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

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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 $KFe_3(SO_4)_2(OH)_6$ and its chromate analog $KFe_3(CrO_4)_2(OH)_6$ was investigated by high-temperature oxide-melt solution calorimetry. The enthalpies of formation (ΔH_f^0) of the latter, as well as of five intermediate compositions in the series $KFe_3(S_{1-z}Cr_zO_4)_2(OH)_6$, were determined, where z corresponds to the Cr content. The variation of ΔH_f^0 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 $KFe_3(CrO_4)_2(OH)_6$ is $\Delta H_f^0 = -3762.5 \pm 8.0$ kJ/mol. In view of this work, and considering literature data, $\Delta G_f^0 = -3305.5 \pm 3.4$ kJ/mol, $\Delta S_f^0 = -1533.6 \pm 29.2$ J/(mol·K), and $S^0 = 487.7 \pm 29.2$ J/(mol·K) are recommended for $KFe_3(CrO_4)_2(OH)_6$.