Oxide melt solution calorimetry of Fe$^{2+}$-bearing oxides and application to the magnetite–maghemite (Fe$_3$O$_4$–Fe$_{8/3}$O$_4$) system

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ABSTRACT

A consistent methodology for obtaining the enthalpy of formation of Fe$^{2+}$-containing binary and multicomponent oxides using high-temperature oxide melt solution calorimetry has been developed. The enthalpies of wüstite (FeO) and magnetite (Fe$_3$O$_4$) oxidation to hematite (Fe$_2$O$_3$) were measured using oxidative drop solution calorimetry in which the final product is dissolved ferric oxide. Two methods were applied: drop solution calorimetry at 1073 K in lead borate solvent and at 973 K in sodium molybdate, each under both oxygen flowing over and bubbling through the solvent, giving consistent results in agreement with literature values. The enthalpies of formation of all three iron oxides from the elements were obtained using a thermodynamic cycle involving the directly measured oxidative dissolution enthalpy of iron metal in sodium molybdate at 973 K and gave excellent consistency with literature data.

The methodology was then applied to the magnetite–maghemite system. The enthalpy of mixing of the Fe$_3$O$_4$–Fe$_{8/3}$O$_4$ spinel solid solution is exothermic and, represented by a subregular (Margules) formalism, $\Delta H_{\text{mix}} = x(1-x)[-63.36 \pm 8.60(1-x) + 17.65 \pm 6.40x] \text{kJ/mol}$, where $x$ is the mole fraction of magnetite. The entropies of mixing of the solid solution were calculated for different assumptions about the distribution of cations, charges, and vacancies in these defect spinels. The different models lead to only small differences in the entropy of mixing. Calculated free energies of mixing show no evidence for a solvus in the magnetite–maghemite system.

Keywords: Iron-bearing oxides, magnetite-maghemite spinel solid solution, enthalpies of mixing, vacancy distribution, high-temperature oxide melt solution calorimetry

INTRODUCTION

Iron oxides are widespread in all parts of the global system as minerals in soils, sediments, and rocks in the lithosphere, as particles in the atmosphere and hydrosphere, and in organisms ranging from bacteria to pigeons in the biosphere (Cornell and Schwertmann 2003). Iron oxides are found on the surface of Mars (Morris et al. 2000). They are often products of corrosion of steel or traces of iron meteorites (Cook et al. 1999; Dunn et al. 2000; Noguchi and Nakamura 2000). Wüstite (Fe$_{1-x}$O) is an end-member of the magnesiowüstite solid solution phase in the Earth’s lower mantle (Lindsley 1991). Ringwood (1977) proposed a model for the Earth’s core with FeO as the major light component. These widespread applications lend great importance to fundamental thermodynamic studies of the Fe-O system to understand core formation and core-mantle interactions. The variation of the properties in magnetic minerals provides one of the most complete records of geological and geomagnetic field history as well as information about palaeoclimate (Van Oorschot and Dekkers 1999). Magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$ or Fe$_{8/3}$O$_4$), the reduced and oxidized end-members of a spinel solid solution, are widely used in ceramic processing, magnetic data storage, catalysis, and microwave radiation shielding (Cornell and Schwertmann 2003). Additionally, magnetite is a corrosion product in the steel containers used for the long-term storage of nuclear waste (Neff et al. 2004). The Fe$^{3+}$ ions in the structure make magnetite a useful reductant for heavy metals, radionuclides, and other toxic compounds (Peterson et al. 1997; White and Peterson 1996; Scott et al. 2005). Maghemite is often an intermediate phase in the oxidation of magnetite to hematite (Gallagher et al. 1968, 1970; Shebanova and Lazor 2003; Gillot et al. 1978; Goss 1988).

Stoichiometric magnetite Fe$_3$O$_4$ has an inverse spinel structure with one Fe$^{3+}$ per formula unit on tetrahedral sites and Fe$^{2+}$ and the remaining Fe$^{3+}$ randomly distributed on the octahedral sites: Fe$^{3+}$(Fe$^{2+}$Fe$^{3+}$)O$_4$. The structure was originally suggested by Verwey and de Boer (1936) to account for its anomalously high room-temperature electrical conductivity through continuous exchange of electrons between Fe$^{2+}$ and Fe$^{3+}$ on the octahedral sites. Later, the fast electron hopping hypothesis was supported by Mössbauer studies (Bauminger et al. 1961). The nature of this exchange process has been interpreted either as a thermally activated hopping process or as a global delocalization of the sixth 3d electron of the Fe$^{2+}$ ions into a conduction band involving the entire octahedral sublattice (Vandenberge and De Grave 1989).

Non-stoichiometric magnetite can be represented as Fe$_{1-x}$O$_4$...