American Mineralogist, Volume 98, pages 1508–1515, 2013

Enthalpies of formation of Fe-Ni monosulfide solid solutions

Amir H. Tavakoli and Alexandra Navrotsky*

Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis, California 95616, U.S.A.

Abstract

Binary and ternary sulfides in the Fe-Ni-S system are of major fundamental and practical interest in environmental, geological, and planetary science. Despite extensive thermodynamic modeling of phase equilibria, the enthalpies of formation of solid solutions in this system have not been measured directly as functions of both nickel/iron and metal/sulfur ratios. This communication reports enthalpies of formation of Fe-Ni monosulfide solid solutions [*mss* = $(Fe_{1-x}Ni_x)_{1-z}S$, $0 \le x \le 1$; $0.875 \le 1-z \le 1$] quenched from 750 °C, representing disordered structural states. Measurements were performed on three series of solid solutions using oxidative solution calorimetry in molten sodium molybdate solvent at 702 °C. The measured enthalpies of formation of $Ni_{1-z}S$ solid solutions from elements are consistent with prior data reported for a few compositions. The enthalpies of formation of ternary compositions, $(Fe_{1-x}Ni_x)_{1-z}S$, are reported for the first time. Within their uncertainties, the enthalpies of formation of the solid solutions, quenched from high temperature, with respect to the end-members (enthalpies of mixing) at 25 °C are zero. An experimentally derived equation is proposed for the calculation of enthalpies of formation of all high-temperature monosulfide solid solutions in the Fe-Ni-S system. The thermodynamic stabilization of these disordered solid solutions arises not from energetic terms but from the configurational entropy.

Keywords: High-temperature pyrrhotite, iron-nickel monosulfide, thermodynamics, enthalpies of formation, oxidative solution calorimetry