Calculation of chemical and phase equilibria via simulated annealing

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We present a new class of techniques for the solution of the chemical and phase equilibria problem for reacting species in a closed system. The minimisation of the Gibbs free energy for all the species in the system is conducted using the technique of simulated annealing (SA). The SA objective function incorporates non-ideal equations of state. This new approach is demonstrably able to solve multi-species and multi-phase LTCE problems in ideal-gas solutions, ideal solutions and mixtures of ideal and non-ideal solutions.

1. Introduction

The determination of the species composition of a reacting, closed system at equilibrium is a problem in chemical physics which is of major industrial importance, and yet one for which no efficient yet flexible solution method has been developed. In this paper, we wish to present the application of a new class of techniques for the solution of this problem, which has resulted in a method that is both highly flexible and applicable to every instance of a chemical equilibrium problem. The new method involves the application of the simulated annealing (SA) algorithms, based on the processes culminating in thermal equilibrium, found in physical annealing [7].

The chemical equilibrium problem arose here in the context of heat exchanger fouling studies [2,5]. In these studies, the chemically frozen boundary layer (CFBL) [8] theory provides a means of calculating condensation deposition, based on an abbreviated flux law for boundary layer mass transport. The resultant species composition is subject to local thermochemical equilibrium (LTCE) constraints and controlled by transport properties predicted by the first order Chapman–Enskog theory [1]. A broad classification of the many other subject areas in which the CE problem arises is given by Smith and Missen [9]. Important examples include chemical kinetics (inorganic, organic and analytical) and energy conversion processes.

Of the two main approaches currently used for the solution of this problem, the first approach requires knowledge of the reaction mechanisms amongst the species in the system [2,5]. These reaction mechanisms are then expressed in terms of equations

which involve the equilibrium constant for each reaction. The equilibrium constant is then calculated for each reaction mechanism from the difference in the Gibbs free energies of the reactants and products. The second, more popular approach, minimises the total Gibbs free energy for all the species in the system. Our previous work has concentrated on the first approach [5] which resulted in good estimates for the LTCE calculation but has several drawbacks including requirement of prior knowledge of the reaction mechanisms and good initial estimates for the main species in the system [1]. In this paper we will outline the formulation and solution of the problem via SA.

Section 2 presents a brief outline of the use of non-ideal equations of phase and how such models can cause significant differences in chemical equilibrium calculations which are based upon ideality. In section 3, we present the main features of the extension of our previous work [6] to a class of problems involving significant non-linearities in the objective function to be minimised, i.e., those which assume more than one phase for the species in the system and where mixtures of ideality and non-ideality are assumed. The extensions embodied in this work demonstrate that the SA method is able to handle multi-phase equilibrium problems in a highly satisfactory way. Computational experiments are reported which show how the algorithm may easily be tailored to specific models for species' equations of state and phase. We will also show how the algorithm produces solutions at least as good as those produced by existing methods, methods which cannot readily be tailored in this way. The method is demonstrated by minimising the highly non-linear and non-ideal non-random two-liquid (NRTL) equation for modelling liquid phases. We then relate the results to existing approaches. In section 4, we discuss the relationship between the extensions to phase variability in the models and techniques used in this paper, and important features of the combustion models, to produce a framework for the prediction of important multi-phase dew-point calculations. Such calculations are, for the class of problems under discussion, highly complex, involving a sequence of successive multi-species chemical and phase equilibria problems.

2.   Non-ideal expressions in chemical and phase equilibria calculations via simulated annealing

In this section we summarise the stoichiometric extensions [6] and relate this to the crucial incorporation of phase variability in the chemical equilibrium calculations. The most important feature of the above approach is that the chemical stoichiometry of the system is independent of the phases in which the species are assumed to exist, and is also independent of the equations used to predict Gibbs free energy in each phase. Thus, the major modifications required to the new approach to handle phase change and/or non-ideal gases and liquids is in the objective functions assumed for such species. In this way, the SA approach benefits from the advantages of the deterministic stoichiometric algorithms [9] without suffering from their local optimisation defects.

The modifications described in the previous paragraph in fact are a feature of the important generalisation of the chemical equilibrium problems to those involving

phase change. This gives rise to a consideration of the phase equilibrium problem, in which, for a closed system of species, the amount of each species occupying each phase must be determined accurately. In the combustion models this problem arises at the dew-points [4,5] of each the given species, where certain amounts of the given species occupy different phases. Thus, at chemical and phase equilibria, we are able to predict the rate of fouling due to the condensation of salts, as well as the temperature this occurs.

A major difficulty in the incorporation of phase equilibrium calculations in the chemical equilibrium calculation is that, in order to obtain accurate estimates from the minimisation procedure for the amounts of salts deposited, a highly non-linear and non-convex equation of state must be used to model the Gibbs energies of species in liquid phases, since such phases are typically non-ideal [9]. As is well-known, such equations of state are powerful in accurately predicting the highly complex behaviour within the species system, and yet are sufficiently complex themselves to defeat most current deterministic optimisation algorithms. The problem is crucial in combustion modelling, since this involves simultaneous chemical reaction and phase change at species dew-points. Hence, each of the species must be modelled as existing simultaneously in two or more phases. This gives rise to non-linearities in the objective function.

3. Minimisation of Gibbs free energy in non-ideal systems via simulated annealing

This section develops the ideas of objective function modification, and its relation to the combustion modelling work. Here we discuss how to implement the non-random two-liquid (NRTL) equation [3] for describing non-ideal liquid phases mixed in the system with ideal gases. This presents a cost function for minimisation which is highly non-linear and non-convex in the objective. The NRTL equation is an equation which has the important property of being able to represent the mixing of multi-component systems via binary parameters. There are three such parameters in each pair of species in liquid form in the system under consideration.

3.1. NRTL equation for non-ideal liquid phases

The following is an example of the NRTL equation [4]; when all species present are in liquid phase,

$$G_L^k = \sum_{i=1}^{n_c} x_{ik} \left(\sum_{j=1}^{n_c} \frac{x_{jk} m_{ij}}{\sum_{l=1}^{n_c} x_{lk} \phi_{lj}} + \ln x_{ik} \right). \tag{1}$$

Note that the gas constant R and the temperature T do not appear explicitly in (1), since they are assumed to be embodied in the appropriate algorithm parameters. Here

x_{ik} is a variable describing the mole fraction of species (i.e., 'component', since no chemical reaction is assumed to occur at this stage) i in phase k, given by

$$x_{ik} = \frac{z_{ik}}{\sum_{i=1}^{n_c} z_{ik}}, \quad i = 1, 2, \ldots, n_c, \ k = 1, 2, \ldots, K, \tag{2}$$

where n_c is the total number of species and K is the number of phases. Here z_{ik} is the variable describing the number of moles of species i in phase K. The entities m_{ij} and ϕ_{ij} are given data in the NTRL model, specific to the system under study and corresponding to an important feature of this model, in that it takes explicit account of (liquid) species molecular interactions. The total number of moles here is denoted by Z,

$$Z = \sum_{i=1}^{N} Z_i, \tag{3}$$

where Z_i is the number of moles of species i and N is the total number of moles equal to n_c. In the general chemical equilibrium problem $N = M + 1$. When liquid and vapour phases are assumed present in the system, as in the combustion models at dew-points, the expression in (1) is modified to

$$G_L^k = \sum_{i=1}^{n_c} x_{ik} \left(\sum_{j=1}^{n_c} \frac{x_{jk} m_{ij}}{\sum_{l=1}^{n_c} x_{lk} \phi_{lj}} + \ln x_{ik} + \ln P_i^{\text{sat}} \right) \tag{4}$$

with P_i^{sat} the saturation pressure of the ith species, and the vapour expression is assumed to be of an ideal form,

$$G_V^k = \sum_{i=1}^{n_c} x_{ik} (\ln x_{ik} + \ln P_i). \tag{5}$$

The following equations are used to derive the parameters above [4]:

$$\phi_{ij} = \exp(-\alpha_{ij} t_{ij}), \tag{6}$$
$$m_{ij} = t_{ij} \phi_{ij}, \tag{7}$$
$$\alpha_{ij} = \alpha_{ji}, \tag{8}$$
$$\alpha_{ii} = 0, \tag{9}$$
$$t_{ii} = 0. \tag{10}$$

Problem-specific values for the terms t_{ij}, ϕ_{ij}, α_{ij} and Z_i are given in the examples following our description of the new extension to the recent SA approach. Finally, assuming no chemical reactions (i.e., only phase equilibrium), the constraints on the problem are

$$\sum_{k=1}^{K} z_{ik} = Z_i, \quad z_{ik} \geqslant 0, \ i = 1, 2, \ldots, n_c, \ k = 1, 2, \ldots, K. \tag{11}$$

The overall expression for Gibbs free energy calculation is thus

$$G(K, t, x, y) = \sum_{k=1}^{K} \sum_{i=1}^{n_c} z_{ik} G_{t_k}^k(x), \qquad (12)$$

where t_k is one of the phase types $\{V, L, S\}$.

Earlier work on the solution of LTCE problems via the SA algorithm [6] discussed the need to incorporate two important extensions within that method; the assumption of non-ideal behaviour of the gases present in combustion models, and the need to predict the amounts of salt deposited in the given systems as a function of temperature. The first problem is effectively solved in the rest of this paper, where we describe how to solve the minimisation of Gibbs free energy for phase equilibrium using SA. The second problem is also solved, by the incorporation of the dew-points of the respective species as saturation pressures within the NRTL equations (2)–(11).

The overall model for determining species phase and chemical equilibria in such systems uses the elemental abundance matrix for specifying the closed nature of the system [9]. In the phase equilibrium problem demonstrated here, the constraints (11) alone require to be satisfied. Nevertheless, for chemical and phase equilibria problems such as those occurring in the combustion models, the modification to the following method is straightforward, requiring only the inclusion of the stoichiometric matrix and associated perturbation operators discussed in the previous section.

Note that due to the assumed interactions between components, a component may exist in more than one liquid phase. Thus, the phase equilibrium problem in its most general form considers the number of phases in which a component is present to be a variable for optimisation [4]. This most general form of the problem is considered here, and the examples solved later involve components existing in more than one liquid phase.

3.2. Solution representation scheme, perturbation operators and linear update mechanisms for NRTL minimisation

The discussions of the previous section highlight the fact that, within the SA-based approach [6], solution representation schemes, perturbation operators and cost update mechanisms used for the phase equilibrium problem here must, in the absence of penalty functions, generate a sequence of solutions (i.e., a sequence of z matrices) which satisfy equation (11), and which asymptotically minimise the Gibbs energy functions described by the addition of (4) and (5). Clearly, the simplest and most efficient such perturbation operator involves the interchange of mole numbers, for a given component, between phases. Thus, for example, if the system composition is described by the matrix z as follows (the species list is reproduced from Mulholland

et al. [6] but the respective mole numbers are cited for example only):

$$z = \begin{array}{c} \\ \text{NaOH} \\ \text{Na}_2\text{SO}_4 \\ \text{Na}_2\text{CO}_3 \\ \text{Na} \\ (\text{NaOH})_2 \\ \text{SO}_2 \\ \text{SO}_3 \\ \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{O}_2 \end{array} \begin{array}{cc} \text{(l)} & \text{(g)} \\ \left[\begin{array}{cc} 0.5 & 0.5 \\ 0.64 & 0.2 \\ 0.24 & 0.4 \\ 0.5 & 0.6 \\ 0.12 & 0.22 \\ 1.25 & 0.55 \\ 1.4 & 0.76 \\ 0.75 & 0.88 \\ 0.6 & 0.12 \\ 0.35 & 0.1 \end{array} \right] \end{array} \tag{13}$$

where (l) and (g) refer to simple liquid and gas phases, respectively, and z_{ik} counts the number of moles per phase for phases $k = \text{(l)}, \text{(g)}$, then a fast perturbation operator can select a species at random from the species list and 'switch' a randomly chosen number of moles between phases. This satisfies the constraints (11), if the random amount is bounded appropriately. For the rest of this discussion, we restrict our attention to the main details of the phase equilibrium problem, noting that the methods presented hereinafter generalise using the mechanism cited for chemical equilibrium calculation.

This generalisation, as discussed later, produces a new method for simultaneously determining not only the amounts of each species present in the system at a given temperature, pressure and initial feed (itself a computationally difficult problem for standard methods), but also the particular phases in which each of the species are present. This can then be used, after suitable parametrisation of the new method, for predicting combustion fouling rates via the models described previously [2,5].

For the purposes of algorithm initialisation, we note that for the problem under discussion, a suitable starting point, satisfying (11), is to take

$$z_{ik} = \frac{Z_i}{k}, \tag{14}$$

that is, to assume initially an equimolar division of each species amongst the various phases. Often, one assumes, after practical experimentation with the real physical system, that only certain species are present at a given temperature and pressure, and so some species will never be present at certain phases [10]. However, the model formulated here, and the new algorithmic approach possess two important properties. Firstly, the system composition arising from the algorithm termination is independent of the initial choice in (14), a property possessed by few of the current methods. Secondly, the algorithm typically finds global minima of the given problem, so determining the actual constituents within the various phases. In fact, any initial values satisfying (11) may be taken.

The calculation of the updated cost function arising from the sum of (4) and (5) can be carried out quickly here due to the simple nature of the perturbation operator described. This is done by calculating the update by a series of additions and subtractions. As an example, we shall assume that V vapour phases, L liquid phases and S solid phases are present in the system and use the following phase indexing system. If phase k is such that $1 \leqslant k \leqslant V$, then this corresponds to a vapour phase, if $V + 1 \leqslant k \leqslant V + L$, then this k corresponds to liquid phase, and if $V + L + 1 \leqslant k \leqslant V + L + S$, then k corresponds to solid phase. Now suppose that $z_{mp} := z_{mp} + \varepsilon$, $z_{mq} := z_{mq} - \varepsilon$, i.e., after random perturbation the amount of species m in the vapour phase p increases by ε moles, and that in some phase q decreases by ε (ensuring molar balance). Thus, the change in contribution to overall Gibbs energy from equation (5) is calculated from

$$(z_{mp})' := z_{mp} + \varepsilon, \qquad (z_{mq})' := z_{mq} - \varepsilon, \quad 1 \leqslant p \leqslant V, \ q \geqslant 1, \qquad (15)$$

$$\sum_{i=1}^{n_c} (z_{ip})' = \sum_{i=1}^{n_c} z_{ip} + (z_{mp})' - z_{mp}, \qquad (x_{mp})' = \frac{(z_{mp})'}{\sum_{i=1}^{n_c} (z_{ip})'}, \qquad (16)$$

and where the new Gibbs energy for vapour phase p can be found by updating the expression (5) when it is written in terms of mole numbers,

$$
\begin{aligned}
G_V^k &= \sum_{i=1}^{n_c} x_{ik}(\ln x_{ik} + \ln P_i) = \sum_{i=1}^{n_c} \frac{z_{ik}}{\sum_{r=1}^{n_c} z_{rk}} \left(\ln z_{ik} - \ln\left(\sum_{r=1}^{n_c} z_{rk} \right) + \ln P_i \right) \\
&= \frac{\sum_{i=1}^{n_c} z_{ik} \ln z_{ik}}{\sum_{r=1}^{n_c} z_{rk}} - \ln\left(\sum_{r=1}^{n_c} z_{rk} \right) + \ln P_i.
\end{aligned}
\qquad (17)
$$

The term $\sum_{r=1}^{n_c} z_{rk}$ in (17) is calculated by the addition and subtraction highlighted in (15) and (16) above, since a single component only is modified in the given perturbation mechanism. The term involving P_i is a constant for each component, and the term in the numerator of the fraction in (17) can also be calculated by such addition and subtraction. Thus, the total number of arithmetical operations required to update the vapour phase Gibbs free energy term is a constant, O(1), independent of number of components n_c. This is because the ideal form assumed for vapour phase Gibbs free energy involves no component interactions. Such interactions, modelled by the more complex expression (4) for NRTL component interactions, involve more intensive computation to derive the effects of perturbation, as highlighted in the following discussion.

For a general perturbed component vector of species, if the phases specified for the interchange of mole numbers are both liquid, e.g., from a liquid phase to another liquid phase, etc., the function (4) can be updated in a way similar to the previous

case. Note that the expression (4) can be simplified by substituting mole numbers for mole fractions, and then simplifying, to yield

$$G_L^k = \sum_{i=1}^{n_c} x_{ik} \left(\sum_{j=1}^{n_c} \frac{z_{jk} m_{ij}}{\sum_{l=1}^{n_c} z_{lk} \phi_{lj}} + \ln x_{ik} + \ln P_i^{\text{sat}} \right)$$

$$= G_V^k + \sum_{i=1}^{n_c} x_{ik} \left(\sum_{j=1}^{n_c} \frac{z_{jk} m_{ij}}{\sum_{l=1}^{n_c} z_{lk} \phi_{lj}} \right). \tag{18}$$

By writing $P_i = P_i^{\text{sat}}$ in (18), and so interchanging the order of summation and making a last substitution, this is equal to

$$G_V^k + \frac{1}{\sum_{r=1}^{n_c} z_{rk}} \sum_{j=1}^{n_c} \frac{z_{jk}}{\sum_{l=1}^{n_c} z_{lk} \phi_{lj}} \sum_{i=1}^{n_c} z_{ik} m_{ij}. \tag{19}$$

Thus, the update of (4) can be calculated after perturbation, if the given perturbation mechanism of (15) and (16) is used, by use of (19). The rightmost sum in (19) under perturbation, for each j, can be calculated by a single addition and subtraction of perturbed and pre-perturbed $z_{ik} m_{ij}$ values, respectively; for each j, this requires 2 arithmetical operations. The denominator in the fraction of (19) can, for each j, be modified similarly, i.e., with 2 arithmetical operations of addition and subtraction. Thus, the two inner sums of (19) are modified in $O(n_c)$ operations using the perturbation mechanism defined, despite the fact that the NRTL equation is a means of calculating highly complex Gibbs energy terms using matrix functions (of z) for component physical properties in (6)–(10). The overall computational effort required to update (19) is therefore dominated by that for the NRTL equation, $O(n_c)$, when compared to that for the vapour phase Gibbs energy also contained in (19), which is $O(1)$ as derived above.

3.3. Examples of algorithm parametrisation and use

Having described the extensions to the new method, and highlighted the modifications to function calculation, solution representation, algorithm operators and cost function update contained in these extensions, we proceed to present the numerical results of testing the above method on two well-known and difficult examples from the literature. It should be clear from the given examples that both problems are relatively small in terms of number of components; an important expression of the difficulty of the chemical and phase equilibria problem is that it is difficult to find test problems in the literature which have been solved to (guaranteed) optimality by another method, and yet which are large enough to test the full generality of new approaches.

However, these examples are used here because they are sufficiently small to enable a complete exposition of the algorithm parametrisation for these cases, and yet possess multiple local minima, meaning that most existing mathematical techniques for their solution are not sufficiently powerful. Also, the examples have been completely solved using other techniques, thus facilitating a direct comparison of execution

times and nearness to optimality (two common measures often combined to estimate minimisation algorithm performance) between the methods here and those in the literature. Finally, both problems represent important industrial problems and possess multi-species in multi-phase, with molecular interactions in the liquid phases.

Example 1. This example is given in McKinnon et al. [4], where it is solved to optimality, and in McDonald and Floudas [3], where it is again solved using different methods. The problem has component list {butyl-acetate, water}, so that $n_c = 2$. The problem concerns determining the amounts of both components in two liquid phases (hence, 'liquid–liquid equilibrium'). Here, using our notation of the previous section, $V = 0$ and $L = 2$. The table of algorithm parameters mentioned in (6)–(10) is given below (see table 1), taken from McKinnon et al. [4] with appropriate modification of symbols.

The set of parameters found suitable for use within the SA/GIBBS algorithm were, $T_0 = 10.0$, $T_\infty = 1.0 \times 10^{-8}$, which under the usual geometric SA schedule gives rise to 20 713 algorithm iterations. However, such iterations in no way correspond in computational requirements to those of McKinnon et al. [4], due to the specialised perturbation operator described in the previous section. In this way, the algorithm is able to carry out a relatively large number of low-effort iterations within a short period of time. The algorithms of McKinnon et al. [4] typically feature a relatively low amount of relatively large-effort iterations. The perturbation step-sizes used on this example, described in the previous section, were bounded in the usual way to retain solution feasibility under perturbation. However, it was found that reducing the randomly chosen mole interchange values improved the accuracy of the method considerably, which is important when searching for trace amounts of certain species, as in column z_{11} above. Using the notation of the previous section, a suitable scaling was found to be $\varepsilon = \varepsilon/10.0$. For the purposes of testing the new method, 10 algorithm runs were carried out; the results of these are given in table 2 together with a summary of statistics.

The accuracy of our method is judged first and foremost by the mean cost statistic. Clearly, the mean cost of these runs compares very favourably with the optimal result given in McKinnon et al. [4] and McDonald and Floudas [3], of -0.0201983; the difference is in the seventh decimal place. In fact, the cost of the solutions obtained in runs 1–7 and 10, calculated using FORTRAN 77 double precision computation, is lower than the 'optimal' solution of the cited works, which is derived within a tolerance of 10^{-5}, i.e., only 5 decimal places. However, admittedly the variation in the corresponding solutions, for our improvements, is low.

Table 1
Example 1. Data.

i	j	t_{ij}	ϕ_{ij}	α_{ij}	Z_i (mol)
1	2	3.00498	0.30794	0.39196	0.5
2	1	4.69071	0.15904	0.39196	0.5

Table 2
Results of SA/GIBBS on example 1. Data.

| Run	Cost	z_{11}	z_{12}	z_{21}	z_{22}
1	−0.020200068	0.000699683	0.4992999	0.1555096	0.3444904
2	−0.020199883	0.000689591	0.49931	0.1555302	0.3444698
3	−0.020199741	0.000684327	0.4993153	0.1549931	0.3450069
4	−0.020199711	0.000683097	0.4993165	0.1554161	0.3445839
5	−0.020200093	0.000701959	0.4992976	0.1558079	0.3441921
6	−0.020198889	0.00066321	0.4993364	0.1553784	0.3446216
7	−0.020199946	0.000692366	0.4993072	0.1554123	0.3445877
8	−0.020198172	0.000649937	0.4993497	0.1545425	0.3454575
9	−0.020180625	0.000522977	0.4994766	0.1519692	0.3480308
10	−0.020199619	0.000680448	0.4993192	0.1548428	0.3451572
Mean	−0.020197675	0.00066676	0.49933284	0.15494021	0.3450597
SD	6.02054E−06	5.29486E−05	5.29471E−05	0.001108748	0.0011087
CV	−0.029808078	7.94117829	0.010603565	0.715597016	0.3213204

Time Series for SA/GIBBS
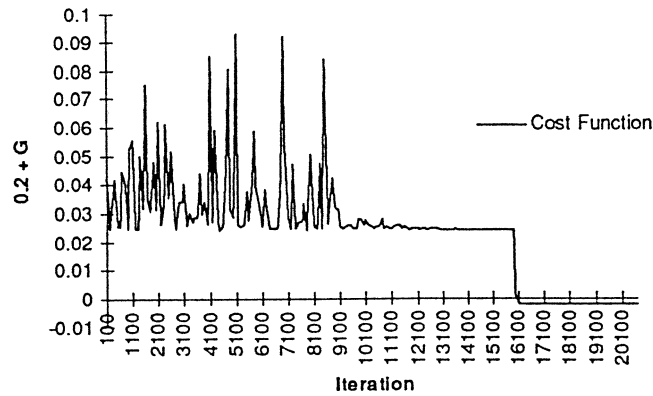
Figure 1.

The reliability of our method on this problem is also excellent. This can be judged from the summary statistics relating to the standard deviation and coefficient of variation (CV). The CV shows here how the cost of the best solutions obtained by the method during the trials varied. The CV for cost is 0.03% (or 3 in 10 000), which is very low and indicates a high degree of consistency in finding near-optimal solutions. The CV for the actual solutions shows a maximum for the variation of component 1 in phase 1, and is 7%, which is again consistent relative to the exceptionally low values of this variable in all near-optimal solutions found. Again, the locations of the solutions found here agree very well with those of the cited works. A typical time series of the run of the SA/GIBBS algorithm on this example is given in figure 1, which graphs the cost of the current solution against algorithm iteration.

Example 2. The second example presented here is also discussed in the cited works of example 1, in both cases solving the problem to guaranteed optimality. This is a 'liquid–liquid–vapour equilibrium' problem involving the species {benzene-acetonitrile-water}, so that each component of this species list can exist simultaneously in a vapour and/or two liquid phases. In this case $n_c = 3$, and using our own notation, $V = 1$ and $L = 2$. McKinnon et al. [4] describe how to derive the appropriate parameters for use in equations (4) and (5), via substitution in (6)–(10). The t values, given in table 3 below, have been derived from the following expression given in McKinnon et al. [4]:

$$t_{ij} = \frac{g_{ij} - g_{jj}}{RT}, \quad R = 1.9872 \text{ cal/K/mol}, \ T = 333 \text{ K}. \tag{20}$$

The t_{ij} values from this equation are listed in table 2, where it is assumed that $t_{ii} = 0$ as in (10). The g_{ij} values in (20) are found from tables 3 and 4, where this data is again taken from McKinnon et al. [4]. Table 5 contains the rest of the data for the problem. Again, 10 runs of the algorithm were presented on this more difficult problem. The parameters used in this problem are the same as in example 1.

Table 3
Values for t_{ij} in example 2.

t_{ij}	$j = 1$	$j = 2$	$j = 3$
$i = 1$	0.0	1.508453	5.868187
$i = 2$	0.099344	0.0	0.54942
$i = 3$	5.817366	1.90770	0.0

Table 4
Values used to calculate t in example 2.

i	j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	α_{ij}
1	2	998.20	65.74	0.88577
1	3	3883.20	3849.57	0.24698
2	3	363.57	1262.40	0.3565

Table 5
Remaining problem data in example 2.

i	P_i^{sat}	P_i (atm.)	Z_i (mol)
1	0.512337709	0.769	0.34483
2	0.485404650	0.769	0.31034
3	0.195255785	0.769	0.34843

4.   Summary and conclusions

Following on from condensation modelling [2,5], and the model solution techniques presented [6], we have discussed how to solve difficult computational minimisation problems related to heat exchanger fouling models, in a way which can incorporate the physical properties of the species involved in these systems, including phase change, multi-phase conditions and phase and chemical equilibria problems. This work, based upon the extensions of the novel SA approach for Gibbs free energy minimisation, is able to take account of the complexities introduced by the existence of a large number of chemically reacting species present in a variety of phases and over a large range of temperatures, pressures and system feed compositions. This is done in a way which exploits the advantages of current approaches to the solution of this problem, such as the utilisation of the concept of chemical stoichiometry, whilst avoiding most of the disadvantages.

In summary, we have presented a method for the solution of chemical and phase equilibria problems which can be identified with the following advantages:

(i) the algorithm can handle any Gibbs potential function and any combination of such functions;

(ii) any equation of state can be used;

(iii) the algorithm iterations are efficient;

(iv) gradient singularities, a problem commonly found in standard techniques, do not occur;

(v) convergence of the algorithm to a local minima of the Gibbs function can be avoided; and

(vi) the final solution produced by the algorithm is independent of starting conditions.

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