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Oxide melt solution calorimetry of sulfides: Enthalpy of formation of sphalerite, galena, greenockite, and hawleyite

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ABSTRACT

Oxidative drop solution calorimetry is being developed as a general method for sulfide thermochemistry. The samples are dropped from room temperature into molten $3Na_2O{\cdot}4MoO_3$ solvent at 975 K, with oxygen bubbling through the melt to ensure rapid and complete conversion of sulfide to dissolved sulfate. Complete dissolution of sulfides and retention of sulfur in the solvent is documented by furnace tests and visual observation, consistent determination of enthalpy of drop solution, and comparison with previous data for the heat of formation of ZnS, PbS, and CdS. Enthalpies of formation (kJ/mol) from the elements (ΔH_f^0) are determined for sphalerite (ZnS) (–206.53 ± 4.03 kJ/mol), galena (PbS) (–98.12 ± 4.37 kJ/mol), greenockite (hexagonal CdS) (–148.79 ± 4.13 kJ/mol), and hawleyite (cubic CdS) (–147.65 ± 4.28 kJ/mol). Thus, hawleyite appears to be energetically very similar to greenockite but possibly slightly metastable by about 1 kJ/mol. The results confirm that oxidative drop solution calorimetry in molten sodium molybdate is a viable method for sulfide thermochemistry. It will be most useful for sulfides with moderate heats of oxidation (e.g., the Fe-S, Co-S, and Ni-S systems), and should be applicable to ternary compounds, e.g., the Fe-Ni-S and Ni-Co-S systems, and systems showing large homogeneity ranges, as well as to other chalcogenides and pnictides.

Keywords: Sulfides, oxide melt solution calorimetry, enthalpy of formation, sphalerite, galena, greenockite, hawleyite