



Formation, stability, and solubility of metal oxide nanoparticles: Surface entropy, enthalpy, and free energy of ferrihydrite

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Abstract

Ferrihydrite (Fh) is an excellent model for understanding nanoparticle behavior in general. Moreover, Fh is one of the most important Fe (hydr) oxides in nature. Fh particles can be extremely small leading to a very high reactive surface area that changes its chemical potential, strongly affecting the solubility, nucleation, and stability. These characteristics can be coupled to the interfacial Gibbs free energy, being $\gamma = 0.186 \pm 0.01 \text{ J m}^{-2}$ for Fh. The surface free energy has a relatively large contribution of surface entropy ($-TS_{\text{surf}} = +0.079 \pm 0.01 \text{ J m}^{-2}$). The surface entropy is primarily related to the formation of surface groups by chemisorption of water ($-17.1 \text{ J mol}^{-1} \text{ K}^{-1}$), for Fh equivalent with $+0.064 \pm 0.002 \text{ J m}^{-2}$ at a surface loading $N_{\text{H}_2\text{O}} = 12.6 \mu\text{mol m}^{-2}$. The entropy contribution of physisorbed water has been estimated by analyzing, as model, the surface enthalpy, entropy, and Gibbs free energy of the principal interfaces of H_2O , i.e. ice–water–gas. It is about 20% of the contribution of chemisorbed water.

The surface enthalpy of Fh is exceptionally low ($H_{\text{surf}} = +0.107 \pm 0.01 \text{ J m}^{-2}$), which can be explained by surface depletion (SD) of relatively unstable Fe polyhedra, or similarly, by additional surface loading of the non-depleted mineral core with specific Fe polyhedra for stabilization. The experimental enthalpy of Fh formation varies linearly with the surface area and correctly predicts the enthalpy value for the mineral core ($-405.2 \pm 1.2 \text{ kJ mol FeO}_{3/2}$), being similar to the literature value for Fh as virtual bulk material ($-406.7 \pm 1.5 \text{ kJ mol FeO}_{3/2}$) obtained with MO/DFT computations. The thermochemical quantities of the mineral core and surface are essentially the same for the entire range of Fh samples, in line with the SD model.

The solubility of Fh suspensions as a whole may differ from the behavior of individual particles due to polydispersity. For 2-line Fh, the overall solubility is $\log K_{\text{so}} \sim -38.5 \pm 0.1$ and for prolongedly aged 6-line Fh, $\log K_{\text{so}} \sim -39.5 \pm 0.1$. The smallest Fh particles in a suspension react according to the Ostwald–Freundlich equation ($RT\Delta\ln K_{\text{so}} = 2/3 \gamma A$), but the suspension as a whole apparently reacts according to the Ostwald equation ($RT\Delta\ln K_{\text{so}} = \gamma A$). This difference can be explained by the observed linear relation between the minimum (d_{min}) and mean (d_{mean}) particle size ($d_{\text{min}} = 2/3 d_{\text{mean}}$) in Fh suspensions.

With best estimates for the surface entropy of goethite, hematite, and lepidocrocite, predictions show that Fh becomes thermodynamically unstable above a diameter of $\sim 8.0 \text{ nm}$ at 298 K, allowing formation of nano-goethite and nano-hematite, as experienced experimentally at Ostwald ripening. More generally, one observes that metal (hydr) oxides with the highest chemical stability also have the highest mean surface Gibbs free energy, which can be considered as the scientific explanation of the empirical rule of Ostwald–Lussac. In addition, it is shown that the surface Gibbs free energies of metal (hydr) oxides increase with the mean metal coordination number of oxygen in the lattices following the order: oxides > oxyhydroxides > hydroxides.

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1. INTRODUCTION

In nature, Fe (hydr) oxides are very important and often present as nanoparticles with particle sizes in the range 1–10 nm (Hochella et al., 2008). In top soils, the nano-oxide fraction creates a reactive surface area of $\sim 3\text{--}30\text{ m}^2/\text{g}$ soil (Hiemstra et al., 2010), which is equivalent with millions of m^2 of oxide surface area per m^2 soil pedon. This huge surface area is able to store large quantities of ions forming the basis of soil system services.

Ferrihydrite is one of the most important Fe oxide minerals in abiotic and biotic environments (Jambor and Dutrizac, 1998; Fortin and Langley, 2005; Guo and Barnard, 2013; Theil et al., 2013). The mineral structure is difficult to grasp with conventional methods (Harrington et al., 2010; Manceau, 2011) because the particles are extremely small in lab and field (Janney et al., 2000; Cismasu et al., 2011). A new mineral structure has been proposed (Michel et al., 2007), that is distinct from the prior model of Drits et al. (1993). High-energy X-ray total scattering (HEXS) suggests that the polyhedral composition of Fh is particle-size dependent (Michel et al., 2010). For the initial precipitate, a defect structure has been proposed. The supposed defects disappear upon aging to ‘FerriFh’ ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$), as it was called. However, Xu et al. (2011) showed that two-line Fh can be dehydrated to almost $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ without significant changes in the mineral structure. Key for understanding this set of observations is the extremely large surface to volume ratio of nanoparticles (Hiemstra, 2013). Fh has a unique polyhedral surface composition that differs from the composition of the mineral core. The mineral core is basically defect-free for all Fh particles, but the surface as an inter‘phase’ is depleted by specific types of Fe polyhedra. Depleted Fh particles neither are supposed to have well-developed crystal terminations nor ideally ordered surfaces. The surface depletion (SD) model (Hiemstra, 2013) explains microscopic observations such as the particle size dependency of the Pair Distribution Function (PDF) and amount of Fe in tetrahedral coordination (Zhao et al., 1994; Maillot et al., 2011; Mikutta, 2011; Peak and Regier, 2012), as well as it explains macroscopic data such as the variable thermogravimetric (TGA) water content (Rancourt and Meunier, 2008; Michel et al., 2010; Xu et al., 2011), mass density (Hiemstra and van Riemsdijk, 2009; Michel et al., 2010; Hiemstra, 2013), and isotopic ^{57}Fe exchange (Rea et al., 1994; Poulson et al., 2005). The presence of surface groups makes 2-line Fh particles water-rich but its mineral core is hydrogen-poor (Hiemstra, 2013).

The large surface to volume ratio not only changes the above-mentioned properties, it also affects the solubility and mineral stability of Fh. Ferrihydrite has a variable collection of chemical bonds with corresponding bond strength, resulting in a variable chemical potential for the Fh particle as a whole. From the thermodynamic perspective, the surface is important and this quantity is represented by the surface Gibbs free energy. For a series of Fh particles, the dissolution enthalpy of Fh has been measured by Majzlan et al. (2004). Deriving from these measurements a value for the surface enthalpy is not an easy

task, particularly without proper insights in the mineral and surface structure. A reliable number for the surface enthalpy is presently missing for Fh in contrast to most other important Fe (hydr)oxides (Navrotsky et al., 2008). Recently, the enthalpy value of Fh as bulk material has been approached by Pinney et al. (2009) using molecular orbital calculations applying density functional theory (MO/DFT). It will be a challenge to link these data to the above-mentioned experimental information and this will be one of the objectives of the current study.

Elucidating the particle-size dependency of Fe(III) dissolution as well as the mineral stability and transformation not only requires insight in the contribution of the surface enthalpy. Actually, information about the interfacial Gibbs free energy is needed. This quantity is a combination of both surface enthalpy H_{surf} and surface entropy S_{surf} . In general, the contribution of surface entropy has been ignored in literature. This may have some justification if the contribution is constant for a set of comparable minerals and/or when it is relatively small. However, the surface enthalpy of Fh is probably very low in comparison to many other Fe (hydr) oxides. In that case, the surface entropy may potentially contribute significantly to the surface Gibbs free energy. It will be intriguing to take steps in this ‘‘Terra Incognita’’ and recent data, collected by Snow et al. (2013) may contribute to gaining insight. Surface hydration and surface entropy are tightly linked and therefore, the SD model may help elucidating these quantities. To evaluate the contribution of physisorbed water, we will collect and derive thermodynamic data for the three principal interfaces of H_2O assuming that the ice–water interface can serve as an interfacial model for mobile water meeting immobile water.

The ultimate goal is relating the obtained thermodynamic properties of the mineral core and surface to experimental data sets on the solubility (Biedermann and Schindler, 1957; Schindler et al., 1963; Fox, 1988; Liu and Millero, 1999; Hiemstra and van Riemsdijk, 2006; Stefansson, 2007), mineral stability of Fh (Michel et al., 2010), as well as its formation by nucleation. Crucial is a well-founded thermodynamic analysis (Enüstün and Turkevich, 1960; Wu and Nancollas, 1999; Godec et al., 2009; Nancollas and Wu, 2009; Kaptay, 2012). More generally, such an analysis is of vital importance for the emerging field of nano-science.

2. SURFACE ENERGETICS

2.1. Interfacial thermodynamics

The standard chemical potential of a mineral (μ°) is defined as the Gibbs free energy change (ΔG_f°) at formation of the bulk mineral from the elements at standard conditions. It generally refers to the bulk material where it represents the Gibbs free energy level of the collection of elements with bonds. Formation of surfaces leads to breaking of bonds usually resulting in a lower metal ion coordination and in the hydrated state, to the formation of new bonds at filling the coordination spheres of the ions at the surface (Goodell et al., 2008). The change in type of

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