

Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, UO_2CO_3 , andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_5$, and grimselite, $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3\text{H}_2\text{O}$

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ABSTRACT

Enthalpies of formation of rutherfordine, UO_2CO_3 , andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_5$, and grimselite, $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})$, have been determined using high-temperature oxide melt solution calorimetry. The enthalpy of formation of rutherfordine from the binary oxides, $\Delta H_{\text{f-ox}}$, is -99.1 ± 4.2 kJ/mol for the reaction UO_3 (xl, 298 K) + CO_2 (g, 298 K) = UO_2CO_3 (xl, 298 K). The $\Delta H_{\text{f-ox}}$ for andersonite is -710.4 ± 9.1 kJ/mol for the reaction Na_2O (xl, 298 K) + CaO (xl, 298 K) + UO_3 (xl, 298 K) + 3CO_2 (g, 298 K) + $5\text{H}_2\text{O}$ (l, 298 K) = $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_6$ (xl, 298 K). The $\Delta H_{\text{f-ox}}$ for grimselite is -989.3 ± 14.0 kJ/mol for the reaction $1.5 \text{K}_2\text{O}$ (xl, 298 K) + $0.5\text{Na}_2\text{O}$ (xl, 298 K) + UO_3 (xl, 298 K) + 3CO_2 (g, 298 K) + H_2O (l, 298 K) = $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3\text{H}_2\text{O}$ (xl, 298 K). The standard enthalpies of formation from the elements, $\Delta H_{\text{f}}^\circ$, are -1716.4 ± 4.2 , -5593.6 ± 9.1 , and -4431.6 ± 15.3 kJ/mol for rutherfordine, andersonite, and grimselite, respectively. Energetic trends of uranyl carbonate formation from the binary oxides and ternary carbonates are dominated by the acid-base character of the binary oxides. However, even relative to mixtures of UO_2CO_3 , K_2CO_3 , and Na_2CO_3 or CaCO_3 , andersonite and grimselite are energetically stable by 111.7 ± 10.2 and 139.6 ± 16.1 kJ/mol, respectively, suggesting additional favorable interactions arising from hydration and/or changes in cation environments. These enthalpy values are discussed in comparison with earlier estimates.