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Formation and Properties of the PuO_{2+x} Phase*

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Kinetics of Reaction Between Plutonium Dioxide and Water at 25°C to 350°C: Formation and Properties of the PuO_{2+x} Phase

by

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Abstract

Results of microbalance, pressure-volume-temperature, and mass spectrometric measurements show that a higher oxide of plutonium, PuO_{2+x} , and hydrogen are formed by reaction of plutonium dioxide with water at 25°C to 350°C. PuO_{2+x} has an intense green color consistent with the presence of Pu(VI). An oxide composition in excess of $\text{PuO}_{2.25}$ is identified, but the maximum value of x is undefined. Reaction rates derived from linear mass-time and pressure-time data are described by an Arrhenius relationship that yields an activation energy of 9.4 ± 0.6 kcal/mol for the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction. X-ray diffraction data for PuO_{2+x} show that the oxide has a fluorite-related structure consistent with substitution of Pu(VI) on cationic lattice sites and accommodation of additional oxygen on interstitial sites. The cubic lattice parameter has a low, but well-defined, linear dependence on the O:Pu ratio, suggesting that PuO_{2+x} forms as a continuous solid solution. The failure of earlier attempts to prepare higher oxides of plutonium is attributed to slow oxidation kinetics and insensitivity of diagnostic techniques. Similarities of the PuO_{2+x} and UO_{2+x} phase are examined and relevance of the results to plutonium technology and environmental issues is discussed.

Introduction

On the basis of thermodynamic estimates, Brewer concluded that oxides with compositions greater than PuO_2 will not form in the plutonium-oxygen system [1]. That conclusion is consistent with the failure of extensive experimental efforts by early workers to prepare higher oxides of plutonium [2-4]. Those attempts to form higher compositions by reacting the dioxide with strong oxidants such as high-pressure O_2 , atomic oxygen, ozone, and nitrogen dioxide were unsuccessful. Although the presence of excess oxygen atoms in the oxide lattice are indicated by data for the thermal decomposition of plutonium peroxide [5], the formation of higher oxides is considered very unlikely.

Interest in the higher oxides and indications of their existence have persisted despite the evidence that binary oxides with compositions greater than PuO_2 appear unstable. The formation of a fluorite-related fcc product with a lattice parameter ($a_0 = 5.38 \pm 0.01$ Å) substantially less than that of PuO_2 ($a_0 = 5.397 \pm 0.001$ Å) during extended heating of Pu_2O_3 in oxygen at 1100°C is associated with possible formation of an "oxygen-rich PuO_2 " phase [6]. Gravimetric measurements made during the atmospheric oxidation of plutonium metal suggest the formation of $\text{PuO}_{2.1}$, but the excess mass of the sample is attributed to

adsorption of moisture by the oxide [7]. Results of more recent studies involving thermal decomposition of the oxygen-rich Pu(VI) compounds such as $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3$ reportedly show no evidence for any higher oxide [8].

However, unusual and intriguing behavior has consistently appeared during investigations involving moist conditions. In addition to the observation of an excess mass gain during early studies of metal corrosion in humid atmospheres [6], subsequent microbalance studies of the hygroscopic behavior of plutonium dioxide show irreversible mass increases during thermal cycles in which PuO_2 was repeatedly equilibrated with saturated water vapor at 27°C and outgassed to constant weight at 100°C before being re-exposed to water in the next cycle [9]. During a kinetic study of plutonium corrosion in salt water at 25°C, H_2 generation occurred in distinct constant-rate steps as a series of solid oxide hydrides and oxides were formed and continued beyond the point at which the PuO_2 stoichiometry was reached [10, 11]. In a recent study providing the first direct evidence for a higher oxide, the presence of a fluorite-related $\text{PuO}_{2.17}$ phase containing Pu(VI) was indicated by x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) analyses of the oxide layer formed on Pu metal during corrosion in water vapor at 250°C [12]. Most recently, pressure-volume-temperature (PVT) and mass spectrometric (MS) results show that H_2 is formed at a constant rate by the reaction of PuO_2 with H_2O vapor at room temperature [13].

The present investigation was initiated in an effort to unequivocally characterize the products and define the kinetics of the interaction between plutonium dioxide and water at elevated temperatures and to address deficiencies in earlier work. Although PuO_2 typically exists on plutonium surfaces instead of Pu_2O_3 , the presence of a second non-equilibrium oxide at the gas-solid interface is questionable [12]. Likewise, formation of a PuO_{2+x} phase by the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction is implied by the appearance of H_2 [13], but the observed extent of reaction (a change of 0.003 in O:Pu after four years) is insufficient to exclude oxidation of a slightly sub-stoichiometric oxide (PuO_{2-x}) to PuO_2 . We repeat the gravimetric adsorption experiments described by Stakebake and Dringman [9] and employ several complementary experimental techniques in examining the chemistry and kinetics of the interaction between plutonium dioxide and water vapor.

Experimental Methods

Kinetic behavior of the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction was investigated over the 100°C to 350°C range using microbalance and PVT methods. Reaction rates and oxide compositions were determined from measured increases in sample mass or pressure over time (t). Gaseous and solid products were analyzed using MS and XRD methods, respectively. Oxide products

have also been characterized by XPS and neutron diffraction, but detailed discussions of those studies measurements are beyond the scope of this report.

The plutonium oxide specimens used in this study were taken from the dioxide used in an earlier investigation [14]. The oxide was formed by atmospheric oxidation of electrorefined alpha-phase metal containing approximately 100 ppm Am as the major metallic impurity. The specific surface area of the oxide was $4.8 \text{ m}^2/\text{g}$, a value that is not altered by heating at temperatures less than 600°C [14]. The initial oxide stoichiometry was determined using the measured lattice parameter and data from the correlation of the cubic lattice parameter (a_o) at fixed O:Pu ratios with temperature reported by Gardner et al. [15]. The derived dependence of a_o for the fcc fluorite sub-cell on composition of the PuO_{2-x} solid solution at room temperature is:

$$a_o (\text{\AA}) = 6.1503 - 0.3789 \text{ O:Pu} . \quad (1)$$

This equation is applicable only within the narrow composition range of the PuO_{2-x} solid solution at 25°C . On the basis of measured a_o (5.4037 \AA) for the oxide used in this study, the initial composition is $\text{PuO}_{1.97}$. Although this stoichiometry is below the $\text{PuO}_{1.98}$ boundary reported for PuO_{2-x} at room temperature, evidence for a two-phase mixture is not seen in the XRD results, and the derived value is within the probable uncertainty in the phase-boundary composition.

Microbalance measurements were made in an inert-atmosphere glovebox with a Cahn RH microbalance at 250°C , 300°C , and 350°C . Oxide specimens (approximately 0.1 g) were accurately weighed using an analytical balance prior to placement in the Pt sample container. Water vapor was introduced into the evacuated balance chamber using a gas manifold system and was maintained at a constant pressure (24 Torr) with a water reservoir held at a fixed temperature. A constant sample temperature was maintained with a programmable controller and was measured by a thermocouple placed near the specimen. The mass of the specimen was measured as a function of time using digital data collection methods. A sample of the oxide product was taken for XRD analysis after completion of these measurements.

Special microbalance measurements were made to characterize behavior during exposure of PuO_2 to H_2O . In one test, oxide was outgassed to constant mass in vacuum at 400°C and was then exposed to water pressure at 15 Torr and 25°C . The temperature was increased stepwise from 25°C to 50°C , 100°C , 150°C , and 250°C over a period of more than 100 hours. In addition, the adsorption experiments of Stakebake and Dringman [9] were repeated using the general procedures for microbalance measurements. The 0.101 g oxide specimen used in this study was also outgassed to constant mass in vacuum at 400°C , cooled to 25°C , and exposed to water vapor at 15 Torr. After a constant sample

mass was attained, the system was evacuated to remove the water vapor, and the specimen was then heated at 100°C until its mass was constant. This adsorption-desorption cycle was repeated four times. Oxide products formed during these cycles were sampled for XRD analysis.

PVT measurements were made at 200°C to 350°C using techniques similar to those described for kinetic measurements at 25°C [13]. Accurately weighed samples (0.05-0.1 g) of oxide contained in Pt or Au crucibles were placed in volume-calibrated (36 cm³) stainless steel reactors sealed with nickel-gasket closures. After evacuation, a reactor was filled with H₂O vapor (24 Torr) supplied by a water reservoir held at constant temperature throughout the test. The sample temperature was measured by a thermocouple located near the specimen and was maintained at the desired constant value using a programmable controller. The system pressure was measured as a function of time using a capacitance manometer and was recorded using digital methods. After completion of the P-t measurements, samples of the gas and solid phase were obtained for MS and for XRD (or XPS analyses), respectively.

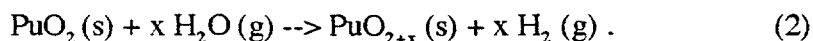
Samples of gaseous atmospheres from PVT reactors were analyzed using a Nuclide magnetic-sector mass spectrometer. Powder x-ray diffraction data of the initial oxide and the products of reaction were obtained by the Debye-Scherrer method with a 114.56-mm-diameter camera and CuK-alpha radiation. Diffraction data were refined and lattice parameters were calculated using the programs DEBVSHAS.FOR and LATPARAS.FOR, respectively.

Kinetic results derived from the mass-time and pressure-time data are area-normalized using the specific surface area of the oxide. Measured mass increases were assumed to result from accommodation of oxygen in the oxide. Ideal gas behavior was assumed for gases. Reaction rates are reported in units of moles of O per m² of oxide surface per hour.

Results and Discussion

PVT Measurements

Results of PVT measurements during exposure of plutonium dioxide to water vapor at 200°C to 350°C and 24 Torr show linear increases in pressure as a function of time. Typical P-t curves for the four experimental temperatures are shown in Figure 1. Mass spectrometric analysis of gas samples taken after termination of the tests show that only H₂O and H₂ are present in the gas phase. These results are identical to those observed at 25°C [13] and show that PuO₂ is oxidized to a higher oxide, PuO_{2+x}, by H₂O over a broad range of temperature.



This equation implies that a fraction of the plutonium is oxidized to an oxidation state greater than Pu(IV), but the PVT-MS results alone do not indicate if x varies continuously across a solid solution or if it is fixed at a value determined by equilibrium compositions bounding a two-phase region. As shown by XRD results presented later in this report, PuO_{2+x} is best described as a non-stoichiometric oxide similar to the UO_{2+x} phase existing at elevated temperatures [16].

A summary of PVT measurements in Table 1 shows that observed values of x are substantial and that the $\text{Pu} + \text{H}_2\text{O}$ reaction continues in the presence of measurable hydrogen over-pressures. The H_2 pressures listed in the table are the values measured at the termination points of the experiments and do not define equilibrium points for the reaction. Results obtained during exposure of high-surface area ($750 \text{ m}^2/\text{g}$) dioxide to liquid water at 25°C are included [10]. As described in a prior report [13], the highest documented composition ($\text{PuO}_{2.265}$) was achieved in that study.

Attainment of equilibrium by Equation 2 is both interesting and of practical importance. At each fixed temperature and H_2O pressure in our test series, the reaction of oxide with water will cease when the equilibrium state is reached. That state defines the maximum H_2 pressure that can be attained during isothermal reaction of oxide with unlimited moisture at constant pressure. Equilibrium oxide compositions and hydrogen pressures were not reached at any temperature in our study. Even if those results were available, they could not be directly applied to sealed storage containers of oxide because the equilibrium H_2 pressure is expected to increase as x decreases. In storage systems, the water supply is limited and the PuO_2 to H_2O ratio is large. For a possible storage configuration (3.0 kg of oxide with 0.5 mass % adsorbed H_2O and 2.0 liters of free volume), complete reaction of the water is capable of increasing the oxide stoichiometry from PuO_2 to $\text{PuO}_{2.08}$ and generating an H_2 pressure of 150 psi. These conditions will not be realized in storage if equilibrium is reached before the reaction of water is complete.

Reaction rates (R) derived from the slopes of the P - t curves and the specific surface area of the oxide are listed in Table 2, with results obtained from microbalance and x-ray diffraction methods. The rate at 25°C is a value obtained from three independent kinetic measurements for the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction [13]. As described in a subsequent section of this report, R at 100°C is derived using XRD results to define the amount of oxygen consumed during the reaction period at that temperature.

Behavior consistent with moisture-catalyzed oxidation of PuO_2 by O_2 [13] was observed during one PVT at 300°C . Difficulties with the experiment were suggested by anomalies in the P - t curve. Subsequent MS analysis of a gas sample showed the presence of N_2 and indicated that failure of a seal had allowed air to enter the reactor. However, the

analysis also showed that neither O_2 nor H_2 were present. These observations are explained by occurrence of reactions in the catalytic cycle that promote the $PuO_2 + O_2$ reaction. Water is simultaneously formed by the catalyzed combination of H_2 and O_2 on the oxide surface and consumed by reaction with the oxide at the rate characteristic of Equation 2. Occurrence of the combination reaction apparently resulted in depletion of both H_2 and O_2 from the gas phase.

Microbalance Measurements

Mass-time data obtained during microbalance measurements at 250°C to 350°C and 24 Torr water pressure show mass increases consistent with the PVT results. Reaction rates listed in Table 2 were derived using Equation 2. The gravimetric values are consistently higher than the corresponding PVT rates, but their close agreement implies that the $PuO_2 + H_2O$ reaction is correctly described by the formation of PuO_{2+x} and H_2 . Short induction periods in which the specimen mass remained constant were frequently observed at beginning of the mass-time measurements.

Experiments to duplicate the adsorption-desorption study by Stakebake and Dringman [9] show that the oxide irreversibly interacts with water during repeated cycles involving saturation with H_2O at 27°C and outgassing at 100°C. The irreversible mass gain observed during four cycles is shown as a function of outgassing time in Figure 2. The mass increased progressively with each cycle and equaled 1.08 mg (1.0%) at the end of the test. A comparable increase of 0.4% was observed after four cycles in the earlier study [9]. If the observed mass increase is assumed to result from reaction of oxide with water according to Equation 2, the calculated rate at 100°C is 95 nmol O/m² h, a value that is a factor of 10 greater than anticipated on the basis of the kinetic results in Table 2. As proposed in the earlier work [9], we conclude that the behavior is most consistent with chemisorption of water. However, a change in stoichiometry of the bulk oxide is also suggested by a decrease in a_o from 5.4037 to 5.3982 Å during the test.

Chemisorption of water at 100°C is also suggested by results of the isobaric test with incremental temperature changes. Exposure of the oxide to 15 Torr water pressure at 25°C and 50°C resulted in a mass increase of 0.4 mg/m², a change corresponding to adsorption of a molecular layer of H_2O on the $PuO(OH)_2$ surface formed by exposing fired oxide to humid air at room temperature [17]. Another weight change corresponding to an increase of 0.4 mg/m² was observed over a 15-hour period after the specimen was heated to 100°C. This mass increase, which may be attributed to adsorption of two H_2O layer or to chemisorption of four OH⁻ surface layers, and the initial gain were lost during a 20-hour heating period at 150°C. Another gain in mass was observed after the specimen

temperature was raised to 250°C. Initially, the behavior was somewhat irregular without an observable change in mass for a period of 1 to 2 hours, but an increase in mass ultimately occurred at a rate (200 nmol O/m² h) characteristic of the Pu + H₂O reaction at 250°C. The mass gain observed at 100°C is most consistent with slow chemisorption of water and formation of high-stoichiometry hydroxide at the oxide surface followed by slow desorption of physisorbed and chemisorbed species at 150°C. The non-linear mass-time data and the sluggish behavior observed initially at 250°C is attributed to simultaneous occurrence of oxidation (mass gain) and desorption (mass loss) reactions.

Composition Dependence of the PuO_{2+x} Lattice Parameter

X-ray diffraction data show that PuO_{2+x} products formed by the PuO₂ + H₂O reaction have a fluorite-related fcc structure derived from that of the dioxide. Intensities of the reflections correspond closely with those reported for PuO₂ [18]. Lattice parameters for oxide compositions prepared in this study are listed in Table 3 along with the value measured for PuO_{2.265} in an earlier study [11]. In addition to these results, the correlation of a_o with O:Pu ratio in Figure 3 includes reference values for the PuO_{2-x} phase at 25°C [15] as well as the a_o value measured for the initial PuO_{1.97} oxide. Lattice parameters for oxide products with compositions defined by microbalance and PVT methods are indicated by filled and open circles, respectively.

The results in Figure 3 define characteristics of the plutonium oxide lattice near the dioxide composition and at compositions substantially in excess of PuO₂. The lattice parameter decreases sharply with composition in the PuO_{2-x} region as defined by Equation 1. The measured lattice parameter (5.3975 Å) for PuO_{2.00} in the present study is slightly larger than the value (5.3960 Å) reported by Gardner et al. [15]. At compositions greater than PuO_{2.00}, a_o increases sharply with O:Pu over a narrow (x < 0.005) composition range and at a surprisingly gradual rate at higher ratios. As defined by the results of eight measurements with O:Pu in 2.016 to 2.169 range from Table 3, the lattice parameter of PuO_{2+x} is a linear function of composition.

$$a_o (\text{\AA}) = 5.3643 + 0.01764 \text{ O:Pu} . \quad (3)$$

The lattice parameter reported for PuO_{2.265} is in excellent agreement with this equation [11]. This result provides independent confirmation of PuO_{2+x} compositions in Table 3 because the PuO_{2.265} stoichiometry is based on direct oxidation of Pu metal to the higher oxide by water.

The Vegard's-law behavior shown by Equation 3 assists in defining important solid-state properties of PuO_{2+x}. The continuous variation of a_o with O:Pu indicates that PuO_{2+x} is a solid-solution oxide similar to the UO_{2+x} phase observed at x values below 0.33. The

composition dependence of a_0 for PuO_{2+x} shows a slight increase in a_0 with O:Pu, not a sharp decrease like that observed for PuO_{2-x} . Values of a_0 change by less than 0.002 Å for each change of 0.1 in x . The origin of this surprising insensitivity of a_0 to composition is suggested by results of XPS and neutron diffraction measurements. XPS results for oxide samples prepared during this study confirm the presence of Pu(VI) in the higher oxide and verify that oxygen is present as O^{2-} , not as OH^- [19]. Neutron diffraction studies show that additional oxygen is accommodated on interstitial sites in the fluorite lattice of PuO_2 [20]. Whereas substitution of Pu(VI) for Pu(IV) on cationic sites of dioxide tends to shrink the lattice, accommodation of oxide ions on vacant sites causes lattice expansion. The opposing changes are apparently of comparable magnitude and the net effect is a low dependence of a_0 on the composition of PuO_{2+x} .

The x-ray diffraction pattern obtained in the initial study showed splitting of the fcc reflections and systematic absences of reflections consistent with a PuO_{2+x} lattice derived by tetragonal distortion of the cubic fluorite structure [11]. Diffraction data obtained in the present study neither show these features nor confirm the formation of a NpH_{2+x} -type tetragonal phase. Since the earlier data were collected by diffractometer analysis of oxide-coated plutonium, systematic absences may have resulted from preferred orientation of the oxide layer on the metal surface. However, as observed during studies of UO_2 oxidation [21], the film method used in the present study may not have resolved closely spaced multiplets in the diffraction pattern. The continuous variation of a_0 with O:Pu is most consistent with a continuous solid-solution oxide formulated as PuO_{2+x} , but we cannot conclude that the earlier observations were inaccurate. Formation of ordered phases is well known for uranium-oxygen [16] and other superstoichiometric fluorite-related fluoride systems with mixed-valence or variable-valence cations [22] and cannot be excluded.

An unusual feature of the lattice parameter-composition correlation in Figure 3 is the sharp increase in a_0 at compositions slightly greater than the dioxide. This behavior implies that the fluorite lattice of PuO_2 expands as additional oxygen is accommodated and then remains essentially constant as the composition increases. The appearance of induction periods during kinetic measurements may have resulted from sluggish lattice dynamics associated with the onset of oxidation.

Comparison of results for Pu-O and U-O systems suggests that the superstoichiometric regions above the dioxide compositions differ substantially. Although early work on the uranium system indicated the existence of a cubic UO_{2+x} solid solution at O:U ratios up to 2.33, subsequent studies show that UO_2 coexists in equilibrium with the tetragonal U_4O_9 phase at temperatures below 300°C, and that the UO_{2+x} phase is stable only at elevated temperatures [16]. Cubic lattice parameters measured for the metastable UO_{2+x} product

suggest that a_o decreases with increasing composition. Although UO_{2+x} and PuO_{2+x} apparently have similar structures, it is evident that the uranium oxides are not a suitable model for phase equilibria of PuO_{2+x} .

Observations made during the course of crystallographic measurements address an intriguing question about the color of plutonium dioxide. In one review, its color is described as normally green with variations caused by differences in preparative methods, purity, and particle size [2]. In contrast, the colors of PuO_2 specimens prepared by firing metal and several compounds at 875°C are reported to vary from dull yellow to khaki [4]. The PuO_{2+x} specimens prepared in this study were green. We conclude that the intense green color characteristic of oxygen-containing compounds of hexavalent plutonium results from the presence of Pu(VI) in the oxide lattice and provides additional evidence for the presence of a higher oxide.

Temperature Dependence of the $PuO_2 + H_2O$ Reaction Rate

Kinetic results for oxidation of plutonium dioxide by water shows that the reaction has a normal temperature dependence over the 25°C to 350°C range. An Arrhenius analysis of the rate data in Table 2 is presented in Figure 4. Results from microbalance, PVT, and XRD measurements are described by a single $\ln R - 1/T$ relationship.

$$\ln R = -6.441 - (4706/T) . \quad (4)$$

The activation energy for reaction is 9.4 ± 0.6 kcal/mol. The uncertainty in E_a results primarily from the uncertainty in the average R at 25°C [13]. Rates from microbalance measurements are in good agreement with those from PVT data, but are consistently higher because of water adsorption on the microbalance and the sample.

The rate measurement at 100°C is based on the change in oxide composition determined by x-ray diffraction. The lattice parameter of the oxide decreased from 5.4037 Å to 5.3982 Å during the four thermal cycles. Reference to Figure 3 shows that the final a_o corresponds to a composition that is either slightly less than or slightly greater than $PuO_{2.00}$. Equation 1 indicates that O:Pu is 1.985 and linear interpolation between the parameters for $PuO_{2.00}$ and $PuO_{2.16}$ in Table 3 gives a value of 2.006. These results are in sufficiently close agreement that the average composition of $PuO_{1.996}$ accurately defines the extent of reaction and yields the oxidation rate listed for 100°C in Table 2. The close agreement of the XRD results with rates measured by microbalance and PVT methods is gratifying because it verifies the consistency of relationships defining rate, composition, and lattice parameter.

The temperature dependence observed for the oxidation rate demonstrates that the reaction of Pu with H_2O is primarily chemical instead of radiolytic. The rate of a purely

radiolytic process is expected to be temperature independent at a fixed water pressure. At isobaric conditions, the measured activation energy of a radiolytic process might actually be slightly positive because the rate is expected to decrease as the equilibrium surface concentration of H_2O adsorbed on the oxide decreases with increasing temperature. If formation of PuO_{2+x} is promoted by radiolysis of H_2O , the largest fractional contribution to the oxidation rate is anticipated at low temperature in a system with a high surface concentration of water. At 25°C , the fastest rate ($0.4 \text{ mol O/m}^2 \text{ h}$) is observed for reaction of oxide in liquid water. However, as shown by the error bars for the room temperature point in Figure 3, results of measurements at different conditions give an oxidation rate ($0.3 \pm 0.2 \text{ mol O/m}^2 \text{ h}$) that is independent of water concentration over a range extending from fractional monolayer coverage of the oxide surface to saturation by liquid water [13]. These results indicate that the radiolytic contribution to the oxidation rate is negligible even at room temperature.

Conclusions

Results of this study confirm observations indicating the existence of a higher oxide and show that plutonium dioxide and water react over the 25°C to 350°C range to form an extended binary solid-solution phase containing interstitial oxygen hexavalent plutonium. Formation of hydrogen by this reaction provides conclusive evidence for the oxidation of plutonium in the PuO_2 lattice to a higher oxidation state. This result is consistent with earlier XPS measurements verifying the presence of Pu(VI) in the product formed during corrosion of plutonium metal by moisture [12] and with similar measurements showing the Pu(VI) state in PuO_{2+x} products prepared by the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction. The higher oxide has an intense green color unlike the yellow to khaki color of the dioxide [4]. Oxide compositions obtained in this study and during prior exposures of PuO_2 to H_2O [10, 11] span a range from $\text{PuO}_{2.00}$ to values in excess of $\text{PuO}_{2.25}$, but the maximum equilibrium value has not been determined for any temperature and water pressure.

Formation of PuO_{2+x} shows that PuO_2 is not the thermodynamically stable oxide in air or humid environments at temperatures below 350°C and contradicts earlier conclusions that higher oxides of plutonium are unstable and cannot be prepared. Failure to observe oxide compositions greater than PuO_2 in prior studies is attributed to a combination of kinetic and experimental factors. Exposure of the dioxide to strong oxidants at high pressure increased the free energy for reaction, but were apparently unsuccessful because of slow reaction kinetics, not unfavorable thermodynamics. For example, dioxide was heated in oxygen and ozone at 400°C and 70 atm pressure, but the O:Pu ratio of the product reportedly did not exceed that of PuO_2 [23]. A favorable free energy for the reaction

existed because $\text{PuO}_{2.17}$ is produced by reaction of dioxide with water at 350°C and 24 Torr pressure. Although the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction has a less favorable free energy than the reaction of O_2 or O_3 , oxidation by water occurs at a sufficiently rapid rate to be observed. Chemisorption of water as hydroxide may promote the oxidation rate by increasing the surface concentration of oxygen on PuO_2 .

Factors other than slow kinetics apparently contributed to the failure of prior attempts to prepare higher oxides. In some cases, the experimental temperatures exceeded 1000°C and were undoubtedly beyond the stability range of PuO_{2+x} [6]. We conclude that the reaction rate of dioxide with water is faster than those for other oxidants, but must emphasize that the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction is not rapid. Reaction periods (0.15 to 12 hours) employed in earlier studies were undoubtedly insufficient to produce composition changes that could be detected using XRD [23]. The method is especially insensitive in this case because of the low dependence of a_0 on the composition of PuO_{2+x} . Difficulty in identifying the higher oxide was also encountered because a_0 was expected to decrease with addition of excess oxygen to the fluorite structure [6]. Characterization of the higher oxide in this study was facilitated by the formation of H_2 , a reaction product that permitted unequivocal definition of the oxide composition. Similar approaches, such as the formation of N_2 by reaction of NO_2 , might be useful for investigating reactions of PuO_2 with other oxidants.

Examination of the literature suggests that the higher oxide was formed during prior studies, but was not identified. Although the excess mass gain observed during corrosion of plutonium metal in moist air was attributed to adsorption of water on the oxide [6], the product was most likely PuO_{2+x} . The a_0 (5.402 Å) of the spalled corrosion product formed during corrosion of metal in water vapor at 250°C corresponds to an oxide composition of $\text{PuO}_{2.15}$ [24]. As described in the preceding discussion, $\text{PuO}_{2.265}$ was formed during an extended study of plutonium corrosion in aqueous solution at 25°C [11]. Mass spectrometric data suggest that the higher oxide might have formed during thermal decomposition of $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3$ [8]. This compound decomposed at 80°C to 120°C and formed PuO_2CO_3 , a product that subsequently lost CO_2 at 150°C to 300°C and O_2 at 260 °C to 320°C. The loss of CO_2 was 90% complete before O_2 formation began. Higher oxide probably existed as a transient product and might be obtained by isothermal decomposition of PuO_2CO_3 in an O_2 atmosphere at 250°C. Formation of the higher oxide during decomposition of plutonium peroxide is also suggested by the liberation of excess oxygen at temperatures above 300°C [5].

Results of our study suggest that substantial revision of the Pu-O phase diagram is necessary in addition to that proposed in an earlier report [11]. Prior studies indicate that an homologous series of oxides described by the general formula $\text{Pu}_n\text{O}_{2n-2}$ are formed by

slow oxidation of Pu_2O_3 on aqueous media at 25°C . Observed values of n (7, 9, 10, and 12) correspond to those found in the Pr-O system and suggest that the plutonium and praseodymium systems are similar for oxygen to metal ratios between 1.5 and 2.0. The present results show that the Pu-O system extends to compositions beyond PuO_2 . At 25°C , the higher oxide phase is stable at compositions in excess of $\text{PuO}_{2.25}$, but the equilibrium behavior and thermodynamic properties of the PuO_{2+x} are presently undefined.

Potential consequences of PuO_{2+x} formation are extensive. Formation of the higher oxide may be involved in promoting the corrosion of plutonium metal in moist air [25]. Reaction of adsorbed water with PuO_2 is of concern because of the potential for overpressurization and rupture of sealed storage containers by H_2 during extended storage [13, 26]. The formation and thermodynamic properties of PuO_{2+x} are important for assessing the stability and behavior of mixed-oxide (MOX) nuclear fuels. The presence of U(VI) is known to increase the solubility of uranium oxide and MOX in aqueous acids [27]. Likewise, the presence of Pu(VI) in PuO_{2+x} is expected to enhance the solubility of plutonium oxide. The slow dissolution rate of "high-fired" plutonium oxide in aqueous acids may result from the absence of Pu(VI) in highly calcined oxide. Reaction of oxide with moisture in environmental systems is expected to form the higher oxide. Leaching of hexavalent plutonium from PuO_{2+x} accounts for the appearance of Pu(V, VI) instead of Pu(IV) in water coexisting with oxide [28, 29]. Contrary to the conclusion that PuO_2 is the solubility-limiting solid phase in the environmental [30], our results suggest that PuO_{2+x} continuously forms in natural systems and is the source for leaching of Pu(VI).

The results of this study demonstrate that present understanding of the plutonium-oxygen system and oxide properties is inadequate. This conclusion is surprising considering the extent of prior work on the system. An extensive experimental effort is needed to define fundamental properties of the PuO_{2+x} phase. Areas of immediate interest include the equilibrium behavior of the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction, phase equilibria of the Pu-O system, and the mechanism of water oxidation, as well as thermodynamic, structural, and spectroscopic properties of PuO_{2+x} . Additional areas of interest are the dissolution and leaching kinetics of PuO_{2+x} and the effects of temperature, pH, chelating agents, and other factors on those processes. Such information is essential for adequately interpreting and predicting the behavior of plutonium oxide in diverse systems of technical importance.

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Table 1. Summary of PVT Results Measured during Exposure of PuO_2 to H_2O Vapor at 24 Torr and Temperatures in the 25°C to 350°C Range

Temperature (°C)	Elapsed Time (h)	Terminal P of H_2 (Torr)	Terminal O:Pu
25 ^a	2938	1140 ± 380	2.265
200	768	8.5	2.040
250	708	15.6	2.098
300	408	17.8 ^b	--
300	512	15.4	2.139
350	165	28.7	2.169

^a. Data for 25°C are from PVT measurements in liquid water [10]. Evaluation of the data is described in a prior report [13].

^b. The reported pressure is the value attained immediately before failure of a seal allowed air to enter the the reactor. The final oxide composition is uncertain.

Table 2. Experimental Rates for Reaction of PuO_2 with H_2O Vapor at 24 Torr and Temperatures in the 25°C to 350°C Range

Experimental Method	Temperature (°C)	R (nmol O/m ² h)
PVT ^a	25	0.25 ± 0.17
XRD ^b	100	13 ± 5
PVT	200	40
PVT	250	107
Microbalance	250	374
PVT	300	209
PVT	300	328
Microbalance	300	604
PVT	350	791
Microbalance	350	1370

^a. The reaction rate for 25°C is the average of three independent measurements in liquid water, D_2O vapor at 16.8 torr, and a 2:1 mixture of D_2 : O_2 [13].

^b. Determination of the rate by XRD is based on the change in oxide composition derived from the lattice parameter of the product and the correlation of a_o with O:Pu.

Table 3. Cubic Lattice Parameters of the Plutonium Oxide Products Formed by Reaction of $\text{PuO}_{1.970}$ with H_2O

Preparative Method	O:Pu	a_0 (Å) ^a
Microbalance	1.993	5.3980
Microbalance	2.000	5.3975
Microbalance	2.016	5.3995
Microbalance	3.034	4.4000
PVT	2.040	5.4002
Microbalance	2.055	5.4005
PVT	2.098	5.4013
Microbalance	2.107	5.4015
PVT	2.139	5.4020
PVT	2.169	5.4025
PVT ^b	2.265	5.404

^a. Uncertainties in a_0 for all but the last entry are less than ± 0.0001 Å.

^b. Data are from measurements on the oxide formed in liquid water at 25°C [11].

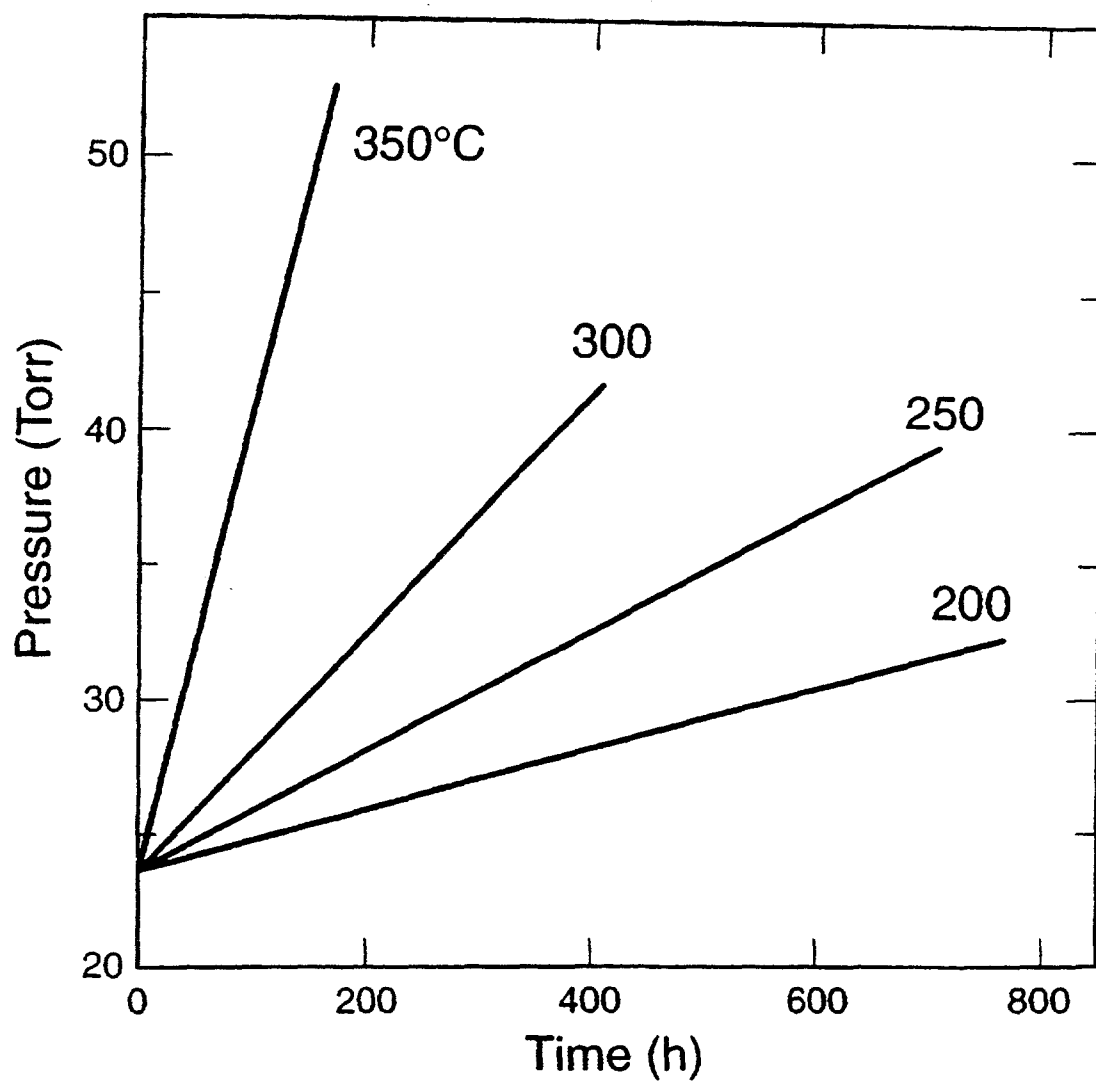


Figure 1. Time dependence of the H_2 pressure during exposure of PuO_2 to H_2O vapor at 24.5°C and 24 Torr pressure.

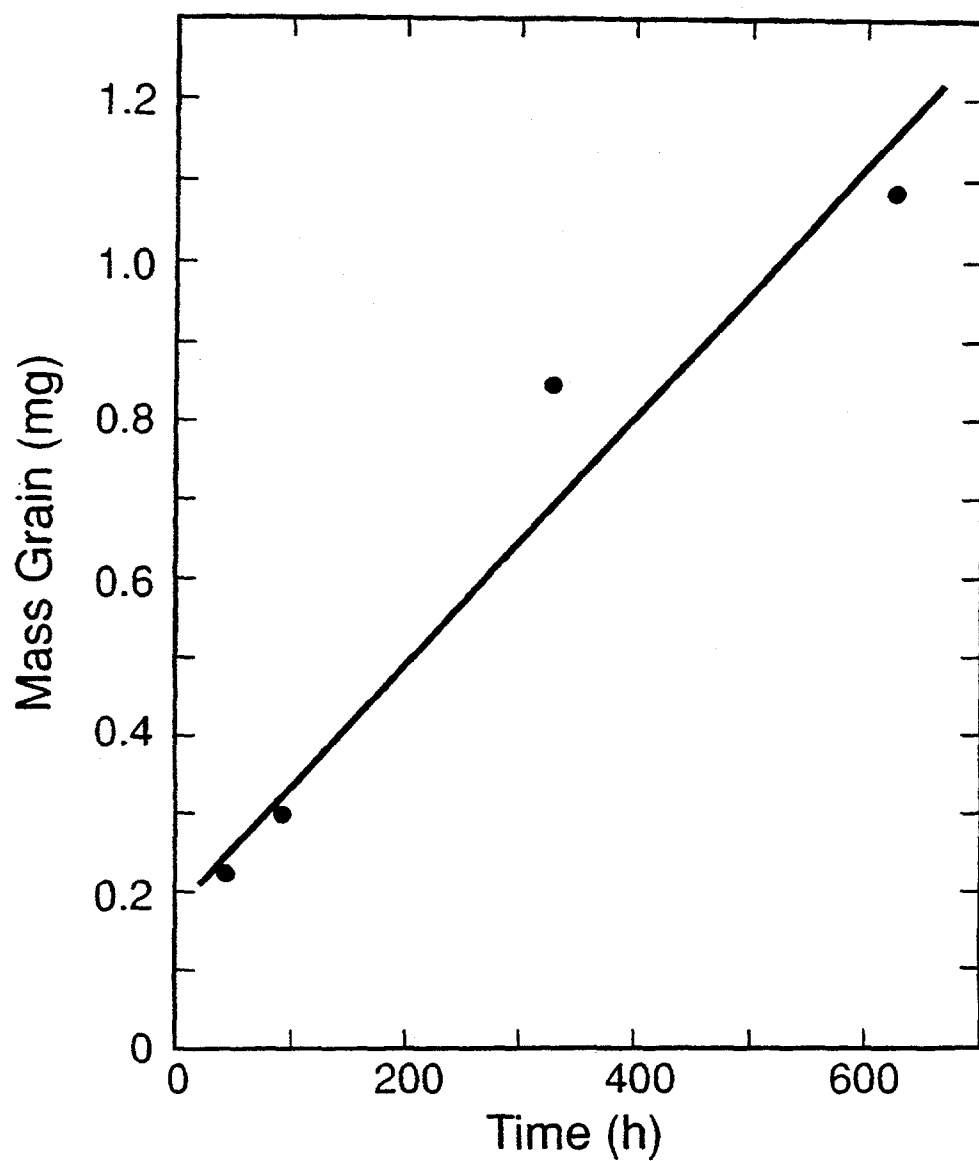


Figure 2. The time dependence of sample mass during four successive thermal cycles in which PuO_2 was heated to constant mass at 100°C after exposure to water vapor at 25°C .

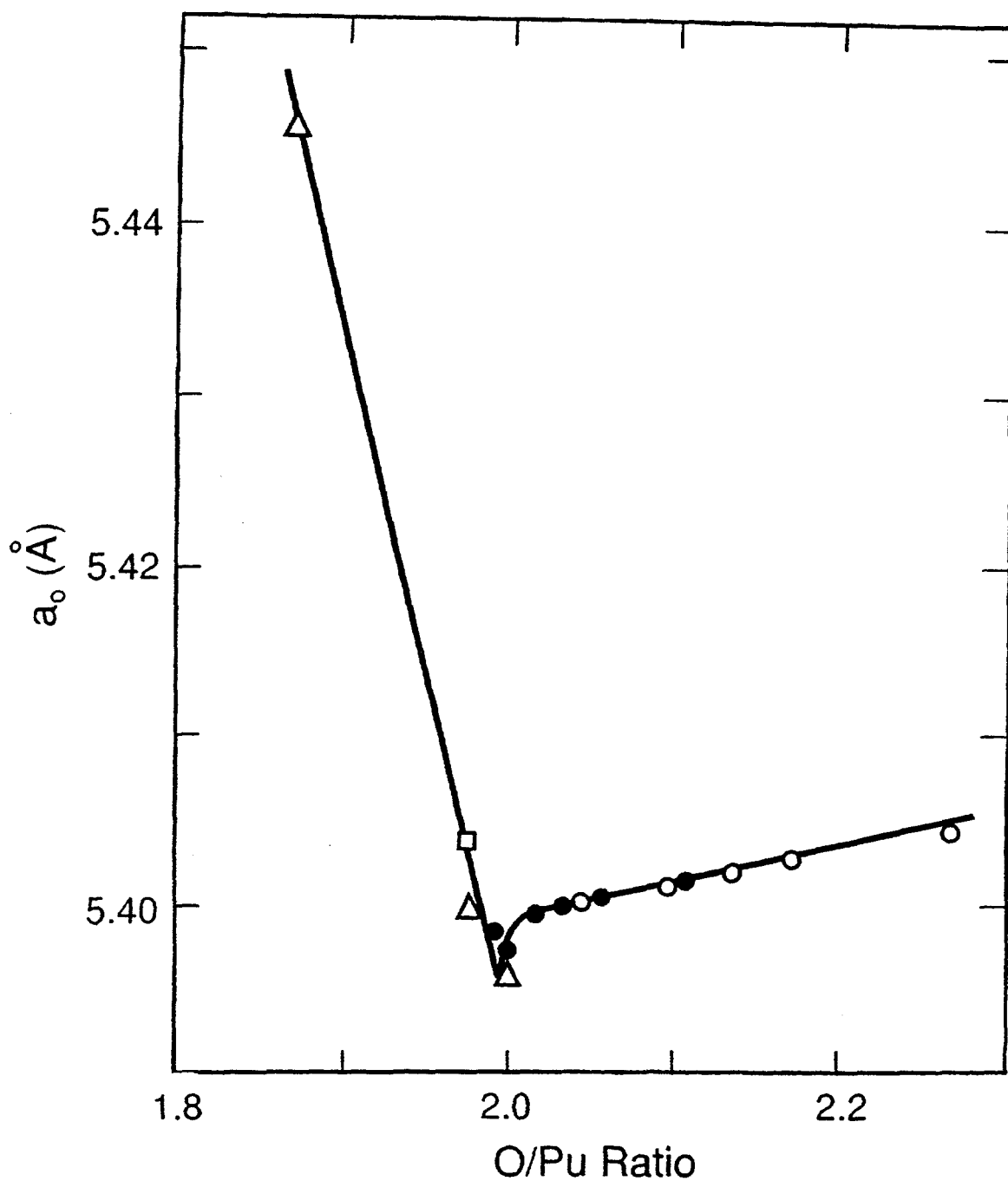


Figure 3. Dependence of the cubic lattice parameter on the O:Pu ratio of the PuO_{2-x} and PuO_{2+x} phases at room temperature. Data points for the fcc fluorite sub-cell (a_o of the sub-cell = half a_o of the body centered cubic cell) of PuO_{2-x} [15] are indicated by triangles. The lattice parameter of the initial oxide ($\text{PuO}_{1.97}$) is identified by a square. Lattice parameters obtained for oxide samples prepared by microbalance and PVT methods are indicated by filled and open circles, respectively.

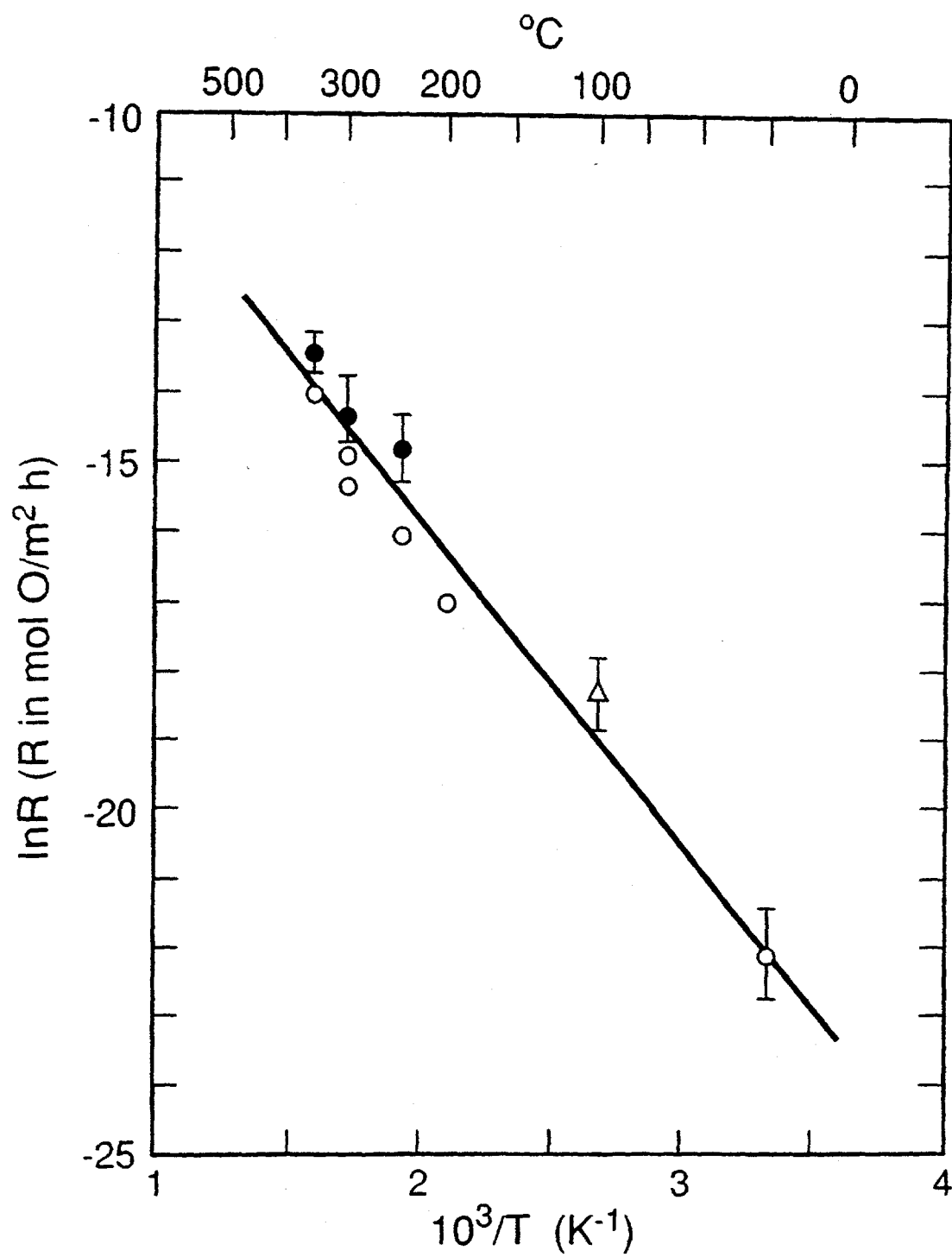


Figure 4. Arrhenius results for the $\text{PuO}_2 + \text{H}_2\text{O}$ reaction at 25°C to 350°C . Data from microbalance, PVT, and XRD measurements are shown by filled circles, open circles, and a triangle, respectively. The data point at 25°C is from a prior PVT study [13].