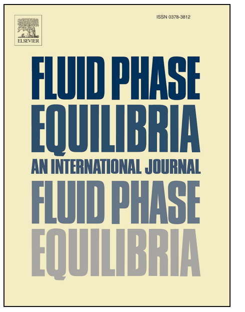

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A volume-based approach to phase equilibrium calculations at pressure and temperature specifications

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Abstract

Phase equilibrium calculations at pressure and temperature specifications, consisting in the minimization of the Gibbs free energy with respect to mole numbers, are the most commonly used and are well documented in the literature. A very attractive alternative is given by the volume-based calculations, in which the volume and mole numbers, which are the natural variables for pressure explicit equations of state (EoS) are treated as independent variables; in this case pressure equality is an additional equation for each phase and there is no need to solve the EoS for volume. The problem is a bound- and linear inequality-constrained optimization problem; the objective function is a formal Gibbs free energy. A major disadvantage is that, unlike in conventional calculations, the successive substitution method cannot be used, thus robust modified Newton iterations are required. Using the block structure of the Hessian matrix, a link is established between conventional and volume-based Newton iterations and it is shown that the latter are inherently slower than the former due to a lower implicitness level in the Hessian. A modified Cholesky factorization (to ensure a descent direction) and a two-stage line search procedure (ensuring that iterates remain in the feasible domain and the objective function is decreasing between two iterations) are used in Newton iterations. Numerical experiments carried out on several test mixtures show that two-phase volume-based flashes initialized from the ideal equilibrium constants pose systematic convergence problems near phase boundaries, while the algorithm is rapid and robust when initial guesses from stability testing are used. The proposed algorithm is not dependent on the thermodynamic model and any pressure explicit EoS can be used, provided the required partial derivatives are available.

Keywords: flash calculations, volume-based method, Newton method, modified Cholesky factorization, convergence

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