Gibbs Energy Minimization Using Simulated Annealing for Two-phase Equilibrium Calculations in Reactive Systems

A. Bonilla-Petriciolet,[a,*] U. I. Bravo-Sánchez,[a] F. Castillo-Borja,[a] S. Frausto-Hernández,[a] and J. G. Segovia-Hernández[b]

[a]Instituto Tecnológico de Aguascalientes, Departamento de Ingeniería Química
Av. López Mateos 1801, CP 20256, Aguascalientes, Ags. México
[b]Universidad de Guanajuato, Facultad de Ciencias Químicas,
Noria Alta s/n, C.P. 36050, Guanajuato, Gto. México

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Phase equilibrium calculations in systems subject to chemical reactions are involved in the design, synthesis and optimization of reactive separation processes. Until now, several methods have been developed to perform simultaneously physical and chemical equilibrium calculations. However, published methods may face numerical difficulties such as variable initialization dependence, divergence and convergence to trivial solutions or unstable equilibrium states. Besides, these methods generally use conventional composition variables and reactions extents as unknowns which directly affect the numerical implementation, reliability and efficiency of solving strategies. The objective of this work is to introduce and test an alternative approach to perform Gibbs energy minimization in phase equilibrium problems for reactive systems. Specifically, we have employed the transformed composition variables of Ung and Doherty and the stochastic optimization method Simulated Annealing for two-phase equilibrium calculations in reacting systems. Performance of this strategy has been tested using several benchmark problems and results show that proposed approach is generally suitable for the global minimization of transformed Gibbs energy in reactive systems with two-phase equilibrium.

Key words:

Global optimization, Gibbs energy minimization, simulated annealing, chemical equilibrium, phase equilibrium

Introduction

Phase equilibrium calculations in reacting systems are often required for designing processes of the chemical, petrochemical and metallurgical industries. During the last years, there has been a growing interest for developing new numerical tools to model the thermodynamic behavior of mixtures under physical and chemical equilibrium.[1] Until now, several methods have been proposed to perform reactive phase equilibrium calculations.[1–12] Principally, these methods have been developed to model reactive distillation process and they are based on equilibrium constant (*K*-value) method or Gibbs energy minimization techniques.[11] Also, they can be classed as either stoichiometric or nonstoichiometric, depending on the way in which the elemental abundance constraints are used in the algorithm.[13]

Strong interactions among components, phases and reactions may cause that this thermodynamic problem exhibits highly nonlinear behavior. By consequence, there are frequently computational difficulties in these calculations and published methods could not be reliable generally. Specifically, there are initialization troubles, the presence of trivial solutions or local minimums of Gibbs energy and numerical methods may also present slow convergence or divergence. It is important to note that few global solving methods have been proposed for this area.[2,7,9,10] Specifically, McDonald and Floudas[2] proposed a deterministic global optimization method which guarantees the global minimization of Gibbs energy in reacting mixtures using solution models. Also, Jalali and Seader[7] have successfully applied a nonlinear optimization based on homotopy continuation and Lagrange function while Burgos-Solórzano *et al.*[10] have used a reliable stability analysis, based on interval mathematics, to validate the results of phase and chemical equilibrium calculations.

The stochastic optimization methods such as Simulated Annealing (SA), Tabu Search (TS) or Genetic Algorithm (GA) have not been extensively studied in thermodynamic calculations for reacting mixtures. These methods have a great potential in

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[*] Corresponding author:
tel: (52) 4499105002 ext. 127, e-mail: petriciolet@hotmail.com

this area because they are reliable numerical tools that can be applied for multivariable and nonconvex problems and, by consequence, they are suitable for performing phase equilibrium calculations in reactive systems. For example, Reynolds *et al.*[14] have outlined a general procedure for the global minimization of Gibbs energy in non-reactive and reactive mixtures using SA method and a nonstoichiometric approach. Unfortunately, these authors have reported results for only non-reactive systems.

On the other hand, we consider convenient to remark that most of published methods use reaction extents and mole fractions as independent variables. For example, in this category the methods proposed by McDonald and Floudas[2] and Jalali and Seader[7] are classed. A suitable choice to reduce the problem dimensionality, and to favor the numerical performance of solution algorithms, consists in using techniques of variable transformation.[4,15] Only a few methods have used these transformed variables with the aim of improving the numerical behavior (efficiency and reliability) of solving strategies.[3,4,8,9] These kinds of algorithms are very attractive for the simulation of separation process and favor the study of complex multireactive multicomponent systems. Moreover, these approaches, in combination with stochastic optimization techniques, can be used to develop reliable strategies for phase equilibrium calculations in reactive systems.

The objective of this work is to introduce an alternative approach for performing two-phase equilibrium calculations in reactive systems. We use the transformed variables of Ung and Doherty[3,15,16] and the stochastic optimization method Simulated Annealing for the global minimization of Gibbs energy in reacting mixtures with two-phase equilibrium. Numerical performance of this strategy is tested using several multicomponent reactive mixtures and our results show that it is generally a suitable method to perform this kind of thermodynamic calculations.

Thermodynamic problem statement

Ung and Doherty[3,15,16] proposed the use of transformed composition variables with the objective of developing a simpler thermodynamic framework for modeling reactive systems. These transformed variables depend only on the initial composition of each independent chemical species and are constant as the reactions proceed. 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. These characteristics allow that all of the procedures used to obtain thermodynamic properties of non reacting mixtures can be extended to reacting systems and, by consequence, the non-reactive phase equilibrium algorithms can be easily modified to account for the equilibrium reactions.[9] Also, reactive phase diagrams in transformed coordinates look very similar to the non-reactive ones in the standard mole fraction coordinates. The main difference is in the shape of the composition space, which depends on the type of reaction in the system and could change if different reference components are selected.[9] Transformed amount fractions X_i are defined as

$$X_i = \frac{x_i - v_i N^{-1} x_{ref}}{1 - v_{TOT} N^{-1} x_{ref}} \quad i = 1, \dots, c - R \qquad (1)$$

where c is the number of components, R is the number of independent reactions, x_{ref} is the column vector of R reference component mole fractions, v_i is the row vector of stoichiometric number of component i for each reaction, v_{TOT} is a row vector where each element corresponds to the sum of the stoichiometric coefficients for all components that participate in reaction r, and N is a square matrix formed from the stoichiometric coefficients of the reference components in the R reactions.[3,15] It is important to note that eq. (1) provides constant values of tranformed mole fractions in single-phase reactions, or constant overall mole fractions in heterogeneous reactions:

$$Z_i = \frac{z_i - v_i N^{-1} z_{ref}}{1 - v_{TOT} N^{-1} z_{ref}} \quad i = 1, \dots, c - R.$$

In multiple-phase reactions, X_i-values in coexistent phases are variable and subject to phase equilibria requirements.

The reference mole fractions x_{ref} are calculated using eq. (1) and the equilibrium constants for each reaction K_{eq}^r by solving a system of R nonlinear equations given by

$$K_{eq}^r = \prod_{i=1}^{c} a_i^{v_i^r} \quad r = 1, \dots, R \qquad (2)$$

where a_i is the activity of component i and v_i^r is the stoichiometric number of component i in the reaction r, respectively. When we know the R reference mole fractions, for a set of $c - R$ specified transformed variables X_i, the corresponding mole fractions of $c - R$ non-reference components are calculated using eq. (1). In this work, we used the bisection method to find the mole fraction of reference component in all examples with only one reaction. Our experience indicates that bisection method works very well for this purpose.[17] On the other hand, for multireactive mixtures, the Newton method can be used to find the mole fractions of reference components.[3,15]

Classical thermodynamics indicates that minimization of Gibbs energy is a natural course for calculating the equilibrium state of a system. Gibbs energy minimization algorithm was introduced by White *et al.*[18] and, for reactive mixtures, minimizing Gibbs energy is equivalent to minimizing the transformed Gibbs energy.[19] In a multicomponent multireaction mixture, with c components and R independent chemical reactions, the dimensionless transformed molar Gibbs free energy of mixing can be defined as[9]

$$\begin{aligned}\frac{\Delta\hat{g}}{R_gT} &= \frac{\hat{g}-\hat{g}_0}{R_gT} = \sum_{i=1}^{c-R} X_i\left(\frac{\Delta\hat{\mu}_i\{X\}}{R_gT}\right) = \\ &= \sum_{i=1}^{c-R} X_i \ln(x_i\gamma_i\{X\}) = \sum_{i=1}^{c-R} X_i \ln\left(\frac{x_i\hat{\varphi}_i\{X\}}{\varphi_i}\right)\end{aligned} \tag{3}$$

where R_g is the gas universal constant, T is the temperature, $\frac{\Delta\hat{\mu}_i}{R_gT} = \frac{\hat{\mu}_i\{X\}-\mu_i^0}{R_gT}$ is the transformed chemical potential of component i, $\hat{g}_0$ is the pure component free energy, $\hat{g}$ is the transformed molar Gibbs free energy, φ_i is the fugacity coefficient of pure component, $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture and γ_i is the activity coefficient of component i, respectively. Note that $\hat{\varphi}_i$ and γ_i are functions of the transformed composition variables $\boldsymbol{X}$. Also, calculations of pure component free energies are avoided, which do not influence the equilibrium and stability calculations, if instead of $\hat{g}$ we use the transformed molar Gibbs energy of mixing $\frac{\Delta\hat{g}}{R_gT}$.[9]

For a feed with a global transformed composition Z that splits in π phases, $\frac{\Delta\hat{g}}{R_gT}$ is given by

$$\frac{\Delta\hat{g}}{R_gT} = \sum_{j=\alpha}^{\pi} \Phi^j \sum_{i=1}^{c-R} X_i^j\left(\frac{\Delta\hat{\mu}_i^j}{R_gT}\right) \tag{4}$$

The equilibrium transformed mole fractions X_i^j for all phases must satisfy the material balance

$$Z_i - \sum_{j=\alpha}^{\pi} \Phi^j X_i^j = 0 \quad i=1,\dots,c-R \tag{5}$$

where Φ^j is the transformed amount fraction for phase j. All transformed variables are subject to the following restrictions

$$\sum_{j=\alpha}^{\pi} \Phi^j = 1 \tag{6}$$

$$\sum_{i=1}^{c-R} X_i^j = 1 \quad j=\alpha,\dots,\pi \tag{7}$$

We note that Φ^j is defined as

$$\Phi^j = \phi^j \frac{(1-\nu_{TOT}N^{-1}x_{ref}^j)}{(1-\nu_{TOT}N^{-1}z_{ref})} \quad j=\alpha,\dots,\pi \tag{8}$$

being ϕ^j the mole fraction of phase j whose feasible domain is (0, 1) and, in accordance with,[16] is subject to $\sum_{j=\alpha}^{\pi}\phi^j = 1+\nu_{TOT}\xi$ where ξ is the column vector of R extents of reaction and z_{ref} is the column vector of R reference component mole fractions associated to the transformed feed Z, respectively.

At equilibrium, $\frac{\Delta\hat{g}}{R_gT}$ must be at the global minimum which is a necessary and sufficient condition for a thermodynamically stable state.[3,9,15,19] However, the global minimization of transformed Gibbs energy is a challenging optimization problem due to the objective function is nonconvex and may have multiple local optimums even for two-phase reacting systems modeled with simple thermodynamic equations. Considering this fact, local optimization methods are not suitable to solve this problem and a robust optimization strategy must be used. In the following section we describe the optimization procedure used to perform the global minimization of transformed Gibbs energy for two-phase equilibrium calculations in reactive systems.

Optimization approach

In this paper we have extended the optimization strategy proposed by Rangaiah,[20] which was originally developed to non-reactive mixtures, to perform an unconstrained Gibbs energy minimization in two-phase reactive systems. Using this approach, the transformed Gibbs energy minimization problem can be simplified by using a set of new variables instead of the transformed mole numbers or fractions as decision variables in the optimization strategy. The introduction of these variables eliminates the restrictions imposed by material balances, reduces problem dimensionality and the optimization problem is transformed to an unconstrained one. This approach is more suitable than the Lagrange multiplier formulation due to the significant reduction of problem dimensionality. So, for two-phase reacting systems where all transformed mole fractions have values in the range $X_i \in (0,1)$ or its phase equilibrium region satisfies this restriction, real variables λ_i in the range [0, 1] are defined and employed as optimization variables using the next equations

$$\hat{n}_i^{\alpha} = \lambda_i \hat{n}_i^{T} \quad i = 1,\ldots,c - R \tag{9}$$

$$\hat{n}_i^{\beta} = \hat{n}_i^{T} - \hat{n}_i^{\alpha} \quad i = 1,\ldots,c - R \tag{10}$$

where $\hat{n}_i^T = \hat{n}_i^\alpha + \hat{n}_i^\beta$ is the transformed mole number of component *i* in the feed, $\hat{n}_i^j = n_i - v_i^T N^{-1} n_{ref}$ is the transformed mole number of component *i* at phase *j* and λ_i is the optimization variable of the unconstrained optimization problem, respectively. The benefit of this modification is that all trial compositions will satisfy the material balance which allows the easy application of optimization strategies. It is important to note that this formulation can be used if $\hat{n}_i^T \neq 0$ for all $i = 1,\ldots c - R$.

Transformed Gibbs energy function is minimized using the simulated annealing (SA) stochastic optimization method. SA is a robust numerical tool that presents a reasonable computational effort in the optimization of multivariable functions; it is applicable to ill-structure or unknown structure problems, it requires only calculations of the objective function and can be used with all thermodynamic models.[21,22] In fact, SA has the attributes of a good numerical optimization method if is properly implemented: generality, acceptable computational time, reliability and ease of use.[23–25] It is considered as global optimization strategy and is one of the most used stochastic methods in engineering applications.[26] Specifically, in the field of thermodynamics, this method has been successfully used in phase stability and equilibrium calculations[14,17,20–22,27] and nonlinear parameter estimation.[28,29] This work introduces the application of this optimization strategy in the minimization of transformed Gibbs energy in reactive mixtures.

SA is a generalization of a Monte Carlo method and its concept is based on the thermodynamic process of cooling of molten metals to achieve the lowest energy state. Generally, it can locate the global optimum independently of initial guesses if the values for its algorithm parameters are properly selected. We have used the algorithm proposed by Corana *et al.*[30] because of its proved reliability in thermodynamic calculations.[17,20–22,29] In this algorithm, a trial point, randomly chosen within the step length ***VM*** (a vector of length *n* optimization variables) is the starting point. The function evaluated at this trial point is compared to its value at the initial point. The Metropolis criterion,[31] with a parameter termed annealing temperature T_{SA}, is used to accept or reject the trial point. If the trial point is accepted, the algorithm moves on from that point. If the trial is rejected, another point is chosen for a trial evaluation. After having adjusted each element of ***VM*** periodically, half of all function evaluations in that direction are acceptable. The temperature reduction factor *RT* is used to decrease T_{SA} employing $T_{SA}^{j+1} = RT \cdot T_{SA}^{j}$ where *j* is the iteration counter. Thus, as T_{SA} declines, downhill moves are less likely to be accepted and the percentage of rejections rises. As T_{SA} declines, ***VM*** falls and the method focuses upon the most promising area for optimization. If the final function values from the last temperatures (*NEPS* = 4) differ from the corresponding value at the current temperature by less than a tolerance value (*EPS*) and the final function value at the current temperature differs from the current optimal function value by less than this tolerance value, algorithm execution terminates. Corana *et al.*[30] provide a full description of this algorithm and we used the subroutine implemented by Goffe *et al.*[32] Fig. 1 shows the flow diagram of this algorithm.

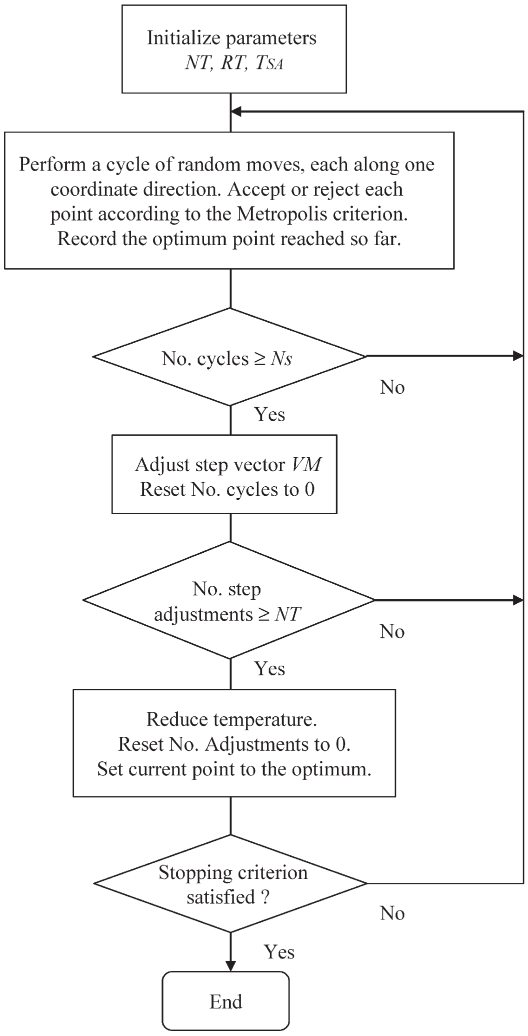

Fig. 1 – *Flow diagram of SA optimization algorithm*[29]

Numerical performance (reliability and efficiency) of SA method is significantly affected by the cooling schedule which is linked to the parameters T_{SA}^{0}, $R\,T$ and NT. These parameters require pre-calibration for new problems. We have tuned these parameters by performing several flash calculations for the reactive mixture: acetic acid + *n*-butanol ⇌ water + *n*-butyl acetate at 25 °C. Thermodynamic properties of this mixture were modeled with UNIQUAC equation using the model parameters reported by Wasylkiewicz and Ung.[9] Based on these calculations (not reported in this paper) and our numerical experience in phase stability analysis for several reactive mixtures,[17] we have defined that SA works acceptably well using the following conditions: $T_{SA}^{0} = 10$, $RT = 0.85$, $NT = 5 \cdot (c - R)$ where NT is the iteration number before annealing temperature reduction.

Results and discussion

We have tested the numerical performance of proposed method using several examples with different dimensionality and thermodynamic models. Most of our examples are standard benchmark in the literature of reactive distillation process, prediction of reactive homogeneous and heterogeneous azeotropes, multiple steady states in reactive separation units and phase stability analysis. All examples were solved several times using different feed conditions (temperature, pressure, chemical equilibrium constants or feed compositions). We have assumed that all chemical reactions are reversible and they occur in both phases. For variable transformation, in all examples we have selected arbitrarily the reference components. Also, tested conditions were arbitrary but we consider that they are sufficient to demonstrate the numerical performance of proposed strategy.

To determine the computational behavior of our algorithm, 100 runs are performed for each example using random initial values for decision variables λ_i and random number seeds for SA. We have defined a tolerance value of $ESP = 1 \cdot 10^{-6}$ for the convergence of SA method. Since stochastic optimization methods do not provide an accurate solution of the global optimum,[25,33] we have considered that the global minimization of transformed Gibbs energy is successful upon satisfying the condition

$$|OBJ_{calc} - OBJ_{\min}| < |OBJ_{\min}| \cdot 10^{-4} + 10^{-5} \quad (11)$$

where $OBJ_{\min}$ is the global minimum of the transformed Gibbs energy and OBJ_{calc} is the calculated value for this thermodynamic function with the optimization method, respectively. Eq. (11) has been used in several applications of other stochastic optimization methods.[33–35] We must remark that the global optimum $OBJ_{\min}$ for all examples was determined by solving the equality of transformed chemical potentials using several initial estimations. The stable two-phase solutions obtained by this procedure were considered as the corresponding global optimum $OBJ_{\min}$ values.

On the other hand, the numerical performance of our optimization strategy is characterized using widespread criterions reported in the literature of stochastic optimization methods;[25,33,36,37] a) success rate (*SR*) of finding the global minimum given as percent of calculations performed that satisfies eq. (11), b) mean total number of function evaluations (*NFEV*) during the optimization procedure, c) mean computational time and d) mean absolute percentage deviation of the calculated compositions from the known compositions at global minimum

$$AAD = \frac{100}{2(c-R)} \sum_{i=1}^{2} \sum_{j=1}^{c-R} \left| \frac{X_{ij}^{\min} - X_{ij}^{Calc}}{X_{ij}^{\min}} \right| \quad (12)$$

where $X_{ij}^{\min}$ is the global optimum value for the transformed composition of component *i* at phase *j* and X_{ij}^{Calc} is the calculated value for the transformed composition of component *i* at phase *j* using the stochastic method, respectively. Criteria a) and d) are used to characterize the reliability of optimization strategy while remaining ones are indicators of algorithm efficiency.[25] Mean values of *NFEV*, *AAD* and computational time are calculated considering only the successful calculations. All calculations were performed on a Processor Intel Pentium M 1.73 GHz with 504 MB of RAM using Fortran 4.0 software.

Phase stability analysis of calculated equilibrium compositions was performed using the Reactive Tangent Plane Distance Function (RTPDF) which is given by[9,19]

$$RTPDF = \sum_{i=1}^{c-R} X_i (\hat{\mu}_i|_X - \hat{\mu}_i|_Z) \quad (13)$$

where the global minimum of *RTPDF* is ≥ 0 for stable mixtures. This function was globally minimized also using SA optimization method. Bonilla-Petriciolet *et al.*[17] have reported that SA is robust to perform phase stability analysis in reacting and non-reacting mixtures. All reported solutions in this work are thermodynamically stable.

Finally, the overall method is outlined as follows for a flash calculation in a multicomponent reactive system:

1. Input n_i^0, equilibrium constants and model parameters.

2. Calculate z_i by $z_i = \dfrac{n_i^0}{\sum_{i=1}^{c} n_i^0}$ and Z_i using eq. (1). Do a phase stability analysis using Z and eq. (13). Continue with step 3 if the global optimum of RTPDF < 0, otherwise propose other n_i^0 and repeat step 2.

3. Calculate $\hat{n}^T = \sum_{i=1}^{c} n_i^0 - v_{TOT} N^{-1} \boldsymbol{n}_{ref}^0$.

4. Guess $\lambda_i \in (0,1)$ for $i = 1, \ldots, c - R$.

5. Calculate $\hat{n}_i^\alpha$ and $\hat{n}_i^\beta$ using eq. (9) and (10).

6. Calculate $X_i^j = \dfrac{\hat{n}_i^j}{\hat{n}^j}$ and $\Phi^j = \dfrac{\hat{n}^j}{\hat{n}^T}$ where $\hat{n}^T = \hat{n}^\alpha + \hat{n}^\beta$ and $\hat{n}^j = \sum_{i=1}^{c-R} \hat{n}_i^j$.

7. Define x_i^j as function of X_i^j and $\boldsymbol{x}_{ref}^j$.

8. Introduce x_i^j in the equations of equilibrium constants for each reaction K_{eq}^r.

9. Determine $\boldsymbol{x}_{ref}^j$ by solving the system of R nonlinear equations formed with K_{eq}^r. This step is performed for both phases to determine their composition in conventional mole fractions $\boldsymbol{x}$.

10. Calculate transformed Gibbs energy using eq. (4).

11. Check for minimum; proceed with SA method with new $\lambda_i \in (0,1)$ and repeat steps 5–11 until satisfy the convergence criterion of SA method.

This algorithm has been applied for all calculations performed in this paper. In the following text, we describe the results obtained for several reacting systems using this strategy.

Example 1. Our first example is a hypothetical reacting ternary mixture $A_1 + A_2 \rightleftharpoons A_3$ with liquid – liquid equilibrium. This system was introduced by Ung and Doherty[15] in their series of publications related to their transformed variables for reacting mixtures. Transformed mole fractions, considering third component as reference component, are given by

$$X_1 = \frac{x_1 + x_3}{1 + x_3} \tag{14}$$

$$X_2 = \frac{x_2 + x_3}{1 + x_3} = 1 - X_1 \tag{15}$$

where $X_i \in (0,1)$. Margules solution model with the data reported by Ung and Doherty[15] is used to calculate thermodynamic properties

$$\frac{G^{ex}}{R_g} = \frac{1}{2} \sum_i \sum_j A_{ij} x_i x_j \tag{16}$$

with $A_{12} = 478.6, A_{13} = 1074.484$ and $A_{23} = 626.9$, respectively. We have studied this system at 323.15 K and phase equilibrium calculations are performed for different values of the reaction equilibrium constant $K_{eq} \in (2.25, 30)$ and feed compositions. Based on our formulation, we have only two optimization variables for this example. Table 1 shows the results of equilibrium calculations for this reacting mixture. For all calculations performed, the proposed optimization strategy is very reliable to find the equilibrium compositions corresponding to the global minimum of transformed Gibbs energy. With respect to efficiency of SA method, mean *NFEV* ranged from 40 068 to 41 489 where this numerical effort is equivalent to 5 s of computational time. For this mixture, *AAD* is around $6.1 \cdot 10^{-03}$ %.

Table 1 – *Numerical performance of simulated annealing in the unconstrained global minimization of Transformed Gibbs energy for the reacting mixture $A_1 + A_2 \rightleftharpoons A_3$ at 323.15 K (Margules solution model)*

Feed conditions		Equilibrium conditions			Numerical performance[1]	
Z_1	K_{eq}	X_1^α	X_1^β	transformed Gibbs energy $\frac{\Delta \hat{g}}{R_g T}$	*NFEV*	*SR*, %
0.408	2.25	0.3921	0.4239	–0.4918	40068 ± 1584	100
0.5	2.5	0.4863	0.7400	–0.5237	40785 ± 1458	100
0.7	3	0.4936	0.8069	–0.4267	40582 ± 1437	100
0.55	4	0.5000	0.8606	–0.6761	40977 ± 1381	100
0.776	5	0.5030	0.8851	–0.4343	40748 ± 1269	100
0.6329	7.5	0.5065	0.9124	–0.7844	41100 ± 1375	100
0.75	10	0.5080	0.9243	–0.6246	41073 ± 1225	100
0.887	15	0.5094	0.9354	–0.3576	41105 ± 1169	100
0.535	20	0.5101	0.9406	–1.4197	41489 ± 1238	100
0.706	30	0.5107	0.9457	–1.0340	40598 ± 1471	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

Example 2. Butyl acetate is widely used as solvent in coating, adhesives and paint industries and it can be produced via the liquid-phase reaction of butanol and acetic acid in the presence of a suitable acidic catalyst.[11] This reaction is given by acetic acid (1) + *n*-butanol (2) $\rightleftharpoons$ water (3) + *n*-butyl acetate (4). Khaledi and Bishnoi[11] have modeled the production of butyl acetate via reactive distillation process. In this work, we have calculated several tie-lines for this mixture at 25 °C. UNIQUAC model is used to predict thermodynamic properties with the parameters reported by Wasylkiewicz and Ung.[9] The chemical equilibrium constant is calculated using $\ln K_{eq} = \frac{450}{T} + 0.8$ where T is given in K. Transformed compositions are defined using *n*-butyl acetate as reference component and are given by

$$X_1 = x_1 + x_4 \tag{17}$$

$$X_2 = x_2 + x_4 \tag{18}$$

$$X_3 = x_3 - x_4 = 1 - X_1 - X_2 \tag{19}$$

where $X_1, X_2 \in (0,1)$ and $X_3 \in (-1,1)$. Transformed Gibbs energy is minimized considering three optimization variables. Calculated tie-lines for this system are shown in Fig. 2 and the numerical performance of optimization strategy appears in Table 2. In this table, we also report the slopes of tie-lines X'_{12} which are calculated using

$$X'_{1j} = \frac{X_j^\alpha - X_j^\beta}{X_1^\alpha - X_1^\beta} \quad j = 2, \ldots, c - R \tag{20}$$

where $\sum_{j=2}^{c-R} X'_{1j} = -1$. Our results show that proposed algorithm is reliable to find the equilibrium compositions and it generally exhibits a 100 % success rate. Only for two feeds, it shows a poor performance. In these cases, SA method converged to trivial solutions (local optimums) where its value of transformed Gibbs energy is very near to the global one. For example, at Z(0.394, 0.274, 0.332), the trivial solution ($Z_i = X_i^\alpha = X_i^\beta$) has a transformed Gibbs energy value of –1.115 167 while the global optimum is equal to –1.115 171. We note that these local optimums satisfy the condition given by eq. (11). However, the phase stability analysis helped us to identify these failures of the proposed optimization method. As indicated by Burgos-Solozarno *et al.*,[10] phase stability analysis is a fundamental procedure which must be used to validate the results of any phase equilibrium calculation. On the other hand, for these difficult cases, it is convenient to modify the cooling schedule of SA algorithm to favor the convergence to the global optimum of transformed Gibbs energy. Specifically, an increment on T_{SA}^0 and NT provides a better performance, of course, at the cost of a greater computational effort. Also, we can improve the performance of SA method in these difficult problems using a proper initialization strategy. For example, we can use the results of phase stability as initial values for Gibbs energy minimization.[4] Finally, with respect to effi-

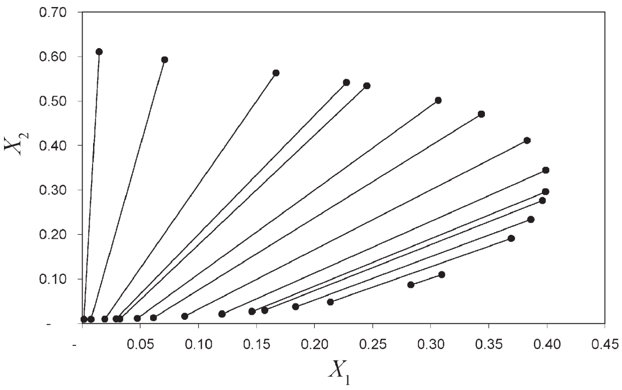

Fig. 2 – *Calculated tie-lines in transformed mole fractions for the reaction (1) acetic acid + (2) n-butanol ⇌ (3) water + (4) n-butyl acetate at 25 °C. UNIQUAC solution model.*

Table 2 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture (1) acetic acid + (2) n-butanol ⇌ (3) water + (4) n-butyl acetate at 25 °C (UNIQUAC solution model)*

	Equilibrium conditions		Numerical performance[1]	
Z	X'_{12}	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	$NFEV$	SR, %
(0.01, 0.4, 0.59)	46.0948	–0.2217	93757 ± 2543	100
(0.1, 0.2, 0.7)	2.6796	–0.4533	94477 ± 2839	100
(0.15, 0.5, 0.35)	3.7574	–0.8034	94357 ± 2744	100
(0.2, 0.3, 0.5)	1.8920	–0.7867	94537 ± 2491	100
(0.3, 0.3, 0.4)	1.3410	–0.9934	94273 ± 2655	100
(0.3, 0.4, 0.3)	1.6227	–1.1063	93985 ± 2454	100
(0.397, 0.294, 0.309)	1.0649	–1.1496	91297 ± 3413	0
(0.394, 0.274, 0.332)	1.0323	–1.1152	91789 ± 3620	3
(0.3, 0.15, 0.55)	0.9692	–0.7847	94237 ± 2435	100
(0.27, 0.1, 0.63)	0.9176	–0.6617	93961 ± 2244	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

ciency, the computational effort in terms of mean function evaluations ranged from 91 297 to 94 537 while mean computation time is around 40 seconds and *AAD* is lower than $4.5 \cdot 10^{-02}$ % for all tested conditions.

Example 3. Third example is the reaction of isobutene (1), methanol (2) and methyl *tert*-butyl ether (3) with *n*-butane (4) as an inert. MTBE is an important industrial chemical and has been used an anti-knock agent to replace tetra-ethyl lead in gasoline. Several simulation and experimental researches have been performed to study the MTBE reactive distillation process.[38] For example, Okansinski and Doherty[39] have studied the effect of the reaction equilibrium constant on the existence and location of reactive homogeneous azeotropes in this mixture. In this work, we have considered the vapor – liquid equilibrium for this reaction at p = 10.1325 bar and ϑ = 100 °C. Transformed mole fractions are defined using MTBE as reference component and are given by

$$X_1 = \frac{x_1 + x_3}{1 + x_3} \tag{21}$$

$$X_2 = \frac{x_2 + x_3}{1 + x_3} \tag{22}$$

$$X_4 = \frac{x_4}{1 + x_3} = 1 - X_1 - X_2 \tag{23}$$

where all transformed mole fractions ranged from 0 to 1. Wilson solution model and Antoine equation are used to calculated thermodynamic properties. Model parameters are taken from Maier *et al.*[40] and the reaction equilibrium constant is calculated using $\Delta G^0_{rxs} / R_g = -4205.05 + 10.0982\,T - 0.2667\,T \ln T$ where T is given in K. For ideal gas behavior, transformed Gibbs energy is given by[41]

$$\frac{\Delta \hat{g}}{R_g T} \cong \sum_{i=1}^{c-R} X_i \ln\left(\frac{x_i p}{p_i^{sat}}\right) \tag{24}$$

where p_i^{sat} is the vapor pressure of pure component i. For this reacting mixture, we also have three optimization variables. Calculated tie-lines for this mixture appear in Fig. 3 and details of equilibrium calculations are reported in Table 3. For all calculations performed, SA method shows a 100 % reliability where phase equilibrium compositions are located without numerical problems. In the other hand, mean value of *NFEV* ranged from 93 949 to 94 813 for all calculations performed while mean computation time is around of 85 s. For this reacting mixture, *ADD* ranged from $6.2 \cdot 10^{-03}$ to $7.48 \cdot 10^{-02}$ %. It is important to note that some published methods cannot handle the presence of inert components.[3] The inert components do not participate in any of the reactions, but have an influence on the phase equilibrium. Based on these results, it appears that proposed strategy is robust even when inert components are considered.

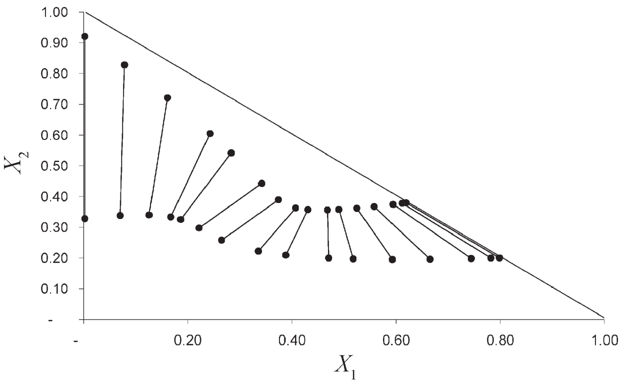

Fig. 3 – *Calculated tie-lines in transformed mole fractions for the reaction (1) isobutene + (2) methanol ⇌ (3) methyl tert-butyl ether and (4) n-butane as inert at 100 °C and 10.13 bar. Wilson model and Antoine equation.*

Table 3 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture (1) isobutene + (2) methanol ⇌ (3) methyl tert-butyl ether and (4) n-butane as inert at 100 °C and 10.13 bar. (Wilson solution model and ideal gas).*

	Equilibrium conditions		Numerical performance[1]	
Z	X'_{12}	transformed Gibbs energy $\frac{\Delta \hat{g}}{R_g T}$	*NFEV*	*SR*, %
(0.278, 0.365, 0.357)	1.2106	–1.3846	94285 ± 2756	100
(0.3, 0.3, 0.4)	1.2028	–1.4343	94381 ± 2415	100
(0.35, 0.25, 0.4)	1.9706	–1.4894	94177 ± 2658	100
(0.4, 0.25, 0.35)	3.4749	–1.5332	93949 ± 2966	100
(0.5, 0.3, 0.2)	–5.7654	–1.5961	94729 ± 2721	100
(0.7, 0.25, 0.05)	–1.1764	–1.3969	94177 ± 2620	100
(0.6713, 0.316, 0.0127)	–1.0483	–1.3990	94201 ± 2499	100
(0.15, 0.6, 0.25)	10.7574	–0.9409	94429 ± 2519	100
(0.00251, 0.42965, 0.56784)	–11621.85	–0.4909	94813 ± 2360	100
(0.6, 0.3, 0.1)	–1.5955	–1.5417	94141 ± 2888	100

[1] *NFEV* is the mean total number of function evaluations involved in the minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

Example 4. This example is also a hypothetical reacting ternary mixture $A_1 + A_2 \rightleftharpoons A_3$ with liquid – liquid equilibrium. We have considered a reaction equilibrium constant independent of temperature and thermodynamic properties are calculated using the Margules solution model where

$$\frac{g^E}{R_g T} = 3.6x_1x_2 + 2.4x_1x_3 + 2.3x_2x_3 \qquad (25)$$

Considering third component as reference component, transformed compositions are given by eqs. (14) and (15). Iglesias-Silva *et al.*[41] used this system to introduce the concept of equal area rule for multiphase equilibrium in reacting mixtures based on transformed variables. Based on their paper, this mixture shows three-phase equilibrium at $K_{eq} = 0.980019$ and $Z_1 \in (0.218336,\ 0.815122)$. We have performed phase equilibrium calculations for different values of K_{eq} and feed compositions that show a transformed Gibbs function with multiple local minima. With illustrative purposes, $\frac{\Delta\hat{g}}{R_g T}$-surface for some tested conditions appears in Fig. 4 where the tangent planes for stable and unstable equilibriums are indicated. Fig. 4 shows that this mixture can present unstable two-phase equilibrium states where a local optimization method can be easily trapped. For example, at $Z(0.6,\ 0.4)$ and $K_{eq} = 0.9825$ this system has two unstable phase equilibrium states: $X^{\alpha}(0.3677, 0.6323)$, $X^{\beta}(0.8104, 0.1896)$ with $\frac{\Delta\hat{g}}{R_g T} = -0.1425$ and $X^{\alpha}(0.2197,\ 0.7803)$, $X^{\beta}(0.8143, 0.1857)$ with $\frac{\Delta\hat{g}}{R_g T} = -0.1442$. So, this example is a good choice to test the reliability of the proposed optimization strategy. Two optimization variables are considered in the minimization of transformed Gibbs energy and results of phase equilibrium calculations are reported in Table 4. Again, for all tested conditions, SA method is capa-

Table 4 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture $A_1 + A_2 \rightleftharpoons A_3$ (Margules solution model $\frac{g^E}{R_g T} = 3.6x_1x_2 + 2.4x_1x_3 + 2.3x_2x_3$)*

Feed conditions		Equilibrium conditions			Numerical performance[1]	
Z_1	K_{eq}	X_1^{α}	X_1^{β}	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	*NFEV*	*SR*, %
0.6	0.9825	0.4845	0.8150	–0.1445	37772 ± 724	100
0.35	0.985	0.2184	0.4824	–0.1495	39857 ± 376	100
0.75	0.995	0.4891	0.8147	–0.1439	39996 ± 659	100
0.5	0.975	0.2156	0.8167	–0.1448	41105 ± 1202	100
0.63	0.95	0.2037	0.8240	–0.1389	41553 ± 723	100
0.559	1.0	0.4907	0.8146	–0.1507	39905 ± 1169	100

[1] *NFEV* is the mean total number of function evaluations involved in the minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

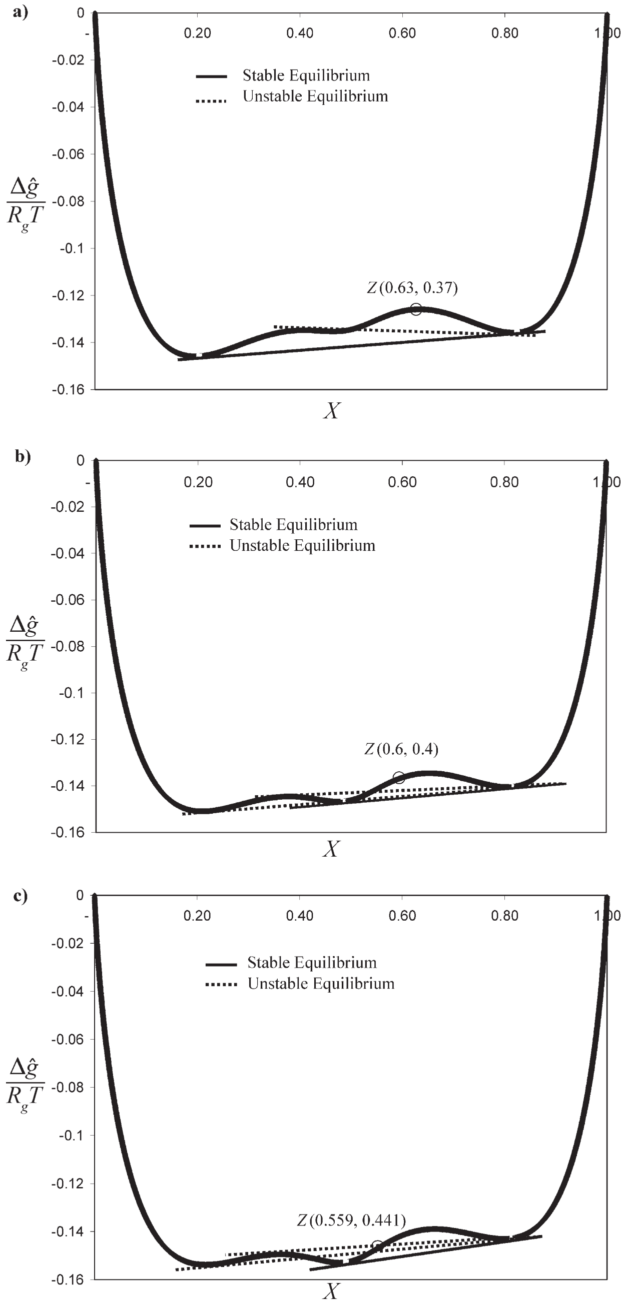

Fig. 4 – *Transformed Gibbs energy surface of a hypothetical reacting mixture $A_1 + A_2 \rightleftharpoons A_3$ (Margules solution model $\frac{g^E}{R_g T} = 3.6x_1x_2 + 2.4x_1x_3 + 2.3x_2x_3$) a) $K_{eq} = 0.95$, b) $K_{eq} = 0.9825$ and c) $K_{eq} = 1.0$*

ble of finding the global minimum of transformed Gibbs energy without numerical problems. On the other hand, *NFEV* ranged from 37 772 to 41 553 while computation time is around 2.5 s. *ADD* is lower than 0.02 % for all cases.

Example 5. *Tert*-amyl methyl ether (TAME) is an important chemical for gasoline and is produced by liquid-phase synthesis from methanol and iso-amylenes catalyzed by a sulfonic acid ion exchange resin.[38] In this reaction, five components take part: methanol, 2-methyl-1-butene, 2-methyl-2-butene, TAME and *n*-pentane as inert component. In this work, we have considered the lumped single reaction which can be written as: 2-methyl-1-butene (1) + 2-methyl-2-butene (2) + 2 methanol (3) $\rightleftharpoons$ 2 TAME (4) with *n*-pentane (5) as an inert solvent.[12,38] In first instance, VLE of this reaction without *n*-pentane as inert is studied. Transformed mole fractions, considering TAME as reference component, are given by

$$X_1 = \frac{x_1 + 0.5x_4}{1 + x_4} \tag{26}$$

$$X_2 = \frac{x_2 + 0.5x_4}{1 + x_4} \tag{27}$$

$$X_3 = \frac{x_3 + x_4}{1 + x_4} = 1 - X_1 - X_2 \tag{28}$$

All transformed fractions ranged from 0 to 1. Wilson and ideal gas models have been used to calculate thermodynamic properties of this mixture where thermodynamic parameters are taken from Chen *et al.*[38] Reaction equilibrium constant is calculated using $K_{eq} = 1.057 \cdot 10^{-04}\, e^{4273.5/T}$ where T is given in K. Phase equilibrium calculations are performed for several feeds at 335 K and 1.52 bar. Details of calculations are reported in Table 5 and calculated tie-lines reported in transformed mole fractions appear in Fig. 5. Only for one feed, the SA method shows a success rate lower than 100 %. For remaining calculations, this method is very reliable to find the global minimum of transformed Gibbs energy. With respect to efficiency, *NFEV* ranged from 93 781 to 94 873 where mean computational time is around 83 s and *AAD* is lower than $1.5 \cdot 10^{-02}$ % for all tested conditions.

In our second scenario for this example, we have considered the presence of *n*-pentane as inert. Transformed mole fractions are defined by eqs. (26) – (27) and

$$X_3 = \frac{x_3 + x_4}{1 + x_4} \tag{29}$$

$$X_5 = \frac{x_5}{1 + x_4} = 1 - X_1 - X_2 - X_3 \tag{30}$$

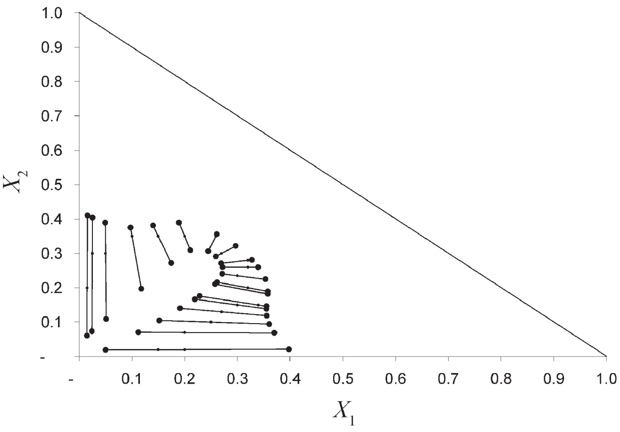

Fig. 5 – *Calculated tie-lines in transformed mole fractions for the reaction (1) 2-methyl-1-butene + (2) 2-methyl-2-butene + + (3) 2 methanol ⇌ (4) 2 tert-amyl methyl ether at 335 K and 1.52 bar. Wilson model and ideal gas.*

Transformed Gibbs energy is minimized considering four optimization variables. Phase equilibrium calculations are performed at 335 K and 1.52 bar where the details of calculations and numerical

Table 5 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture (1) 2-methyl-1-butene + (2) 2-methyl-2-butene + (3) 2 methanol ⇌ (4) 2 tert-amyl methyl ether at 335 K and 1.52 bar (Wilson model and ideal gas)*

	Equilibrium conditions		Numerical performance[1]	
Z	X'_{12}	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	*NFEV*	*SR*, %
(0.3, 0.15, 0.55)	–0.2072	–1.0868	94453 ± 2354	100
(0.32, 0.2, 0.48)	–0.2800	–1.2179	94393 ± 2554	100
(0.354, 0.183, 0.463)	–0.2856	–1.2264	93089 ± 2881	63
(0.2, 0.07, 0.73)	–0.0076	–0.7003	94345 ± 2935	100
(0.15, 0.02, 0.83)	0.0064	–0.3950	94429 ± 2519	100
(0.27, 0.3, 0.43)	0.8089	–1.2913	93781 ± 2205	100
(0.2, 0.35, 0.45)	–3.6767	–1.2218	94573 ± 2549	100
(0.1, 0.35, 0.5)	–8.5301	–0.9623	94477 ± 2335	100
(0.05, 0.3, 0.65)	–162.6184	–0.7089	94873 ± 2418	100
(0.025, 0.3, 0.675)	327.5080	–0.5787	94117 ± 2614	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

Table 6 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture (1) 2-methyl-1-butene + (2) 2-methyl-2-butene + (3) 2 methanol ⇌ (4) 2 tert-amyl methyl ether with (5) n-pentane as inert at 335 K and 1.52 bar (Wilson model and ideal gas)*

	Equilibrium conditions		Numerical performance[1]	
Z	(X'_{12}, X'_{13})	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	*NFEV*	*SR*, %
(0.15, 0.02, 0.8, 0.183)	(0.0099, –1.2428)	–0.5104	170006 ± 4526	100
(0.1, 0.1, 0.6, 0.2)	(0.9406, –5.8340)	–1.0432	170412 ± 4236	100
(0.05, 0.05, 0.85, 0.05)	(0.8069, –6.2438)	–0.4882	169857 ± 4033	100
(0.1, 0.15, 0.7, 0.05)	(6.0243, –13.4445)	–0.8726	170177 ± 3726	100
(0.15, 0.15, 0.6, 0.1)	(0.8465, –4.0396)	–1.1136	170091 ± 4150	100
(0.07, 0.17, 0.64, 0.12)	(7.9130, –18.0152)	–0.9581	169558 ± 3937	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

performance of SA method for some feeds are reported in Table 6. For all tested conditions, this method is capable of finding the transformed equilibrium compositions with 100 % reliability. We note again that the presence of inert component does not affect the performance of proposed method. With respect to the efficiency *NFEV* ranged from 169 518 to 170 412, which is equivalent to 199 s of computational time. Finally, AAD is lower than $3.0 \cdot 10^{-02}$ % for all feeds.

Example 6. In this example we have considered the reacting mixture of propene (1) + water (2) ⇌ 2-propanol (3) which has been studied by Castier *et al.* [42] and Stateva and Wakeham.[5] Equilibrium constant is considered independent of temperature and flash calculations are performed using $K_{eq} = 23$ at 353.15 K.[5] We have used the SRK EoS with conventional mixing rules and all interaction parameters equal to zero. Parameters of pure components are taken from Smith and Van Ness.[43] For this reaction, transformed mole fractions are defined using 2-propanol as reference component and are given by eqs. (14) – (15). Equilibrium calculations are performed for different pressures and feed compositions. Numerical results of calculations performed are reported in Table 7. With the exception of one feed, the SA method showed a 100 %

Table 7 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture (1) propene + (2) water ⇌ (3) 2-propanol at 353.15 K (SRK EoS)*

		Equilibrium conditions			Numerical performance[1]	
p/kPa	Z_1	X_1^α	X_1^β	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	*NFEV*	*SR*, %
100	0.025	0.0002	0.3745	–0.0912	40982 ± 1437	100
	0.001			–0.0038	41035 ± 1256	100
	0.370			–1.3479	39089 ± 1802	41
1000	0.8	0.5663	0.9149	–0.7365	41025 ± 1370	100
	0.621			–1.3089	41057 ± 1254	100
	0.840			–0.5766	40977 ± 1420	100
3000	0.934	0.8649	0.9800	–0.3125	41377 ± 1291	100
	0.942			–0.2771	40881 ± 1156	100
	0.959			–0.2018	40646 ± 1230	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

success rate to find the global optimum of transformed Gibbs energy. For all calculations performed, mean value of NFEV ranged from 39 089 to 41 377 and computational time is around 30 s. This computational time is very reasonable considering that an EoS model is used. With respect to solution accuracy, AAD is lower than 0.4 % for all cases.

Example 7. Our final example is a hypothetical quaternary system that follows the two reactions: $A_1+A_2 \rightleftharpoons A_3$ and $2A_3 \rightleftharpoons A_4+A_2$. We have considered ideal behavior for both liquid and vapor phases, where the Antoine equation is used to calculate the vapor pressures of pure components with the parameters reported by Ung and Doherty.[3] The transformed mole fractions are defined using A_3 and A_4 as reference components and they are given by

$$X_1 = \frac{x_1 + x_3 + 2x_4}{1 + x_3 + 2x_4} \tag{31}$$

$$X_2 = \frac{x_2 + x_3 + x_4}{1 + x_3 + 2x_4} = 1 - X_1 \tag{32}$$

where X_1 and $X_2 \in (0,1)$. The chemical equilibrium constants are calculated using $K^1_{eq} = \exp\left(-22.57 + \frac{7368}{T}\right)$ and $K^2_{eq} = \exp\left(-7.0265 + \frac{6844.1}{T} - \frac{1391790}{T^2}\right)$ where T is given in K. Two optimization variables are considered for the global minimization of transformed Gibbs energy. So, flash calculations are performed for five arbitrary feeds at 1.01325 bar and 310 K, and our results are reported in Table 8. In general, the Simulated Annealing is robust to minimize the transformed Gibbs energy for the performed calculations. Specifically, for only one feed, the success rate of SA method is lower than 100 %. On the other hand, the computational time is around 12 s and the mean value of NFEV ranged from 40 753 to 41 041, respectively. We note that this computational time is lower than that obtained for other examples with the same dimensionality. This result is due to the use of algebraic approach to find the reference mole fractions inside the stage of variable transformation. Finally, ADD is lower than 0.03 % for all calculations performed.

For all systems with only one reaction, we note that the computational time involved in the stage of variable transformation can be reduced significantly by using Newton method for finding the mole fraction of reference component. Unfortunately, the Newton method is highly sensitive to initial values while bisection method is more reliable for this purpose.

Conclusions

In this paper, we have introduced and tested an alternative approach for performing two-phase equilibrium calculation in reactive systems based on transformed Gibbs energy minimization using Simulated Annealing optimization method. In fact, this work introduces the use of a stochastic optimization strategy for the global minimization of Gibbs energy in reactive systems using transformed variables. Our results show that the SA method generally can locate the global optimum of Gibbs energy in two-phase systems; it can be applied with multicomponent reactive systems (with or without inert components) using many thermodynamic model without problem reformulations and requires a reasonable computational time. Although we can not offer a theoretical guarantee for the global

Table 8 – *Numerical performance of simulated annealing in the unconstrained global minimization of transformed Gibbs energy for the reacting mixture $A_1+A_2 \rightleftharpoons A_3$ and $2A_3 \rightleftharpoons A_4+A_2$ at 310 K and 1.01325 bar (Ideal Gas and Ideal Solution)*

	Equilibrium conditions			Numerical performance[1]	
Z_1	X_1^{α}	X_1^{β}	transformed Gibbs energy $\frac{\Delta\hat{g}}{R_g T}$	*NFEV*	*SR*, %
0.7	0.4399	0.9541	–1.6283	41041 ± 1407	100
0.445			–1.2980	40933 ± 1536	79
0.56			–1.4470	40809 ± 1240	100
0.92			–1.9133	40753 ± 1395	100
0.63			–1.5376	40833 ± 1619	100

[1] *NFEV* is the mean total number of function evaluations involved in the global minimization of transformed Gibbs energy and *SR* is the success rate to find the transformed phase equilibrium compositions. 100 trials performed with random initial values for optimization variables and random number seeds.

minimization of transformed Gibbs energy using SA method, it appears that this strategy is a suitable numerical tool for the analysis and study of phase equilibrium behavior of multicomponent reacting systems.

In future work, we will test and compare the numerical performance of SA method with respect to others stochastic optimization methods, as Genetic Algorithm or Tabu search, in this kind of thermodynamic calculations.

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Nomenclature

a – activity, mol dm^{-3}
A_{ij} – parameter of Margules solution model
AAD – mean absolute percentage deviation
c – number of components
$\hat{g}$ – transformed molar Gibbs free energy, J mol^{-1}
K_{eq} – chemical equilibrium constant
n – mole number
N – square matrix formed for all components that participate in reaction r
NT – iteration number of Simulated Annealing optimization method
OBJ – objective function value
p – pressure, bar
ref – reference component
R – reaction number
R_g – universal gas constant, J mol^{-1} K^{-1}
RT – temperature reduction factor of Simulated Annealing optimization method
T – thermodynamic temperature, K
T_{SA} – temperature of Simulated Annealing optimization method
v_i^r – stoichiometric number of component i
X – transformed mole fraction
X'_{12} – slope of tie-line
x – mole fraction
Z – transformed feed composition
z – feed mole composition

Greek letters

α, β – phase at equilibrium
ϕ – phase mole fraction
γ – activity coefficient
φ – fugacity coefficient
λ – optimization variable
μ – chemical potential, J mol^{-1}
ξ – adimensional extent of reaction
Φ – transformed phase mole fraction
ϑ – temperature, °C

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