Calculation of constrained equilibria by Gibbs energy minimization

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Received 29 September 2005; received in revised form 28 November 2005; accepted 30 November 2005

Available online 27 December 2005

Abstract

The Gibbs energy minimization encompasses active use of the chemical potentials (partial molar Gibbs energies) of the constituents of the system. Usually, these appear at their equilibrium values as a result of the minimization calculation, the mass balance constraints being the necessary subsidiary conditions. Yet, there are several such physico-chemical circumstances where the system is also constrained by other factors, such as surface effects, potential fields or even by chemical reaction kinetics. In this paper a particular method is presented by which constrained chemical potentials can be applied in a multi-phase Gibbs energy minimization. The constrained potentials arise typically from work-related thermodynamic displacements in the system. When Gibbs energy minimization is performed by the Lagrange method, these constraints appear as additional Lagrangian multipliers. Examples of the constrained potential method are presented in terms of the electrochemical Donnan equilibria in aqueous systems containing semi-permeable interfaces, the phase formation in surface-energy controlled systems and in systems with affinities controlled by chemical reaction kinetics. The methods have been applied successfully in calculating distribution coefficients for metal ions together with pH-values in pulp suspensions, in the calculation of surface tension of alloys, and in thermochemical process modeling involving chemical reaction rates.

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1. Introduction

With the improving numerical capacity of present day computers, Gibbs energy minimization has gained increasing interest not only in the calculation of complex chemical equilibria and phase diagrams, but also in performing complicated process simulations. The advantage of the thermodynamic method is that it avails a common basis for complex chemical problems in multi-phase systems with various proportions and conditions. Both industrial processes and small scale laboratory systems can be calculated successfully with the Gibbs energy method.

However, the multi-phase Gibbs energy minimization technique has not been applicable to more complicated problems where the thermodynamic system is subjected to a displacement caused by a generalized work coefficient or when the chemical or phase change is constrained by slow reaction kinetics. Such problems are often encountered in practical materials science and in the simulation of processes, notably including such topics as membrane separated electrochemical equilibrium systems, complex surface energy equilibria and finally time-dependent systems controlled with chemical reaction rates. A common feature of all these phenomena is that the total Gibbs energy is affected by an additional physical constraint, which is due to a work-related thermodynamic displacement, including the affinity of kinetically controlled chemical reactions.

In the conventional Gibbs energy minimization calculation, the system is subjected to the mass balance constraints which are deduced from the input amounts of the components of the equilibrium system. The Gibbs free energy minimum is often solved by using the Lagrange method of undetermined multipliers with the mass balances of the system components as the necessary subsidiary constraints. The chemical potentials of the constituents of the multi-component system can then be solved in terms of the elements of the mass conservation (stoichiometric) matrix and the Lagrange multipliers. As the elements of the matrix are dimensionless factors, the Lagrange multipliers represent chemical potentials of the system components. By extension of the matrix, one may introduce additional constraints for a desired set of constituents and thus take into account additional Gibbs energy terms due to the surface tension, electrochemical potential or affinity of a kinetically controlled reaction. In what follows, we present a
Lagrangian method, which allows a number of such phenomena to be calculated with Gibbs energy minimization.

2. Theory

2.1. Overview of the Lagrangian method

The Gibbs energy of the multicomponent system is written in terms of the chemical potentials as follows

\[ G = \sum_\alpha \sum_k n_k^\alpha \mu_k^\alpha \]  

(1)

where \( \mu_k^\alpha = \mu_k^\alpha(T, p, n_k^\alpha) \) is the chemical potential of the species \( (k) \) in the respective phase \( \alpha \) and \( n_k^\alpha \) is its molar amount. The Gibbs energy is an extensive state variable and the chemical potential \( \mu_k^\alpha \) is the partial molar Gibbs energy of the constituent \( k \).

For the Lagrangian method, the mass balance equations are needed as follows [1,2]:

\[ \phi_j = b_j - \sum_\alpha \sum_k \sum_l a_{kj}^\alpha n_k^\alpha = 0 \quad (j = 1, 2, \ldots, l) \]

(2)

where \( b_j \) is the total input amount of a system component and \( a_{kj}^\alpha \) refers to the stoichiometric number of component \( k \) in constituent \( j \), in its respective phase \( \alpha \). The number of phases is denoted by \( \Psi \), and \( N_\alpha \) is used for the number of constituents in phase \( \alpha \). A system component is typically, but not necessarily, a chemical element. The total number of system components is \( l \). The individual mass balances are denoted for brevity as \( \phi_j \).

The Lagrangian function is then written in terms of the Gibbs energy and the mass balance conditions:

\[ L = G - \sum_{j=1}^l \lambda_j \phi_j \]

(3)

where the \( \lambda_j \)s are the undetermined multipliers of the Lagrange method. The minimum condition of the Gibbs energy is the same as this condition for the Lagrangian function \( L \), and is received at constant temperature and pressure by finding the extremum points for the respective partial derivatives:

\[ \left( \frac{\partial L}{\partial n_k} \right)_{j \neq k} = \mu_k - \sum_{j=1}^l a_{kj} \lambda_j = 0 \quad (k = 1, 2, \ldots, N) \]

(4)

Conditions (2) and (4) together give a set of \( N + l \) equations with an equal number of unknowns to be solved \( (N \) is the total number of constituents). The solution gives the molar amounts \( (n_k) \) at equilibrium for the closed system when temperature and pressure are held constant. In addition, the undetermined multipliers \( (\lambda_j) \) become solved. By definition of (3), they connect the mass balances of each system component to the Gibbs energy. In fact, the solution of the undetermined multipliers produces each \( \lambda_j \) as representing the chemical potential of the respective system component \( j \). To emphasize, we denote this potential by \( \pi_j \) and get, for the chemical potentials of any constituent \( k \):

\[ \mu_k = \sum_{j=1}^l a_{kj} \pi_j \quad (k = 1, 2, \ldots, N) \]

(5)

Eq. (5) gives the chemical potential of any constituent \( k \) as a linear combination of the respective potentials of the system components [1]. The respective \((N \times l)\) conservation matrix is

\[
A = \begin{pmatrix}
a_{1,1}^{(1)} & \cdots & a_{1,l}^{(1)} & a_{1,l+1}^{(1)} \\
\vdots & \ddots & \vdots & \vdots \\
a_{N,1}^{(1)} & \cdots & a_{N,l+1}^{(1)} & a_{N,l+1}^{(1)} \\
\vphantom{a_{1,1}^{(1)}} \vdots & \ddots & \vdots & \vdots \\
(\Psi) & \cdots & a_{N,l}^{(\Psi)} & a_{N,l+1}^{(\Psi)}
\end{pmatrix}
\]

(6)

In the conventional CALPHAD methods, the system components represent stoichiometric building blocks of the constituents and the matrix elements \( a_{kj} \) are the respective stoichiometric coefficients. For example, the chemical potential of carbon dioxide \( (\text{CO}_2) \) in an equilibrium system with the elements carbon \( (C) \) and oxygen \( (O) \) as system components will be given in terms of their potentials. Carbon dioxide consists of one unit of carbon and two units of oxygen, and the chemical potential is accordingly \( \mu_{\text{CO}_2} = \mu_C + 2\mu_O \). The condition is equivalent to the requirement that the affinity of all possible chemical reactions is zero at equilibrium.

The independent components of the system may be chosen to represent stoichiometric entities other than chemical elements. These include, for example, chemical substances, ions and electronic charge, which characteristically may occur as independent components of a phase constituent. The stoichiometric coefficients given in the transformed matrix must be consistent with the conservation of mass in the system, which is defined in terms of the total mass \( (\text{m}_\text{tot}) \) as \( \sum_{j=1}^l b_j M_j = \text{m}_\text{tot} \). Here, \( M_j \) is the molecular mass of the system component \( j \).

2.2. Setting additional constraints with the conservation matrix

The conservation matrix \( A \) has a row for each species and a column for each independent conservation equation [1,3]. The conservation matrix is thus made up of the coefficients of the conservation equations valid in the system. As stated above, in chemical reactions, atoms of elements and electric charge are conserved. Sometimes, additional conservation equations are required, for example to denote conserved molecular groups [4]. The new constraint appears as an additional column in the conservation matrix:

\[
A = \begin{pmatrix}
a_{1,1}^{(1)} & \cdots & a_{1,l}^{(1)} & a_{1,l+1}^{(1)} & \cdots \\
\vdots & \ddots & \vdots & \vdots & \ddots \\
a_{N,1}^{(1)} & \cdots & a_{N,l+1}^{(1)} & a_{N,l+1}^{(1)} & \cdots \\
\vphantom{a_{1,1}^{(1)}} \vdots & \ddots & \vdots & \vdots & \ddots \\
(\Psi) & \cdots & a_{N,l}^{(\Psi)} & a_{N,l+1}^{(\Psi)} & \cdots
\end{pmatrix}
\]

(7)

Here the matrix elements for the phase constituents remain equivalent to those in Eq. (6), but the additional column with
subscript \(l+1\) represents the new conservation equation. Thus, the element \(a^q_{k,l+1}\) is 0 for all those constituents \(k\) which are not affected by the additional constraint, whereas \(a^q_{k,l+1}\) is not zero for those constituents which are affected by the said constraint. Thus, for example, the number of aromatic groups to be conserved in each aromatic compound can be attached to the Gibbs energy calculation by the new pseudoelement [4]. It is obvious that the mass balance of the total system is not affected if the molecular mass of the pseudoelement \(M_{l+1}\) is chosen to be zero.

The additional constraint affects the chemical potential of the phase constituents through Eq. (5). As the elements of the matrix are dimensionless factors, the Lagrangian multipliers represent additive contributions to the chemical potentials of the constituents. Applying this property, one may introduce additional conditions for a desired set of constituents, thus generalizing the conservation matrix to applicable physical constraints of the system. Such constraints may be set for the electroneutrality condition of phases [5], or for an affinity related metastable or kinetically conserved species [6,7]. Further, a constraint set for the surface area of the system is similarly linked to the surface energy of the system and it can be used to predict the surface tension and surface compositions of multi-component mixtures [8]. In what follows, three simple examples are presented to detail the use of the additional constraint when calculating surface tensions of multi-component alloys, to determine Donnan equilibria in membrane-separated multi-phase aqueous systems, and to conserve the affinity of a kinetically conserved chemical reaction in a multi-phase system.

3. Calculation examples

3.1. Computation of surface tension

Surface energy can appear as an additional factor in the Gibbs energy function of a multi-component system. If the (flat) surface layer is assumed to be one monolayer thick, the total Gibbs energy of the system is:

\[
G = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_b} A_k n_k^b
\]  

Here superscripts and subscripts \(b\) and \(s\) have been used for the bulk and surface phases, respectively. As the same species can be assumed to be present both in the bulk and in the surface, with \(N\) being the total number of species, we have \(N_b = N_s = N/2\) and the same subscript denotes the same chemical species in both the bulk and the surface phase. The surface tension is a function of temperature and composition, \(\sigma = \sigma(T, x_1)\). Each constituent of the surface phase occupies a characteristic molar surface area \(A_k\). The total surface area is assumed to be constant at equilibrium:

\[
\sum_{k=1}^{N} A_k n_k^s = A
\]

Considering the two phases, Eq. (9) may also be written as

\[
A/A_0 - \sum_{\alpha=1}^{N} \sum_{k=1}^{\alpha} (A_k^q / A_0) n_k^q = 0
\]  

where the molar surface for any species in the bulk phase is zero. The area terms are divided by a normalization constant \(A_0\) with dimensions of \(m^2/mol\). This equation then shows the constraint of constant surface area, in analogy to the mass balance conditions of Eq. (2). It is then mathematically possible to consider Eq. (10) as an additional constraint of a multi-component system, where the surface layer is introduced as a separate phase and the surface area as an additional system component [6].

Using (8) in (3) and by applying (2) and (10), the Lagrangian function of the multi-component surface system becomes

\[
L = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_b} A_k n_k^b
\]

\[
- \sum_{j=1}^{l+1} \lambda_j \left( b_j - \left( \sum_{k} a^b_{kj} n_k^b + \sum_{k} a^s_{kj} n_k^s \right) \right)
\]

Here, summation of the constraints extend over all system components, that is, \(j = 1, 2, \ldots, l, l + 1\), where the last constraint is the one deduced from the surface area, with \(b_{l+1} = A/A_0\), and \(a^b_{k,l+1} = A_k^q / A_0\). From Eqs. (4) and (11), the partial derivative conditions become:

\[
\left( \frac{\partial L}{\partial n_k^b} \right)_{i \neq k} = \mu_k^b - \sum_{j=1}^{l} a^b_{kj} \lambda_j = 0
\]

\[
\left( \frac{\partial L}{\partial n_k^s} \right)_{i \neq k} = \mu_k^s + A_k \sigma - \sum_{j=1}^{l+1} a^s_{kj} \lambda_j = 0
\]

At equilibrium, the chemical potential of each species is independent of phase, that is, \(\mu_k^b = \mu_k^s = \mu_k\). From Eqs. (12) and (13), it follows that the surface tension of the mixture is obtained as the additional Lagrange multiplier:

\[
\sigma \cdot A_0 = \pi_{l+1}
\]

The numerical value of the constant \(A_0\) can be chosen arbitrarily, but for practical calculation reasons it can be advantageous if the ratio \(A_k/A_0\) is a value close to unity, being of the same order of magnitude as the stoichiometric coefficients appearing in the conservation matrix.

To perform the calculations with a Gibbs energy minimizing program, such as ChemApp [9], the input data must be arranged in terms of the standard state and excess Gibbs energy data of chemical potentials of the system constituents. It is sufficient here to state that the chemical potentials of species \(k\) in the bulk and surface phases can be written in terms of the respective activities as follows:

\[
\mu_k^b = \mu_k^0 + RT \ln a_k^b
\]

\[
\mu_k^s = \mu_k^0 s + RT \ln a_k^s - A_k \sigma
\]

where the superscript \(0\) refers to the standard state, and \(a_k^b\) and \(a_k^s\) are the activities of the constituent \(k\) in the bulk phase and
calculation of the multi-phase Donnan equilibrium with Gibbs energy minimization. Thus, the distribution of ions in the two compartments, together with formation of precipitating phases for example, can be calculated.

In Table 2 an example of the stoichiometric matrix for a two-compartment Donnan system is presented. For the two solution phases present, notations ′ and ″ have been used. The constancy of the amount of water in the second compartment is ascertained by setting the respective matrix element to unity. As there is no molecular mass assigned for this system component, the mass for the constituent H₂O in the second solution volume (solvent″) is obtained from the respective system components O (for oxygen) and H (for hydrogen). The electronic charge of aqueous ions is introduced to both aqueous phases in terms of the negative charge numbers, and an additional electroneutrality constraint has been set for the secondary aqueous phase, denoted in the matrix as q″. The immobile anion (Anionq) has been positioned as a constituent for the secondary aqueous phase ″. For clarity, just values different from zero are shown.

With the given matrix conditions, by using Eq. (5) for the chemical potentials of charged species at equilibrium, we have

\[
\mu_k'' = \mu_k'^0 + RT \ln a_k''
\]

where the chemical potentials of the primary and secondary aqueous phases have been written in terms of their respective activities (a′ and a″). The additional term (z_k p q″) deduced from Eq. (5) is due to the supplementary electroneutrality constraint set for the secondary aqueous phase. Eq. (18) is comparable to the general form of electrochemical equilibrium of charged species [11]:

\[
\mu_k'' + RT \ln a_k'' = \mu_k'^0 + RT \ln a_k' + z_k F \Delta \phi
\]

where F is the Faraday constant and \( \Delta \phi \) is the electrical potential difference between the primary and secondary aqueous phases. It follows that the solution of the Gibbs problem with the additional electroneutrality constraint gives this potential difference as the Lagrange multiplier \( \pi_{q''} \):

\[
F \Delta \phi = \pi_{q''}
\]

Similarly, from Eq. (5) one may deduce the chemical potential of water in the two aqueous phases in terms of the Lagrangian multipliers. Obviously, these two chemical potentials are not equal, but differ by the Lagrange multiplier \( \pi_{q_{solvent}} \). This is because the Gibbs energy model does not include the effect of the contractive forces of the membrane system, which prevent the transport of water from the primary compartment to the secondary volume. Yet the model can be applied to determine the activity difference of the two aqueous phases and thus to define the expected pressure difference in various membrane systems [12,13]. Assuming incompressibility, i.e. that the partial molar volume of water is constant in the moderate pressure range of the membrane systems, we have

\[
-\pi_{solvent''} = (p'' - p') V_{solvent}' = RT \ln \left( \frac{a'_{solvent}}{a''_{solvent}} \right)
\]
Fig. 1. Surface composition and surface tension as a function of bulk composition in a Fe–FeO mixture at 1970 K.

Table 2
Example of the stoichiometric matrix for a Donnan equilibrium system with two membrane-separated compartments containing ionic solutions

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>H</th>
<th>Na</th>
<th>C</th>
<th>Ca</th>
<th>Solvent''</th>
<th>Anion_m</th>
<th>ε''</th>
<th>q''</th>
</tr>
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<tbody>
<tr>
<td>H₂O</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH⁻</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO⁻</td>
<td>3</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂⁻</td>
<td>3</td>
<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH⁻</td>
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<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>2</td>
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<td></td>
</tr>
<tr>
<td>HCO⁻</td>
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<tr>
<td>CO₂⁻</td>
<td>3</td>
<td>1</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Anion_m</td>
<td></td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CaCO₃

The partial molar volume of the solvent (water) is denoted by \( V_{\text{solvent}}^{m} \). The constraining factor \( \pi_{\text{solvent}}'' \), emerges as the potential difference due to the different activities of solvent water in the two different compartments. Thus, the pressure drop across the membrane \( (p'' - p') \) can be calculated on the basis of either the activities of the solvent in the two volumes or the potential \( \pi_{\text{solvent}}'' \).

An example calculation of the above described Donnan equilibrium system is a pulp fiber suspension where the fibers absorb both water and solute ions. Fibers contain carboxylic acid groups of hemicellulose and phenolic groups of the lignines. The anions of these groups are generally bound to the fiber, but the protons of these acidic functional groups can be dissolved and transferred through the fiber to an external bulk solution. Charge neutrality prevails both within the fiber structure and in the external solution, and thus the dissociation of the functional groups may lead to ion exchange between the cell structure of the fiber and the bulk solution. The stoichiometric Donnan equilibrium theory has been used already by Neale (1929) and Farrar and Neale (1952) to characterize electrolyte interactions with cellulose fibers [14,15]. In 1996 Towers and Scallan published their Donnan model, which could be used to calculate the ionic distribution of mixtures of mono- and divalent cations and monovalent anions in pulp suspensions [16]. The solution model was further extended by Riisäinen et al. to include the presence of multivalent anions as well as the formation of hydroxyl complexes and ligands [17]. The multi-phase Gibbs energy model of the fiber suspension, introduced by Koukkari, Pajarre and Pakarinen (2002), enables the calculation of the solution equilibria (including the distribution of the charged species) while precipitating solids and the dissolution of gaseous constituents are also taken into account [5].

The Gibbs energy model of the fiber suspension is essentially based on the electrochemical theory described above, the fibers representing the secondary aqueous phase containing both mobile and immobile ions. The basic input data of the multi-phase Donnan model is similar to any characteristic aqueous solution model, requiring the incoming amounts of substances and equilibrium temperature and pressure. The water content of pulp fibers is based on experimental water retention values and given as additional model input.
Furthermore, to characterize the immobile anionic species in the fiber phase, their amounts and Gibbs energy data must be specified. Unlike the mobile ions and neutral solutes, the bound acidic groups are included only in the fiber phase. As no reactions that would change the total amount of these groups is assumed to take place, the chemical potential of the undissociated forms of these groups can be set to zero, while the chemical potential of the anionic forms can be calculated based on the thermodynamic relation

$$\Delta G_i = -RT \ln K_i$$  \hspace{1cm} (22)

where the acidic dissociation constants ($K_i$) and the corresponding molar amounts are determined experimentally by potentiometric or conductometric titration. This data is sufficient to perform the equilibrium calculations, and the chemical structure of the acids needs not to be known. It has been found quite customarily that both the $K_i$-values and amount of charge are characteristic to a given form of cellulose or pulp with a known treatment history. Consequently, this data appears comparable with standard Gibbs energy data of known substances [18,19]. In Fig. 2, typical ionic distributions and phase formation in terms of changing pH in various pulp suspensions have been calculated from thermodynamic equilibrium data and compared with the experimental results of Towers and Scallan [16]. The input amounts (Table 3) are from the same source. At low pH of the external solution, the acidic groups within the fiber phase remain undissociated, their anionic charge is small and the cations, such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$ typically, are evenly distributed between the fiber and the external solution. With decreasing acidity, the pH in the external solution is raised and the acid groups in the fiber are dissociated. This feature triggers the ion exchange between the two aqueous phases, the protons are transported to the external solution and the corresponding charge in the fiber phase becomes compensated with the metal cations. At high enough pH, precipitating carbonates and hydroxides are formed as solid phases. The practical perspective of the multi-phase equilibria in pulp suspensions lies in the improved control of pH buffering of paper machines and in metal management of pulp bleaching solutions [18].

### Table 3

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>89.12 kg</td>
</tr>
<tr>
<td>H$_2$O$_f$</td>
<td>1.4 kg</td>
</tr>
<tr>
<td>Bound acid (pK = 4)</td>
<td>0.085 mol</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>0.0282 mol</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>0.0174 mol</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>0.00166 mol</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.0615 mol</td>
</tr>
<tr>
<td>HCl</td>
<td>varied for pH control</td>
</tr>
</tbody>
</table>

H$_2$O denotes the water inside the fibers, H$_2$O the amount of the rest of the aqueous solution (corresponding to the 1. solution volume in Table 2).
of conserved groups as additional system components to the stoichiometric matrix in the Lagrangian method of Gibbs energy minimization was originally used by Alberty [4] to preserve aromatic rings in a benzene flame model. With a further matrix extension, this technique was shown to be applicable to kinetically conserved species [6] and could be applied to several related problems [7]. In what follows, the method is shown to include the characteristics of the potential constraint technique, in the sense that it conserves the (non-zero) affinity of the rate controlled reactions step as the additional Lagrange multiplier.

As a simple example, calculation of titanium oxyhydrate (TiO(OH)2) slurry is considered, referring to the formation of titanium dioxide powder in a calciner. The feed consists of (wet) titanium oxyhydrate slurry, the chemical composition being approximated as TiO(OH)2 * nH2O. During calcination, the slurry is dried and finally the hydrate decomposes, leaving the product titanium dioxide in the bed. From the oxyhydrate, at relatively low temperatures (ca. 200°C) the crystalline form anatase, TiO2(An), is formed first, and only in the high temperature zone of the furnace end, the thermodynamically stable rutile form TiO2(Ru) appears as the desired product. The reactions are as follows:

TiO(OH)2 * nH2O ↔ TiO2(An) + (n + 1)H2O ↑ (I)  
TiO2(An) ↔ TiO2(Ru). (II)

Rutile is the thermodynamically more stable form of these two titanium dioxide species (Table 4). Thus a thermodynamic calculation, such as Gibbs free energy minimization, would at all temperatures result in rutile and water. This would lead to a 100% rutilisation of the titania already at temperatures where the Ti-oxyhydrate is all but calcined by reaction (I). Yet it is well known from practical experience that the rutilisation reaction (II) is slow and only takes place with a finite rate at elevated temperatures (above 850°C). The simulation of the calcination reactions must take this feature into account [21].

In Table 5, the stoichiometry of the calcination system is presented. The three first columns with system components oxygen (O), hydrogen (H) and titanium (Ti) show the elemental abundance-constrained stoichiometry of the equilibrium system. The additional column (R) represents the additional kinetic constraint, affecting the conservation of rutile content in each Gibbsian calculation sequence.

The formation of the Lagrangian function from Eq. (3) by using the equilibrium matrix is straightforward, as well as the solution of the (zero) affinities for the stoichiometric reactions (I) and (II) from the equilibrium condition in Eq. (4). (For simplicity, the Ti-oxyhydrate has been written without the bound water molecules.) When the additional constraint is taken into account, the Lagrangian function becomes:

\[ L(n) = \sum_{k=1}^{2} n_k \left( \mu_k^0 + \ln \frac{n_k}{n_1 + n_2} \right) + \sum_{k=1}^{N=5} n_k \mu_k \]

where the first term on the right is the chemical potentials of the two gaseous species in terms of their partial pressures, the second is formed from the three condensed species, and the last term is deduced from the mass balances (a single ascending value has been used for the constituent index \(k\)). The total number of mass balance constraints is \(l^p = 4\), including the additional zero-mass ‘rutility’ of the formed titanium dioxide. From (4) and (23), the following conditions are obtained:

\[ \mu_4 + \left( \mu_2^0 + \ln \frac{n_2}{n_1 + n_2} \right) - \mu_3 = 0 \]  
\[ \mu_4 - \mu_5 = \pi_4. \]  

Eq. (24) is the equilibrium condition for the fast reaction (I) which forms anatase and water from the oxyhydrate at elevated temperatures. Condition (25) gives the additional Lagrange multiplier as the affinity of reaction (II) and is dependent on the value of the constraint \(b_k\). In a sequential computation, the kinetic constraint is defined as a function of the extent of such a given reaction \([b_R = f(\xi_R)]\) and is set as the input of the Gibbsian calculation. The reaction rate parameters of the rutilisation example are given in Table 4, where the reaction kinetics are deduced from the experimental study of McKenzie [22] (model of contracting spheres). The integrated reaction rate is obtained as a dimensionless ‘degree of rutilisation’, which equals the extent of reaction (II). At each sequence of calculation, the constraint \(b_k = \xi \times (\text{number of TiO(OH)}_2 \text{mole in the input})\). As \(\xi\) is dimensionless, the unit of \(b_k\) is moles.

With the procedure described above, the kinetically constrained Gibbs energy calculation can be performed in a sequential procedure, provided that there is a means to define the value of the additional system component (\(b_R\) as

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H(1000,^\circ C)) (kJ mol(^{-1}))</th>
<th>(\Delta G(1000,^\circ C)) (kJ mol(^{-1}))</th>
<th>Reaction rate equation</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(A) (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(OH)(_2) ↔ TiO(_2)(An) + H(_2)O ↑</td>
<td>43.5</td>
<td>−83.6</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>TiO(_2)(An) ↔ TiO(_2)(Ru)</td>
<td>−6.6</td>
<td>−5.9</td>
<td>(\xi = 1 - (1 - kt)^3)</td>
<td>441.99</td>
<td>1.80E+17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Index ((k))</th>
<th>Species</th>
<th>O</th>
<th>H</th>
<th>Ti</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O(_2)-gas</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)O-gas</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>TiO(OH)(_2)</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>TiO(_2)(An)</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>TiO(_2)(Ru)</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Substance index (\(k\)) is shown in the left-hand column.
program input. For the ChemApp program, which applies the Lagrange method and is hence suitable for the calculation of the constrained problems, we have developed a more indirect procedure, which allows for the control of a kinetically constrained reaction either in its forward or reverse mode [7,9,23].

The thermodynamic (Gibbs energy) data for the species are from standard sources [26], yet the estimates for the standard enthalpy, entropy and heat capacity of TiO(OH)\textsubscript{2} were used as in [24]. The kinetic calculation is then performed in 60 steps with 10 min intervals to cover the experimental data of McKenzie, ranging up to 10 h at 995 °C. For each step, the Gibbs energy of the system is minimized and, as a result, the composition and the Gibbs energy of the system are calculated. The calculation method has been described in more detail in [23]. The results are shown in Fig. 3. The rutile fraction rises from zero to one according to the given reaction rate. It is worth noticing that, with the Gibbsian approach, the thermodynamic properties of the system also become calculated for each sequential step. The Gibbs energy of the reactive system is a monotonically descending curve at any constant temperature. As the anatase-rutile transformation is an exothermic reaction, it is practical interest to also follow the enthalpy change of the system during the gradual process.

Additional constraints may be set to include a more complex reaction mechanism. Each kinetically conserved species will then be annexed to a rate constraint [23]. It seems viable that a systematic approach, which embeds the necessary reaction rates as source terms to the multi-phase Gibbsian calculation, can be developed on the basis of the additional constraints. It is emphasized, however, that the method provides a technique to connect the experimentally found reaction rates with the thermodynamic calculation, but includes no attempt to predict reaction rates from thermochemical theory.

4. Summary

The method of constrained potentials provides an extension of the applicability of the Gibbs energy minimization method to a variety of problems encountered in chemical thermodynamics. A common feature of all these problems is that there is a conservation factor additional to that of mass balance. Above, we have presented three examples, where

![Graph](image_url)

Fig. 3. Measured points and model curves for the rutile fractions are presented at four temperatures (left). The respective Gibbs energies of the system at the same temperatures are calculated as monotonically descending curves (right).

<table>
<thead>
<tr>
<th>System</th>
<th>Constraint</th>
<th>Potential equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>( \sum A_k n_k^r = A )</td>
<td>( \sigma \cdot A_k = \pi_{\text{surface}} )</td>
</tr>
<tr>
<td>Electro-chemical</td>
<td>( \sum_{k=1}^{q^o} z_k n_k = 0 )</td>
<td>( F_{\mu_k} = \pi_{\mu_k} )</td>
</tr>
<tr>
<td>Kinetic</td>
<td>( \sum_k v_k n_k = h_r )</td>
<td>( \sum_{\text{Reacts}} \mu_k - \sum_{\text{Products}} \mu_k = \pi_R )</td>
</tr>
</tbody>
</table>

Table 6: Potential constraints for surface energy, electro-chemical and reaction rate systems
suspensions and other membrane separated systems (e.g. [18]). One may expect similar applications in related electrochemical problems. The constraining of reaction rate-dependent affinities in the Gibbsian calculation extends the applicability of the thermodynamic method to process simulations in systems where it is essential to follow both chemical and energy changes and their interdependence. Finally, as there are many analogous phenomena in chemical thermodynamics where an additional displacement factor affects the chemical potential of one or several species, we expect that the method presented will also find applications other than those mentioned in this text.

References
