Chemistry and kinetics of the pyrophoric plutonium hydride-air reaction

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Abstract

The chemistry and kinetics of the pyrophoric reaction of the plutonium hydride solid solution (PuH_x , $1.9 \leq x \leq 3$) are derived from pressure-time and gas analysis data obtained after exposure of $\text{PuH}_{2.7}$ to air in a closed system. The reaction is described by two sequential steps that result in reaction of all O_2 , partial reaction of N_2 , and formation of H_2 . Hydrogen formed by indiscriminate reaction of N_2 and O_2 at their 3.71:1 molar ratio in air during the initial step is accommodated as PuH_3 inside a product layer of Pu_2O_3 and PuN . H_2 is formed by reaction of O_2 and partial reaction of N_2 with PuH_3 during the second step. Both steps of reaction are described by general equations for all values of x . The rate of the first step is proportional to the square of the O_2 pressure, but independent of temperature, x , and N_2 pressure. The second step is a factor of ten slower than step one with its rate controlled by diffusion of O_2 through a boundary layer of product H_2 and unreacted N_2 . Rates and enthalpies of reaction are presented and anticipated effects of reactant configuration on the heat flux are discussed.

1. Introduction

The pyrophoric reactions of plutonium hydride and partially hydrided plutonium metal are of continuing concern because of associated thermal and dispersal hazards [1]. An exothermic reaction of the cubic solid-solution hydride (PuH_x , $1.9 \leq x \leq 3$) initiates spontaneously upon exposure to air at room temperature. The corrosion rate of Pu in dry air is limited by diffusion of oxygen through a surface layer of PuO_2 . The rate is catalytically increased by a factor of 10^{10} if the metal surface is coated with hydride. Aerosolizable and respirable particles are formed by an autocatalytic reaction in which an $\alpha\text{-Pu}_2\text{O}_3$ layer formed by oxidation of the PuH_x surface promotes disproportionation of adsorbed O_2 and N_2 , and facilitates transport of the resulting O^{2-} and N^{3-} ions to the product-metal interface [1]. Reaction of oxygen and the concurrent Pu_2O_3 -catalyzed reaction of nitrogen in air at 1 bar penetrate the metal at a combined linear rate of 1 mm min^{-1} until all the Pu is consumed. Concern about the thermal hazards posed by the reactions of hydride and metal is compounded because the heats of those reaction are released in sharp spikes, not at rates that allow heat to dissipate with a modest temperature excursion. During exposure of hydride-coated metal to O_2 or air at low O_2 partial pressure ($< 50 \text{ mbar}$), the temperature rise at the sample surface is insufficient for maintaining the catalytic Pu_2O_3 surface. The resulting formation of a PuO_2 surface layer forces the reaction into a slow diffusion-controlled kinetic regime [1] with thermal consequences that are negligible and beyond the scope of this study.

The chemistry and kinetics of PuH_x -coated Pu with O_2 and air at 1 bar are described in prior reports [1-3]. In these cases, the rates of the catalyzed reactions are independent of temperature ($E_a=0$) and proportional to the square of the O_2 pressure [1]. Hydrogen is not formed as a gaseous product, but is accommodated as a PuH_3 core within a shell of Pu_2O_3 formed by reaction of O_2 or within a shell of $\text{Pu}_2\text{O}_3\text{-PuN}$ formed by indiscriminate reaction of N_2 and O_2 at the 3.71:1 ratio of those gases in air. In contrast to these observations for reaction of hydride-coated Pu, results show that exposure of PuH_x to air produces substantial amounts of H_2 and that consumption of N_2 is incomplete [2]. Hydride and unreacted air remain after the PuH_x -catalyzed reaction of metal is complete, but continuing reaction with the release of H_2 is not observed. Resolution of this difference in behavior of PuH_x -coated Pu and PuH_x is needed because formation of hydrogen expands the hazardous potential of the PuH_x -air reaction.

The kinetics of a corrosion reaction is an important consideration in hazard assessment because it determines the rates at which dispersible particles form and heat is produced. The nuclear material hazards posed by corrosion of plutonium during exposure to air are addressed in a report on particle-size distributions of products [2]. Promotion of the corrosion rate by hydride on the metal surface was observed and kinetics of the PuH_x -catalyzed reaction of Pu metal were determined. The reaction of hydride particles with air was also investigated and experimental data were reported, but neither the chemistry nor the kinetics of the complex reaction was determined. Here, we use rate data collected during the earlier study [2] to quantify the chemistry and kinetics of the PuH_x -air reaction

and to identify factors that determine hydride pyrophoricity and the extents of heat generation for different reactant configurations.

2. Experimental methods

Multiple experiments were conducted to investigate the reaction of plutonium hydride with air at 25°C. PuH_x samples (25.0 g) were prepared by reacting Ga-stabilized δ -phase Pu with excess H₂ at pressures of 3-4 bar in a stainless steel reactor (0.040 l) fitted with a pressure transducer. After cooling to 25°C and evacuation to 10⁻⁶ mbar, the reactor was filled with air by expansion from a pressurized (1.04 bar) reservoir (2.78 l) to a theoretical initial pressure of 1.01 bar. The pressure of the combined system and the gas-phase temperature were measured over time. The reactor and reservoir were isolated after completion of the reaction and gas samples from those volumes were analyzed by mass spectrometry.

Use of experimental conditions and observations to derive essential properties of the PuH_x products is necessary because determinations of x and the particle-size distribution were precluded by the possibility of pyrophoric reaction during handling outside the Ar-filled glovebox. Since hydrides with x values near 3 are stable at room temperature only if the equilibrium hydrogen pressure is present [4, 5], the products would have readily lost H₂ until x reached 2.7 during evacuation to remove unreacted H₂ at 25°C [6]. The sizes of PuH_x particles formed by the Pu-H₂ reaction increase as the pressure-dependent rate increases [1, 3] and relatively coarse products are expected at the preparative conditions. Since the size distribution and specific area of the hydride might be changed by spallation of product during the reaction with air, residues from air-exposure tests were compared with samples of unreacted hydride in the inert-atmosphere glovebox. Particle sizes (0.1-1.0 mm) were not observably altered by spallation. A geometric area of 11.5±1.5 cm² g⁻¹ is calculated for a hydride comprised of 0.5-mm-diameter particles. The molecular-scale (Braunauer-Emmett-Teller, BET) specific area of 230±30 cm² g⁻¹ is obtained using an experimental result showing that the BET area obtained by adsorption of Ar at -196 °C is a factor of 20 greater than the geometric area [1].

3. Results and discussion

3.1. Chemistry

As shown by a typical gas pressure-time (P-t) curve (Figure 1) published previously [2], attainment of an initial pressure near 1.0 bar immediately after expansion of air into the reactor was followed by a v-shaped pressure variation that was identified as a consequence of experimental design. The pressure measured in the reactor decreased sharply over a 0.05 min period and increased to a value greater than 1 bar during the following 0.05 min period as the gas-phase temperature increased to approximately 150°C. A stable pressure of 1.00±0.01 bar was reached after the reactor had cooled. Gas analysis showed a mixture of 75% H₂ and 25% N₂ in the reactor and 7% H₂ in the air reservoir. Data for all tests show that N₂ and O₂ were consumed at an average molar ratio

of 1.6±0.5:1 until pressurization of the reactor by product H₂ and unreacted N₂ prevented entry of additional air from the reservoir.

The formation of H₂ during rapid exposure of PuH_x to air suggests that, unlike the other hydride-catalyzed reactions [1], product H may not be accommodated as PuH₃ in the solid. The reaction products for PuH_{2.7} are accurately described by two sequential steps (Eqns. 1 and 2, Table 1) that forms the trihydride before continuing reaction yields the net products (Eqn. 3). The net reaction agrees with the single-step reaction (Eqn. 4) that forms H₂ by direct reaction of PuH_{2.7}. For both pathways, the theoretical composition (74% product H₂, 26% unreacted N₂) of the final gas mixture agrees with the experimental results. Although N₂ and O₂ are consumed at the 3.71:1 ratio of air in Eqn. 1, their consumption at a lower ratio (1.5:1) during the second step is necessary to give a net value of 1.6:1. General formula describing the two-step sequence (Eqns. 5-7) and the single-step reaction (Eqn. 8) for all compositions of the cubic PuH_x solid solution are also given in Table 1. The predicted N₂:O₂ reaction ratio is 1.6:1 for all x values using Eqn. 8, but progressively decreases from 1.9 to 1.5 as x increases from 2 to 3 if Eqn. 7 is used.

Accurate description of chemistry for the PuH_x-air reaction is contingent on determining if the process occurs via the single-step or the two-step pathway. For x=2, the ΔG° values derived from Gibbs energies of formation [1] show that Eqn. 8 (-298 kJ mol⁻¹) is more favorable than Eqn. 5 (-86 kJ mol⁻¹), but the observed path of a reaction is determined by kinetics. After H is formed by reaction of air, its movement into the underlying PuH_x should be facile relative to hydrogen formation that requires countercurrent transport of H to the surface and diffusion of H₂ through the reacting gas. Formation of PuH₃ is facilitated by rapid movement of H in PuH_x, a superionic conductor with highly mobile H [1]. The v-shaped time dependence of reactor pressure is consistent with a two-step process of pressure loss and gain, but not with Eqn. 4 in which each mole of air forms 2.35 mol of H₂. Indiscriminate reaction of O₂ and N₂ is observed for adherent PuH_x on Pu and is expected during the initial reaction between particulate hydride and air. However, consumption of air at a N₂:O₂ ratio less than 3.71:1 during the first step of the PuH_x-air reaction merits consideration. Calculations for the case in which 10% of the N₂ did not react show that the pressure of accumulated N₂ in the reactor would reach 0.99 bar when reaction of the hydride was only 43% complete and x of the PuH_x was 2.8. Complete reaction of O₂ and N₂ during an initial step of the PuH_x-air reaction is implied because the extent of air consumption shown by Fig. 1 and the high H₂ percentage found in the residual gas after over-pressurization of the reactor are contingent on complete consumption of air during the initial step or reaction.

3.2 Kinetics

Identification of a two-step path for the PuH_{2.7}-air reaction is confirmed by using the P-t data to derive kinetic properties. Results are evaluated assuming that the reaction proceeds by indiscriminate consumption of O₂ and N₂ (Eqn. 1) during the descending segment of the v-shaped P-t curve and to formation of H₂ by further reaction of product PuH₃ with air (Eqn. 2) during the ascending segment. **Occurrence of Eqn. 1 during the initial step of reaction is consistent with indiscriminate reaction of O₂ and N₂ during**

reaction of PuH_x-coated Pu with air. Results of PVT and gas-analyses for the reactor and reservoir show that 9.1 mmol of H₂ was formed. Eqn. 2 shows that 3.5 mmol of air would have reacted during step two. The amount of air consumption via Eqn. 1 is the difference between the final moles of gas in the system and the calculated net increase in moles of gas (5.6 mmol) during the second step. Since the initial and final system pressures were identical (1.0 bar), 5.6 mmol of air reacted during the first step. According to Eqn. 1, that amount of air would have consumed 0.1047 mol (25.3 g) of PuH_{2.7}. The calculated rate, R, is 0.087±0.009 g PuH_{2.7} cm⁻² min⁻¹ in air at 1 bar pressure. Studies show that the reaction rates of PuH_x-coated Pu with O₂/air and PuH_x with O₂ are independent of temperature, P_{N2}, and x, but proportional to (P_{O2/air})² [1]. If those dependencies are applied to PuH_x-air, the rate of Eqn. 1 is:

$$R \text{ (in g PuH}_x \text{ cm}^{-2} \text{ min}^{-1}) = 0.087(P_{\text{air}})^2 \text{ (P in bar, BET area).} \quad (9)$$

Comparison of the rate constants for the general rate equation, $R = C(P_{\text{O}_2})^2$, for the hydride-catalyzed reactions of O₂/air with PuH_x-coated Pu and PuH_x shows (Table 2) that kinetic behavior is related in two ways. The ratio of C(Pu):C(PuH_x) is 20, the factor by which the BET area of the PuH_x layer on the Pu exceeds the geometric area of the hydride-coated sample [1]. In a more complex way, the values of C(air) for Pu and PuH_x are a factor of 0.23-0.24 less than the corresponding values for C(O₂). The energetically favorable Pu-N₂ reaction is sluggish at temperatures above 1000 °C [7] and N₂ is used as inert atmosphere for handling Pu, **but PuH_x-catalyzed nitriding via Eqn. 5 consumes hydride at a rate that is 5.57 times faster than the simultaneous rate of hydride consumption by O₂.** If R is independent of P_{N2}, replacement of oxygen at 1 bar by air at 1 bar should decrease the rate by a factor of 0.246, the net result of the 5.57-fold increase in Pu consumption and the decrease of (0.21)² due to the lower P_{O2}. Prediction of C for the PuH_x-air reaction using experimental C ratios for the reactions of PuH_x-coated Pu with O₂/air and PuH_x with O₂ (Table 2) both gives values of 0.085 for Eqn. 9.

Kinetic results confirm that the reactions of PuH_x and PuH_x-coated Pu with O₂ or air proceed via the same reaction sequence that forms a core of PuH₃ inside a product layer of Pu₂O₃ or Pu₂O₃+PuN. A conceptual description of the process for PuH_x-air is presented schematically in Figure 2. The proposed mechanism accounts for appearance of the v-shaped P-t curve in Figure 1. The air pressure instantly rose to near 1 bar while onset of Eqn.1 was briefly delayed by formation of the catalytic Pu₂O₃ surface layer on PuH_{2.7}. The subsequent rate of air consumption by the reaction exceeded the rate of air flow into the reactor and the transient pressure in the reactor **steadily decreased** until the initial step of reaction was complete. During the reaction of hydride-coated plutonium with O₂ or air, product H is rapidly transported to the hydride-metal interface, forms hydride until the metal is consumed, and ultimately transforms the hydride core to PuH₃. **Characterization of the hydride-Pu interface [8, 9] at slow hydriding rates show that a two-phase (hydride + metal) zone is formed as H penetrates the metal and suggests that a similar intermediate layer may exist during the rapid macroscopic reaction of PuH_x-coated Pu with air.** The product layers obtained with coated metal are inherently thicker than those obtained with hydride particles.

The derived rate for PuH₃-air (Eqn. 2) is a factor of ten slower than that for the PuH_{2.7}-air reaction. Formation of 9.1 mmol H₂ during the 0.05 min period of reaction

consumed 1.47 g (~6%) of the trihydride before being stopped by pressurization of the reactor. The derived R value is $0.0051 \text{ g PuH}_3 \text{ cm}^{-2} \text{ min}^{-1}$ (BET area). The kinetic effects of temperature, gas concentrations, and extent of reaction are not known.

Formation of H_2 via Eqn. 6 is a unique feature of the PuH_x -air reaction and examination of a likely reason for that behavior is merited. The thickness of the product layer encasing the PuH_3 is determined by sample area, the extent of Eqn. 1, and x, with the value approaching zero as x approaches 3. The average calculated thickness of the Pu_2O_3 +PuN layer formed during the test with $\text{PuH}_{2.7}$ is ~400 nm. Thicknesses varied from ~80 nm for 0.1-mm-diameter particles to ~800 nm for particles with diameters of 1.0 mm. Transport of O and N to the underlying PuH_3 and countercurrent movement of product H to the surface are necessary for reaction. Failure to observe H_2 after relatively thick (0.5-1.0 mm) product layers were formed during the reactions of PuH_x -coated Pu with O_2 [1] or air is consistent with limitation of those transport processes. Transport through a Pu_2O_3 +PuN layer formed by air may also be more favorable than through the Pu_2O_3 layer formed by O_2 because of differences in morphology of the layers. The porosity of a mixed-phase product comprised of small oxide and nitride grains is likely to be greater than that of a single-phase product in which growth of larger grains is possible.

3.3 Thermal hazards

The heat flux generated by reaction of air with PuH_x is determined by the kinetics and thermodynamics of hydriding. As outlined in Table 3, a progressive decrease in heat production via Eqn. 5 with increasing x is accompanied by an increase in the heat for the second step (Eqn. 6). ΔH° values for the net reaction vary by less than 10% over the composition range of PuH_x . Occurrence of the reaction for x greater than 2.7 at room temperature is unlikely due to spontaneous loss of H_2 at higher compositions. The enthalpies for all reactions are linear functions of x and readily derived by interpolation.

Results of this study demonstrate that the extent of heat generation may be limited by physical constraints. Such behavior was observed in this study when reaction ceased because the reactor was pressurized above 1 bar by product H_2 and unreacted N_2 . Eqn. 7 shows that a standard liter of gas mixture is formed by the reaction of air with 7 g of PuH_2 . In the case of a containment breach for a system or vessel containing hydride, the likelihood of a large thermal excursion may be substantially diminished if the PuH_x -air reaction is throttled by the rate at which air reaches the hydride [1].

Reaction of unconfined PuH_x in air is complex and presents significant potential for a thermal excursion if the hydride is disturbed. The reaction initiates spontaneously and is evidenced by a pale blue flame at a distance of 1-2 cm above the solid [1, 10]. That observation is consistent with burning of product H_2 formed by Eqn. 6. Formation of the Pu_2O_3 catalyst and initiation of the H_2 - O_2 reaction are promoted by heat from step one. However, reaction of the PuH_3 product via Eqn.6 apparently depends on the thickness of the surface product. Reaction of the trihydride is likely because the calculated thickness (~100 nm) of the Pu_2O_3 +PuN layer formed during reaction of PuH_2 powder ($0.20 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$ BET area) prepared by slow reaction at low temperature and low H_2 pressure [1] is

a factor of four less than that for PuH_{2.7} sample in this study. ΔH° values for Eqn. 6 (Table 3) are increased by the production of additional heat from formation of H₂O (g) (-242 kJ mol⁻¹). Further oxidation of PuN to Pu₂O₃ (-529 kJ mol⁻¹ PuN) has been reported [1], but neither the rate of PuN-O₂ reaction nor that of ultimate PuO₂ formation (-456 kJ mol⁻¹ Pu₂O₃) is described.

Appearance of flame at a discernable distance from the surface during the pyrophoric reaction of hydride suggests that the H₂-O₂ reaction is limited by the concentration of oxygen at the gas-solid interface. Both the rate of the PuH₃-air reaction (Eqn. 6) and attainment of a flammable mixture for burning of product H₂ are apparently controlled by transport through an oxygen-deficient barrier of N₂ and H₂. In a similar system, the rate of the Pu₂O₃-catalyzed oxidation of Pu in static air at 1 bar increases with temperature below 500°C, but is constant above that point because diffusion of O₂ through an N₂-rich layer becomes the slow step [1]. If the Pu₂O₃-catalyzed PuH_x-air reaction is sufficiently fast that its rate is controlled by diffusion through a N₂+H₂ barrier, the rates of the two reactions should be similar. Division of the rate (0.14 g Pu cm⁻² min⁻¹, geom. area) for the diffusion-controlled Pu-air reaction [1] by 20 gives 0.0070 g Pu cm⁻² min⁻¹ (BET area), a value consistent with the 0.0051 g PuH₃ cm⁻² min⁻¹ (BET area) result obtained for Eqn. 2.

Reaction of hydride-coated Pu with O₂ or air undoubtedly proceeds as described for PuH_x (Eqn. 5), but with increased extents of reaction and heat production due to hydride-catalyzed involvement of the metal. Except for the PuH_x core, all Pu is transformed to Pu₂O₃ and PuN with an enthalpy of -379 kJ mol⁻¹ Pu (or per 0.537 mol air). If the Pu surface is partially covered by hydride, the corrosion rate for all hydride-coated areas in air is described by R (Table 2), but the area-normalized rate is reduced as determined by the fractional hydride coverage of the metal surface. The PuH_x-catalyzed reaction continues until all Pu is consumed and all hydrogen is present as PuH₃. Partial coverage of the metal by hydride is possible because the amounts of hydrogen typically available from chemical and radiolytic sources in storage are small and the formation of PuH_x is localized by autocatalytic reaction at a limited number of surface sites [1]. H₂ formed during concurrent reaction of spalled PuH_x product (Eqn. 7) and partially hydrided Pu with air does not pressurize the container [2], but reacts with the metal [11].

4 Conclusions

Results of this study show that the reaction kinetics of PuH_x and PuH_x-coated Pu with O₂ and air are described by a single equation with rate constants related by differences between the geometric and BET surface areas of hydride and by consequences of N₂ participation as a diluent and as a kinetically neutral reactant. The results imply that the reactions of hydride and metal proceed via the same mechanism. Contrary to an earlier conclusion [2], data evaluation shows that the v-shaped P-t curve observed for the PuH_x-air reaction is due to the combined effect of limited air flow and rapid reaction of air in addition to experimental configuration. Pu₂O₃ formed at the hydride surface via Eqn. 5 promotes further reaction by catalyzing dissociation of O₂ and transporting the product O to the oxide-hydride interface. Direct correlation of the rate

constant for the PuH_x -air reaction with that for the PuH_x - O_2 reaction (Table 2) implies that catalytic Pu_2O_3 is formed during exposure of hydride to air or that an oxide nitride product [1] is equally catalytic. H produced by the ensuing reaction advances into the underlying PuH_x . N_2 in air or other nitrogen-oxygen mixtures participates in the catalyzed reaction by altering the rate of Pu/PuH_x consumption without involvement of P_{N_2} in the rate equation.

Insight into the pyrophoric nature of PuH_x has been gained. The reaction initiates spontaneously after exposure of the hydride to air at room temperature because reaction of oxygen immediately forms a Pu_2O_3 surface that catalyzes continuing reaction of both O_2 and N_2 . Formation of a gas-phase diffusion barrier during the initial step (Eqn. 5) is precluded by rapid and complete reaction of N_2 at a 300-fold faster rate than observed for nitriding of Pu at 1000 °C [12]. Although 85% of the PuH_x is consumed by N_2 during the first step and ΔH° for PuN formation is 18% of that for Pu_2O_3 , the heat flux for catalyzed reaction of PuH_2 via Eqn. 5 is 6.5-fold greater than that estimated for catalyzed, but diffusion controlled, oxidation of the dihydride in static air. In large measure, the effectiveness of using N_2 dilution methods to reduce hydride pyrophoricity in glovebox atmospheres [1, 8] is not only due to the decrease in O_2 pressure, but to amplification of the kinetic effect by the dependence of R on $(\text{P}_{\text{O}_2})^2$.

The oxidation kinetics of the PuN and Pu_2O_3 products of Eqn. 7 are undefined and the origin of the squared dependence on the PuH_x oxidation rate on O_2 pressure is unknown. Additional investigation is needed to address these deficiencies.

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Table 1. Equations describing the two-step and the single-step reactions of PuH_{2.7} and PuH_x with air.^a

Reactions of PuH_{2.7}

Reactions of PuH_x

a. Eqn. 3 is the sum of Eqns. 1 and 2; Eqn. 7 is the sum of Eqns. 5 and 6.

Table 2. Comparison of the measured rate constants, C, for the reactions of PuH_x-coated Pu and PuH_x with O₂ at 1 bar and at 0.21 bar in air.^a

Gas Phase (1 bar)	Experimental C		C(Pu):C(PuH _x)
	PuH _x -coated Pu (geom. area)	PuH _x (BET area)	
O ₂	7.4 ^b	0.37	20.2
Air	1.72	0.087	19.5
C(air):C(O ₂)	0.23	0.24	

a. At each condition, C (in g Pu or PuH_x cm⁻² bar⁻² min⁻¹) is defined by $R = C(P_{O_2})^2$ (geom. or BET area, P_{O2} in bar).

b. The experimental value of C for the reaction of PuH_x-coated Pu with O₂ at 1 bar is derived from the rate (78.1 g Pu cm⁻² min⁻¹) measured at a median O₂ pressure of 3.25 bar [2].

Table 3. Dependence of ΔH° on x for step one (Eqns. 5), step two (Eqn. 6), and the net reaction (Eqn. 7) after exposure of PuH_x to air.^a

x	ΔH° (kJ mol ⁻¹ PuH_x) ^{b,c}		
	Eqn. 5	Eqn. 6	Eqn. 7
2.0	-104	-166	-270
2.7	-31	-224	-255
3.0	0	-248	-248

a. Values are derived using tabulated enthalpies of formation [1].

b. ΔH° values correspond to the sequence of equations formulated per mole of PuH_x initially reacting via Eqn. 5 (Table 1).

c. Enthalpies for intervening values of x are determined by interpolation.

Figure 1. The time dependence of gas pressure and temperature after exposure of $\text{PuH}_{2.7}$ to air at 25°C and 1.01 bar.

Electrons from PuH_x ($1.9 \leq x < 3$) **catalytically** promote dissociative chemisorption of O_2 and N_2 to form O^{2-} and N^{3-} via concerted surface reactions.

Reaction of O^{2-} and N^{3-} with PuH_x forms catalytic Pu_2O_3 , PuN , and H^- that moves into the non-stoichiometric hydride and increases x as electrons from the hydride move to the surface. **Reaction proceeds as Pu_2O_3 in the product layer catalyzes dissociation of O_2 and N_2 to form O^{2-} and N^{3-} and transport those ions to the PuH_x interface.**

As the $\text{Pu}_2\text{O}_3 + \text{PuN}$ layer grows, reaction of product H^- (δ moles) with PuH_x maintains charge balance (δ moles e^-) and continues until $x + \delta = 3$.

After reaction is complete, each particle has a PuH_3 core encased in a $\text{Pu}_2\text{O}_3 + \text{PuN}$ layer with a thickness determined by x and particle size.

Figure 2. Schematic description of the initial reaction of air with a PuH_x particle (Eqn.1). A segment of an ideal spherical particle is shown.