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Thermodynamics of Fe oxides: Part II. Enthalpies of formation and relative stability of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe_2O_3)

JURAJ MAJZLAN,[1,*] KLAUS-DIETER GREVEL,[1,2] ALEXANDRA NAVROTSKY[1]

[1]Thermochemistry Facility and Department of Geology, University of California at Davis, Davis, California 95616, U.S.A.
[2]Ruhr-Universität Bochum, Institut fur Geologie, Mineralogie und Geophysik, 44780 Bochum, Germany

ABSTRACT

The enthalpy of formation from the elements at 298.15 K (ΔH_f^0) of lepidocrocite (γ-FeOOH) and maghemite (γ-Fe_2O_3) has been measured by acid-solution calorimetry as –549.4 ± 1.4 and –808.1 ± 2.0 kJ/mol, respectively. The ΔH_f^0 of goethite (α-FeOOH) was measured by high-temperature transposed temperature drop and acid-solution calorimetry as –559.5 ± 1.1 and –560.7 ± 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 $\Delta H_f^0 = -561.9$ kJ/mol and entropy at standard pressure and temperature (S^0) = 59.2 J/K·mol; using VW brackets, we arrived at $\Delta H_f^0 = -561.4$ kJ/mol and $S^0 = 59.5$ 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 ± 1.2, –480.1 ± 1.4, and –727.9 ± 2.0 kJ/mol, for goethite, lepidocrocite, and maghemite, respectively. Only hematite (α-Fe_2O_3) and goethite have a stability field in the Fe_2O_3-H_2O system at low to moderate pressures; maghemite and lepidocrocite are metastable at all pressures and temperatures. Goethite is 1.0 ± 1.4 kJ/mol metastable in ΔG with respect to hematite and liquid water, and 2.0 ± 1.4 kJ/mol metastable with respect to hematite and water vapor at 298 K and 50% relative humidity.