On the thermochemistry of the solid solution between jarosite and its chromate analog

CHRISTOPHE DROUET,1 DIRK BARON,2 AND ALEXANDRA NAVROTSKY1,*

1Thermochemistry Facility, University of California at Davis, One Shields Avenue, Davis, California 95616, U.S.A.
2Department of Physics and Geology, California State University, Bakersfield, California 93311, U.S.A.

ABSTRACT

Minerals of the jarosite group can be a significant environmental sink for hexavalent Cr by substitution of chromate for sulfate. The thermochemistry of the synthetic solid solution between jarosite KFe3(SO4)2(OH)6 and its chromate analog KFe3(CrO4)2(OH)6 was investigated by high-temperature oxide-melt solution calorimetry. The enthalpies of formation (ΔHf°) of the latter, as well as of five intermediate compositions in the series KFe3(S1−zCrzO4)2(OH)6, were determined, where z corresponds to the Cr content. The variation of ΔHf° with Cr content deviates from ideality, and negative enthalpies of mixing between jarosite and its chromate analog are observed, suggesting some ordering of the sulfate/chromate groups in the solid solution. The measured enthalpy of formation from the elements of the end-member KFe3(CrO4)2(OH)6 is ΔHf° = −3762.5 ± 8.0 kJ/mol. In view of this work, and considering literature data, ΔGf° = −3305.5 ± 3.4 kJ/mol, ΔSf° = −1533.6 ± 29.2 J/(mol·K), and S° = 487.7 ± 29.2 J/(mol·K) are recommended for KFe3(CrO4)2(OH)6.

INTRODUCTION

Chromium (VI) has become an increasingly recognized and common environmental contaminant in soils and groundwater (Handa 1988; Mayer 1988; Puls et al. 1994). Although this contamination is mostly a consequence of human industrial activity, there are also reports of naturally elevated levels of Cr⁶⁺ in groundwater (Robertson 1975; Robles-Camacho and Armienta 2000). The ion CrO⁴²⁻, whose carcinogenic and mutagenic properties are well known (Bose et al. 1998; Hamilton et al. 1998), is among the most frequently cited pollutants in hazardous waste sites (National Research Council 1991), and is therefore at the center of many environmental concerns.

Although most relatively insoluble solid phases containing Cr immobilize it in the trivalent state, there are some crystalline solids that incorporate Cr in its hexavalent form. Among such precipitates, the chromate analog of jarosite, KFe3(CrO4)2(OH)6, has been identified for the first time in contaminated soils by Baron et al. (1996). Because the precipitation of such Cr⁶⁺ phases modifies the mobility of Cr in the surrounding soils and groundwater, it is crucial to have accurate thermodynamic data for these phases to predict and understand their formation and dissolution as a function of external conditions.

In addition, one of the most promising new technologies for the in-situ treatment of Cr⁶⁺-contaminated groundwater consists of permeable, reactive-iron barriers (e.g., Blows et al. 1997; Powell et al. 1995). Several of these barriers are now installed at sites around the U.S. (e.g., Puls et al. 1999). The basic principle behind these barriers is that reaction with Fe metal will reduce chromate and then immobilize it. One of the important issues associated with the long-term performance of these barriers is the formation of secondary Fe-Cr precipitates in the barrier itself or down gradient from it. The thermodynamic data for such potential precipitates, including KFe3(CrO4)2(OH)6 and solid solution between jarosite KFe3(SO4)2(OH)6 and the KFe3(S1−zCrzO4)2(OH)6 solid solution, are essential to assess the conditions under which these precipitates may form, and to evaluate the aqueous chromate concentrations for waters in equilibrium with these phases.

In another context, the precipitation of jarosite-like phases could be exploited to remove undesired CrO⁴²⁻ ions from aqueous solutions in a similar way as the precipitation of jarosite is used to eliminate Fe impurities from processing solutions in Zn hydrometallurgy (Arregui et al. 1979). However, to put this into practice at an industrial scale, knowledge of the conditions of formation of such precipitates is essential.

Only a few studies have been dedicated to the thermochemistry of KFe3(CrO4)2(OH)6 or its solid solution with jarosite, and the lack of thermodynamic data for these compounds is obvious. Recently, Baron and Palmer (1996) determined the free energy of formation (ΔGf°) of KFe3(CrO4)2(OH)6 from dissolution experiments, as well as the solubility products of intermediate compositions KFe3(S1−zCrzO4)2(OH)6 (Baron and Palmer 2002). For KFe3(CrO4)2(OH)6, these authors reported the value ΔGf° = −3305.5 ± 3.4 kJ/mol. Ball and Nordstrom (1998) also estimated ΔGf° for this phase from the free energy of the constituting ions, and the value calculated by these authors (−3307.2 ± 5.2 kJ/mol) is in close agreement with that measured by Baron and Palmer (1996).

Although the free energy of formation at ambient conditions is important, the enthalpy of formation and entropy are required to constrain the temperature dependence of solubility. Such data also allow better understanding of the relation between crystal chemistry and energetics for substitutions such as K⁺ → Na⁺, Fe³⁺ → Al³⁺, and S⁶⁺ → Cr⁶⁺. To our knowledge, no measurements of the enthalpy of formation of the jarosite-chromate analog series have been reported, and this is the objective of the present work.