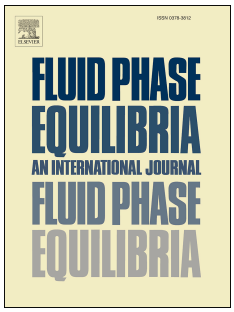

Phase stability testing and phase equilibrium calculation at specified internal energy, volume, and moles

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Phase stability testing and phase equilibrium calculation at specified internal energy, volume, and moles

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Abstract

We have developed a fast and robust algorithm for the general multi-phase equilibrium calculation at constant internal energy, volume, and moles (specification UVN). The algorithm is based on the direct maximization of the total entropy of the system subject to the internal energy-, volume-, and mole-balance constraints. The algorithm uses the Newton-Raphson method with line-search and modified Cholesky decomposition of the Hessian matrix to produce a sequence of states with increasing values of the total entropy of the system. Unlike the previously published formulations, our method uses results of the UVN-phase stability testing for initialization of the UVN-flash calculation. As the number of phases is not known a-priori, the proposed strategy is based on repeated UVN-stability testing and UVN phase-split calculation until a stable phase split is found. The performance of the algorithm is demonstrated on many examples of different complexity.

Keywords: phase equilibrium calculation, UVN specification, isochoric-isoenergetic flash problem, entropy maximization, modified Newton method, modified Cholesky factorization

1. Introduction

Investigation of phase stability and multi-phase equilibrium calculation for multicomponent mixtures are basic problems in chemical engineering with numerous applications in the industry. The most frequently encountered formulation of these problems uses pressure P, temperature T, and mole numbers $N_1, \ldots, N_n$ (or mole fractions $z_1, \ldots, z_n$) as specification variables – this is the case of the so called PTN-stability and PTN-flash equilibrium calculation. These problems have been treated extensively by many authors building mainly on the the classical works of Michelsen [1–3], see e.g. [4, 5]. In this work, we are interested in developing methods for phase stability testing and phase equilibrium calculation in a different variables specification – namely internal energy U, volume V, and mole numbers $N_1, \ldots, N_n$. This is the problem of the UVN-stability and UVN-phase equlibrium computation.

Compared to PTN-stability and PTN-flash, other variables specifications are less common. Notable problems are the specification in terms of temperature T, volume V, and mole numbers $N_1, \ldots, N_n$ (TVN-based formulation) and the UVN-formulation. The TVN-formulation can be used e.g. for simulations of equilibria in a closed vessel of known volume at constant temperature (see e.g. [6–8]), or in compositional simulation [9] where the flash calculation is performed locally on each finite element of the discretized domain at each time step under the assumptions of constant temperature and local thermodynamic equilibrium. On the other hand, the UVN-formulation is useful in non-isothermal problems as, for example, in the dynamic simulation of separation vessels [10, 11] or dynamic filling of a process vessel [12]. In these problems, temperature changes during the simulation must be computed using the energy balance and the assumption of the local thermodynamic equilibrium. As evolution of the internal energy is provided by solving the energy balance equations, it is natural to solve the phase equilibrium using the UVN-formulation.

There are only few papers concerning the UVN-flash. First, Michelsen has proposed a general framework for other variables specifications in [13], including the UVN- and TVN-formulations. His approach uses PTN-flash in

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