Enthalpies of formation of pyrrhotite Fe$_{1-0.125x}$S ($0 \leq x \leq 1$) solid solutions

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ABSTRACT

Binary iron sulfides are of major interest and importance in environmental, geological, and planetary science. Oxidative high-temperature oxide melt drop-solution calorimetry in molten sodium molybdate (3Na$_2$O·4MoO$_3$) solvent at 975 K was applied to determine the energetics of formation of the binary iron monosulfide solid solution (pyrrhotite) (Fe$_{1-0.125x}$S, $0 \leq x \leq 1$). The enthalpies of formation from elements are consistent with earlier data in the literature, available for a few compositions. Within the experimental errors, the enthalpies of formation of the solid solution from the end-members Fe$_{0.875}$S and FeS ($\Delta H_{\text{form}}$, kJ/mol) at 25 °C equal to zero. Under the assumption of random distribution of Fe vacancies, the Gibbs free energies of mixing of Fe$_{1-0.125x}$S ($0 \leq x \leq 1$) are estimated. Our data support the two-sublattice model proposed by Waldner and Pelton (2005).

Keywords: Pyrrhotite, iron sulfides, thermodynamics, enthalpy of formation, oxidative high-temperature oxide melt solution calorimetry

INTRODUCTION

Iron sulfides are of major interest and importance in environmental, geological, and planetary science. The binary iron-sulfur (Fe-S) system has a complex phase diagram, with broad range of composition of Fe$_{1-0.125x}$S ($0 \leq x \leq 1$) phases (Nakazawa and Morimoto 1971; Nath et al. 2003; Rao and Pisharody 1976; Ward 1970). A wide variety of iron sulfide structures accommodates atomic substitution and non-stoichiometry. Metal-metal interactions allow for diverse magnetic (Hirone et al. 1954; Horwood et al. 1976; Li and Franzen 1996; Ward 1970) and electronic (Fleet 2006; Gosselin et al. 1976) properties. Iron sulfides have been recognized as advanced inorganic materials with non-conventional applications, such as high-energy density batteries, diagnostic materials, materials for photoelectrolysis, solar energy materials, and so on (Bonneau et al. 1991; Chin et al. 2005; Ferrer et al. 1994; Michel et al. 2005). Iron sulfides are major ore-forming minerals (Toulmin and Barton 1964) and have been proposed to play an important role in the origin of life (Russell et al. 1990; Williams 1990). Pyrrhotite, associated with pentlandite [(Fe,Ni)$_2$S$_3$] and other sulfides, occurs in basic igneous rocks, veins, and metamorphic rocks. It is also often found with pyrite, marcasite, and magnetite. Its magnetic powers vary with the number of iron vacancies in the crystal structure. A related species with no vacancies is called troilite and has been found in meteorites and rarely terrestrially (Dana 1944). Troilite may be the most common sulfide in the solar system, while pyrite is the most common sulfide in the crust (Fleet 2006). Sulfides are also an intrinsic and essential part of the global biogeochemical iron and sulfur cycles. Consequently, iron sulfides are central to our understanding of the evolution of the Earth (Rickard and Luther 2006, 2007; Rickard and Morse 2005).

Because of the scientific and industrial importance of Fe-S systems in materials science and geological science, thermodynamic properties of iron sulfides are required and continue to be of interest. Several methods have been used to obtain thermodynamic properties of sulfides. These include methods for both free energy determination (Lin et al. 1977; Rau 1976; Toulmin and Barton 1964), entropy (Grønvold and Stølen 1992; JANAF 1976), and heat of formation (Bugli et al. 1972; Cemić and Kleppa 1988). However, few methods are of general applicability and most of them evaluate the thermodynamic data at high temperature (generally, higher than 500 °C). Both $\Delta H$ and $\Delta S$ terms derived from a given free energy or activity, are often available only over a small temperature range. Thus the enthalpy and entropy values are often model-dependent and may be of limited accuracy. Also, direct reaction calorimetry (Bugli et al. 1972; Cemić and Kleppa 1988) is not general by virtue of the necessary rapid formation of the sulfide in situ. The samples formed directly may be heterogeneous and are not always well characterized.

Recently, high-temperature oxide melt solution calorimetry has been successfully applied to sulfides (MeS, Me = Zn, Cd, Pb) (Deore and Navrotsky 2006). In this method, small pellets of powdered, well-characterized sample are dropped into molten sodium molybdate (3Na$_2$O·4MoO$_3$) oxide solvent at 975 K. Sulfide (S$^2$-) is completely oxidized to dissolved sulfate (SO$_4^{2-}$). Obviously, investigation of thermodynamic data of pyrrhotite (Fe$_{1-0.125x}$S, $0 \leq x \leq 1$) solid solutions at room temperature is still needed for comprehending phase stability and materials compatibility. Here, we extend our calorimetric methodology to binary iron sulfides. The proposed calorimetric scheme for iron sulfides is illustrated as follows:

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\text{Pyrrhotite } \text{Fe}_{1-0.125x}\text{S (s, 298 K)} + (9 - 0.375x) \text{O}_2 (g, 975 K) = (1 - 0.125x) \text{Fe}^{2+} \text{(soln, 975 K)} + \text{SO}_4^{2-} \text{(soln, 975 K)} + (1 - 0.125x)/2 \text{O}^2- \text{(soln, 975 K)}
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