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Computational methods for reactive transport modeling: A Gibbs energy minimization approach for multiphase equilibrium calculations

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ABSTRACT

We present a numerical method for multiphase chemical equilibrium calculations based on a Gibbs energy minimization approach. The method can accurately and efficiently determine the stable phase assemblage at equilibrium independently of the type of phases and species that constitute the chemical system. We have successfully applied our chemical equilibrium algorithm in reactive transport simulations to demonstrate its effective use in computationally intensive applications. We used FEniCS to solve the governing partial differential equations of mass transport in porous media using finite element methods in unstructured meshes. Our equilibrium calculations were benchmarked with GEMS3K, the numerical kernel of the geochemical package GEMS. This allowed us to compare our results with a well-established Gibbs energy minimization algorithm, as well as their performance on every mesh node, at every time step of the transport simulation. The benchmark shows that our novel chemical equilibrium algorithm is accurate, robust, and efficient for reactive transport applications, and it is an improvement over the Gibbs energy minimization algorithm used in GEMS3K. The proposed chemical equilibrium method has been implemented in Reaktoro, a unified framework for modeling chemically reactive systems, which is now used as an alternative numerical kernel of GEMS.

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1. Introduction

Typically, reactive transport simulations for subsurface flow assume many reactions in thermodynamic equilibrium [46–48]. This is in fact a reasonable assumption for some reactions that have time scales in the order of microseconds to minutes compared to others with time scales in the order of thousands of years. For example, reactions involving aqueous and gaseous species, and fluid-rock reactions that are considerably faster than others (e.g., calcite dissolves much faster than quartz) are in general assumed to be in equilibrium. As a result, reactive transport simulations require efficient and robust chemical equilibrium solvers, since the number of equilibrium calculations per time step is proportional to the number of mesh nodes. In large-scale simulations, this number can easily reach millions to billions, and the computational cost of all equilibrium calculations can be more than 2/3 of the total cost of the simulation for complicated chemical systems.

The equilibrium state of a chemical system corresponds to a compositional state that minimizes its Gibbs energy at prescribed temperature, pressure, and elemental amounts. The compositional state of a chemical system can be represented by the number of moles of every species. For physical reasons, a non-negative condition for the molar amounts of the species is also imposed. In addition, when charged species are considered, a charge balance condition is equally required. Thus, a chemical equilibrium problem can be mathematically formulated as a constrained minimization problem, where the objective function being minimized is the total Gibbs energy of the system, and the constraints are the molar amounts of the elements, the charge of the system, and the non-negative condition on the molar amounts of the species.

Although a chemical equilibrium problem can be elegantly defined as a minimization problem [18,25,57], the usual algorithmic approach for its solution does not directly minimize the Gibbs energy of the system. Instead, law of mass-action (LMA) equations (i.e., the equations that govern the stationary state of reactions) are adopted. Despite the fact that the solution found by conventional LMA formulations corresponds to the minimum of Gibbs energy of the system, their methodologies are in many cases not as straightforward and extensible as Gibbs energy minimization (GEM) methods. For example, GEM methods are capable of determining the set of stable phases without techniques that are dependent on the type of phases and species, and thus can be easily applied to chemical systems composed by a variety of phases. Most LMA formulations, however, have different approaches for each type of phase. For pure minerals, for

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example, an iterative technique in which minerals are added or removed from the calculation based on their saturation indices is usually used [see [6] for a more detailed description of this technique].

There is a plenitude of codes for geochemical equilibrium calculations. These include WATEQ [51], MINEQL [56], WATEQ4F [5], THERIAC [8], ChemSage [3,4,10], MINTEQA2 [1], EQ3/6 [58], MINEQL+ [38], CHESS [53], PHREEQC [35], The Geochemist's Workbench [6], HCh [41,42], CHIM-XPT [36,37], Selektor-C [7,19] and GEM-Selektor [21,55]. From all these codes, THERIAC, ChemSage, HCh, FactSage, and GEM-Selektor are based on a Gibbs energy minimization approach, while the others adopt a law of mass action approach that can be traced back to the work of [33]. Additionally, all reactive transport simulators reviewed in [49], such as MIN3P [31], HYDROGEOCHEM [60], TOUGHREACT [59], CrunchFlow [45], and PFLOTRAN [30] adopt such LMA approach. Despite its less popularity in reactive transport modeling codes, however, we show in this paper that Gibbs energy minimization methods can also be successfully used in such applications. We recognize that other authors have already accomplished this [13,20].

Thus, we present in this work a novel chemical equilibrium algorithm for general multiphase systems based on a Gibbs energy minimization approach. This method constitutes a substantial improvement over an earlier algorithm presented in [25] that was later successfully applied in a chemical kinetics algorithm in [26]. We realized that many global convergence strategies adopted in the former algorithm were instead making it less robust. These strategies were borrowed from the trust-region interior-point filter method of [52] and [43], and although these authors successfully tested them on a large range of optimization problems, their application in chemical equilibrium calculations were ineffective and unstable, especially when good initial guesses were available from previous calculations, as it is the case in a warm-start approach for reactive transport simulations.

In contrast with the algorithm of [25], we use now a simpler approximation for the Hessian matrix of the Gibbs energy function. In [25], the exact Hessian of the Gibbs energy function was used, which required the exact partial molar derivatives of the activities of every species. The advantage of using an exact Hessian matrix in a Newton method is the quadratic convergence rates attained near the solution that results in convergence within a few iterations if good initial guesses are provided [34]. Its drawback is the resultant dense linear systems at every Newton iteration, which makes it more expensive to solve, especially for large chemical systems with many species. In this work, however, we adopt a sparse diagonal approximation for the Hessian matrix of the Gibbs energy function that *(i)* does not require expensive thermodynamic derivative calculations, *(ii)* produces linear systems with a sparsity pattern that can be solved more efficiently and cheaply, and *(iii)* also allows convergence within a couple of iterations when good initial guesses are provided. For more challenging chemical systems and/or chemical states (e.g., near a phase boundary where a strong non-ideal phase is appearing or disappearing), an exact Hessian matrix scheme might be needed for robustness and efficiency purposes, which will then inevitably require the solution of larger and dense linear systems.

All previously outlined features of the algorithm are assessed in this work. The presented chemical equilibrium method was successfully applied in porous medium reactive transport simulations. The FEniCS Project [28,29] was used for solving the governing partial differential equations of chemical species transport in unstructured meshes using finite element methods. In all simulations, we benchmarked our equilibrium calculations with the code GEMS3K [21], the numerical kernel of the geochemical modeling package GEM-Selektor, which has been under active development for over 25 years. This not only allowed us to ensure that our results match another algorithm's results, but also to compare their performance, both in terms of iterations and time spent on every node of the mesh for every time step.

The algorithm presented here has been implemented in Reaktoro (www.reaktoro.org), a unified framework for modeling chemically reactive systems, which includes methods for multiphase chemical equilibrium and kinetics calculations, as well as reactive transport simulations. This algorithm is now one of the alternatives to the equilibrium method of [19] used in the numerical kernel of the family of geochemical applications GEMS (http://gems.web.psi.ch), which includes GEM-Selektor, GEMS3K [21,55] and GEMSFITS [32]. This has been achieved by combining both codes GEMS3K and Reaktoro in a new GEMS4R code as a kernel for the next generation of GEMS software.

2. Mathematical formulation

Let a chemical system be constituted by N species $\{\alpha_i\}_{i=1}^{\mathrm{N}}$ distributed among Π phases $\{\pi_k\}_{k=1}^{\Pi}$, and constructed from a set of E elements $\{\lambda_j\}_{j=1}^{\mathrm{E}}$. Let the *formula matrix* of the chemical system be defined as the matrix W, with dimension $\mathrm{E} \times \mathrm{N}$, whose entry W_{ji} denotes the stoichiometry of the jth element in the ith species. Thus, given the molar composition vector $n \in \mathbb{R}^{\mathrm{N}}$, whose entry n_i denotes the number of moles of the ith species, the molar abundance vector $b \in \mathbb{R}^{\mathrm{E}}$ of the elements, whose entry b_j denotes the number of moles of the jth element, can be calculated using the *balance equation*:

$$b = Wn. \tag{1}$$

In our formulation, the word *element* should be understood in a broad sense. It can either refer to the chemical elements that compose a chemical species, as well as to its electrical charge. For example, the aqueous species OH^- can be represented by *elements* H, O, and Z, with stoichiometries 1, 1, and −1 respectively, where Z is our adopted symbol for charge. Therefore, Eq. (1) not only accounts for the mass balance of chemical elements, but also for the balance of charges. Hence, an electroneutrality condition implies that the component in the b vector corresponding to charge is zero.

2.1. Equilibrium problem

The *fundamental chemical equilibrium problem* can be formulated as follows: given temperature T, pressure P and molar amounts of elements b, find the equilibrium composition n of the chemical system that minimizes the Gibbs energy of the system:

$$\min_n G(n) \quad \text{subject to} \begin{cases} Wn = b \\ n \geq 0 \end{cases}, \tag{2}$$

where G is the *Gibbs energy function* of the system:

$$G(n) = \sum_{i=1}^{\mathrm{N}} n_i \mu_i(n), \tag{3}$$

μ_i is the *chemical potential function* of the ith species:

$$\mu_i(n) = \mu_i^\circ + RT \ln a_i(n), \tag{4}$$

with μ_i° and a_i denoting the *standard chemical potential function* and *activity function* of the ith species, respectively. For simplicity reasons, the dependency on temperature and pressure of the functions G, μ_i, μ_i°, a_i has been omitted.

The standard chemical potentials μ_i° of the species are functions of temperature and pressure. They refer to the chemical potentials of the species at their standard and reference states in their respective aggregate states and phases. In this work, we use the SUPCRT [17] database together with the equations of state of [15,16,39,50] and [40] to compute μ_i° for aqueous, gaseous, and mineral species. However, it suffices in general to create interpolation tables for these thermodynamic properties over temperature and pressure ranges of interest,

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