Thermodynamic properties of iron oxides and hydroxides.
II. Estimation of the surface and bulk thermodynamic properties of ordered and disordered maghemite (\(\gamma-\text{Fe}_2\text{O}_3\))

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Abstract: A consistent set of the thermodynamic properties of ordered and disordered maghemite (\(\gamma-\text{Fe}_2\text{O}_3\)) was generated from literature data by accounting for the effect of surface thermodynamic properties. The experimental high-temperature heat-capacity measurements for ordered and disordered maghemite are consistent with the equations: \(C_p^0 = 87.84 + 0.07518T\) (300–700 K) and \(C_p^0 = 52.94 + 0.1713T\) (300–600 K), respectively. The standard enthalpy of formation of ordered and disordered maghemite at 298.15 K (\(\Delta H^0 = -805.8 \pm 5.7\) kJ/mol) was generated from the measured enthalpy of transition of maghemite to hematite, using the apparent surface enthalpy of maghemite derived from the measured enthalpy of solution of this mineral as a function of surface area. The surface Gibbs energy of maghemite (\(G_A = 690 \pm 200\) mJ/m²) was calculated from the experimental surface enthalpy and estimated surface entropy. In the absence of low-temperature heat-capacity data and because of large scattering of estimated values, the standard entropy of ordered maghemite at 298.15 K was taken to be that of hematite (\(S^0 = 87.4\) J/mol K, Hemingway, 1990). Consequently, the standard entropy of disordered maghemite was calculated as 91.4 J/mol K. Using the standard entropies and enthalpy of formation, the standard Gibbs energies of formation at 298.15 K were derived as \(\Delta G^0 = -723.9 \pm 6.4\) and \(\Delta G^0 = -725.1 \pm 6.4\) kJ/mol for ordered and disordered maghemite, respectively. Stability of maghemite with respect to hematite was examined for temperatures up to 1150 K.

Key-words: maghemite, surface thermodynamic properties, Gibbs energy, solubility, \(\gamma-\text{Fe}_2\text{O}_3\).

Introduction

Maghemite (\(\gamma-\text{Fe}_2\text{O}_3\)) is a common mineral under conditions at the Earth’s surface. It is invariably found in subtropical and tropical soils (Schwertmann, 1988; Schwertmann & Cornell, 1991) where it can account for up to 5 wt% of soil material (Fabris et al., 1995). This mineral is responsible for magnetic properties of certain rocks, for example, Chinese loess (Eyre & Shaw, 1994). Recent data on Icelandic basalt mineralogy revealed the presence of maghemite in partially oxidised lavas (Helgason et al., 1992; Steinthorsson et al., 1992). Maghemite is also present among the oxidation products of iron-nickel meteorites (Golden et al., 1995) and is an important phase in steel corrosion processes (Schwarz, 1972; Nasrazadani & Raman, 1993). Additionally, magnetic and infrared characteristics of Martian regolith have been explained in several studies by the presence of maghemite (Burns, 1993; Bell et al., 1995). Maghemite is formed in natural systems mostly by the oxidation of magnetite and ilmenite (Schwertmann, 1988; White et al., 1994; Banfield et al., 1994) which are the two most commonly occurring Fe minerals in the Earth’s crust (totalling about 2 wt% of the crust according to Ronov & Yaroshovsky, 1971). Thus, the understanding of the processes of maghemite formation and its relative stability are vital for the reconstruction of...