



Efficient chemical equilibrium calculations for geochemical speciation and reactive transport modelling

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Abstract

Chemical equilibrium calculations are essential for many environmental problems. It is also a fundamental tool for chemical kinetics and reactive transport modelling, since these applications may require hundreds to billions equilibrium calculations in a single simulation. Therefore, an equilibrium method for such critical applications must be very efficient, robust and accurate. In this work we demonstrate the potential effectiveness of a novel Gibbs energy minimisation algorithm for reactive transport simulations. The algorithm includes strategies to converge from poor initial guesses; capabilities to specify non-linear equilibrium constraints such as pH of an aqueous solution and activity or fugacity of a species; a rigorous phase stability test to determine the unstable phases; and a strategy to boost the convergence speed of the calculations to quadratic rates, requiring only few iterations to converge. We use this equilibrium method to solve geochemical problems relevant to carbon storage in saline aquifers, where aqueous, gaseous and minerals phases are present. The problems are formulated to mimic the ones found in kinetics and transport simulations, where a sequence of equilibrium calculations are performed, each one using the previous solution as the initial guess. The efficiency and convergence rates of the calculations are presented, which require an average of 1–2 iterations. These results indicate that critical applications such as chemical kinetics and reactive transport modelling can potentially benefit by using this multiphase equilibrium algorithm.

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1. INTRODUCTION

In a chemical equilibrium state, the forward and reverse rates of the reactions in a system are equal, and therefore no changes in the concentrations of its species are observed with time. It is possible to demonstrate, with the use of the first and second laws of thermodynamics, that a chemical system undergoing an isobaric and isothermal process progress towards a state of minimum Gibbs free energy.

Other conditions also apply during this process, such as mass conservation of the chemical elements.

Therefore, an equilibrium problem consists of finding the number of moles of the chemical species that simultaneously minimises the Gibbs free energy of the system and satisfies a system of equilibrium constraints (Smith and Missen, 1982). In addition, a non-negativity constraint for the number of moles is required in order to guarantee a physically feasible molar composition.

The applicability of chemical equilibrium solvers for environmental problems is wide. For instance, speciation modelling of aquatic systems, calculation of solubilities of gases and minerals, analysis of the effect of pH on the dissolution of a mineral, investigation of water-gas-rock effects during carbon storage in geological formations, and radioactive waste disposal modelling are all examples of

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Nomenclature

Greek symbols

α_i	the i th species in the chemical system
α_i^π	the i th species in the π th phase
α_r	the convergence rate of an equilibrium calculation, see Eq. (4.2)
α	the set of species in the chemical system
α^π	the set of species in the π th phase
ε	the set of elements in the chemical system
ε_Λ	the phase stability tolerance
ε_j	the j th element in the chemical system
φ_i	the fugacity coefficient of the gaseous species with index i , see Eq. (2.4)
γ_i	the activity coefficient of the aqueous species with index i , see Eq. (2.3)
Λ_π	the stability index of the π th phase, see Eq. (3.12)
$\hat{\mu}$	the constant perturbation parameter used when the watchdog strategy is active
$\hat{\mu}$	the perturbation parameter of the interior-point method, see Eq. (3.9)
μ_i	the chemical potential of the i th species, see Eq. (2.2)
μ_i°	the standard chemical potential of the i th species, see Eq. (2.3)
μ_w	the threshold used to activate the watchdog strategy
Ω_π	the generalised saturation index of the π th phase, see Eq. (3.12)
Π	the number of phases in the chemical system

Roman symbols

a_{H^+}	the activity of the ionic species H^+ , see Eq. (2.13)
a_i	the activity of the i th species, see Eq. (2.3)
a_i^\star	the specified activity of the i th species, see Eq. (2.14)
\mathbf{b}	the molar abundance vector of the elements, see Eq. (2.5)
b_j	the molar abundance of the j th element, see Eq. (2.5)
b_j^\star	the specified number of moles of the j th element, see Eq. (2.8)
\mathbf{c}	the equality constraint function in a optimisation problem, see Eq. (3.1)
\mathbf{D}	the diagonal scaling matrix of the primal variable \mathbf{x} , see Eq. (3.10)
\mathbf{e}	the vector of all ones, see Eq. (3.9)
E	the number of elements in the chemical system
$\mathbf{F}_{\hat{\mu}}$	the residual function of the perturbed KKT conditions, see Eq. (3.9)
f	the objective function in a optimisation problem, see Eq. (3.1)
G	the Gibbs free energy function of the chemical system, see Eq. (2.1)
\mathbf{h}	the vector-valued equilibrium constraint function, see Eq. (2.1)
\mathcal{I}_π	the set of indices of the species in the π th phase
\mathcal{I}_g	the indices of the gaseous species

i^\star	the local index of the i th species in its phase, see Eq. (3.13)
\mathcal{L}	the Lagrange function of a optimisation problem, see Eq. (3.2)
M	the number of equilibrium constraints, see Eq. (2.1)
m	the number of equality constraints in a optimisation problem, see Eq. (3.1)
m_i	the molality of the aqueous species with index i , see Eq. (2.3)
\mathbf{n}	the molar abundance vector of the species, see Eq. (2.1)
N	the number of species in the chemical system
n	the number of variables in a optimisation problem, see Eq. (3.1)
N_π	the number of species in the π th phase
n_i	the number of moles of the i th species, see Eq. (2.2)
P	the pressure of the chemical system, see Eq. (2.1)
P°	the reference pressure for the activity of gaseous species, see Eq. (2.4)
P_i	the partial pressure of the i th gaseous species, see Eq. (2.16)
R	the universal gas constant, see Eq. (2.3)
r_k	the calculation residual at the k th iteration, see Eq. (4.2)
T	the temperature of the chemical system, see Eq. (2.1)
\mathbf{W}	the formula matrix of the chemical system, see Eq. (2.5)
\mathbf{w}_j	the j th row of the formula matrix \mathbf{W} , see Eq. (2.8)
\mathcal{W}	the number of watchdog iterations after which the algorithm checks for filter acceptance
$\bar{\mathbf{x}}$	the scaled primal variables, see Eq. (3.10)
$\hat{\mathbf{x}}$	the primal solution in a previous calculation, see Eq. (3.11)
\mathbf{X}	the diagonal matrix defined by $\mathbf{X} := \text{diag}(\mathbf{x})$, see Eq. (3.6)
\mathbf{x}	the vector of variables in a optimisation problem, see Eq. (3.1)
x_i^g	the molar fraction of the i th species in the gaseous phase, see Eq. (3.13)
x_i^π	the molar fraction of the i th species in the π th phase, see Eq. (2.4)
\mathbf{y}, \mathbf{z}	the Lagrange multipliers of a optimisation problem, see Eq. (3.2)
y_{j,z_i}	the Lagrange multipliers with respect to the j th constraint and i th variable, see Eq. (3.13)
\mathbf{z}_a	the vector of electrical charges of the aqueous species, see Eq. (2.10)

Mathematical symbols

∇_x	the gradient operator with respect to the primal variables \mathbf{x} only
T	the transpose operator of a matrix or vector

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