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Thermochemistry of hydrotalcite-like phases in the MgO-Al_2O_3-CO_2-H_2O 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-Al_2O_3-CO_2-H_2O system. Using high-temperature oxide-melt solution calorimetry, we determined the enthalpies of formation at 298 K from the elements (ΔH_f^0) for the compounds: $Mg_{0.69}Al_{0.31}(OH)_{2.013}(CO_3)_{0.15}\cdot0.30H_2O$, $Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}\cdot0.39H_2O$, $Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.16}\cdot0.69H_2O$, and $Mg_{0.66}Al_{0.34}(OH)_2(CO_3)_{0.17}\cdot0.70H_2O$ to be –1171.55 ± 1.81, –1165.98 ± 2.06, –1284.65 ± 1.97, and –1292.07 ± 2.05 kJ/mol, respectively. We also present the heats of formation of these materials from the single-cation hydroxides [$Mg(OH)_2$ and $Al(OH)_3$] and carbonates ($MgCO_3$) and water (ΔH_f^{scc}); they are energetically stable by 10–20 kJ/mol. Using low-temperature adiabatic heat-capacity measurements we determined the third-law entropy (S^0) for the compound $Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}\cdot0.39H_2O$ [85.58 ± 0.17 J/(mol·K)], neglecting any configurational contributions. From our experimental data for $Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}\cdot0.39H_2O$, we calculated the free energy at 298 K ($\Delta G_f^0 = -1043.08 \pm 2.07$ kJ/mol). Our thermodynamic studies also provide insight into the state of the interlayer water in hydrotalcite, namely the water of hydration appears to exist in a state intermediate in thermodynamic properties between that of ice and liquid water.