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Oxide-melt solution calorimetry of selenides: Enthalpy of formation of zinc, cadmium, and lead selenide

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Abstract

Selenium is an important trace element. Its geochemical cycles involve various oxidation states, including Se^{2-}, yet thermodynamic data for selenides are sparse. A general method for selenide thermochemistry has been developed by using oxidative drop-solution calorimetry in a molten oxide solvent. The samples are dropped from room temperature into molten sodium molybdate ($3Na_2O{\cdot}4MoO_3$) solvent at 975 K, with oxygen bubbling through the melt to ensure rapid and complete conversion of selenide to dissolved selenate species. This method is analogous to that developed for sulfides (Deore and Navrotsky 2006). Complete dissolution of selenides is documented by furnace tests and visual inspection, and supported by consistent results for enthalpy. Enthalpies of formation ($\Delta_f H°$, kJ/mol) from the elements were determined for zinc selenide (ZnSe) (–169.94 ± 4.31 kJ/mol), cadmium selenide (CdSe) (–139.04 ± 6.13 kJ/mol), and lead selenide (PbSe) (–99.26 ± 6.06 kJ/mol). These three $\Delta_f H°$ values agree with previously published data, often obtained by less direct means. This is the first report of the enthalpy of formation of CdSe measured by any calorimetric method. For ZnSe, a more reliable $\Delta_f H°$ value is proposed since prior data are quite scattered. The results confirm that oxidative drop-solution calorimetry is an available method for selenide thermochemistry. It should be applicable to binary and multinary selenides with large homogeneity ranges, to solid solutions, and to nanophase materials.

Keywords: Selenides, thermodynamics, enthalpy of formation, calorimetry, oxide melt solution calorimetry, optical properties, semiconductors