# Kinetics of the High Temperature Oxygen Exchange Reaction on $^{238}PuO_2$ Powder*

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**Abstract**

Oxygen exchange reactions performed on $PuO_2$ suggest the reaction is influenced by at least three mechanisms: an internal chemical reaction, surface mobility of active species/defects, and surface exchange of gaseous oxygen with lattice oxygen. Activation energies for the surface mobility and internal chemical reaction are presented. Determining which mechanism is dominant appears to be a complex function including at least specific surface area and temperature. Thermal exposure may also impact the oxygen exchange reaction by causing reductions in the specific surface area of $PuO_2$. Previous $CeO_2$ surrogate studies exhibit similar behavior, confirming that $CeO_2$ is a good qualitative surrogate for $PuO_2$, in regards to the oxygen exchange reaction. Comparison of results presented here with previous work on the $PuO_2$ oxygen exchange reaction allows complexities in the previous work to be explained. These explanations allowed new conclusions to be drawn, many of which confirm the conclusions presented here.

*Keywords* – oxygen exchange; kinetics; internal chemical reaction; surface exchange; surface mobility; plutonium (IV) oxide

*Abbreviations*: SSA – specific surface area, RPS – radioisotope power system

## 1 Introduction

Isotopic oxygen exchange reactions are used in the production of $^{238}PuO_2$ based Radioisotope Power Systems (RPS) employed in space exploration to help minimize the ($\alpha$,n) reaction that occurs between the $\alpha$ radiation emitted by $^{238}Pu$ and the naturally abundant $^{17}O$ (0.037%) and $^{18}O$ (0.204%) isotopes [1-7]. Neutron radiation is a significant safety concern for personnel as well as an operational concern for some spacecraft and their scientific payload. Fortunately, the ($\alpha$,n) reaction does not occur with $^{16}O$, so neutron emission rates can be minimized through use of an oxygen exchange reaction. This

reaction reduces the amount of detrimental $^{17}O$ and $^{18}O$ in the $^{238}PuO_2$, and replaces it with $^{16}O$. While a number of publications have proven the principle of the oxygen exchange reaction on $PuO_2$, there is very little published kinetic or mechanistic information. Obtaining a better understanding of the mechanisms and kinetics that govern the oxygen exchange is valuable because it will help RPS programs apply the oxygen exchange reaction in an efficient manner and help them adapt to processing changes without the need for extensive development work.

Recently, an extensive campaign of oxygen exchange experiments was performed using $CeO_2$ as a non-radioactive surrogate for $PuO_2$ [8,9]. Results from those experiments showed that the oxygen exchange behavior of $CeO_2$ is complex. Three different mechanisms were observed on several different $CeO_2$ powders as the temperature was varied from 600 to 1100 $^oC$: i) an unidentified chemical reaction occurring within the bulk and not at the material surface, ii) the surface mobility of active surface species or surface defects, and iii) the surface exchange of gaseous oxygen with lattice oxygen. Winter's [10,11] and Novakova's [12] extensive work on the oxygen exchange behavior of metal oxides clearly indicates that the surface exchange and surface mobility mechanisms should be observable on most metal oxides. The internal chemical reaction, however, was a fascinating observation as it represents a novel stage in the oxygen exchange reaction on $CeO_2$.

Previous reports on the oxygen exchange behavior of $PuO_2$ were not able identify the internal chemical reaction or obtain any activation energy data [7], leaving a significant gap in our knowledge of the oxygen exchange reaction on $PuO_2$. Using the oxygen exchange behavior of $CeO_2$ as a guide, the experiments presented here were specifically designed to look for the internal chemical reaction. Results will show that the internal chemical reaction does occur in $PuO_2$, and activation energies for the internal chemical reaction and the surface mobility reaction on $PuO_2$ will be reported for the first time. Additionally, results presented in this report show that that the complex mechanistic behavior of oxygen

exchange on $CeO_2$ is qualitatively similar to $PuO_2$, confirming that for the oxygen exchange reaction, $CeO_2$ is a good qualitative surrogate. Finally, since previous $PuO_2$ oxygen exchange work was limited in scope with almost no experimental replication, the results presented here help validate the previous $PuO_2$ oxygen exchange work through independent verification.

## 2 Theory

Winter's extensive and seminal work on the oxygen exchange reaction with metal oxides indicates that the exchange rate is typically limited by a surface exchange mechanism at moderately high temperatures and that as temperature increases the exchange rate will eventually become limited by the surface mobility mechanism [10,11]. Figure 1 provides a cartoon depiction of these oxygen exchange mechanisms to aid in comprehension. Surface exchange is a generalized term that describes the series of reactions that are necessary to take oxygen from the gas phase and incorporate it into the material lattice (Figure 1, top left). Surface mobility is a generalized term that describes the series of reactions that are necessary for an adsorbed oxygen species to move around the surface of the material until it finds a location where exchange with the lattice can occur (Figure 1, top right). Unfortunately, determining the specific reactions that limit these mechanisms is very challenging. As a result, the concepts of surface exchange and surface mobility are often referenced in the literature as elementary steps in the oxygen exchange reaction.

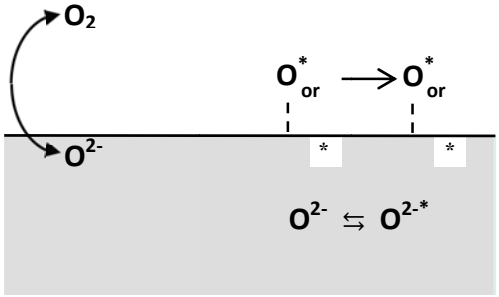


**Figure 1.** Cartoon depiction of the three known mechanisms that can influence the oxygen exchange reaction of $CeO_2$ at high temperatures. Top Left – surface exchange of oxygen from the gas phase with the lattice. Top Right – surface mobility of an active surface species or surface defect. Bottom Right – the novel internal chemical reaction. * - denotes an active species, or a species that is not in a standard state for this system.

Despite not fully understanding the exact rate limiting steps involved in surface exchange and surface mobility, some $CeO_2$ surface chemistry has been associated with these mechanisms. Since it is likely that $PuO_2$ will exhibit surface chemistry that is similar to $CeO_2$, there is value in reviewing what is known regarding $CeO_2$ surface chemistry.

### *2.1 Surface Exchange on $CeO_2$*

In general, oxygen exchange reactions are typically classified into one of three categories: homoexchange, simple heteroexchange, and multiple heteroexchange [10-13]. Homoexchange is defined as isotopic exchange that does not include oxygen from the solid oxide, such as:

$$^{18}O_{2\,(g)} + {}^{16}O_{2\,(g)} \leftrightarrows 2\,{}^{18}O^{16}O_{\,(g)} \quad (1)$$

Homoexchange can occur as the result of catalytic activation at the oxide surface, in which case the exchange rate is most likely limited by an adsorption-desorption reaction [14].

Simple heteroexchange is defined as isotopic exchange that includes only one oxygen atom from the solid oxide and one oxygen atom from the gas phase, such as:

$$^{18}O_{2\,(g)} + {}^{16}O_{\,(s)} \leftrightarrows {}^{18}O^{16}O_{\,(g)} + {}^{18}O_{\,(s)} \quad (2)$$

A triatomic surface intermediate (i.e., $O^-_{3\,(ads)}$) has been suggested as a factor in some isotopic exchange reactions that include simple heteroexchange [15-17]. Other reports have suggested that surface oxygen vacancies can also induce simple heteroexchange [14].

Multiple heteroexchange is defined as isotopic exchange that includes two oxygen atoms from the solid oxide and both oxygen atoms from the gas phase molecule, such as:

$$^{18}O_{2\,(g)} + 2\,{}^{16}O_{\,(s)} \leftrightarrows {}^{16}O_{2\,(g)} + 2\,{}^{18}O_{\,(s)} \quad (3)$$

Two potential intermediate steps have been proposed for the multiple heteroexchange reaction. The first is an associative mechanism that includes a tetratomic (i.e., $O^-_{4\,(ads)}$) surface intermediate [17,18].

The second involves the displacement of an oxygen molecule associated with the surface of the oxide by a gas phase oxygen molecule, and is referred to as a "place-exchange" mechanism [17,19].

Above ~500 $^{o}$C, several reports suggest that isotopic oxygen exchange reactions on $CeO_2$ are most likely dominated by multiple heteroexchange [14,18,19]. In the report by Cunningham *et al*., it was noted that the isotopic ratios produced by the oxygen exchange reaction on $CeO_2$ performed between 450-650 $^{o}$C were indicative of a multiple hetero exchange mechanism driven by place-exchange [18]. Below 500 $^{o}$C, however, Martin and Duprez observed that the oxygen exchange reaction on $CeO_2$ occurred via a combination of simple and multiple heteroexchange, and it was hypothesized that the simple heteroexchange portion of the reaction was driven by oxygen vacancies found at the oxide surface [14]. Therefore, it is likely that at temperatures above ~500 $^{o}$C the surface exchange reaction on $CeO_2$ is limited by a place-exchange mechanism, and that below ~500 $^{o}$C the presence of oxygen vacancies can cause the exchange rate to be influenced by simple heteroexchange.

### *2.2 Surface Mobility on $CeO_2$*

Oxygen mobility has been linked to $O^{2-}$–$M^{n+}$ bonds at the oxide surface, suggesting that surface basicity is correlated to the rate of surface mobility. Martin and Duprez tested this hypothesis and confirmed a correlation between surface basicity and surface mobility for 4 of the 6 oxides they tested, with the two exceptions to this trend being pure $CeO_2$ and $Al_2O_3$ doped with 12% $CeO_2$ [14]. The surface mobility on these two $CeO_2$ containing samples was observed to be so fast, that the surface basicity trends could not completely explain the surface mobility rate. Based on their data, Martin and Duprez were able to hypothesize that this very high surface mobility was a complex function of surface chemistry that included at least surface basicity and surface oxygen vacancies [14].

Several surface di- and triatomic oxygen species have been proposed as a result of oxygen adsorbing to the surface of $CeO_2$ [20-22]. Superoxides ($O_2^-$) were observed by EPR [23-25], while

peroxides ($O_2^{2-}$) were observed by FTIR on partially pre-reduced samples [26]. Martin and Duprez were able to observe a highly mobile diatomic species on the surface of $CeO_2$, but they were unable to positively identify the species [14]. Huang and Beck, on the other hand, were able to observe 3 different active oxygen species (i.e., $O_2^-$, $O_2^{2-}$, and $O_3$) on the surface of $CeO_2$ using FTIR and Raman spectroscopy [27]. It is important to note, that despite the observation of these active oxygen species and their potential mobility at the $CeO_2$ surface, this is not a positive indication that any of these species play a direct role in the rate limiting step of the surface mobility mechanism.

### *2.3 Internal Chemical Reaction*

Recently, another rate limiting mechanism in the oxygen exchange reaction was observed in $CeO_2$ at very high temperatures, and this novel mechanism was observed to be independent of atmospheric composition and most particle properties, including specific surface area [8]. Winter [10,11] and Novakova [12] both very clearly indicate that the surface exchange and surface mobility reactions have a strong dependence on the specific surface area of the material. This led to the conclusion that the novel mechanism must be occurring within the bulk of the material, not the surface.

It was also determined that this novel mechanism is not related to oxygen diffusion [8,9]. We recognize that this conclusion will challenge the perception that many have regarding oxygen motion through solid materials. Therefore, the evidence presented in Ref. 8 and 9 will be reviewed so that a diffusion based mechanism can be refuted. First, when data obtained from the oxygen exchange reaction was fit to the appropriate diffusion equations, the resulting graph did not exhibit diffusion-like behavior. Second, the rate of this novel mechanism was determined to be independent of particle size, grain size, and specific surface area. Diffusion, by definition, must have a second-order dependence on size, while diffusion under a potential (e.g., oxygen ion mobility in the presence of a voltage) must have a first-order dependence on size. Third, the oxygen diffusion constant ($D$) through a $CeO_2$ single crystal

lattice at 1000 $^{o}$C can be calculated from the activation energies published by Yamaguchi *et al*. to be $D$ = $1.5x10^{-9}$ $cm^2$ $s^{-1}$ [28]. Using the method described by Deaton and Wiedenheft to obtain $D$ from oxygen exchange data [29], the novel mechanism at 1000 $^{o}$C produced a *hypothetical* $D$ = $9x10^{-17}$ $cm^2$ $s^{-1}$, which is an irrationally small result. Finally, using the calculated value of $D$ = $1.5x10^{-9}$ $cm^2$ $s^{-1}$ it is possible to calculate a mean free path for oxygen during 1 second to be 390 nm (mean free path = $(Dt)^{1/2}$). This value is huge compared to the 20-100 nm average grain size of the $CeO_2$ powders [9]. Rearranging these calculations indicates that on average, an oxygen ion will take only 0.067 seconds to travel across the entire distance of a 100 nm grain. This rate of transport is so fast, that it cannot possibly be the limiting factor in a reaction that typically takes ~600 seconds to complete. This information clearly indicates that the observed novel mechanism cannot be associated with oxygen ion diffusion through the material lattice.

"Internal chemical reaction" was therefore adopted as the descriptor for this novel mechanism in order to clearly articulate that this mechanism is not occurring at the surface and is not related to diffusion.

Unfortunately, beyond ruling out both a surface and a diffusion based mechanism, the exact nature of the internal chemical reaction is unknown. However, it is possible to deduce that the internal chemical reaction is most likely related to a step that permits, or activates, the motion of oxygen through the lattice, but is not directly related to the actual diffusion of the oxygen. One hypothesis that was presented previously that fits these characteristics is the movement of an oxygen ion away from its lattice position towards, or completely into, the interstitial space found inside the fluorite atomic space grouping ($Fm\bar{3}m$; #225) adopted by $CeO_2$ [9]. This motion would be similar to the formation of an oxygen ion Frenkel defect (using Kröger-Vink notation):

$$O_O^x \leftrightarrows V_O^{\bullet\bullet} + O_i^{''} \qquad (4)$$

It is well-known that oxygen diffusion in both $CeO_2$ [30] and $PuO_2$ [31] occur via oxygen vacancies, so the formation of an oxygen vacancy via the displacement reaction shown in Equation 4 may then create a pathway for nearest neighbor lattice oxygen ions to begin diffusion.

Another hypothesis that could represent the activation of oxygen ion motion without being directly tied to diffusion could be based on the fact that both $CeO_2$ [32,33] and $PuO_2$ [34] exhibit significant orbital mixing, resulting in partially ionic and partially covalent behavior in the oxygen-metal bonding. A diffusing oxygen ion will clearly not be able to maintain this orbital mixing while it is in motion. As a result, a certain amount of energy will need to be added to the system to activate the oxygen ion and allow the separation of the mixed orbitals.

It is important to reiterate that there is currently no empirical evidence to directly support/refute either hypothesis presented here. However, we felt it was important to include these potential mechanisms in our discussion so the skeptical reader can see that there are indeed chemical reactions that can occur within the bulk of the material and activate oxygen diffusion without being directly tied to the process of diffusion.

## 3 Experimental

### *3.1 Instrumentation*

Instrumental design was based on designs described previously [8] and adapted for use in a radiological glove box, with a schematic of the glove box and atmosphere controlled reaction chamber presented in Figure S1 (Supplementary Information). Major differences to this design will be discussed here. A fused silica reaction chamber (~500 mL internal volume) and fused silica sample vessel were fabricated in-house. Fused silica tubing was used to bring the inlet gases into the reaction chamber and was positioned such that the end of the fused silica tube would blow the gases directly over the sample bed. Incoming gases passed through a flow meter that was set to a flow rate of 2.2 mL/s. A series of

ball valves and stainless steel tubing controlled the flow of gases into and out of the reaction chamber, while a vacuum pump was used to remove the reagent gases after the exchange was complete. A sampling line was included in this design to allow the analysis of gases in the reaction chamber, but was not utilized in this work.

Reaction rates were monitored by observing the change in neutron emission rates with an NP-2A Portable Neutron Monitor from Nuclear Research Corporation/Canberra (Meriden, CT). The sensor on the NP-2A was attached to the bottom exterior of the glovebox, directly below the location of the $PuO_2$ sample. Characterization of the analytical quality of the NP-2A in the described configuration is discussed in Section S1 of the Supplemental Information.

### *3.2 Materials*

A sample of plutonium (75% as $^{238}Pu$) oxalate was precipitated from a 1.3 g $L^{-1}$ solution of plutonium nitrate with nominally 0.15 M $HNO_3$ by the addition of ~25-fold excess of solid oxalic acid. The solution was agitated and allowed to settle over the course of a week. After filtration of the solid plutonium oxalate, an additional ~12-fold excess of solid oxalic acid (based on the original plutonium concentration) was then added to the filtrate to improve the plutonium recovery. This solution was agitated and allowed to settle over the weekend before filtration. Calcination of the collected plutonium oxalate was performed at 700 $^{o}C$ for 90 min with a ramp rate of 20 $^{o}C$ $min^{-1}$. A calculated final sample mass of 234.0 mg $PuO_2$ (154.7 mg $^{238}Pu$) was then transferred to the fused silica sample vessel; calculations were based on the plutonium concentrations in the nitrate solution before and after precipitation. All experiments were performed on this sample of $PuO_2$.

BET measurements of the SSA on the $^{238}PuO_2$ sample were not obtained because of material transport and sample size concerns. It was estimated that nearly the entire $PuO_2$ sample would have been required to obtain an accurate BET measurement. Therefore, the risk to the oxygen exchange

experiment was deemed too high compared to the value of the BET measurements. Fortunately, the reduction of SSA at temperatures above the original calcination temperature is a well-known phenomenon in $PuO_2$ [35,36], so we are confident that changes in SSA can be discussed with accuracy, even if absolute SSA values are not known.

Exchange gas containing 52% $^{18}O$ was obtained from Isotec, Inc. (Miamisburg, OH) and was provided as a mixture of 21% $O_2$ and 79% $N_2$ to minimize safety concerns with utilizing pure oxygen. Compressed air and 99.999% purity argon were obtained from Air Liquide (Houston, TX). Oxalic acid was obtained in its dihydrate form from J. T. Baker (Center Valley, PA).

### *3.3 Methods*

The sample vessel was placed into the reaction chamber, and the reaction chamber was placed into the furnace while the system was still at room temperature. Once the furnace and sample were at thermal equilibrium with the desired temperature, the reaction chamber was evacuated, flushed with argon for several minutes, and then evacuated again to minimize the amount of residual glove box air. Exchange gas was then introduced to the reaction chamber and the rate of the exchange was monitored by recording the neutron emission rate from the sample as a function of time. Neutron emission rates were recorded every 20 s until the reaction was complete. After the exchange reaction was complete, the reaction chamber was evacuated and the reverse reaction was performed using compressed air (i.e., $^{16}O$). Upon completion of the reverse reaction, the reaction chamber was evacuated, flushed with argon for several minutes, and then evacuated again prior to any subsequent experiments. Both forward and reverse exchange reactions were considered complete when the measured neutron emission rate became constant.

Previous results from $CeO_2$ suggest that the thermal history of the sample can have a significant impact on the exchange rate, which is most likely due to reductions in porosity and SSA resulting from

exposure to high temperatures [8,9]. This strongly suggests the thermal experimental profile is a very important factor when interpreting data from a single sample of $PuO_2$. Therefore, the order in which the experiments were performed is described here. The first two experiments were performed at 700 $^{o}$C prior to exposure to higher exchange temperatures. This temperature is unlikely to cause significant changes to SSA because this was the calcination temperature of the material. After the 700 $^{o}$C experiments, four experiments were performed at 1000 $^{o}$C, which resulted in the sample being exposed to 1000 $^{o}$C for ~3 hours. Subsequent experiments were performed at 900 (x2), 800 (x2), 700 (x1), 850 (x2), and 950 (x2) $^{o}$C, in that order. Data from the second run at 800 $^{o}$C were not utilized because the first 800 $^{o}$C reaction was inadvertently stopped before the exchange was completed. This complicated the results of the second 800 $^{o}$C exchange, but the data from the first 800 $^{o}$C reaction could be salvaged by extrapolating the expected end-of-experiment neutron emission rate from other runs.

### *3.4 Oxygen Exchange Rate Law*

Rate constants were obtained using the rate law equations derived previously [8] and are defined by the rate constant (k) as modified by a set of probability constants that can be defined as the fraction of reaction remaining (*F*):

$$\text{Rate} = k * F \tag{5}$$

$$F = \frac{n_t - n_{eq.}}{n_i - n_{eq.}} \tag{6}$$

Where $n_i$, $n_{eq.}$, and $n_t$ are the measured neutron emission rates before the exchange, at equilibrium, and at time *t*, respectively. It is important to note that this rate is referred to as the apparent rate of exchange because the true rate of exchange never changes. For clarification, after the isotopic ratios in the gas phase and the oxide reach equilibrium, the oxygen exchange reaction will continue to occur because the chemical and atmospheric conditions within the reaction tube have not actually changed.

However, the rate of $^{18}O$ entering the oxide will be exactly equal to the rate of $^{18}O$ entering the gas phase, so the apparent exchange – from a neutron emission standpoint – will appear to stop.

Both of the previous peer-reviewed literature reports on the oxygen exchange of $PuO_2$ with oxygen gas have shown that the exchange rate has a first-order dependence on ($[\%\ ^{18}O]_t - [\%\ ^{18}O]_\infty$), where the subscripts describe the values at time *t* and infinity/equilibrium, respectively [2,7]. Algebraic manipulation shows that the rate law used in these previous reports is functionally equivalent to Equation 5 (Section S2, Supplemental Information).

Reagent gas flow rate can be another important factor in determining the rate of the isotopic oxygen exchange reaction [37]. Fortunately, if the reagent gas flow rate is much faster than the rate of exchange, it is possible to assume that the gas phase around the sample is at a steady state composition that is identical to the composition of the gas phase reagent. The gas flow rate of 2.2 mL $s^{-1}$ used in these experiments corresponds to a molar flow rate of $9.0 \times 10^{-5}$ mol $s^{-1}$, which is 15-fold faster than the anticipated molar production rate during the first second of the reaction (i.e., $6.2 \times 10^{-6}$ mol $s^{-1}$ using the 1000 $^{o}$C rate constant reported by Deaton and Wiedenheft [7]). From a kinetic perspective, steady state gas phase conditions in a flow reaction are functionally equivalent to a batch reaction where the moles of gas phase reagent are much larger than the moles of sample. In both cases, it is possible to assume that the composition of the gas phase is constant. Since the $CeO_2$ surrogate studies were performed as batch reactions where the moles of gas phase are much larger than the moles of sample, the results presented here are directly comparable to the $CeO_2$ surrogate studies [8,9].

## 4 Results

Figure 2 presents the results obtained from these experiments as individual data points in an Arrhenius plot (individual numerical results are presented in Table S1, Supplemental Information). Three different exchange mechanisms appear to be occurring over the temperature range studied. The

first mechanism was observed in the 1000, 950, and the non-thermally treated 700 °C experiments (Figure 2, ■). This mechanism has an activation energy ($E_a$) of 17.9 ± 0.9 kJ $mol^{-1}$ and is most likely the internal chemical reaction.

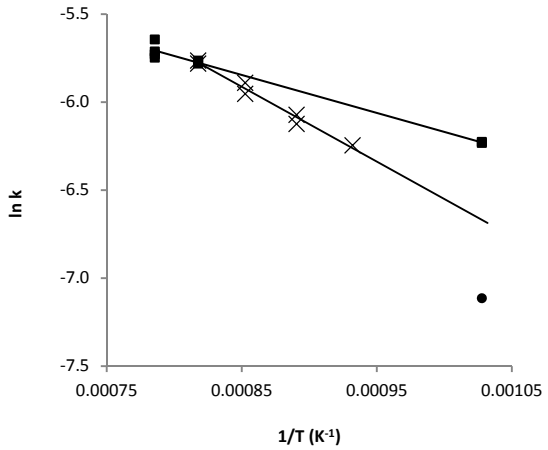


**Figure 2.** Arrhenius plot obtained from $PuO_2$ oxygen exchange experiments showing that the rate can be influenced by up to three different mechanisms: internal chemical reaction (■), surface mobility (X), and either a pure surface exchange or a competitive surface exchange and surface mobility based mechanism (●).

The assignment of the internal chemical reaction was made primarily due to the four replicate runs performed at 1000 °C exhibiting reproducible results. One of the well-known properties of both $CeO_2$ [9] and $PuO_2$ [35,36] powders is that exposure to high temperatures – such as 1000 °C – tends to reduce the SSA of the material. Therefore, performing the oxygen exchange reaction at 1000 °C should cause the SSA of the material to decrease during the experiment. Since both the surface exchange and surface mobility mechanisms have a strong dependence on SSA, changing the SSA during the experiment would result in an exchange rate that was dynamically changing. Replicate experiments at 1000 °C would also result in rates that were becoming progressively slower. Neither condition was observed, suggesting that the rate limiting mechanism is independent of SSA, and oxygen exchange rates that are independent of SSA are most likely being dominated by the internal chemical reaction (cf. Section 2.3).

The second mechanism observed in Figure 2 occurs during the 950, 900, 850, and 800 $^{o}$C experiments. This mechanism has an $E_a$ = 35.3 $\pm$ 2.3 kJ mol$^{-1}$ and is most likely representing surface mobility (Figure 2, X). The 950 $^{o}$C experiments were used in determining the $E_a$ for both the internal chemical reaction and surface mobility because the mathematical intersection of these trendlines occurs at 950 $^{o}$C. The assignment of the surface mobility mechanism is supported by a number of observations. First, the surface mobility is expected to succeed the internal chemical reaction as the dominant mechanism as temperature decreases [9]. Second, Winter predicts that the surface mobility on any metal oxide is expected to occur at very high temperatures and, as a general rule, have an $E_a \leq$ 40 kJ mol$^{-1}$ [10,11]. Observing an $E_a$ = 35.3 kJ mol$^{-1}$, therefore meets the expected guidelines for the surface mobility mechanism on a metal oxide. Finally, the experiments performed at 900, 850, and 800 $^{o}$C did not fall on the internal chemical reaction trendline, despite the fact that the initial 700 $^{o}$C experiment did fall on the trendline. This is a strong indication that the 1000 $^{o}$C exchange experiments caused a significant reduction in the $PuO_2$ SSA. Prior to the thermal exposure at 1000 $^{o}$C, the $PuO_2$ had a larger SSA. Large SSA would have resulted in very fast surface exchange and surface mobility mechanisms, which would have left the internal chemical reaction as the rate limiting mechanism. The fact that the 900, 850, and 800 $^{o}$C experiments do not fall on the internal chemical reaction trendline implies that the SSA was reduced by the exposure to 1000 $^{o}$C, causing the surface mobility reaction to slow down enough to become the rate limiting mechanism.

When the $PuO_2$ sample was exchanged at 700 $^{o}$C after it had been exposed 1000 $^{o}$C for ~3 hours (Figure 2, ●), two major observations were made. First, the rate is significantly slower than the 700 $^{o}$C experiments performed before exposure to 1000 $^{o}$C. This suggests a significant reduction in the SSA of the material, which subsequently caused one of the surface mechanisms to slow down enough to become the rate-determining mechanism. Second, the rate did not fall on the surface mobility trendline, which strongly suggests that the exchange rate was influenced by the surface exchange

mechanism. Previous studies on $CeO_2$ suggest that there is a large temperature range where the surface mobility and surface exchange mechanisms are competitive [9]. Unfortunately, the sensitivity of the neutron counter was not high enough to determine if the post-thermal treatment experiment at 700 $^oC$ was operating under a purely surface exchange-based mechanism or under a regime where the surface mobility and surface exchange are competitive. Due to the departure from the surface mobility trendline in Figure 2, however, it is clear that this 700 $^oC$ experiment was at least being influenced by the surface exchange.

## 5 Discussion

### *5.1 Comparison with $CeO_2$ Surrogate Studies*

A comparison of the results presented here to previous $CeO_2$ surrogate studies has value because proving that $CeO_2$ is a useful surrogate allows future experiments to use $CeO_2$ as a guide for $PuO_2$ behavior. Additionally, upon validating the usefulness of $CeO_2$ as a surrogate, the much more detailed and extensive knowledge base regarding the chemistry of the oxygen exchange reaction on $CeO_2$ can be used to guide the conclusions obtained from $PuO_2$ experiments.

On a qualitative level, the oxygen exchange behaviors of $PuO_2$ and $CeO_2$ appear to be similar. When temperature is high and SSA values are large, the exchange rate appears to be dominated by the internal chemical reaction. As temperature decreases, the material becomes dominated by a different mechanism that appears to fit the expected behavior of the surface mobility mechanism. As temperature continues to decrease, the material becomes influenced by a third mechanism that appears to fit the expected behavior of the surface exchange mechanism. This suggests that it is possible to extrapolate the qualitative mechanistic information obtained on $CeO_2$ to the $PuO_2$ system with confidence.

Table 1 compares the $E_a$ values for the surface mobility and internal chemical reaction obtained for $PuO_2$ to $E_a$ values available from the literature [10,38-41]. Quantitatively speaking, the $E_a$ values for $PuO_2$ are notably larger than on $CeO_2$. One hypothesis that could justify these larger values relates to how strongly the oxygen atoms are bound. Another well-known property of $PuO_2$ and $CeO_2$ is that in the presence of very low oxygen potentials, these materials can be slightly reduced and become substoichiometric (i.e., $PuO_{2-x}$). Literature data on this topic were compiled by Lindemer, who developed a semi-empirical method to predict the relationship between x, temperature, and oxygen potential for $CeO_2$ [42]. Later, Besmann and Lindemer repeated this process for $PuO_2$ [43,44]. Besmann and Lindemer's equations are considered the best method for estimating the energy necessary to separate the metal and oxygen atoms under the conditions presented in this report because they account for: i) the chemical thermodynamics of the dioxide and sesquioxide of each material and ii) the stability that is generated by the $CeO_{2-x}/PuO_{2-x}$ defect structure. Besmann and Lindemer's models clearly show that significantly more energy is required to remove oxygen and form $PuO_{2-x}$ compared to $CeO_{2-x}$, which further suggests that the metal-oxygen interaction is stronger in $PuO_2$.

**Table 1.** Known Activation Energies (kJ $mol^{-1}$) for the Oxygen Exchange Reaction

| | $PuO_2$ | | $CeO_2$ | |
|---|---|---|---|---|
| | This Work | Historical[b] | Ref. [9] | Other Lit.[c] |
| Internal Chemical Reaction | 17.9 ± 0.9 | 20.6 ± 5.5 | 11.0 ± 0.4 | --[a] |
| Surface Mobility | 35.3 ± 2.3 | --[a] | 29.1 ± 1.2 | --[a] |
| Surface Exchange | --[a] | --[a] | 114 ± 8 | 116 ± 17 |

[a] No data for this mechanism
[b] Original data points taken from Ref [7] with $E_a$ values derived in this work
[c] Average and standard deviation from the values reported in Refs. 10 and 38-41

It is important to note a few details regarding the comparison of $E_a$ values presented in Table 1. First, the $E_a$ for the surface exchange on $PuO_2$ has not been measured, so an analysis of any potential

differences in the surface exchange reaction cannot be made at this time. Second, there is some unique chemistry that is observed in the $PuO_2$ system that may impact the oxygen exchange reaction, such as the high radiation field produced by the $^{238}Pu$ and the potential presence of $PuO_{2+x}$. Unfortunately, since the exact nature of the surface exchange, surface mobility, and internal chemical reaction are unknown, predicting how these factors will influence the oxygen exchange behavior will be very challenging. Future experiments that study the effects of radiation fields and $PuO_{2+x}$ on the exchange rate are likely to be the best way to obtain answers to these questions.

### *5.2 Impact of Thermal Exposure*

Both $CeO_2$ and $PuO_2$ appear to experience a significant decrease in SSA upon heating to high temperatures (e.g., 1000 $^{o}$C), which is likely caused by generic reductions in surface area and the closing of particle porosity [9,35,36]. Since the surface mobility and surface exchange mechanisms are dependent on SSA, decreasing SSA could cause a significant change in the rate and/or mechanism to occur in subsequent runs, or it could even cause a dynamic change to occur during the exchange experiments. To clarify, if the temperature and SSA values are high, the surface mobility and surface exchange mechanisms will be fast; meaning that the internal chemical reaction will be the rate-determining mechanism. As the SSA decreases, eventually the surface mobility and surface exchange will become slow enough that one (or both) will influence the rate of exchange. This effect was observed in Figure 2 when the 900, 850, and 800 $^{o}$C experiments departed from the internal chemical reaction trendline. In addition, if the exchange rate is being limited by the surface mobility or surface exchange mechanisms, exposure to the exchange temperature could cause reductions in SSA while the experiment is being performed. This could cause the experiment to produce a dynamic change in the exchange rate, which could result in very confusing and inconsistent behavior. Historical literature discussing the oxygen exchange behavior on $CeO_2$ indicates that the exchange rate is unstable at

temperatures above 700 $^{o}$C [38,45], while prior work on $PuO_2$ was only able to obtain limited kinetic information because of "the complexities in the data" [7]. These historical observations are consistent with thermal exposure causing reductions in SSA between experiments and/or a potential dynamic change in the exchange rate.

These changes in $PuO_2$ SSA due to thermal treatment are not surprising. Thermal treatment of $PuO_2$ is frequently used to obtain desirable particle properties. For example, RPS programs sometimes utilize a special blend of "low-fired" and "high-fired" $^{238}PuO_2$ [46]. This blend has particle properties that help produce a desirable microstructure for the $^{238}PuO_2$ ceramic fuel pellets.

While thermal treatment at high temperatures can cause a significant reduction in SSA, it also appears to create a surface that is relatively stable when exposed to lower temperatures. For example, after exposure to 1000 $^{o}$C for 2 to 3 hours, the surfaces of $CeO_2$ powders studied previously [9] and $PuO_2$ powders studied in this report appear to be stable because replicate oxygen exchange experiments performed at $\leq$ 950 $^{o}$C produce repeatable results. If the SSA was changing significantly during these experiments, then a more complicated rate behavior should be observed. This suggests that a high-temperature thermal treatment at 1000 $^{o}$C stabilized the surface enough that subsequent short-term exposure to lower temperatures did not significantly reduce SSA.

This result is very beneficial because it means that exposure to high temperatures can be used to stabilize the surface of a $PuO_2$ sample and help ensure that reproducible surface mobility and surface exchange rates are obtained. It is important to note that this stability has only been observed in the timeframe of several oxygen exchange experiments. Long term exposure to lower temperatures (i.e., significantly more than 2 to 3 hours) has not been tested.

### *5.3 Comparison with Previous $PuO_2$ Exchange Studies*

Prior to this work, the only peer-reviewed manuscript that presented rate constants for the oxygen exchange reaction on $PuO_2$ was published in 1972 by Deaton and Wiedenheft [7]. Unfortunately, the authors observed that their data were very complex. As a result, they were not able to obtain any activation energies and the mechanistic information was minimal. Using the results obtained from the work presented here and in previous $CeO_2$ surrogate studies [8,9], it is possible to provide explanations for the complexities observed by Deaton and Wiedenheft. This allows for a reanalysis of the previous $PuO_2$ data, which will produce results that corroborate the data and conclusions presented here.

### *5.3.1 Evaluation of the Internal Chemical Reaction*

Table 2 presents the data published by Deaton and Wiedenheft on their oxalate precipitated $PuO_2$ particles [7]. One important feature to note from this table is that all of the samples were thermally pretreated (i.e., sintered) at different temperatures. Since $PuO_2$ is expected to undergo sintering behavior above ~1200 $^{o}$C (i.e., one-half the melting point), it is anticipated that the different thermal pretreatments presented in Table 2 will cause drastically different particle size, grain size, and SSA. Despite these anticipated changes, $PuO_2$ results from two oxalate precipitated samples that were exchanged at 1000 $^{o}$C and sintered at either 1000 or 1550 $^{o}$C produced rate constants that were similar, suggesting that the rate limiting step being observed in these two experiments is independent of particle size, grain size, and SSA. Rates that are independent of these material properties are indicative of the internal chemical reaction (cf. Section 2.3).

While this contradicts the surface mechanism conclusion published by Deaton and Wiedenheft, their conclusions were understandable when placed within the right context. A surface-based mechanism was the prevailing theory at the time for high-temperature oxygen exchange rates on metal oxides [10-12]. It would have been hard for Deaton and Wiedenheft to draw strong conclusions from

the two non-replicated data points presented in their report because they would have contradicted the very large, and well-respected, body of work. In this context, concluding that the rate was limited by a surface mechanism is understandable. However, with the additional knowledge gained from both this report and the recent $CeO_2$ surrogate studies [8,9], it is possible to conclude that their rate was actually limited by the internal chemical reaction.

**Table 2.** Rate Constants for the $PuO_2$ Oxygen Exchange Reaction from Ref [7]

| Exchange T ($^oC$) | Sintering T ($^oC$) | Oxalate k ($min^{-1}$) | Hydroxide k ($min^{-1}$) |
|---|---|---|---|
| 1550 | 1550 | 0.858 | |
| 1300 | 1300 | 0.663 | |
| 1000 | 1550 | 0.362 | |
| 1000 | 1000 | 0.307 | |
| 700 | 700 | 0.277 | |
| 1550 | 1550 | | 0.225 |
| 1550 | 1550 | | 0.251[a] |
| 1550 | 1550 | | 0.264[b] |
| 1550 | 1550 | | 0.355[c] |

[a] New precipitation of $PuO_2$
[b] Sintered an additional 6 hours
[c] Particle fines

Deaton and Wiedenheft were hesitant to calculate an $E_a$ from their oxalate experiments because of the potential complexities that could be present due to the different sintering temperatures [7]. Fortunately the internal chemical reaction has been shown to be independent of the changes caused by sintering temperature, allowing a calculation of the $E_a$ to be made from the historical $PuO_2$ data. Figure 3 shows that a linear trendline is obtained between 700 and 1550 $^oC$, which suggests that the exchange rate is being dominated by a single mechanism over this temperature range. The slope of this trendline corresponds to $E_a = 20.6 \pm 5.5$ kJ $mol^{-1}$, which is statistically similar ($P < 0.05$) to the $E_a = 17.9 \pm 0.9$ kJ $mol^{-1}$ obtained in this work. This statistical similarity in $E_a$ supports the conclusion that the exchange rates observed previously were dominated by the internal chemical reaction. It also helps confirm the

accuracy of these $E_a$ values by showing that the value presented here was independently reproduced elsewhere.

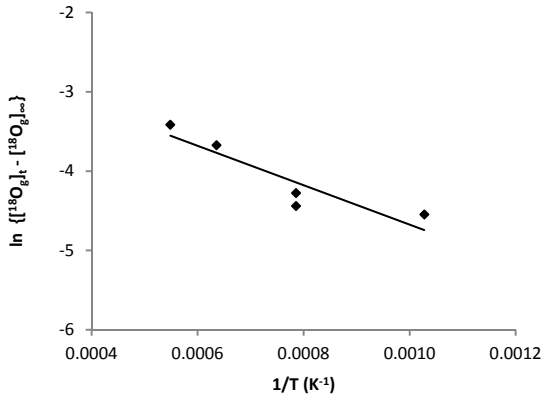


**Figure 3.** Arrhenius plot of the exchange rates reported in Ref. [7] for $PuO_2$ synthesized from an oxalate precipitate.

### *5.3.2 Evidence of the Surface Mobility and Surface Exchange Mechanisms*

Data presented by Deaton and Wiedenheft for their hydroxide precipitated particles are considerably more complex than their oxalate precipitated particles. This is most likely due to the hydroxide precipitation process producing particles that are much larger. For reference, the hydroxide process produced particles that were 125–297 μm, whereas the oxalate process produced particles that were ~1 μm [7]. Table 2 shows that when the hydroxide precipitated particles were sintered and exchanged at 1550 $^{o}$C, it was possible to obtain exchange rates that were relatively constant. Interestingly, when the significantly smaller hydroxide fines (i.e., 10–125 μm) were analyzed, the exchange rate was significantly faster. Photomicrographs of the hydroxide precipitated particles indicate that the SSA of these particles is directly tied to their size, so the hydroxide fines have a significantly larger SSA [7]. Since the exchange rates on these hydroxide particles show a significant dependence on SSA, it is possible to deduce that the rate is limited by surface based mechanism, such as surface mobility or surface exchange.

Deaton and Wiedenheft also noted that when the exchange temperature was $\leq$ 1300 $^{o}$C, the hydroxide particles produced a rate that was influenced by two different mechanisms, which they attributed to a transition from a surface exchange-based mechanism to lattice diffusion [7]. While this was a good conclusion based on the understanding of the oxygen exchange process at that time, exchange data on the $CeO_2$ surrogate appear to indicate a different conclusion. $CeO_2$ exchange studies exhibited a large temperature range where the surface mobility and surface exchange rates were competitive [9]. Rate law plots generated from data obtained in this competitive regime produce results that are qualitatively similar to the $\leq$ 1300 $^{o}$C hydroxide results (compare Figure 4 from Ref. [7] to Figure 2 from Ref. [9]). Therefore, while there are no results that can specifically refute the diffusion-based conclusion made by Deaton and Wiedenheft, we find it more likely that the results indicate a region where the surface mobility and surface exchange are competitive.

### *5.4 Mechanisms of Oxygen Exchange on $PuO_2$*

Since $CeO_2$ appears to be a good qualitative surrogate for the oxygen exchange behavior of $PuO_2$, it is possible to correlate most of the current body of knowledge on $CeO_2$ to $PuO_2$ (cf. Section 2). Therefore, the internal chemical reaction on $PuO_2$ is expected to be the rate limiting step for the oxygen exchange reaction when both temperature and SSA are high. The exact mechanism governing the internal chemical reaction on $PuO_2$ is also most likely related to a reaction that permits, or activates, the diffusion of oxygen through the lattice, but is not actually a form of oxygen diffusion. Surface mobility rates on $PuO_2$ are most likely much faster than the rates observed on many other metal oxides, and the rate is most likely governed by a complex function of surface chemistry that includes at least surface basicity and surface vacancies. While it is tempting to make a comparison of the surface exchange mechanism, we hesitate to do so because the surface exchange rate and activation energy were not definitively measured in this report.

## 5 Conclusions

The behavior of the oxygen exchange reactions with $PuO_2$ is controlled, or influenced, by at least three different mechanisms: an internal chemical reaction, surface mobility, and surface exchange. The surface exchange and surface mobility mechanisms exhibit a dependence on SSA, while the internal chemical reaction is independent of particle properties. Determining which mechanism is dominant appears to be a complex function that includes at least temperature and SSA. Since the SSA of $PuO_2$ can be affected by thermal treatment, the oxygen exchange behavior of $PuO_2$ can be significantly influenced by thermal treatment and processing. This suggests that under some circumstances the exchange temperature could cause a change in the SSA to occur during the experiment, which could generate very confusing results. Fortunately, high-temperature thermal treatment appears to generate a relatively stable SSA, which can allow subsequent lower temperature oxygen exchange experiments to perform consistently.

When studying the oxygen exchange behavior of $PuO_2$, $CeO_2$ appears to be a good qualitative surrogate. This allows use of the much more extensive body of work on the oxygen exchange behavior of $CeO_2$ to help explain the behavior of $PuO_2$. Quantitatively, $PuO_2$ has a stronger metal-oxygen interaction, which may explain why the surface mobility and internal chemical reaction mechanisms have higher activation energies.

Results from this report allow a detailed reinterpretation of past $PuO_2$ oxygen exchange work based on new findings. This allowed several of the previous complexities observed in the oxygen exchange reaction to be explained and clarified. Qualitative behavior extracted from the previous oxygen exchange work and new activation energies obtained from the previous data on $PuO_2$ confirm the results presented here.

**Acknowledgments**

The University of Dayton Research Institute was funded by the U.S. Department of Energy under contract #: DE-NE0000422. Oak Ridge National Laboratory was funded by the U.S. Department of Energy under contract #: DE-AC0500OR22725. The authors would like to acknowledge Raymond Vedder from Oak Ridge National Laboratory for some technical assistance with performing the oxygen exchange experiments. Additional thanks goes to Dr. Michael Stoll and Lia Brodnax of Los Alamos National Laboratory for useful discussions regarding the impacts of this work to the $^{238}PuO_2$ heat source program.

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