

Thermochemistry of metastudtite and amorphous UO_3

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Metastudtite, $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2$, is one of the few minerals containing peroxide and maybe an important alteration phase in geological repositories or nuclear plant accidents, as well as some natural geologic settings. Decomposition of synthetic metastudtite was characterized by thermogravimetry (TG) and differential scanning calorimetry (DSC) with ex-situ X-ray diffraction analysis of its products. Three decomposition steps were observed in both oxygen and inert atmospheres, with water loss around 220 °C associated with an endothermic heat effect accompanied by amorphization, following by slowing oxygen loss prior to recrystallization, eventually reduction to U_3O_8 . Standard formation enthalpy of metastudtite was obtained from high temperature solution calorimetry in sodium molybdate melt and from the heat effect on reduction to U_3O_8 during transposed temperature drop calorimetry at 700 °C. The obtained value -1780 ± 2 kJ/mol [1, 2] agrees with earlier reports and estimates from thermal analysis. Amorphous UO_3 (*am*- UO_3) with surface area 8.8 m²/g was prepared by decomposition of metastudtite at 400 °C. Enthalpy of water adsorption on metastudtite and *am*- UO_3 was measured directly by gas adsorption calorimetry providing integral enthalpy of chemisorption as -84 kJ/mol at 4.1 H₂O/nm² for *am*- UO_3 , and -116 kJ/mol at 2.8 H₂O/nm² for metastudtite. These coverages represent the transition from chemisorbed to physisorbed water.

[1] Cordfunke, *et al* (1063) *Recl. Trav. Chim. Pays-Bas*, **82**, (3). [2] Cordfunke (1966) *Thermodynamic properties of hexavalent uranium compounds*, IAEA: Vienna, Austria, Vol. **2**, 483-495