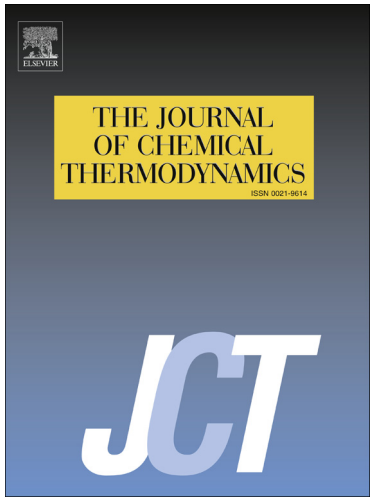

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Thermodynamic assessment of the neptunium-oxygen system: mass spectrometric studies and thermodynamic modelling

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Abstract

Knudsen effusion mass spectrometry measurements on neptunium dioxide are reported in this work, which have allowed to improve the understanding of its vaporization behaviour and solved discrepancies noticed in the literature: the enthalpy of formation of NpO_2(g) has been re-assessed and the composition of neptunia at congruent vaporization has been determined at 2262 K. In addition, a thermodynamic model for the neptunium-oxygen system has been developed using the CALPHAD method. The non stoichiometric NpO_{2-x} phase is described herein using the compound energy formalism with ionic constituents $(Np^{3+}, Np^{4+})_1(O^{2-}, Va)_2$, while the liquid phase is represented with the ionic two-sublattice model $(Np^{4+})_P(O^{2-}, Va^{Q-}, O)_Q$. The reliability and consistency of all optimized Gibbs energies have been verified by calculating the phase equilibria, thermodynamic data, oxygen chemical potential and equilibrium partial pressures. Finally, a number of ill-defined data in the Np-O system have been identified after critical review of the literature and comparison with the present experimental results and CALPHAD model.

Keywords: CALPHAD, Knudsen effusion mass spectrometry, neptunium-oxygen system

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