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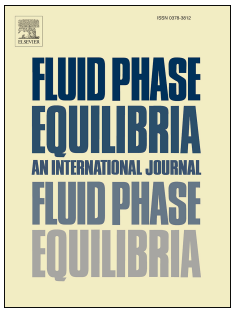

New unconstrained minimization methods for robust flash calculations at temperature, volume and moles specifications

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New unconstrained minimization methods for robust flash calculations at temperature, volume and moles specifications

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Abstract

In this paper, a new method for phase equilibrium calculations at constant temperature, volume and moles (VTN flash) is presented. The problem is formulated as an unconstrained minimization of the Helmholtz free energy with respect to mole numbers. Volume is a dependent variable and its dependence on mole numbers is taken into account by solving a nonlinear equation (the volume balance equation) for pressure at each iteration level. By analyzing the block structure of the Hessian matrix in the constrained minimization of the Helmholtz free energy with respect to mole numbers and volume (used in previous approaches), it is shown that the Hessian in the proposed method has a higher implicitness level and Newton iterations converge faster (in terms of number of iterations). The calculation framework is similar to that in flash calculations at pressure and temperature specifications (PT flash). A combined successive substitution - Newton method is used, with mole numbers or natural logarithms of equilibrium constants as independent variables. The iterations in the VTN flash are "PT-like" (for a sequence of pressures converging to the pressure at which the volume specification is met) and the number of iterations required for convergence is comparable to that of the PT flash performed at the final pressure. The proposed method is tested for several mixtures of various complexities and proved to be rapid and robust. For vapor-liquid equilibrium, the convergence is obtained starting from the ideal equilibrium constants, even very close to phase boundaries and at near-critical conditions. Existing codes for PT flash calculations can be easily modified to incorporate the new method for VTN flash calculations.

Keywords: VTN flash, Helmholtz free energy, unconstrained minimization, Newton method, equilibrium constant, convergence, number of iterations

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