Robust resolution of chemical equilibrium by the methods of parametrization and cartesian representations

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The calculation of chemical equilibrium of a single-phase system amounts to finding the quantities of chemical species that minimize the Gibbs free energy under constant temperature and pressure, with mass conservation and non-negativity constraints. This problem can be expressed as the solution of a nonlinear system of equations that presents many numerical difficulties. In particular, Newton's method faces difficulties to converge when one of the species tends to disappear. The remedy usually employed is to work in the logarithm of the concentrations, which improves the situation for small concentrations but significantly degrades the convergence for large ones.

The objective of this work is to develop resolution strategies better adapted to these two operating regimes. To do so, we extend to our setting the parametrized form of the switching-variable technique proposed in [1] for the Richards equation. Alternatively, we propose to reformulate the problem by introducing new variables which relax the logarithm of concentrations and whose relation with the concentrations is expressed by a well-balanced Cartesian representation designed to control the partial derivatives. We implement and test these methods on geochemical systems consisting of an aqueous phase at equilibrium. The first results show a clear improvement of the robustness in terms of convergence compared to those of the literature.

References

[1] K. Brenner and C. Cancès. Improving Newton's method performance by parametrization: the case of the Richards equation. *SIAM Journal on Numerical Analysis*, 55(4):1760–1785, 2017.