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Oxide melt solution calorimetry of Fe^{2+}-bearing oxides and application to the magnetite–maghemite (Fe_3O_4–$Fe_{8/3}O_4$) system

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Abstract

A consistent methodology for obtaining the enthalpy of formation of Fe^{2+}-containing binary and multicomponent oxides using high-temperature oxide melt solution calorimetry has been developed. The enthalpies of wüstite (FeO) and magnetite (Fe_3O_4) oxidation to hematite (Fe_2O_3) were measured using oxidative drop solution calorimetry in which the final product is dissolved ferric oxide. Two methods were applied: drop solution calorimetry at 1073 K in lead borate solvent and at 973 K in sodium molybdate, each under both oxygen flowing over and bubbling through the solvent, giving consistent results in agreement with literature values. The enthalpies of formation of all three iron oxides from the elements were obtained using a thermodynamic cycle involving the directly measured oxidative dissolution enthalpy of iron metal in sodium molybdate at 973 K and gave excellent consistency with literature data.

The methodology was then applied to the magnetite–maghemite system. The enthalpy of mixing of the Fe_3O_4–$Fe_{8/3}O_4$ spinel solid solution is exothermic and, represented by a subregular (Margules) formalism, $\Delta H_{mix} = x(1-x)[-63.36 \pm 8.60(1-x) + 17.65 \pm 6.40x]$ kJ/mol, where x is the mole fraction of magnetite. The entropies of mixing of the solid solution were calculated for different assumptions about the distribution of cations, charges, and vacancies in these defect spinels. The different models lead to only small differences in the entropy of mixing. Calculated free energies of mixing show no evidence for a solvus in the magnetite–maghemite system.

Keywords: Iron-bearing oxides, magnetite-maghemite spinel solid solution, enthalpies of mixing, vacancy distribution, high-temperature oxide melt solution calorimetry