Thermochemistry of hydrotalcite-like phases in the MgO-Al₂O₃-CO₂-H₂O system: A determination of enthalpy, entropy, and free energy

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ABSTRACT

Interest in hydrotalcite-like compounds has grown due to their role in controlling the mobility of aqueous metals in the environment as well as their use as catalysts, catalyst precursors, and specialty chemicals. Although these materials have been studied in a number of contexts, little is known of their thermodynamic properties. Here we present a complete thermochemical study of hydrotalcite-like compounds of the MgO-Al₂O₃-CO₂-H₂O system. Using high-temperature oxide-melt solution calorimetry, we determined the enthalpies of formation at 298 K from the elements (ΔfH) for the compounds: Mg₀.₆₉Al₀.₃₁(OH)₂.₀₁₃(CO₃)₀.₁₅·₀.₃₀H₂O, Mg₀.₇₄Al₀.₂₆(OH)₂(CO₃)₀.₁₃·₀.₃₉H₂O, Mg₀.₆₇Al₀.₃₃(OH)₂(CO₃)₀.₁₃·₀.₄₀H₂O, and Mg₀.₇₆Al₀.₂₄(OH)₂(CO₃)₀.₁₃·₀.₆₉H₂O. The structure of hydrotalcite (Fig. 1) is similar to that of the mineral talc, in which trivalent cations substitute for divalent cations alternating layers, or interlayers, containing anions that balance the positive charge resulting from the substitution. The remaining sites in the interlayers are occupied by water molecules.

INTRODUCTION

The mineral hydrotalcite occurs in nature as white crystals, similar in appearance to the mineral talc, in foliated and contorted plates and/or fibrous masses. Hydrotalcite-like solids form in association with other phases such as serpentinite and calcite. Takovite [Ni₆Al₂(OH)₁₆(CO₃)·₄H₂O], a Ni-bearing hydrotalcite-like phase, occurs in karstic bauxites and with minerals such as gaspeite, nepoutite, and carrboydite in weathered Ni-sulfide deposits (Bish 1980). The structure of hydrotalcite (Fig. 1) was first elucidated by Allmann (Allmann 1970) for the CO₃-Mg,Al system (hydrotalcite), and by Taylor (Ingram and Taylor 1967) for CO₃-Mg,Fe compounds (pyroaurite). The structure of hydrotalcite can be visualized as being composed of brucite-type layers and/or plates and/or similar in appearance to the mineral talc, in foliated and contorted plates and/or

Now the term hydrotalcite-like compound (HTLC) encompasses a growing class of minerals and materials that possess this type of layered structure. These materials possess a general stoichiometry: M⁺ₓM⁺ⁿ⁺(OH)₂[A⁻ⁿ]ₓ·mH₂O, where “x” represents the mole fraction of the trivalent cation in the brucite-layer (based on one mole of cations), “A⁻” is the intercalating anion, and “m” represents the water content. These materials contain a variety of cations including Mn²⁺, Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺, Fe³⁺, Al³⁺, Fe⁺, and Cr⁶⁺, as well as interlayer anions such as CO₃²⁻, NO₃⁻, Cl⁻, and SO₄²⁻.

Interest in HTLCs has grown due to their use as catalysts, catalyst precursors, and specialty chemicals (Cavani and Trifrò 1991), as well as their potential use as anion-exchange materials (Cavani and Trifrò 1991; Miyata 1980, 1983; Miyata and Okada 1977; Reichle 1986a, 1986b). Hydrotalcites are also interesting because of their role in controlling the mobility of aqueous metals in the environment (d’Espinos de la Caillerie et al. 1995a, 1995b; Scheidegger et al. 1997, 1998; Thompson et al. 1999a, 1999b, 2000; Towle et al. 1997).

Even though numerous applications have been developed for HTLCs, and a great deal of research has centered upon their effects on total dissolved concentrations of transition metals in the environment, little is known about their energetics. Standard-state thermodynamic data are essential for design calculations for the development of novel chemical processes and new materials, as well as for more accurate calculations in environmental chemistry. For example, solubility products for HTLCs are necessary for calculations involving their equilibrium with minerals in natural waters and generating phase diagrams. Similarly, solubility data are necessary for determining the capacity of HTLCs...