ABOUT NECESSITY TO USE THERMODYNAMIC POTENTIALS IN CALCULATIONS WITH FINITE-RATE CHEMICAL KINETICS

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Abstract: The problem of arising of a nonphysical stationary state ("dynamic" equilibrium) in chemical kinetic calculations is considered. The "dynamic" equilibrium is characterized by ring-like chains of finite-rate reactions. It is shown that the correction of a kinetic scheme for eliminating the "dynamic" equilibrium can result in a very essential variation in the nonequilibrium evolution of the process and the reaction heat effect. It is shown that the widespread practice in calculating backward reaction rates based on the forward reaction rates and thermodynamic potentials eliminates both the possibility of arising of the nonphysical "dynamic" equilibrium and the possibility of nonphysical evolution of a nonequilibrium process in numerical calculations.

Keywords: equilibrium constant; thermodynamic potential; reaction heat effect; kinetic scheme

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