

EVALUATION OF HYDROGEN GENERATION MODEL IN DOE STANDARD 3013 FOR LONG-TERM STORAGE OF PLUTONIUM-BEARING MATERIALS

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ABSTRACT

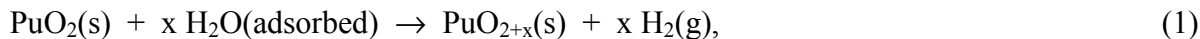
Ambient room-temperature equilibrium constants have been determined for the physical and chemical reactions within the $\text{PuO}_2\text{-H}_2\text{O-H}_2\text{-O}_2$ system characteristic of stored plutonium oxides, from data for nine Hanford items studied in the materials identification and surveillance (MIS) program at Los Alamos National Laboratory. Our analysis led to the conclusion that under the low temperature and water content conditions for the investigation, the vapor pressure of water, or chemical activity of the adsorbed water in equilibrium with the vapor, would be very low for pure and impure plutonium oxide that had been stabilized for transportation or storage. The pure or impure plutonium oxide would getter any free oxygen in a strong equilibrium to reduce its concentration to minor levels in the storage package, and, together with the very weak equilibrium for the dissociation of water bound to the solid, it would prevent both further oxidation of the oxide material and any significant buildup of hydrogen. These findings imply that for the low temperatures investigated, it would not be necessary to render inert packages of plutonium oxides that had been stabilized for transportation and storage.

These are benign results compared with the much higher hydrogen pressures over plutonium oxides that would be determined from the model given in the Appendix of DOE-STD-3013. For various estimated upper-limit temperatures that depend on the power density within the plutonium oxide, the DOE-STD-3013 model assumes hydrogen pressures derived by extrapolation from results of experiments by Haschke, Allen and Morales at temperatures between 25 and 350°C that did not achieve equilibrium. Therefore, further analysis in the ongoing MIS program could be directed toward determination of the upper-limit temperatures for plutonium oxides with higher power densities and the equilibrium constants associated with those temperatures.

INTRODUCTION

At first, it was assumed [1] that the adsorbed water on plutonium oxides would be completely dissociated by radiolysis to give a 2:1 $\text{H}_2\text{:O}_2$ inventory that would pressurize the DOE-STD-3013 [1] can during long-term storage of its plutonium oxide contents. That assumption was nonconservative in that it did not consider the possibility of additional pressures that might arise from a deflagration or detonation of such a gaseous mixture. But it was overly conservative in that it did not take into consideration the catalytic recombination of those gases over PuO_2 that was demonstrated by Morales [2].

Haschke and Allen [3] and Haschke, Allen and Morales [4] studied the reaction between PuO_2 (at temperatures from 25 to 350°C) with water from a reservoir at 24-25°C that had a vapor pressure of ≈ 24 torr. They observed production of hydrogen with no production of oxygen in the gas phase under those conditions. X-ray diffraction analysis (XRD) identified the solid phase for this reaction as $\text{PuO}_{2+x}(\text{s})$, where x represents a hyperstoichiometric amount of oxygen in the solid that was equivalent to the molar amount of hydrogen formed in the gas. Consequently, their conclusions were that the equation for the chemical reaction was



and that PuO_{2+x} was a solid solution of PuO_3 and PuO_2 . The latter conclusion has been controversial in that no previous thermodynamics basis for the existence of PuO_3 had been established. Because equilibrium was not achieved in those experiments, 1996, 1999, and 2000 editions of DOE-STD-3013 [5] assumed that the above reaction would go to completion to pressurize a 3013 storage can with the hydrogen inventory equivalent to the number of gram moles of H_2O adsorbed on the PuO_2 contents of the storage can.

By examining cans with both pure and impure plutonium oxides Mason et al. [6] demonstrated that this was not the case for cans that had been sealed in air and stored at ambient room temperatures for periods between 1 and 18 years. Hydrogen pressures were very low under those conditions, except for one case in which moderate hydrogen pressure was observed; and in that case, no oxygen was observed within the precision limits for the head space gas measurements. In all cases in which the head space gases were analyzed, except for one leaking can, most of the oxygen in the as-sealed cans had reacted with the solid oxide material.

In summary, the experiments by Haschke, Allen and Morales [4] were a valuable contribution to understanding the chemistry of the PuO_2 - H_2O - H_2 - O_2 system. However, equilibrium conditions which might be achieved with plutonium oxides, under conditions of long-term storage, were not achieved in those experiments. Therefore, as pointed out by Morales [2] and concluded from our analysis of the results given by Mason et al. [6], the assumption of complete reaction of the water adsorbed on stored plutonium oxides to generate hydrogen could be an unrealistic basis for the current hydrogen generation model in the Appendix of DOE-STD-3013. It also appears that equilibrium might have been precluded in the experiments of Haschke, Allen and Morales, in that the vapor pressure of the water adsorbed on the oxide could have been much less than the 24 torr vapor pressure of the water reservoir source. Under those conditions, water would have continuously distilled over to the PuO_2 surface and eliminated the possibility of attaining equilibrium there. Or perhaps PuO_{2+x} is a metastable solid that would never exist under equilibrium conditions; because in the reverse of the reaction depicted by Eq. 1, it ultimately might react completely with hydrogen to give back PuO_2 and H_2O .

From examination of the results and conclusions of the above-cited Los Alamos National Laboratory (LANL) investigations, a chemical thermodynamics model was formulated to describe the equilibrium conditions for storage of plutonium oxide materials. Provisional values of equilibrium constants for this model were derived from limited information obtained through the materials identification and surveillance (MIS) program by Mason et al. [6] and can be further developed with information from planned future MIS studies by Behrens et al. [7]. Interpretation of those results should include analysis of the effects of such variables as temperature, chemical composition, and surface characteristics on those thermodynamics constants.

EXPERIMENTAL BASIS FOR THE CHEMICAL THERMODYNAMICS MODEL

Baker, Ness and Orman [8] studied the time dependence of constituents in the gas phase during reaction of uranium metal that were initiated with a gaseous 3:2 O_2 : H_2O mixture. It was found that the amount of gaseous oxygen was reduced to zero in ≈ 300 h. During that period of oxygen

depletion, some hydrogen was formed, but its partial pressure did not exceed 1.5 μ while oxygen remained; and its concentration showed only a barely perceptible upward trend in that period. The water vapor pressure remained constant and the oxygen pressure fell linearly. When the oxygen pressure became zero there was an immediate rise in hydrogen concentration and a fall in water vapor pressure. To determine whether the small amount of hydrogen formed in the presence of oxygen was in static or dynamic equilibrium, hydrogen was injected into the reacting system. The added hydrogen was not consumed and the reaction proceeded normally to completion.

Similar behavior appears to be the case for the reaction of oxygen and water with plutonium oxides in (long-term storage) cans that were opened in the MIS program at LANL [6]. That conclusion is based upon examination of the gaseous constituents of the opened inner cans that were initially sealed in air. Very little oxygen was left in the cans. The major gaseous constituent of the opened cans was nitrogen, with minor levels of oxygen, water vapor, carbon dioxide, helium, argon, and small amounts of hydrogen (presumably) from the reaction of PuO_2 (or its impurities) with its adsorbed water.

SUMMARY OF MIS STUDIES AT LANL

Nine items sent to LANL from Hanford and twenty-four from the Rocky Flats Environmental Technology Site (RFETS) were evaluated in the 1999 MIS status report. The plutonium, uranium, and impurity contents, as well as the wattage, of all as-received Hanford and RFETS items were determined. In addition, thermal analysis, surface area and particle size analysis, XRD and thermogravimetric analysis (TGA) studies, loss on ignition (LOI), supercritical fluid extraction (SFE) and density measurements, as well as chemical and interstitial gas analysis and surveillance testing, were performed on all of the as-received materials from Hanford and RFETS. The items were then calcined at 600 and 950°C and subsequently measured. Laura Worl at LANL [9] has advised us that the SFE measurements are a more reliable measure of the moisture content than the traditional LOI measurements, which reflect the presence of volatile impurities, particularly for as-received item ARF-102-85-295 that had a chloride content >20 wt.%.

Five of the nine items from Hanford, prefixed ARF, consisted of RFETS items that were canned in the RFETS atmosphere of \approx 620 torr, sent to Hanford, and stored there for several years. Two of those items, ARF-102-85-355 and ARF-102-85-295, were opened at Hanford for chloride analysis; and they were then resealed using a Hanford glovebox atmosphere of <742 torr. All nine cans were sealed in air gloveboxes.

Head space gases for the inner and outer cans for all nine items from Hanford were analyzed by mass spectrometry. Also, head space gas compositions were measured for small reactors loaded with selected 10-g samples of those nine items sealed in air, and several head space gases were analyzed for 10-g samples sealed in helium. From analysis of the Hanford cans, it was found that hydrogen buildup during extended storage of those items was minimal, except for ARF-102-85-365. Even in that item, hydrogen buildup was moderate and no oxygen was observed within the precision limits for the head space measurements.

ANALYTICAL MODEL

Vapor Pressure over Stored Plutonium Oxides

The vapor pressure of adsorbed water over stored oxides at the nominal room temperatures in the nine Hanford cans was very low. This weak equilibrium condition may be represented by the equilibrium equation



in which the forward reaction is driven by the chemical activity $a_{\text{H}_2\text{O}}$ of the water adsorbed on the oxide, and the backward reaction is driven by the vapor pressure of water over the oxide. The thermodynamics constant K_1 for that equilibrium is defined by the relation

$$K_1 = \frac{P_{\text{H}_2\text{O}}}{a_{\text{H}_2\text{O}}} = \frac{P_{\text{H}_2\text{O}}}{\mathcal{G}_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}}, \quad (3)$$

where $C_{\text{H}_2\text{O}}$ is the concentration of moisture adsorbed on the oxide and $\gamma_{\text{H}_2\text{O}}$ is its activity coefficient, which may depend on the chemistry and surface characteristics of the oxide. The product of those two quantities is the activity of the adsorbed water. It should be noted that the rates of the forward and reverse reactions for this equilibrium, and the consequent equilibrium constant, are dependent on the temperature of the oxide. Therefore, at a given temperature, the effective equilibrium constant would be given by

$$K_1(\text{eff}) = \mathcal{G}_{\text{H}_2\text{O}} K_1 = \frac{P_{\text{H}_2\text{O}}}{C_{\text{H}_2\text{O}}}, \quad (4)$$

where the definition of the activity coefficient could be derived from extensive studies of the effects of such factors as the surface-to-mass ratio (S/M) and chemistry of the oxides on $K_1(\text{eff})$.

Oxidation of Hyperstoichiometric and Hypostoichiometric PuO₂

From the results of the head space gas composition measurements, the oxidation of the plutonium oxide depleted most or all of the oxygen in the air atmosphere within the sealed cans. Therefore, the reaction of oxygen with the plutonium oxide content of those cans appears to involve a fairly strong equilibrium. If future experimental investigations corroborate the contention of Haschke, Allen and Morales [4] that PuO₃ can form (non-metastable) solid solutions with PuO₂, the equilibrium for the reaction of oxygen with stoichiometric or hyperstoichiometric PuO₂ would be represented by the expression



where x and $1-x$ are the mole fractions of PuO₃ and PuO₂, respectively, in the solid solution at equilibrium. Equation 5 represents the solid solution somewhat differently from Haschke's representation of it as PuO_{2+x} in his past publications. But x , the mole fraction of PuO₃ in the solid solution, is also identical to the (alleged) hyperstoichiometry of the PuO₂, i.e., PuO_{2+x}. This follows from the oxygen inventory for the hyperstoichiometric PuO₂, given as

$$\frac{O}{Pu} = 3x + 2(1 - x) = 2 + x. \quad (6)$$

The equilibrium constant for Eq. 5 may be given by

$$K_2 = \frac{1}{\sqrt{P_{O_2}}} \frac{a_{PuO_3}}{a_{PuO_2}}, \quad (7)$$

where a_{PuO_3} and a_{PuO_2} are the activities of (alleged) PuO_3 and PuO_2 , respectively, in the solid solution at equilibrium, and P_{O_2} is the equilibrium partial pressure of oxygen over the solid. Haschke, Allen and Morales [4] have shown XRD evidence that the crystal lattice constants of such resultant solid solutions do not change drastically over a wide range of hyperstoichiometric additions. Therefore, this model assumes that the activity coefficients of both PuO_2 and PuO_3 would be the same at equilibrium in the (alleged nonmetastable) solid solution of those constituents. Accordingly, their concentrations would be substituted for their activities in the equilibrium constant for this reaction, so that with the PuO_3 -to- PuO_2 mole-fraction ratio of $x/(1-x)$ in the solid solution, the equilibrium constant for Eq. 5 would be represented as

$$K_2 = \frac{1}{\sqrt{P_{O_2}}} \frac{\hat{K}_E}{\hat{K}_E} \frac{x}{1-x} \hat{\sim}. \quad (8)$$

There is a thermodynamics basis for the existence of PuO . Therefore, hypostoichiometric PuO_2 , i.e., PuO_{2-x} , may be considered a solid solution of PuO and PuO_2 , where the mole-fraction of PuO is identical to x , from the relation

$$\frac{O}{Pu} = x + 2(1 - x) = 2 - x. \quad (9)$$

Accordingly, the equilibrium for oxidation of hypostoichiometric PuO_2 may be given by an alternative form of Eq. 5, namely,



Because XRD results from Haschke, Allen and Morales [3] showed that hypostoichiometric plutonium oxides with O/Pu values >1.95 exhibit lattice constants very close to that of pure PuO_2 , it is assumed that the activity coefficients of PuO and PuO_2 in such solid solutions are equal, so that the equilibrium constant for Eq. 10 for that condition may be given by

$$K_2 = \frac{1}{\sqrt{P_{O_2}}} \frac{\hat{K}_E}{\hat{K}_E} \frac{1-x}{x} \hat{\sim}. \quad (11)$$

Dissociation of Water Adsorbed on PuO₂

In addition, there is radiolysis of the water in the system. In structuring this model the equilibrium constant for radiolysis of water at the oxide surfaces (to give hydrogen and oxygen) was analyzed. But, because as shown in Eq. 2, the water vapor would be in equilibrium with the water adsorbed on the oxide surfaces, analysis of the equilibrium constant for the radiolysis at the oxide surfaces would be equivalent to analyzing the equilibrium constant for radiolysis of the water vapor.

From experiments with pulsed radiolysis of liquid water, after decay of the intermediate free-radical products, H₂O₂ is the end product in the liquid and an equivalent amount of H₂ is released to the gas space. Any small amount of H₂O₂ released to the small vapor space in such experiments would be decomposed there to H₂O and O₂, because H₂O₂ is unstable as a gas. But the radiolytic products would essentially be gaseous hydrogen and oxygen for water adsorbed on PuO₂ in a transportation or storage package, because the ratio of free gas volume to the volume of adsorbed water would be very large in that system.

Morales [2] has shown that there can be recombination of radiolytic H₂ and O₂ products catalyzed at the PuO₂ surface; so that an equilibrium would exist between the adsorbed water and its dissociation products at that surface according to the equation

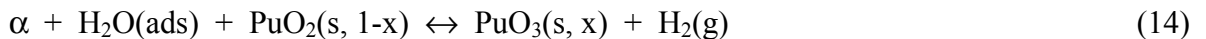


It is assumed that the radiolysis reaction would depend on the energy decay rate of the α radiation per gram of oxide F_a , the concentration of adsorbed water on the oxide $C_{\text{H}_2\text{O}}$, and the activity coefficient of the adsorbed water under radiolytic conditions γ_α , where γ_α should reflect the dependence of the equilibrium constant on the surface characteristics and chemistry of the particular stored oxide. The reverse (thermally dependent) recombination would be proportional to the product of the partial pressure of hydrogen and the square root of the partial pressure of oxygen. Accordingly, the constant for this equilibrium is given by the relation

$$K_3 = \frac{P_{\text{H}_2} \sqrt{P_{\text{O}_2}}}{C_{\text{H}_2\text{O}} F_a \gamma_\alpha}. \quad (13)$$

From the results given by Mason et al. [6], this would be a weak equilibrium, consistent with the observation that very little hydrogen was detected in the cans that were sampled, at the highly depleted oxygen concentrations in those cans. Even in one atypical case, the hydrogen inventory was only 47.5 mole % of the head space gases, with no detection of oxygen.

It should be pointed out that for the (alleged) hyperstoichiometric PuO₂, the sum of Eq's. 5 and 12 yields



and

$$K_4 = \frac{P_{\text{H}_2}}{C_{\text{H}_2\text{O}} F_a \gamma_\alpha} \frac{\hat{a}_{\text{PuO}_3} x}{\hat{a}_{\text{PuO}_2} (1-x)}. \quad (15)$$

Similar equations would be valid for hypostoichiometric PuO₂.

Equation 14 is similar to Haschke's equation for the forward reaction [4], i.e., the chemical reaction of water vapor with PuO₂ that he studied as a function of temperature over the temperature range from 25 to 350°C. However, Haschke contends that the chemical reaction for this forward chemical reaction was both temperature-dependent and faster than that for radiolysis. It is quite possible that for the conditions of his experiments, that was the case. For that possibility, the trend of derived values of K_3 (with and without the α -dependent terms) with C_{H_2O} were compared for a various conditions in the data given by Mason et al. [6]. From results given below in Table 4 of the thermodynamics analysis section of this paper, it appears that the variation of the derived equilibrium constant with C_{H_2O} was more consistent with the assumption that the forward reaction for the dissociation of water over PuO₂ was driven by radiolysis at the nominal room temperatures of the Hanford cans that were analyzed. The issue of the driving force for that dissociation could be investigated further for upper limit temperatures determined for high power density plutonium oxides in the ongoing MIS program.

THERMODYNAMICS ANALYSIS OF RESULTS FROM THE MIS PROGRAM

Vapor Pressure over Stored Plutonium Oxides

The vapor pressures of only three head space gases from the nine Hanford cans were within the detection limits for the sampling and mass spectrometric measurements. The partial pressure of water was determined for each of those three cans from the percentage of H₂O in its head space gas and the measured (total) pressure of the can. $K_1(eff)$ for each can was calculated from Eq. 4, and rounded off to account for the very limited precision in the measurement of the water composition in the cans. The results for the sampling of the cans, i.e., full-scale tests, are given in Table 1, where $K_1(eff)$ is the ratio of the vapor pressure of water (in atmospheres) to its concentration (in wt.%) in the oxide.

Table 1. Vapor pressures at room temperature of selected Hanford items

Item	% Pu	Condition	Test	C_{H_2O} (wt.%)	P_{H_2O} (torr)	P_{H_2O} (atm)	$K_1(eff)$
PPSL-365	83	As-Received	Full-Scale	0.006	0.6	8E-04	0.13
PBO-47-09-0112-023	87	As-Received	Full-Scale	0.040	0.6	8E-04	0.02
ARF-102-85-365	15	As-Received	Full-Scale	0.150	1.4	1.8E-03	0.01

From these results it can be seen that the vapor pressure over plutonium oxides at the ambient room temperatures of those cans is very low, much less than the 24-torr vapor pressure used as a constant water reservoir for the experiments of Haschke and Allen [3] and Haschke, Allen and Morales [4]. It also appears that the decrease in the effective equilibrium constant has no correlation to plutonium content and appears to be due to the decrease in activity coefficient of the adsorbed water with its concentration in the oxide.

Oxidation of Hypostoichiometric PuO₂

The XRD analysis of the Hanford and RFETS items identified the solid phases of each item with such general designations as PuO₂, PuO₂ + NaCl, Pu-U-O solid solution, and U₃O₈. But O/Pu values were obtained for two cases, the as-received relatively pure PPSL-365 and the impure as-received ARF-102-85-295, from data that were generously made available from the original LANL data file by Mason [10]. Both items were hypostoichiometric with O/Pu values of 1.958 and 1.967 for PPSL-365 and ARF-102-85-295, respectively. The head space gas of the original PPSL-365 storage can, i.e., the full-scale test given in Table 2, and the head space gas of the small storage can that contained a 10-g sample of as-received ARF-102-85-295, both contained measurable amounts of oxygen. Therefore, for both of those cases, equilibrium constants for the air oxidation of the plutonium oxides within the cans could be calculated from Eq. 11. Those results are also given in Table 2.

From these two cases, it can be seen that K_2 is fairly independent of the purity of the plutonium oxide and appears to be primarily dependent on the partial pressure of oxygen and the ratio of the mole-fractions of PuO and PuO₂, as predicted from Eq. 11.

Table 2. Equilibrium constants for the oxidation of hypostoichiometric PuO₂

Item	% Pu	Condition	Test	P_{O_2} (atm)	x_{PuO}	K_2
PPSL-365	83	As-Received	Full-Scale	3.8E-02	0.042	117
ARF-102-85-295	28	As-Received	10-g Sample	9.7E-02	0.033	94

Furthermore, it is a fairly strong equilibrium constant that explains the active gettering action of (at least hypostoichiometric) PuO₂ for oxygen in the air environments of those storage cans.

Dissociation of the Water Adsorbed on PuO₂

Table 3 gives information for headspace gas analysis of long-term storage cans as-received from Hanford, i.e., full-scale tests, which had amounts of both hydrogen and oxygen that could be measured within the precision limits of the mass spectrometer instrumentation.

Table 3. Head gas values from selected items stored in air for periods ≥ 1 y

Item	F_a (W/g)	Test	Condition	C_{H_2O} (wt.%)	P_{O_2} (atm)	P_{H_2} (atm)
PPSL-365	2.25E-03	Full-Scale	As-Received	0.006	3.8E-02	8E-04
PSU-84-06-05	5.01E-04	Full-Scale	As-Received	0.134	8E-04	2.3E-03
ARF-102-85-223	1.58E-03	Full-Scale	As-Received	0.140	9.4E-02	8E-04

As shown in Table 4, assuming that the dissociation of water on PuO₂ is driven by radiolysis, the effective variation of the equilibrium constant with C_{H_2O} ,

$$K_3(\text{eff}) = g_a K_3(\text{rad}) = \frac{P_{H_2} \sqrt{P_{O_2}}}{C_{H_2O} F_a}, \quad (16)$$

is more consistent with the data than if it were a pure chemical reaction, i.e.,

$$K_3(\text{eff}) = g_{H_2O} K_3(\text{chem}) = \frac{P_{H_2} \sqrt{P_{O_2}}}{C_{H_2O}}. \quad (17)$$

Assuming that the dissociation of water was driven by radiolysis, the activity coefficient γ_α was normalized to a value of 1.0 for the test on PPSL-365. It is reasonable that PPSL-365 had the highest effective equilibrium constant, since oxides with a lower surface-to-mass ratio (S/M), i.e., less porosity, and higher water content would be more restrictive on the rate of escape of the radiolytic products of H_2 and O_2 through the porosity of the oxide before they could recombine on the inner surfaces within the pores of the oxide. That effect would decrease the effective dissociation constant for the radiolysis of water, which is proportional to γ_α . However, such a conclusion is based on only several cases and on limited surface-to-mass information. With more extensive and more precise data, better correlation might be drawn between the effective equilibrium constant and other factors such as the chemistry of the material.

Table 4. Equilibrium constants for dissociation of water over plutonium oxides

ITEM	Test Duration (y)	$K_1(\text{eff})$ Chemical	$K_1(\text{eff})$ Radiolytic	γ_α	C_{H_2O} (wt.%)	S/M (m^2/g)
PPSL-365	1.0	2.6E-02	12	1.0	0.006	2.33
PSU-84-06-05	13	5E-04	1	0.08	0.134	0.64
ARF-102-85-223	13	1.8E-03	1	0.08	0.140	—

Actually, with available S/M values for all of the oxides, values of F_a could be expressed in units of W/cm^2 , and C_{H_2O} could be expressed in units of $moles/cm^2$, both of which might be an improvement over W/g and $wt.\%$, respectively, in defining the equilibrium constant for radiolysis of the adsorbed water.

Nevertheless, this analysis implies that the combined equilibria for the oxidation of (at least the hypostoichiometric) plutonium oxides and for radiolytic dissociation of water, limit the oxidation of such oxides at ambient room temperatures. Furthermore, it also prevents the buildup of any significant amounts of either oxygen or hydrogen in the system.

SUMMARY

Based on limited data from the materials identification and surveillance (MIS) program at Los Alamos National Laboratory, we determined ambient room temperature equilibrium constants for the physical and chemical reactions that occur within the PuO_2 - H_2O - H_2 - O_2 system characteristic of stored plutonium oxides. We found that under the low temperature and water content for the conditions of the investigation, the vapor pressure of water, or chemical activity of the adsorbed

water in equilibrium with the vapor, would be very low in pure and impure plutonium oxide that had been stabilized for transportation or storage. The pure or impure plutonium oxide would getter any free oxygen in a strong equilibrium to reduce its concentration to minor levels in the storage package, and together with the very weak equilibrium for the dissociation of water bound to the solid, it would both prevent any further oxidation of the oxide material and any significant buildup of hydrogen. These findings imply that for the low temperatures investigated, it would not be necessary to render inert packages of plutonium oxides for transportation and storage.

These are benign results when compared with the excessive hydrogen pressures for plutonium oxides that would be determined from the model given in the Appendix of DOE-STD-3013. For various estimated upper-limit temperatures that depend on the power density within the plutonium oxide, that model assumes hydrogen pressures derived by extrapolation from results of experiments by Haschke, Allen and Morales at temperatures between 25 and 350°C that did not achieve equilibrium [3]. Therefore, further analysis in the ongoing MIS program could be directed toward determination of the upper-limit temperatures for plutonium oxides with higher power densities and the equilibrium constants associated with those temperatures. Surface-to-mass and water-vapor measurements for all items, in addition to other measurements planned by Behrens et al. [7], would be valuable information for future thermodynamics analyses. Ultimately, with more extensive and precise data, a more complete thermodynamics model could be developed as a predictive tool for the safety analysis of packages for the transportation or storage of plutonium oxide-bearing materials.

Also, it should be pointed out that *O/Pu* data were available for only two of the solids investigated, both of which were hypostoichiometric, and from which equilibrium constants for the gettering of oxygen by those oxides could be determined. It is still an open question, of considerable importance to the packaging of plutonium oxides for transportation or storage, whether or not hyperstoichiometric oxide can be formed under (nonmetastable) equilibrium conditions from the gettering of oxygen by stoichiometric PuO₂. Therefore, it would be desirable to have XRD and *O/Pu* values for all of the oxides that will be used in future MIS investigations, in order to confirm the possible existence of PuO_{2+x} in typical packages for transportation or storage of plutonium oxides.

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