

Thermodynamic properties of antlerite, brochantite, and posnjakite

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Weathering of primary copper minerals (e.g., chalcopyrite, bornite) leads to the formation of secondary copper sulfates, phosphates, and arsenates. In this work, we focused on Cu sulfate-hydroxide minerals antlerite ($\text{Cu}_3\text{SO}_4(\text{OH})_4$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) and posnjakite ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$). We synthesized these phases in the laboratory and measured their thermodynamic properties.

The synthesis procedure was a titration of a 0.1 M sodium hydroxide solution into a 0.001 M solution of copper sulfate. The temperature of the CuSO_4 solution ranged from 25 to 80 °C and the end-point pH was set between 6 and 11. By variations of temperature and the end-point pH, the precipitates contained brochantite, posnjakite, or tenorite (CuO). We were able to determine systematic variations of the nature of the precipitated product with temperature and pH. Antlerite was synthesized as described in [1]. All these samples were characterized by X-ray diffraction (XRD). Subsequently, the best samples were analyzed by scanning electron microscopy (SEM) for phase purity and prepared for calorimetric measurements.

The calorimetric measurements were carried out by an acid-solution calorimeter at $T = 298$ K in 5 N HCl as the solvent with the calibration compound KCl, using CuO , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and H_2O as the reference compounds. For all measurements, appropriate thermochemical cycles were constructed. The formation enthalpies ($\Delta_f\text{H}_0$) of antlerite, brochantite and posnjakite are -1734.6 ± 5.3 kJ/mol, -2158.1 ± 7.0 kJ/mol, and -2456.0 ± 7.0 kJ/mol, respectively. Measurements of heat capacity are finished and standard entropies for each phase were calculated as 274.3 ± 5.5 J/mol•K, 343.1 ± 6.9 J/mol•K, and 390.9 ± 7.8 J/mol•K, for antlerite, brochantite, and posnjakite, respectively. The standard Gibbs free energies of formation of antlerite, brochantite and posnjakite are -1454.7 ± 5.6 kJ/mol, -1819.2 ± 7.3 kJ/mol and -2031.3 ± 7.3 kJ/mol, respectively. The ultimate goal of this study is a comprehensive model of Cu- and sulfate-rich fluids present in oxidation zones of ore deposits and tailings of Cu ores.

[1] Lin'ko et al. (2001) Russ J Inorg Chem+ 46, 298-301.