# Enabling Gibbs energy minimization algorithms to use equilibrium constants of reactions in multiphase equilibrium calculations

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## ARTICLE INFO

## ABSTRACT

The geochemical literature provides numerous thermodynamic databases compiled from equilibrium constants of reactions. These databases are typically used in speciation calculations based on the law of mass action (LMA) approach. Unfortunately, such LMA databases cannot be directly used in equilibrium speciation methods based on the Gibbs energy minimization (GEM) approach because of their lack of standard chemical potentials of species. Therefore, we present in this work a simple conversion approach that calculates apparent standard chemical potentials of species from equilibrium constants of reactions. We assess the consistency and accuracy of the use of apparent standard chemical potentials in GEM algorithms by benchmarking equilibrium speciation calculations using GEM and LMA methods with the same LMA database. In all cases, we use PHREEQC to perform the LMA calculations, and we use its LMA databases to calculate the equilibrium constants of reactions. GEM calculations are performed using a Gibbs energy minimization method of Reaktoro — a unified open-source framework for numerical modeling of chemically reactive systems. By comparing the GEM and LMA results, we show that the use of apparent standard chemical potentials in GEM methods produces consistent and accurate equilibrium speciation results, thus validating our new, practical conversion technique that enables GEM algorithms to take advantage of many existing LMA databases, consequently extending and diversifying their range of applicability.

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## 1. Introduction

A large body of geochemical literature is devoted to applications of chemical equilibrium speciation codes based on law of mass action (LMA) algorithms. These algorithms rely on thermodynamic databases that contain equilibrium constants of reactions typically written in the *canonical form*, where *primary species*, a subset of linearly independent species, serve as components for the other species, the *secondary species* (Morel and Morgan, 1972; Smith and Missen, 1982; Reed, 1982; Lichtner, 1985; Steefel and Cappellen, 1990). LMA equilibrium methods solve the law of mass action equations that govern the equilibrium state of the reactions in the system:

$$\ln K_m = \sum_{i=1}^{N} \nu_{mi} \ln \alpha_i \qquad (m = 1, \ldots, M), \tag{1}$$

where $K_m$ denotes the equilibrium constant of the $m$th reaction; $\nu_{mi}$ the stoichiometric coefficient of the $i$th species in the $m$th reaction,

with negative $\nu_{mi}$ for reactants and positive $\nu_{mi}$ for products; $a_i$ the activity of the $i$th species; N is the number of species in the chemical system; and M is the number of reactions, with $M \leq N$. We assume that these reactions are linearly independent, so that they can be written as:

$$0 \rightleftharpoons \sum_{i=1}^{N} \nu_{mi} \alpha_i \qquad (m = 1, \ldots, M), \tag{2}$$

where $\alpha_i$ denotes the $i$th species. The reactions (2) are not necessarily in canonical form.

An equilibrium speciation calculation consists of finding mole amounts, $n_i$, of chemical species that correspond to the state of minimum Gibbs energy of the system at a prescribed temperature, $T$, and pressure, $P$ (Smith and Missen, 1982). Commonly, this is done by solving the system of mass action Eq. (1) instead of directly minimizing the Gibbs energy of the system. The problem is non-linear, since the activities, $a_i$, of the species depend on the concentrations of the species in their respective phases (e.g., the activities of aqueous species depend on their molalities). In contrast, the equilibrium constants, $\ln K_m$, depend on temperature only, although some pressure corrections may be applied as well (Appelo et al., 2014). Values of $\ln K_m$ are sometimes

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calculated using interpolation tables from thermodynamic databases that contain equilibrium constants at different temperature and pressure points. The activities, $a_i$, of the species are calculated from thermodynamic models that describe the non-ideal behavior of phases (see Anderson, 2005, for a description of models for aqueous, gaseous, and solid phases).

There are N unknowns in an equilibrium problem, namely the molar amounts, $n_i$, of the species. However, there are only M < N mass action equations in Eq. (1), which are insufficient to solve the problem. The necessary additional $E = N - M$ equations consist of imposing the molar amounts of elements (alternatively, one can impose the total amounts of basis or primary species, Bethke, 2007):

$$\sum_{i=1}^{N} A_{ji} n_i = b_j \quad (j = 1, ..., E), \tag{3}$$

where $A_{ji}$ denotes the stoichiometry of the $j$th element in the $i$th species; $b_j$ the molar amount of the $j$th element; and E the number of elements in the system.

Equilibrium methods based on the law of mass action (LMA) equations remain very popular in geochemical modeling in general and in reactive transport simulations in particular. A plenitude of LMA codes exist, such as WATEQ (Truesdell and Jones, 1974); MINEQL (Westall et al., 1976); WATEQ4F (Ball et al., 1987); SOLMINEQ.88 (Kharaka et al., 1988); MINTEQA2 (Allison and Kevin, 1991); EQ3/6 (Wolery, 1992); MINEQL + (Schecher and McAvoy, 1998); CHESS (van der Lee and de Windt, 2002); PHREEQC (Parkhurst and Appelo, 1999, 2013); The Geochemist's Workbench (Bethke, 2007); and CHIM-XPT (Reed and Spycher, 2006; Reed et al., 2010). These numerical simulators take advantage of the rich collection of thermodynamic databases that contain equilibrium constants for thousands of reactions for aqueous and gaseous species, surface complexes, and minerals, starting from classical compilations such as Smith and Martell (1976) and ending with modern databases such as THERMODDEM (Blanc et al., 2012) and PSI-Nagra 12/07 (Thoenen et al., 2014).

Despite their lower popularity in aquatic chemistry, Gibbs energy minimization (GEM) methods are widely used in petrology, hydrothermal geochemistry, and metallurgy. This is because GEM methods are capable of naturally determining the set of stable phases at equilibrium, even for phases with highly complex non-ideal behavior (Karpov et al., 1997; Wagner et al., 2012; Kulik et al., 2013; Leal et al., 2016a). LMA methods can in principle also achieve this, however, this usually requires ad-hoc (e.g., basis swapping) or non-straightforward means (e.g., trial addition/removal of minerals). See Leal et al. (2013, 2014, 2015, 2016a) for an in-depth discussion. In addition, see Leal et al. (2016b) for a revised law of mass action (rLMA) approach that has the advantages of both GEM and LMA methods.

In GEM methods, it is not possible to directly use LMA-style thermodynamic databases containing equilibrium constants of reactions. This is because GEM calculations require standard chemical potentials (also known as standard Gibbs energies) of all chemical species

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TITLE Example 3, part A.--Calcite equilibrium at log Pco2 = -2.0 and 25C.
SOLUTION 1   Pure water
        pH       7.0
        temp     25.0
EQUILIBRIUM_PHASES
        CO2(g)          -2.0
        Calcite          0.0
SAVE solution 1
END
TITLE Example 3, part B.--Definition of seawater.
SOLUTION 2   Seawater
        units    ppm
        pH       8.22
        pe       8.451
        density 1.023
        temp     25.0
        Ca               412.3
        Mg               1291.8
        Na               10768.0
        K                399.1
        Si               4.28
        Cl               19353.0
        Alkalinity       141.682 as HCO3
        S(6)             2712.0
END
TITLE Example 3, part C.--Mix 70% ground water, 30% seawater.
MIX 1
        1        0.7
        2        0.3
SAVE solution    3
END
TITLE Example 3, part D.--Equilibrate mixture with calcite and dolomite.
EQUILIBRIUM_PHASES 1
        Calcite          0.0
        Dolomite         0.0
USE solution 3
END
--TITLE Example 3, part E.--Equilibrate mixture with calcite only.
EQUILIBRIUM_PHASES 2
        Calcite          0.0
USE solution 3
END
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Listing 1. The PHREEQC input file ex3 distributed with PHREEQC v3.3.7 (Parkhurst and Appelo, 2013).