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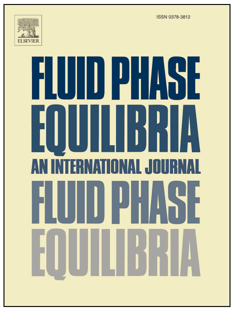


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# Volume-based phase stability testing at pressure and temperature specifications

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**Abstract**

Conventional phase equilibrium calculations at temperature and pressure specifications require the resolution of the equation of state (EoS). In volume-based calculations, the EoS must not be solved for volume, which is a primary variable. The tangent plane distance (TPD) function can be expressed in terms of mole numbers and volume or of component molar densities. The stationary points of the TPD function, as well as the location of the stability test limit locus (STLL) are different for the two formulations. A modified TPD function in terms of mole numbers and volume is proposed here. Using the block structure of the Hessian matrix, it is shown that Newton iterations in volume-based stability are inherently slower than those in the conventional PT stability, since the Hessian matrix is evaluated at a lower implicitness level. The minimization of several TPD functions (in volume-based and conventional stability testing) is analyzed using various sets of independent variables and scaling procedures. A modified Cholesky factorization and a two-stage line search procedure ensure a sequence of decreasing TPD functions in all cases. The proposed methods are tested for several mixtures, with emphasis on the vicinities of singularities (STLL and spinodal). With proper scaling, the modified Newton iterations are robust and converge very fast for most conditions and reasonably fast for very difficult conditions. The proposed algorithm is not model-dependent; any pressure explicit EoS can be used, provided the required partial derivatives are available.

**Keywords:** phase stability, Tangent plane distance, volume-based method, Newton method, Hessian, convergence

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