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D17

The Reaction of Plutonium with Water: Phases in the Pu + O + H System

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In early reports, the reaction of plutonium with water is described as "very slow at room temperature" [1]. The product is a finely divided black solid which prior workers have identified as hydrated oxide or hydroxide [2]. Results of recent experiments with synthetic sea water show that the Pu + H_2O reaction is quite rapid and that the quantities of H_2 produced are less than half those expected for the formation of $Pu(OH)_3$ or $Pu(OH)_4$ [3]. The primary measurement described in this report was designed to determine the reaction rate of Pu with 1.0 *M* $CaCl_2$ solution, but kinetic measurements which continued for more than 450 days have provided valuable insight into the chemistry of the complex Pu + U + H system.

Kinetic measurements and the preparation of solid hydrolysis products for analysis were made with a stainless steel system fitted with a glass liner for containment of the reactants. Rates and extents of reaction at 23 ± 2 °C were monitored by PVT methods. Both α-phase and δ-stabilized Pu were reacted with aqueous salt solutions having a wide range of concentrations. Samples of the initial hydrolysis product were isolated by removing residual water under dynamic vacuum or with molecular sieve.

The reaction of Pu with H_2O to form the black product is rapid when catalyzed by salt. The reaction rate R (mgPu cm^{-2} hr^{-1}) is dependent on the anion concentration X (mol l^{-1}) as follows: $R = 1.2X^{0.7}$ for $10^{-7} \leqslant X \leqslant 1$ *M*. Small variations are observed for different anions and cations and for α- and δ-phase Pu.

When the quantity of H_2 formed during the extended experiment (α-Pu + 1.0 *M* $CaCl_2$ solution) is graphed against time, a series of linear curves with successively lower slopes is observed. Each linear (constant rate) section is attributed to the occurence of a specific equilibrium hydrolysis reaction. During the first linear segment, Pu is completely converted to black product. During the second segment, that product reacts with water at a slower rate to produce additional H_2 and a third product, *etc.* It is convenient to formulate the quantity of H_2 as mol H_2 produced per mol Pu because this ratio is directly correlated with the net chemical reaction; *e.g.*, this ratio is 1.5 and 2.0 for formation of $Pu(OH)_3$ and $Pu(OH)_4$, respectively. Least squares analysis of the data for the extended test show that sharp slope changes occur at the following H_2/Pu ratios: 0.507, 1.078, 1.455, 1.716, 1.763, 1.803, 1.831 and 1.993. Eight different hydrolysis products apparently form in succession. The breaks near 1.5 and 2.0 correspond to the formation of products containing trivalent and tetravalent Pu. The products existing at 0.50 and 1.07 must either have Pu in a valence state less than three or contain hydride, while those formed between the 1.50 and 2.00 ratios are mixed-valent.

The black product formed at $H_2/Pu = 0.50$ has been identified as plutonium monoxide monohydride, Pu(O)H. This assignment is based on the results of chemical, TG, XRD, and XPS analyses. The data show that the product is not an hydroxide or hydrated oxide and that it is chloride-free. XRD results for wet and dry products give identical fcc patterns with a = 540.1(2) pm. Although the parameter is similar to those of PuH_2 (a = 535.9 pm) and PuO_2 (a = 539.7 pm), thermal decomposition results show that the product is not a mixture of hydride and oxide. The observed parameter is consistent with that expected for a fluorite-related oxide hydride. Hydrolysis of Pu is described by the reaction: $Pu + H_2O \rightarrow Pu(O)H + 1/2H_2$. XRD results are given in Table I.

TABLE I. X-ray Diffraction Intensities for the Plutonium Monoxide Monohydride.

hkl	I/I_0 (%)
111	100
200	34
220	45
311	42
222	8
400	5
331	11
420	10
422	8
333	9

Our identification of the other hydrolysis products is based on results for the initial product and on the well-known phase relationships of Pr + O [4]. Particularly important observations are: (a) The product does not contain hydroxide, and this anion is not expected to exist in subsequent products. (b) The metals occupy fcc positions, and their rearrangement in subsequent phases at room temperature is unlikely. The observed H_2/Pu ratios at which slope changes occur are in excellent agreement with the theoretical values for the following sequence of products: Pu(O)H (0.500), $Pu_7O_9H_3$ (1.071), Pu_2O_3 (1.500), Pu_7O_{12} (1.714), Pu_9O_{16} (1.778), $Pu_{10}O_{18}$ (1.800) $Pu_{12}O_{22}$ (1.833) and PuO_2 (2.000). All these phases are expected to have metal atoms on fcc positions with the anion positions of fluorite occupied at Pu(O)H and PuO_2. During hydrolysis of the oxide hydride phases, the metal presumably remains trivalent while ordered defects are created on anion sites until the formation of C-type Pu_2O_3 is complete. As hydrolysis continues, ordered occupancy of anion sites occurs as Pu(III) is converted to Pu(IV). The mixed-valent oxides proposed for Pu are identical to those of Pr. $Pu_7O_9H_3$ is considered to be an analog of Pu_7O_{12}. Our results suggest that six previously unknown phases exist in Pu + O + H.

Although our characterization of the product formed by thermal decomposition of Pu(O)H in dynamic vacuum at 100–200 °C is incomplete, all observations suggest that it is metastable plutonium monoxide, PuO.

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D18

Oxygen Nonstoichiometry in Calcium and Strontium Uranates ($CaUO_{4-x}$ and $SrUO_{4-x}$): Lattice Parameters and Enthalpies of Formation[+]

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Nonstoichiometric calcium monouranate, $CaUO_{3.50}$, was prepared by reducing $CaUO_4$ in a hydrogen stream at 900 °C. $CaUO_{3.64}$ and $CaUO_{3.81}$ were prepared by heating mixtures of $CaUO_{3.50}$ and $CaUO_4$ in evacuated quartz tubes at 900 °C for 50 h. Nonstoichiometric strontium monouranates with compositions $SrUO_{3.62}$, $SrUO_{3.70}$, and $SrUO_{3.87}$ were prepared by heating mixtures of $SrUO_{3.52}$ and α-$SrUO_4$ in evacuated tubes at 300 °C for 100 h. Chemical analyses were carried out for the products. These are all rhombohedral ($R\bar{3}m$). The lattice c-parameter decreases at a much larger rate than the a-parameter with increasing oxygen amount, but there exist two-phase regions at $CaUO_{3.81}$ and $SrUO_{3.87}$.

The effect of heating conditions for these phases was examined. The enthalpies of formation of these compositions were measured. The variation of these data as a function of nonstoichiometry is discussed.

D19

Magnetic Properties of the Rhomboedral Ferrites $LuFe_2O_4$ and $LuMgFeO_4$

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D20

Two New Families of Lanthanoide Ferrites $Ln_2Fe_4O_9$ and $Ln_4Fe_6O_{15}$

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D21

Synthesis, Structural Study and Electrical Properties of Hydride–Oxides: LaHO, $LaH_{1+2x}O_{1-x}$ and $LaH_{1+y}O_{1-x}$ (y = 2x)

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