reached in all calculations performed. Algorithm parameters: $NS \times NT$ ($=NP$) = $10n_{var}$.

cially for F_1 (i.e., constrained formulation) and if SC1 is used alone as the stopping condition (Fig. 1). SR of SA increases with $Iter_{max}$ and its *GSR* ranges from 51 to 87% for constrained formulation using SC1. But, SA showed the best performance (i.e., 100% *GSR* at $Iter_{max} \geq 500$) using transformed composition variables even without quasi-Newton method. On the other hand, maximum *GSR* of DETL is 59 and 94% for constrained and unconstrained problems, whereas GA showed maximum *GSR* of 1 and 68% for these problems using SC1 as the termination criterion (Fig. 1).

In unconstrained Gibbs free energy minimization, DETL and SA can often find solutions very close to the global optimum even without applying the local method and using SC1 as the stopping condition (Fig. 1). In general, value of the best solution obtained by these methods is nearer to the global minimum as $Iter_{max}/Gen_{max}$ increases. It is clear that GA without local strategy is the worse performer for both stopping conditions and problem formulations (Fig. 1). If SC2 is used as the stopping condition, reliability of DETL without quasi-Newton method is higher compared to GA and SA for both constrained and unconstrained functions (Fig. 2). In fact, DETL offers the best performance and can give high reliability of $GSR \cong 90\%$, if proper values of Sc_{max} are used, for Gibbs free energy minimization employing transformed composition variables (see results in Fig. 2). SA performed worse than all other stochastic methods tested for unconstrained problems using SC2 as the stopping condition with and without local optimization. In summary, all stochastic methods improve its performance with the application of intensification step in Gibbs free energy minimization using both conventional and transformed composition variables, irrespective of the convergence criterion used (i.e., SC1 and SC2). In particular, the intensification stage using the quasi-Newton method plays a major role for improving numerical performance of stochastic methods in constrained approach, while it appears that its use has less impact for increasing the reliability of stochastic methods in the unconstrained problems tested.

Usually, it is expected that the performance of the optimization methods for solving unconstrained problems is better than those obtained for constrained problems because the optimization can be executed without worrying about the feasibility [44]. For constrained problems, the variance of solutions obtained by the stochastic method without local optimization may be large. This is mainly related to the capability of each stochastic method for searching the feasible region of the total search space. For illustration, % of the infeasible solutions versus $Iter_{max}/Gen_{max}$ for selected problems is given in Fig. 3. The infeasible solutions generated at different levels of computational effort by the stochastic methods, indicate that DETL is very effective for handling constraints and the percentage of infeasible solutions decreases from 30 to 5% as the optimization search progresses. This may be due to the ability of DE to exploit and intensify the search as iterations increase. It is interesting to observe that approximately 40% of function evaluations for SA correspond to infeasible solutions and this proportion practically remains constant throughout the tested range of $Iter_{max}$. Although this percentage is higher than those reported for DETL, SA shows high reliability for constrained problems especially using SC1 as the convergence criterion. On the other hand, GA fails frequently to identify feasible optimal solutions in the constrained Gibbs free energy minimization of reactive systems (see Fig. 3). Other studies have recognized this drawback of GA for solving constrained optimization problems [45]. Literature also indicates that GA performs well in the diversification of the search space but may fail in the intensification of the solutions found [46]. Overall, the present results suggest that the diversification mechanisms in DETL and SA are more effective than those of GA, to escape from the infeasible region and to locate the global optimum.

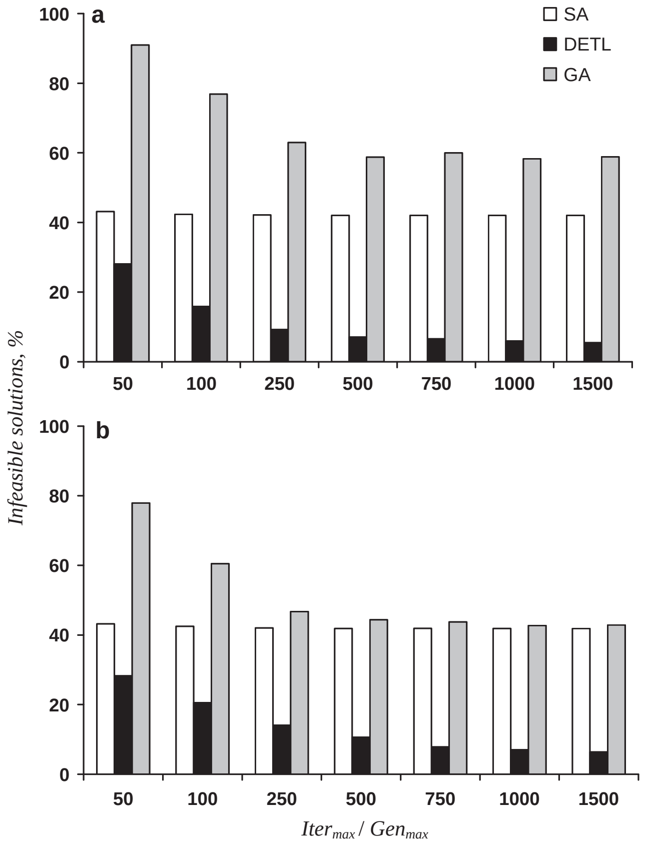

Fig. 3. Infeasible solutions versus $Iter_{max}/Gen_{max}$ (without using Sc_{max}) of SA, DETL and GA for the constrained Gibbs free energy minimization for selected reactive systems: No. 1 (top plot) and No. 5 (lower plot). Algorithm parameters: $NS \times NT = NP = 10n_{var}$.

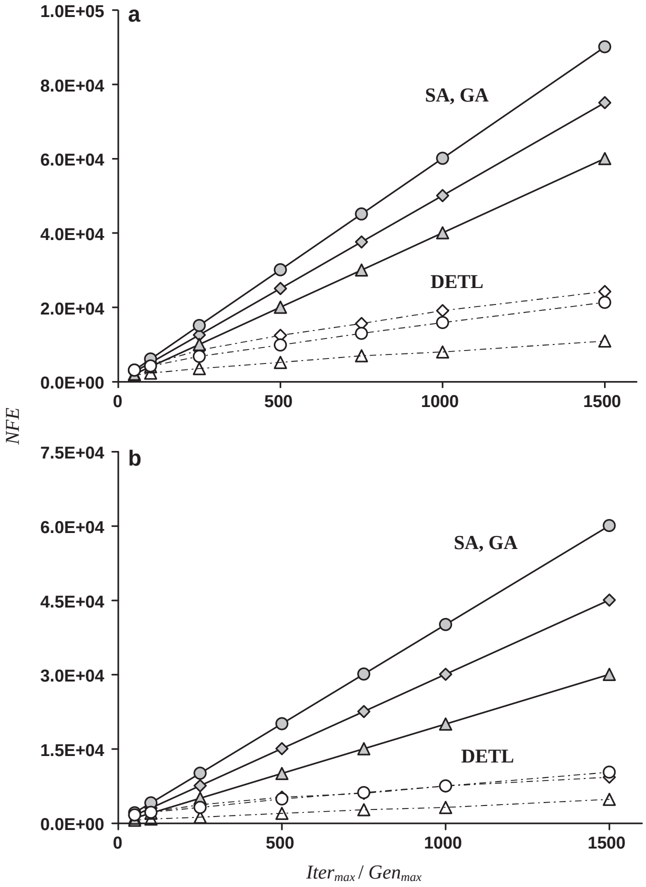

Fig. 4. NFE of SA, DETL and GA each followed by the quasi-Newton method for solving constrained (top plot) and unconstrained (lower plot) Gibbs free energy minimization problems in reactive systems using SC1 alone as the stopping criterion. Reactive system: (◊, ♦) No. 1, (Δ, ▲) No. 5, and (○, ●) No. 6. Unfilled symbols are for DETL and filled symbols are for SA and GA. Algorithm parameters: $NS \times NT = NP = 10n_{var}$.

Comparing the performance of stochastic methods, each followed by the quasi-Newton method, all the three methods provide similar *GSR* for both SC1 and SC2 using constrained approach (see Figs. 1 and 2). However, Fig. 1 shows that *GSR* of SA and DETL is better than that obtained for GA using SC1 as the stopping condition, at low iterations. But, as the number of generations increases, GA can achieve a $GSR > 70\%$. Though GA followed by the quasi-Newton method showed the worst performance in the unconstrained approach using SC1, its success rate can be still considered competitive for several reactive problems if a larger number of function evaluations is permitted. DETL has good performance and requires fewer NFE than the other two stochastic methods using SC1 alone as the stopping criterion for the reactive problems tested (see Fig. 4 and Table 5). NFE of SA and GA is almost the same when SC1 is used as the stopping criterion, and the percentage reduction in NFE of DETL compared to SA and GA for SC1 is summarized in Table 5. The percentage reduction in NFE of DETL ranged from 1.4 to 81.9% for constrained functions and from 0.2 to 65.0% for unconstrained problems compared to the other stochastic methods tested. So, NFE reduction of DETL is more significant for constrained Gibbs free energy minimization problems. As stated earlier, DETL is a hybrid strategy that integrates the strong features of DE and TS. In contrast to SA and GA, DETL can achieve a good tradeoff between the capabilities to effectively explore the search space and to exploit the experience accumulated during the optimization. The tabu concept has considerable influence on the performance of DETL resulting in lower NFE [28]. However, the improvement in the convergence rate of DETL may not be the same for all the functions and depends on problem dimensionality and complexity.

If SC2 is used as the convergence criterion (along with $Iter_{max}/Gen_{max}$ set at 1500 to avoid indefinite looping), the results indicate that DETL can achieve a higher *GSR* than those obtained for GA and SA with and without local optimization and for both constrained and unconstrained formulations (see Fig. 2). At tested values of SC2, SA, DETL and GA gave similar *GSR* for constrained problems. However, in unconstrained formulation, DETL is the best performer and can achieve a $GSR > 90\%$ with or without local optimization. Also, NFE of DETL is lower than that of SA and GA using SC2 in both constrained and unconstrained approaches especially for problems with several decision variables, as shown in Table 6. For this stopping condition, SA generally required more NFE than GA and DETL. These results again confirm that the diversity introduced in DETL using TS concept has a significant impact on its performance.

When we examine the results for individual problems, the three stochastic methods, each followed by the quasi-Newton method, show high reliability for reactive problems No. 1–3, 6, and 8, irrespective of the stopping criterion used (i.e., $Iter_{max}/Gen_{max}$ or Sc_{max}), for constrained formulation (results not shown for brevity). In fact, the global optimum is found even using low values of these stopping conditions. In the case of unconstrained approach, only DETL showed a high success rate for both SC1 and SC2 in almost all reactive problems, while the reliability of SA is high for tested examples and using SC1 only. Further, GA failed to find the global optimum several times in almost all Gibbs free energy minimization problems using transformed composition variables. In general, performance of stochastic optimization methods is dependent on the problem under study and, as a consequence, the numerical effort for escaping from local minima depends on the problem. For any global optimization problem, all stochastic methods converge to a global minimum as NFE → ∞ [46]. Therefore, for difficult constrained and unconstrained optimization problems, the performance of all stochastic methods could be improved using larger $Iter_{max}/Gen_{max}$ (i.e., >1500) or Sc_{max} (i.e., >$24n_{var}$) but at the expense of significant computational effort.

Overall, our results indicate that the reliability of SA, DETL and GA is better using SC1 compared to that of SC2 for both constrained and unconstrained problems. This may be because of slow convergence and/or more iterations/generations are required for escaping from the local minimum region reached in the initial iterations. However, maximum number of generations/iterations to find the global optimum cannot be judged *a priori* for an arbitrary function. In some problems, this may lead to unnecessary function calls when the minimum is reached long before the maximum number of generations/iterations, thus increasing computational effort. Therefore, to avoid the premature convergence and reduce computational effort, it is better to employ both SC1 and SC2 with suitable values as the stopping conditions (i.e., the algorithm terminates after satisfying either $Iter_{max}/Gen_{max}$ or Sc_{max}).

In the tests performed on the reactive problems using the constrained approach, the CPU time ranged from 0.003 to 0.83 s for SA, from 0.01 to 0.79 s for DETL, and from 0.005 to 0.98 s for GA, respectively. Using transformed composition variables (i.e., unconstrained approach), these CPU times ranged from 0.04 to 18.6 s for SA, from 0.03 to 3.5 s for DETL, and from 0.05 to 18.9 s for GA. The computational time of stochastic methods increases proportionally with the number of decision variables. On average, there is a 14:1 (for SA), 4:1 (for DETL) and 12:1 (for GA) ratio between the computational times for minimizing F_2 and F_1 (i.e., between the application of transformed and conventional composition variables). As expected, implementation of the unconstrained approach using reaction-invariant composition variables requires larger computing time compared to that for the constrained formulation using conventional variables. This is because the transformation procedure $X \rightarrow x$ must be performed for each objective function evaluation, and this procedure requires another numerical method for determining the composition of reference components.

In summary, our results indicate that DETL offers the best compromise between reliability and efficiency for solving both the constrained and unconstrained Gibbs free energy minimization in reactive systems. In particular, the constrained Gibbs free energy minimization approach (using conventional composition variables) has the advantage of requiring smaller computing time, is straightforward and suitable for modeling systems subject to chemical reactions.

5. Conclusions

In this work, performance of DETL, GA and SA is studied for Gibbs free energy minimization in reactive systems using both conventional and transformed composition variables. For both constrained (involving conventional composition variables) and unconstrained (involving transformed composition variables) problems, with and without local optimization, DETL and SA are better than GA in terms of reliability. However, these stochastic methods may face difficulties in finding the global minimum for Gibbs free energy minimization in reactive systems using both transformed and conventional composition variables. The use of local optimization for intensification stage improves the performance of the stochastic methods especially for constrained Gibbs free energy minimization. Our results show that there is a significant increase in the computational effort for solving the unconstrained formulation caused by the use of the transformed variables. They also indicate that DETL offers better reliability and efficiency, and so it is recommended for both constrained and unconstrained Gibbs free energy minimization in reactive systems.

List of symbols

a_i	activity of component *i*
A	amplification factor
B	total number of gram-atoms of element
C	number of components
CR	crossover constant
d	number of gram-atoms of element
$\boldsymbol{e}$	unit vector
f_{ij}	partial fugacity
$f_{0,ij}$	fugacity of pure component
F_{obj}	objective function
g	molar Gibbs free energy of mixing
$\hat{g}$	transformed molar Gibbs free energy of mixing
G	Gibbs free energy function
$\hat{G}$	transformed Gibbs free energy function
ΔG_f	Gibbs free energy of formation
$\Delta\hat{g}$	transformed Gibbs free energy of mixing
Δg	Gibbs free energy of mixing
Gen_{max}	maximum number of generations
$Iter_{max}$	maximum number of iterations
k	iteration counter
K_{eq}	reaction equilibrium constant
m	number of equality constraints
m_e	number of elements
n	mole numbers
$\hat{n}$	transformed mole numbers
n_{inf}	number of infeasible solutions
n_{var}	number of decision variables in the optimization problem
$\boldsymbol{N}$	invertible matrix of stoichiometric coefficients of reference components
N_{prob}	total number of tested problems
NFE	number of function evaluations
NP	population size in genetic algorithm and differential evolution with tabu list
NS	number of cycles of SA for updating decision variables
NT	number of iterations before annealing temperature reduction
p	penalty function for constrained optimization
P	pressure
P_{cros}	crossover probability
P_{mut}	mutation probability
P_i^{sat}	vapor pressure of pure component *i*
r	number of independent chemical reactions
R	universal gas constant
R_1, R_2, R_3	random numbers
Sc_{max}	maximum number of successive iterations without improvement in the best function value
SR	success rate of stochastic method
tls	tabu list size
T	temperature
Tr	tabu radius
T_{SA}	annealing temperature of simulated annealing
U	vector of decision variables
$U_{i,G+1}$	trial vector
$\boldsymbol{V}$	vector of stoichiometric coefficients
ν_i	stoichiometric coefficient of component *i*
$V_{i,G+1}$	mutant vector
VM	step length vector
x	mole fraction

$X_{i,G}$	target vector
X	transformed mole fraction
z	feed mole fraction
Z	transformed feed mole fraction
β_i	decision variable for phase stability and equilibrium calculations
μ_i	chemical potential of component i
$\hat{\varphi}_i$	fugacity coefficient of component i in the mixture
φ_i	fugacity coefficient of pure component i
γ_i	activity coefficient of component i in the mixture
π	phase number

Appendix A.

Thermodynamic data and model parameters for all reactive systems used in this paper are given in Tables A1–A6.

Table A1
Thermodynamic data for Example 1.

Component[a]	Parameters of pure component			τ_{ij} in the NRTL model			
	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
	$\log_{10} P_i^{sat} = A_i - \frac{B_i}{T+C_i}$			$\alpha_{ij} = 0.3$			
	where P_i^{sat} in N/m^2 and T in K.			$\ln \gamma_i = \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{j=1}^{c} G_{ji} x_j} + \sum_{j=1}^{c} \frac{G_{ij} x_j}{\sum_{l=1}^{c} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{l=1}^{c} \tau_{lj} G_{lj} x_l}{\sum_{l=1}^{c} G_{lj} x_l} \right)$			
				$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$			

[a] 1: ethanol, 2: acetic acid, 3: ethyl acetate, and 4: water.

Table A2
Thermodynamic data for Example 2.

Component[a]	Parameters of pure component			V_i	u_{ij} in the Wilson model (cal/mol)			
	A_i	B_i	C_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	–	–
	$\log_{10} P_i^{sat} = A_i - \frac{B_i}{T+C_i}$			$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{c} x_j \Lambda_{ij} \right) - \sum_{k=1}^{c} \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{c} x_j \Lambda_{kj}} \right)$				
	where P_i^{sat} in mmHg and T in $^\circ$C			$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left(\frac{-u_{ij}}{RT} \right)$				

[a] 1: isobutene, 2: methanol, 3: MTBE, and 4: butane.

Table A3
Thermodynamic data for Examples 3 and 6.

Component[a]	Parameters of pure component				V_i	u_{ij} in the Wilson model (J/mol)				
	A_i	B_i	C_i	D_i		1	2	3	4	5
1	74.527	−5232.2	−8.1482	8.474E−06	0.10868	–	478.8	1376.5	−611.75	326.74
2	82.614	−5586.1	−9.4429	1.0858E−05	0.10671	−477.94	–	968.81	−386.04	362.28
3	23.5347	−3661.468	−32.77		0.04069	9772.3	10147	–	4826.3	11,749
4	20.9441	−2936.223	−47.70385		0.13345	951.33	712.33	−177	–	1143.9
5	81.624	−5578.5	−9.2354	9.4522E−06	0.11613	−194.18	−265.49	1946.7	−447.84	–
	$\ln P_i^{sat} = A_i + \frac{B_i}{T} + C_i \ln T + D_i T^2$ for $i = 1,2,5$					$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{c} x_j \Lambda_{ij} \right) - \sum_{k=1}^{c} \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{c} x_j \Lambda_{kj}} \right)$				
	$\ln P_i^{sat} = A_i + \frac{B_i}{T+C_i}$ for $i = 3,4$					$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left(\frac{-u_{ij}}{RT} \right)$				
	where P_i^{sat} in Pa and T in K.									

[a] 1: 2-methyl-1-butene, 2: 2-methyl-2-butene, 3: methanol, 4: TAME, and 5: n-pentane.

Table A4
Thermodynamic data for Example 4.

Component[a]	Q	R_u	u_{ij} in the UNIQUAC model (cal/mol)			
			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	–

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

$$\ln\gamma_i^E = \ln\frac{\phi_i}{x_i} + 5Q_i\ln\frac{\phi_i}{x_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{c} x_j l_j \quad \ln\gamma_i^R = Q_i\left(1-\ln\left(\sum_{j=1}^{c}\theta_j\tau_{ji}\right) - \sum_{j=1}^{c}\left(\frac{\theta_j\tau_{ji}}{\sum_{l=1}^{c}\theta_l\tau_{li}}\right)\right)$$

$$\theta_i = \frac{Q_i x_i}{\sum_{j=1}^{c} Q_j x_j} \quad \phi_i = \frac{R_{u,i}x_i}{\sum_{j=1}^{c} R_{u,j}x_j} \quad l_i = 5(R_{u,i}-Q_i)-(R_{u,i}-1)$$

$$\tau_{ij} = \exp\left(\frac{-u_{ij}}{RT}\right)$$

[a] 1: acetic acid, 2: n-butanol, 3: water, and 4: n-butyl acetate.

Table A5
Thermodynamic data for Example 7.

Component	A_{ij} in the Margules solution model (K)		
	1	2	3
1	0.0	478.6	1074.484
2	478.6	0.0	626.9
3	1074.484	626.9	0.0

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

Table A6
Thermodynamic data for Example 8.

Component	u_{ij} in the NRTL model (cal/mol)				α_{ij}			
	1	2	3	4	1	2	3	4
1	0.0	1850.2001	79.4397	−327.5173	–	0.3	0.3006	0.3044
2	−80.4396	0.0	667.4489	−219.7238	0.3	–	0.2564	0.2997
3	369.0624	3280.604	0.0	−484.8901	0.3006	0.2564	–	0.3
4	256.8999	842.6079	1126.4792	0.0	0.3044	0.2997	0.3	–

$$\ln\gamma_i = \frac{\sum_{j=1}^{c}\tau_{ji}G_{ji}x_j}{\sum_{j=1}^{c}G_{ji}x_j} + \sum_{j=1}^{c}\frac{G_{ij}x_j}{\sum_{l=1}^{c}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{l=1}^{c}\tau_{lj}G_{lj}x_l}{\sum_{l=1}^{c}G_{lj}x_l}\right)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \tau_{ij} = \frac{u_{ij}}{RT}$$

References

[1] W.A. Wakeham, R.P. Stateva, Rev. Chem. Eng. 20 (2004) 1–56.
[2] W. Xiao, K. Zhu, W. Yuan, H.H. Chien, AIChE J. 35 (1989) 1813–1820.
[3] W.D. Seider, S. Widagdo, Fluid Phase Equilib. 123 (1996) 283–303.
[4] S. Ung, M.F. Doherty, Chem. Eng. Sci. 50 (1995) 3201–3216.
[5] E.S. Pérez-Cisneros, R. Gani, M.L. Michelsen, Chem. Eng. Sci. 52 (1997) 527–543.
[6] R.P. Stateva, W.A. Wakeham, Ind. Eng. Chem. Res. 36 (1997) 5474–5482.
[7] Y.S. Teh, G.P. Rangaiah, Chem. Eng. Res. Des. 80 (2002) 745–759.
[8] J. Castillo, I.E. Grossmann, Comp. Chem. Eng. 5 (1981) 99–108.
[9] H. Greiner, Math. Comput. Model. 10 (1988) 529–550.
[10] M. Castier, P. Rasmussen, A. Fredenslund, Chem. Eng. Sci. 44 (1989) 237–248.
[11] C.M. McDonald, C.A. Floudas, Comp. Chem. Eng. 21 (1997) 1–23.
[12] A.V. Phoenix, R.A. Heidemann, Fluid Phase Equilib. 150–151 (1998) 255–265.
[13] F. Jalali, J.D. Seader, Comp. Chem. Eng. 23 (1999) 1319–1331.
[14] Y.P. Lee, G.P. Rangaiah, R. Luus, Comp. Chem. Eng. 23 (1999) 1183–1191.
[15] S.K. Wasylkiewicz, S. Ung, Fluid Phase Equilib. 175 (2000) 253–272.
[16] G.I. Burgos-Solorzano, J.F. Brennecke, M.A. Stadtherr, Fluid Phase Equilib. 219 (2004) 245–255.
[17] P. Koukkari, R. Pajarre, Calphad 30 (2006) 18–26.
[18] A. Bonilla-Petriciolet, G.A. Iglesias-Silva, K.R. Hall, Fluid Phase Equilib. 269 (2008) 48–55.
[19] A. Bonilla-Petriciolet, U.I. Bravo-Sanchez, F. Castillo-Borja, S. Frausto-Hernandez, J.G. Segovia-Hernandez, Chem. Biochem. Eng. Q. 22 (2008) 285–298.
[20] F. Jalali, J.D. Seader, S. Khaleghi, Comp. Chem. Eng. 32 (2008) 2333–2345.
[21] C.C.R.S. Rossi, L. Cardozo-Filho, R. Guirardello, Fluid Phase Equilib. 278 (2009) 117–128.
[22] A. Bonilla-Petriciolet, J.G. Segovia-Hernández, Fluid Phase Equilib. 289 (2010) 110–121.
[23] A. Bonilla-Petriciolet, G.P. Rangaiah, J.G. Segovia-Hernandez, J.E. Jaime Leal, in: G.P. Rangaiah (Ed.), Stochastic Global Optimization: Techniques and Applications in Chemical Engineering, World Scientific, 2010.
[24] D.V. Nichita, S. Gomez, E. Luna, Comp. Chem. Eng. 26 (2002) 1703–1724.
[25] D. Reynolds, A.J. Mulholland, J. Gomatam, J. Math. Chem. 22 (1997) 25–37.
[26] G.P. Rangaiah, Fluid Phase Equilib. 187–188 (2001) 83–109.
[27] M. Srinivas, G.P. Rangaiah, Comp. Chem. Eng. 31 (2007) 760–772.
[28] M. Srinivas, G.P. Rangaiah, Ind. Eng. Chem. Res. 46 (2007) 3410–3421.
[29] G. Nagatani, J. Ferrari, L. Cardozo Filho, C.C.R.S. Rossi, R. Guirardello, J. Vladimir Oliveira, M.L. Corazza, Braz. J. Chem. Eng. 25 (2008) 571–583.
[30] R. Khaledi, P.R. Bishnoi, Ind. Eng. Chem. Res. 45 (2006) 6007–6020.
[31] S.K. Wasylkiewicz, Chem. Eng. Sci. 55 (2000) 5177–5182.
[32] B.V. Babu, R. Angira, Comp. Chem. Eng. 30 (2006) 989–1002.
[33] M. Srinivas, G.P. Rangaiah, Ind. Eng. Chem. Res. 46 (2007) 7126–7135.
[34] S. Kirkpatrick, C. Gelatt, M. Vecci, Science 220 (1983) 671–680.

[35] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, E. Teller, J. Chem. Phys. 21 (1953) 1087–1092.
[36] A. Corana, M. Marchesi, C. Martini, S. Ridella, ACM Trans. Math. Softw. 13 (1987) 262–280.
[37] M.L. Corazza, L.C. Fiho, J.V. Oliveira, C. Dariva, Fluid Phase Equilib. 221 (2004) 113–126.
[38] B. Goffe, G. Ferrier, J. Rogers, J. Econometr. 60 (1994) 65–99.
[39] J.H. Holland, Adaptation in Natural and Artificial Systems, The University of Michigan Press, Ann Arbor, 1975.
[40] J.E. Dennis Jr., R.B. Schnabel, Numerical Methods for Unconstrained Optimization and Nonlinear Equations, Prentice-Hall, Englewood Cliffs, NJ, 1983.
[41] S. Ung, M.F. Dohety, Chem. Eng. Sci. 50 (1995) 23–48.
[42] G.A. Iglesias-Silva, A. Bonilla-Petriciolet, K.R. Hall, Fluid Phase Equilib. 241 (2006) 25–30.
[43] M.J. Okasinski, M.F. Doherty, Chem. Eng. Sci. 55 (2000) 5263–5271.
[44] Z. Michalewicz, D. Dasgupta, R.G. Le Riche, M. Schoenauer, Comp. Ind. Eng. 30 (1996) 851–870.
[45] S.O. Kimbrough, M. Lu, D.H. Wood, D.J. Wu, Lect. Notes Comput. Sci. 2723 (2003) 1148–1159.
[46] C. Blum, A. Roli, ACM Comput. Surv. 35 (2003) 268–308.