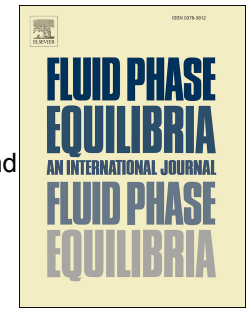

Unified presentation and comparison of various formulations of the phase stability and phase equilibrium calculation problems

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Unified presentation and comparison of various formulations of the phase stability and phase equilibrium calculation problems

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Abstract

In this paper we present general formulations of the phase-equilibrium and phase-stability problems for multicomponent mixtures and verify that these formulations generalize the problems of phase-equilibrium and phase-stability at constant volume, temperature, and mole numbers (VTN-flash), at constant internal energy, volume, and mole numbers (UVN-flash), and at constant pressure, temperature, and mole numbers (PTN-flash). Furthermore, we develop a numerical method for solving the general formulation of phase-equilibrium problems. This algorithm is based on the direct minimization of the objective function with respect to the constraints. The algorithm uses a modified Newton-Raphson method, along with a modified Cholesky decomposition of the Hessian matrix to generate a sequence of states with decreasing values of the objective function. The algorithm was implemented in C++ and using generic programing we have a single, portable solver for all three flash formulations. Properties of the algorithm are shown on phase-equilibria problems of multicomponent mixtures in different specifications and with different levels of difficulty. Complexities and numerical performance of the individual flash formulations are discussed.

Keywords: C++ templates, general formulation, generic programing, phase equilibrium calculation, phase stability testing, modified Cholesky decomposition, multicomponent mixtures, Newton-Raphson method, optimization, VTN-flash, PTN-flash, UVN-flash

1. Introduction

The phase-stability testing and the phase equilibrium calculation of multicomponent mixtures are basic problems in chemical engineering with multiple applications in the industry. Development of fast and robust algorithms to solve these problems is important e.g. for hydrocarbon reservoirs simulation or in CO_2 sequestration.

The traditional formulation of these problems uses pressure P^*, temperature T^*, and mole numbers $N_1^*, \ldots, N_n^*$ (or mole fractions $x_1^*, \ldots, x_n^*$) as specification variables – this is the case of the so called PTN-stability and PTN-flash equilibrium calculation. Problems of PTN-flash and PTN-stability were investigated by many authors building mainly on the the classical works of Michelsen [17, 18, 20], see e.g. [4, 5]. Compared to PTN-stability and PTN-flash, other variables specifications are less common. One of the notable specifications uses volume V^*, temperature T^* and mole numbers $N_1^*, \ldots, N_n^*$ as specification variables (the so called VTN-stability and VTN-flash). The VTN-flash specification can be used e.g. for simulations of equilibria in a closed vessel at constant temperature (see e.g. [11–13]), or in compositional simulation [29] in which 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. First, in [21], Mikyška and Firoozabadi investigated the VTN-stability and derived a criterion for VTN-stability. In [11], Jindrová and Mikyška presented a numerical algorithm of the two-phase VTN-flash calculation. Finally, in [12] they presented a general algorithm of an arbitrary p-phase split VTN-flash calculation and a general strategy for solving the phase equilibrium calculations with an a-priori unknown number of phases. Another notable

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