Thermochemistry of jarosite-alunite and natrojarosite-natrolalunite solid solutions

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Abstract—The thermochemistry of jarosite-alunite and natrojarosite-natrolalunite solid solutions was investigated. Members of these series were either coprecipitated or synthesized hydrothermally and were characterized by XRD, FTIR, electron microprobe analysis, ICP-MS, and thermal analysis. Partial alkali substitution and vacancies on the Fe/Al sites were observed in all cases, and the solids studied can be described by the general formula $K_{1+x-y}Na_y(H_2O)_{1+x}Fe_{2+y}Al_x(SO_4)_{3-y}OH_{6-3/y}(H_2O)_{3-3/y}$. A strong preferential incorporation of Fe over Al in the jarosite/alunite structure was observed. Heats of formation from the elements, $\Delta H_f$, were determined by high-temperature oxide melt solution calorimetry. The solid solutions deviate slightly from thermodynamic ideality by exhibiting positive enthalpies of mixing in the range 0 to +11 kJ/mol. The heats of formation of the end members of both solid solutions were derived. The values $\Delta H_f = -3734.6 \pm 9.4$ kJ/mol and $\Delta H_f = -4912.2 \pm 24.2$ kJ/mol, $\Delta H_f = -3734.6 \pm 9.7$ kJ/mol and $\Delta H_f = -4979.7 \pm 7.5$ kJ/mol were found for $K_{1.08}(H_2O)_{1.07}Fe_{2.06}(SO_4)_{2.87}(OH)_{6.07}(H_2O)_{3.07}$, $K_{1.08}(H_2O)_{1.07}Fe_{2.06}(SO_4)_{2.87}(OH)_{6.07}(H_2O)_{3.07}$, $Na_{0.89}(H_2O)_{1.08}Fe_{2.06}(SO_4)_{2.87}(OH)_{6.07}(H_2O)_{3.07}$, and $Na_{0.89}(H_2O)_{1.08}Fe_{2.06}(SO_4)_{2.87}(OH)_{6.07}(H_2O)_{3.07}$ respectively. To our knowledge, this is the first experimentally-based report of $\Delta H_f$ for such nonstoichiometric alunite and natrolalunite samples. These thermodynamic data should prove helpful to study, under given conditions, the partitioning of Fe and Al between the solids and aqueous solution. Copyright © 2004 Elsevier Ltd