Thermodynamics of Fe oxides: Part II. Enthalpies of formation and relative stability of goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), and maghemite ($\gamma$-Fe$_2$O$_3$)

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ABSTRACT

The enthalpy of formation from the elements at 298.15 K ($\Delta H^0_f$) of lepidocrocite ($\gamma$-FeOOH) and maghemite ($\gamma$-Fe$_2$O$_3$) has been measured by acid-solution calorimetry as $-549.4 \pm 1.4$ and $-808.1 \pm 2.0$ kJ/mol, respectively. The $\Delta H^0_f$ of goethite ($\alpha$-FeOOH) was measured by high-temperature transposed temperature drop and acid-solution calorimetry as $-559.5 \pm 1.1$ and $-560.7 \pm 1.2$ kJ/mol, respectively.

Mathematical programming analysis (MAP) was used to generate an internally consistent data set for goethite and hematite, using the thermodynamic data presented in this study for goethite, and additional thermodynamic data for hematite and synthesis experiments of Baneyeva and Bendeliani (1973) (BB) and Voigt and Will (1981) (VW). Using BB brackets, the thermodynamic values for goethite were refined to $\Delta H^0_f = -561.9$ kJ/mol and entropy at standard pressure and temperature ($S^\circ$) = 59.2 J/K·mol; using VW brackets, we arrived at $\Delta H^0_f = -561.4$ kJ/mol and $S^\circ = 59.5$ J/(K·mol). However, MAP failed to include the magnetic transition in goethite, and the derived data should be used with caution.

Combined with the entropies for the studied phases, the Gibbs free energies of formation from the elements at 298.15 K are $-489.8 \pm 1.2$, $-480.1 \pm 1.4$, and $-727.9 \pm 2.0$ kJ/mol, for goethite, lepidocrocite, and maghemite, respectively. Only hematite ($\alpha$-Fe$_2$O$_3$) and goethite have a stability field in the Fe$_2$O$_3$-H$_2$O system at low to moderate pressures; maghemite and lepidocrocite are metastable at all pressures and temperatures. Goethite is $1.0 \pm 1.4$ kJ/mol metastable in $\Delta G$ with respect to hematite and liquid water, and $2.0 \pm 1.4$ kJ/mol metastable with respect to hematite and water vapor at 298 K and 50% relative humidity.

INTRODUCTION

Previous thermodynamic studies on Fe oxide and oxyhydroxide minerals focused on hematite (Coughlin et al. 1951; Grønvold and Westrum 1959; Grønvold and Samuelsen 1975; Hemingway 1990) and goethite (Barany 1965; King and Weller 1970; Ferrier 1966; Hsu and Marion 1985; Laberty and Navrotsky 1998); the other Fe oxides have received much less attention. Inconsistencies remain even for the relatively well-studied phases, for example, in the heat capacity of hematite above its Néel transition (955 K) (e.g., Robie and Hemingway 1995 vs. Chase 1998). Detailed studies on solubility of Fe-oxides, similar to those performed on Al-oxides (Tagirov and Schott 2001), are missing, perhaps owing to much lower solubility of the former. In this work, we have used acid-solution calorimetry and high-temperature transposed temperature drop calorimetry to measure enthalpy of formation ($\Delta H^0_f$) of goethite, lepidocrocite, and maghemite. The measurements of entropy ($S^\circ$) and heat capacity ($C_p$) of these three phases were presented in the companion paper (Majzlan et al. 2003), and the combination of $\Delta H^0_f$, $S^\circ$, and $C_p$ gives a complete description of the stability or metastability of the studied phases at pressure-temperature conditions relevant to geochemistry and materials science. Mathematical programming analysis generated an internally consistent thermodynamic dataset for hematite and goethite. This is the first study where all thermodynamic properties were determined, with high accuracy and precision, on well-characterized synthetic Fe-oxide samples. We were able to exclude the thermodynamic contribution of impurity metal substitution and high surface area, common flaws of thermodynamic studies done on natural samples. We are also investigating the effect of Al-for-Fe substitution in hematite and goethite and the effect of variable surface area, and the results of these investigations will be reported separately.

METHODS AND MATERIALS

Sample synthesis and characterization

Synthesis and characterization of the goethite, lepidocrocite, and maghemite samples used in this study are described in the companion paper (Majzlan et al. 2003). The fraction of a commercial hematite sample (Johnson Matthey, 99.999% metals basis) that passed through a 63 µm sieve was used in the calorimetric experiments described in this paper. The lattice parameters of the hematite samples were determined by Rietveld refinement of the powder X-ray diffraction (XRD) pattern with GSAS (Larson and von Dreele 1994) as $a = 5.0367(1)$ and $c = 13.7550(4)$ Å. Crystal size calculated from XRD data is 140...