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Computational methods for reactive transport modeling: An extended law of mass-action, xLMA, method for multiphase equilibrium calculations

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ABSTRACT

We present an extended law of mass-action (xLMA) method for multiphase equilibrium calculations and apply it in the context of reactive transport modeling. This extended LMA formulation differs from its conventional counterpart in that *(i)* it is directly derived from the Gibbs energy minimization (GEM) problem (i.e., the fundamental problem that describes the state of equilibrium of a chemical system under constant temperature and pressure); and *(ii)* it extends the conventional mass-action equations with Lagrange multipliers from the Gibbs energy minimization problem, which can be interpreted as stability indices of the chemical species. Accounting for these multipliers enables the method to determine all stable phases without presuming their types (e.g., aqueous, gaseous) or their presence in the equilibrium state. Therefore, the here proposed xLMA method inherits traits of Gibbs energy minimization algorithms that allow it to naturally detect the phases present in equilibrium, which can be single-component phases (e.g., pure solids or liquids) or non-ideal multi-component phases (e.g., aqueous, melts, gaseous, solid solutions, adsorption, or ion exchange). Moreover, our xLMA method requires no technique that tentatively adds or removes reactions based on phase stability indices (e.g., saturation indices for minerals), since the extended mass-action equations are valid even when their corresponding reactions involve unstable species. We successfully apply the proposed method to a reactive transport modeling problem in which we use PHREEQC and GEMS as alternative backends for the calculation of thermodynamic properties such as equilibrium constants of reactions, standard chemical potentials of species, and activity coefficients. Our tests show that our algorithm is efficient and robust for demanding applications, such as reactive transport modeling, where it converges within 1–3 iterations in most cases. The proposed xLMA method is implemented in Reaktoro, a unified open-source framework for modeling chemically reactive systems.

1. Introduction

At equilibrium, all possible reactions in a chemical system must have equal forward and backward rates. The system is then said to have achieved a steady state, in which no net consumption and production of its chemical species are observed. Although the equilibrium state of a system is fundamentally described as the state of minimum total Gibbs energy at prescribed temperature, pressure, and elemental composition, it is also possible to use steady-state conditions of reactions as a means to compute the equilibrium state of the system. This is known as the *stoichiometric approach* (Smith and Missen, 1982), or the *law of mass-action* (LMA) approach, in which the mass-action equations (i.e., the equations accounting for the equilibrium condition of the reactions) are solved. On the other hand, the *non-stoichiometric approach*, or the *Gibbs energy minimization* (GEM) approach, consists of minimizing the Gibbs energy function of the system, which requires no stoichiometric relationship between the species in the form of reactions. Both mathematical formulations are fundamentally equivalent (Van Zeggeren and Storey, 1970), though the algorithms to solve them are very different and each have their advantages and disadvantages. Although much progress has been achieved towards improved LMA and GEM algorithms, a method that combines their advantages has, up to now, not been developed and is the goal of this publication.

The LMA formulation is by far the most frequently used methodology for aquatic equilibrium calculations in geochemical

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solvers and reactive transport codes. These include, for example, WATEQ (Truesdell and Jones, 1974), MINEQL (Westall et al., 1976), WATEQ4F (Ball et al., 1987), MINTEQA2 (Allison and Kevin, 1991), EQ3/6 (Wolery, 1992), MINEQL+ (Schecher and McAvoy, 1992), CHESS (van der Lee and de Windt, 2002), The Geochemist's Workbench (Bethke, 2007), CHILLER (Reed and Spycher, 2006), CHIM-XPT (Reed et al., 2010a), SOLVEQ-XPT (Spycher and Reed, 1989; Reed et al., 2010b), and PHREEQC (Parkhurst and Appelo, 1999; 2013). In addition, all reactive transport simulators reviewed in Steefel et al. (2015), such as MIN3P (Mayer et al., 1999), HYDROGEOCHEM (Yeh et al., 2004), TOUGHREACT (Xu et al., 2006), CrunchFlow (Steefel, 2009), and PFLOTRAN (Lu and Lichtner, 2005; Hammond et al., 2014), adopt the conventional LMA approach that was inspired by the works of Garrels and Thompson (1962); Morel and Morgan (1972); Crerar (1975); Wolery and Walters (1975); and Reed (1982). With respect to reactive transport modeling, Lichtner (1985) was a pioneer in the coupling of mass-action equations and reactive transport equations, whose approach has influenced most reactive transport solvers in the literature.

Why is the LMA approach predominant among most geochemical modeling codes and reactive transport simulators? This is probably due to a combination of factors that include historical reasons, convenience, simplicity, and the availability of thermodynamic data mainly in the form of reaction equilibrium constants. At early times, it made sense for Garrels and Thompson (1962) to use an LMA approach to compute the speciation of a seawater sample, as GEM methods were in their infancy being applied to ideal gas mixtures only (White et al., 1958). In addition, aquatic chemistry and geochemistry were always taught in terms of chemical reactions (e.g. Stumm and Morgan, 1981; 1996) rather than in terms of minimization of Gibbs energy. To summarize, Garrels and Thompson (1962) used (*i*) the total concentrations of dissolved ions obtained by chemical analyses, and (*ii*) the dissociation constants of aqueous complexes to determine the distribution of all dissolved species in a seawater sample. Their approach involved specific assumptions for aquatic systems and simplifications such as the use of constant activity coefficients for aqueous species instead of computing them as a function of ionic strength, which eliminated complicated non-linear terms from the model equations. Ten years later, a major progress was made by Morel and Morgan (1972), who improved upon the speciation methodology of Garrels and Thompson (1962) by applying the Newton–Raphson method to simultaneously solve the mass-balance and mass-action equations for chemical systems containing an aqueous solution and pure minerals.

Besides its popularity, the conventional LMA approach has some disadvantages. Its main drawback stems from the fact that the mass-action equations can only be applied to reactions involving species that are stable at equilibrium (i.e., species contained in phases that exist in positive amounts at equilibrium). For example, the mass-action equations for reactions involving gaseous and aqueous species are only valid when both the gaseous and aqueous phases are stable at equilibrium. As a result, several difficulties are encountered when performing multiphase equilibrium calculations with the conventional LMA equations. Typically, conventional LMA algorithms rely on strategies of addition and removal of phases and reactions to ensure that no mass-action equation involving species from unstable phases is used in the calculation. For pure mineral phases, for example, it is common to use saturation indices as a stability indicator that determines if a pure mineral should be added to, or removed from the calculation (Morel and Morgan, 1972; Reed, 1982; Bethke, 2007). Leal et al. (2013) showed that numerical complications arise during an LMA computation when all phases are considered in the calculation and some of them happen to be absent at equilibrium to ensure the Gibbs' phase rule is respected. A heuristic technique was presented there to circumvent these numerical complications, but the approach was only applied to a chemical system of interest and its general validity was not demonstrated.

Gibbs energy minimization methods, on the other hand, are able to tackle complex non-ideal multiphase systems and can accurately determine their stable phase assemblage in a single run. In contrast to conventional LMA methods, GEM algorithms take advantage of Lagrange multipliers that are helpful in determining the stability of phases in general, without requiring customized techniques for different types of phases. The typical disadvantage of using GEM methods is the larger amount of required thermodynamic input data (i.e., standard chemical potentials for all species corrected to temperatures and pressures of interest) when compared with LMA thermodynamic data (i.e., equilibrium constants of reactions). However, a method recently presented in Leal et al. (2016b) enables GEM algorithms to use equilibrium constants of reactions as well.

Therefore, both LMA and GEM approaches have their advantages and disadvantages. LMA algorithms benefit from simpler formulations, given in terms of equilibrium constants of reactions, but lack generality for chemical systems with non-ideal multicomponent phases. GEM algorithms, on the other hand, can inherently handle complex systems and determine the stable phases at equilibrium, but require more thermodynamic data that are not always immediately available. Therefore, the ideal method would be an LMA approach that can take advantage of all thermodynamic databases available in the literature, while possessing capabilities of a GEM approach to efficiently, robustly, and rigorously handle complex non-ideal multiphase systems.

In this paper, we present such a method that combines the best of both LMA and GEM approaches. What is unique about this algorithm is the use of *extended law of mass-action (xLMA) equations* that are valid even when their corresponding reactions involve chemical species from unstable phases. Therefore, by using these xLMA equations, instead of the conventional ones, we can simultaneously account for all possible phases in the calculation without experiencing numerical complications. As a result, the xLMA equations circumvent the traditional LMA requirement of using only mass-action equations involving species from stable phases, which are often not known a priori, but estimated either during, or at the end of the calculation.

The extended law of mass-action equations are derived directly from the Gibbs energy minimization problem. As such, they satisfy the Gibbs–Duhem equations, so that the number of stable phases at equilibrium respects the Gibbs' phase rule, even when many more phases are initially considered in the calculation as potential stable phases (e.g., many pure minerals might be considered in an equilibrium calculation in the hope that some of them might exist as precipitated solids). The difference between these extended equations and the conventional ones is minimal and yet essential to guarantee a robust and convenient equilibrium speciation calculation for a multiphase chemical system.

We emphasize that the presented xLMA method can take advantage of thermodynamic databases used in both LMA and GEM approaches (i.e., databases composed of either equilibrium constants of reactions or standard chemical potentials of species). This is because the standard chemical potentials of the species obtained from thermodynamic databases such as SUPCRT92 of Johnson et al. (1992) and the ones of Holland and Powell (1998; 2011) can be used to calculate the equilibrium constants of reactions. In Appendix A, we show how a system of linearly independent reactions can be automatically generated from a given list of chemical species. These reactions can be used with our xLMA method, and their equilibrium constants can be directly calculated from the standard chemical potentials of the species.