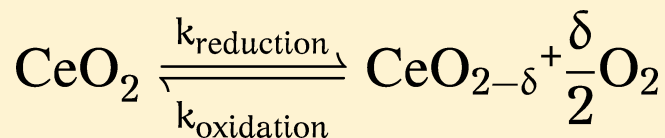


1 Analytical Model of CeO<sub>2</sub> Oxidation and Reduction

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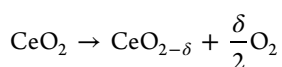
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4 **ABSTRACT:** In this work, an Arrhenius-based model for the  
5 high-temperature reduction and oxidation of CeO<sub>2</sub> is  
6 developed. The model is shown to agree well with both  
7 literature data for the equilibrium oxygen vacancy concen-  
8 tration and novel experimental kinetics of oxidation and  
9 reduction obtained by the authors. The form of the Arrhenius  
10 rate equation was determined from the properties of the reaction. Equilibrium data from the literature was analyzed with respect  
11 to our rate equation. From this analysis, a number of constraints on the model parameters were determined, and some of the  
12 constants of the model were fixed. The model accurately predicts the equilibrium composition of CeO<sub>2</sub> over a wide range of  
13 oxygen partial pressures (10<sup>-2</sup> to 10<sup>-8</sup> bar) and temperatures (1000–1900 °C). Novel results of the experimental reoxidation of  
14 ceria were analyzed to fix the remainder of the constants. Porous cerium dioxide pellets produced by the authors were reduced at  
15 high temperature (1650 °C) and low oxygen partial pressure (10<sup>-5</sup> bar). The reduced cerium pellets were then reoxidized in an  
16 oxygen atmosphere of 1.4 × 10<sup>-4</sup> bar at temperatures in the range 500–1000 °C. The reoxidation was conducted in a sealed  
17 vacuum chamber. The reaction was monitored via the change in pressure and gas composition measured by a manometer and  
18 mass spectrometer. The results from this reoxidation experiment allowed us to fix the values of the activation energies and  
19 frequency factors of the oxidation and reduction. The model was then compared with experimental reaction kinetics of thermal  
20 oxidation and reduction and showed good agreement.

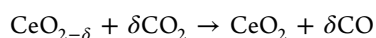
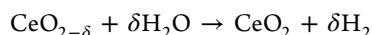


## 21 ■ INTRODUCTION

22 Cerium dioxide has found many applications due to its unique  
23 properties. At high temperatures, it is an oxide conductor and is  
24 also noted for its oxygen storage and redox properties.<sup>1–3</sup> This  
25 makes it a good material for applications in catalysis and solid  
26 oxide fuel cells.<sup>4–7</sup> Ceria has also been heavily investigated for  
27 its use in converting heat energy to fuels.<sup>8–13</sup> It can be  
28 thermally reduced at high temperatures, releasing oxygen.



29 The reduced ceria can then be used to split H<sub>2</sub>O or CO<sub>2</sub>.<sup>14–16</sup>



30 Together, these products form syn-gas, which can be  
31 converted into denser diesel-type fuel using the Fischer–  
32 Tropsch process.<sup>17</sup> This means there are many options for fuel  
33 conversion, with the possibility of producing hydrogen, syn-gas,  
34 or diesel-type fuels. The reaction can be driven using  
35 concentrated solar power as the heat input, making these  
36 fuels renewable.<sup>18–20</sup> A number of reactor designs for such fuel  
37 conversion have been proposed,<sup>21,22</sup> and some prototypes have  
38 been constructed.<sup>14,15,23</sup> Alternatively, these reactions could  
39 conceivably be driven by any high-temperature heat source,  
40 making this a very attractive energy conversion technology.

41 In the past, studies have been conducted into developing  
42 numerical models of the phase diagrams and composition of  
43 CeO<sub>2</sub> over a wide range of conditions.<sup>24–26</sup> These models,  
44 however, give us no information about the reaction kinetics of

the reduction and oxidation of ceria. It is interesting to note  
45 that ceria remains in the fluorite phase throughout the range of  
46 temperatures and pressures of interest for these fuel conversion  
47 cycles.<sup>13,24</sup> Even with large numbers of oxygen vacancies, the  
48 fluorite phase is still stable. The fact that no phase changes  
49 occur should allow the development of a reasonably simple  
50 model of the reactions.

51 The lack of such a simple analytical model for the reaction  
52 kinetics of ceria reduction makes the modeling of the  
53 performance of the above reactions difficult. If one has a  
54 simple model, which depends only on the concentrations of the  
55 reactants, the temperature, and the oxygen partial pressure,  
56 then it can easily be linked to heat flow and diffusion  
57 simulations.<sup>27</sup> This will greatly improve reactor design  
58 capabilities and allow for more accurate assessment of this  
59 proposed fuel production technology.

60 In this work, an analytical model for the reduction and  
61 oxidation of ceria in an oxygen atmosphere is developed. The  
62 model should predict both the equilibrium composition and  
63 reaction kinetics if it is to accurately simulate the performance  
64 of the reactions. It should prove to be an invaluable tool in the  
65 development of the discussed fuel production technology. It  
66 could also be of use in any cerium dioxide high-temperature  
67 redox processes. The model itself is of theoretical interest as it  
68 should allow for a better understanding of the role of diffusion  
69 and surface reactions in ceria reduction and oxidation.

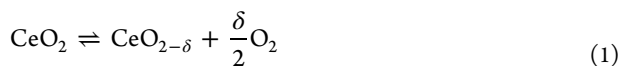
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## 71 ■ MODEL

72 The model is based on the Arrhenius equation. Because it is an  
73 equilibrium reaction, both reduction and oxidation reactions are  
74 taking place at any given time.



76 The reaction does not proceed to complete decomposition in  
77 this regime. If enough oxygen is removed, then the fluorite  
78 phase will no longer be stable and a phase transition will be  
79 inevitable. If there is a phase change, then the fundamental  
80 properties of the reaction kinetics will change and our equation  
81 will no longer be valid. Therefore, it is assumed that not all of  
82 the oxygen can be removed by this reaction and that it is  
83 proceeding toward a certain maximum value of  $\delta$ , say  $x$ .



85 The reduction reaction depends on the concentration of  
86 removable oxygen, and the oxidation reaction depends on the  
87 concentration of vacancies and the concentration of oxygen gas.  
88 Initially, oxygen diffusion in the bulk shall be ignored, and the  
89 vacancy concentration is assumed to be constant throughout.  
90 The rate of change of the oxygen vacancy concentration is the  
91 rate at which oxygen leaves  $\text{CeO}_2$  (reduction) minus the rate at  
92 which it recombines (oxidation).

$$93 \quad \frac{d[\text{O}_{\text{vac}}]}{dt} = [\text{O}_{\text{Ce}}]k_{\text{red}} - [\text{O}_{\text{vac}}][\text{O}_{\text{gas}}]^n k_{\text{ox}} \quad (3)$$

94 Here  $k_{\text{red}}$  and  $k_{\text{ox}}$  are the rate constants of reduction and  
95 oxidation, respectively. These rate constants take the Arrhenius  
96 form.<sup>28</sup>

$$97 \quad k_a = A_a \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

98 The concentration terms can be made unitless by dividing eq  
99 3 by the concentration of cerium  $[\text{Ce}]$ , which is a constant.

$$100 \quad \frac{1}{[\text{Ce}]} \frac{d[\text{O}_{\text{vac}}]}{dt} = \frac{[\text{O}_{\text{Ce}}]}{[\text{Ce}]} k_{\text{red}} - \frac{[\text{O}_{\text{vac}}]}{[\text{Ce}]} [\text{O}_{\text{gas}}]^n k_{\text{ox}} \quad (5)$$

101 The rate is now in terms of moles of oxygen vacancies per  
102 mole of cerium per second or simply per second. From eqs 1  
103 and 2, the values  $[\text{O}_{\text{Ce}}]/[\text{Ce}]$  and  $[\text{O}_{\text{vac}}]/[\text{Ce}]$ , which are both  
104 unitless, can be defined in terms of the stoichiometry  
105 parameters  $\delta$  and  $x$ .

$$106 \quad \frac{[\text{O}_{\text{Ce}}]}{[\text{Ce}]} = x - \delta \quad (6)$$

$$107 \quad \frac{[\text{O}_{\text{vac}}]}{[\text{Ce}]} = \delta \quad (7)$$

108 The oxygen gas concentration is directly proportional to the  
109 oxygen partial pressure  $P_{\text{O}_2}$ . Therefore, the constant of  
110 proportionality can simply be included as part of the rate  
111 constant  $k_{\text{ox}}$  and the oxygen gas concentration is taken to be  
112 the oxygen partial pressure. Initially, we wish to look at  
113 equilibrium data, so we set the rate to zero. Setting eq 5 equal  
114 to zero and using eqs 4, 6, and 7, we get an equilibrium  
115 condition.

$$(x - \delta)A_{\text{red}} \exp\left(\frac{-E_{\text{red}}}{RT}\right) - \delta P_{\text{O}_2}^n A_{\text{ox}} \exp\left(\frac{-E_{\text{ox}}}{RT}\right) = 0 \quad (8) \quad 116$$

At equilibrium, the rate of oxidation is equal to the rate of  
117 reduction. We can now express our equilibrium oxygen vacancy  
118 concentration as a function of temperature and oxygen partial  
119 pressure. 120

$$\left(\frac{\delta}{x - \delta}\right) = \frac{A_{\text{red}} P_{\text{O}_2}^{-n}}{A_{\text{ox}}} \exp\left(\frac{-(E_{\text{red}} - E_{\text{ox}})}{RT}\right) \quad (9) \quad 121$$

The difference in activation energies  $E_{\text{red}} - E_{\text{ox}}$  shall be  
122 labeled throughout the remainder of the manuscript as  $\Delta E$ . 123

**Equilibrium Composition.** It is common in the literature  
124 for equilibrium data obtained at constant temperature and  
125 varied pressure to plot  $\log(\delta)$  versus  $\log(P_{\text{O}_2})$ . If the logarithm  
126 of eq 9 is taken, it is clear that a more suitable plot can be made. 127

$$\log\left(\frac{\delta}{x - \delta}\right) = -n \log(P_{\text{O}_2}) + \log\left(\frac{A_{\text{red}}}{A_{\text{ox}}} \exp\left(\frac{-\Delta E}{RT}\right)\right) \quad (10) \quad 128$$

From eq 10, it is clear that a plot of  $\log(\delta)$  versus  $\log(P_{\text{O}_2})$   
129 will yield a straight line with slope  $-n$  but only when  $\delta \ll x$ .  
Supporting this, both Panlener and Dawicke<sup>29,30</sup> found that in  
131 the region  $0.001 < \delta < 0.004$  this plot yields a straight line, and  
132 the pressure dependence was well-characterized by the relation  
133  $\delta \propto P_{\text{O}_2}^{-1/5}$ . 134

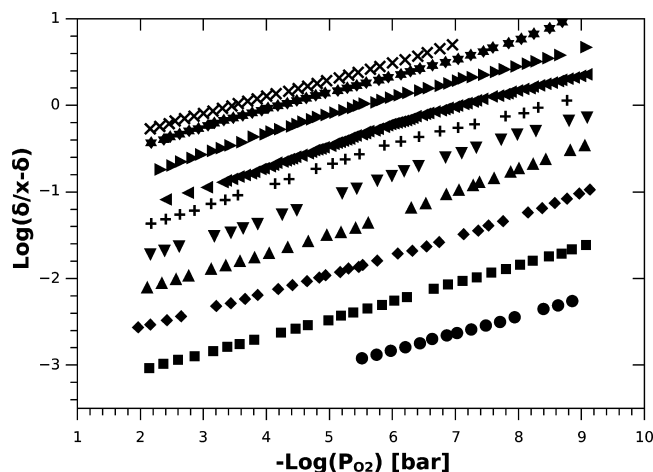
Because we are not dealing with a dilute species reaction, it  
135 may not be possible to use the law of mass action to accurately  
136 find  $x$  and  $n$ . It can, however, provide a good starting point.  
137 From eq 2, the law of mass action predicts that  $n = x/2$ . Using  
138 the findings of Panlener et al., as an estimate of  $n = 0.2$ , a good  
139 starting point would be to set  $x = 0.4$ . Using these parameters,  
140 experimental equilibrium data can be analyzed. Data in the  
141 range 1000–1500 °C were extracted from the experimental  
142 work of Panlener et al.<sup>29</sup> For temperatures above this, the  
143 numerical model of Zinkevich et al.<sup>24</sup> was used, which is in  
144 good agreement with experimental findings.<sup>29–33</sup> We look at  
145 pressures in the range of  $10^{-2}$  to  $10^{-9}$  bar. 146

The analysis of data from the literature is presented in Figure  
147 1, with the parameter  $x = 0.35$ . For constant temperature, the  
148 data show linear dependencies over a wide range of pressures.  
149 This is in contrast with the plots made previously of  $\log(\delta)$   
150 versus  $\log(P_{\text{O}_2})$ ,<sup>29</sup> where the data begin to deviate from the  
151 linear dependence as  $\delta$  increases and drastically so for values of  
152  $\delta$  greater than 0.1. This is as predicted by eq 8, providing strong  
153 evidence in support of our analytical model. 154

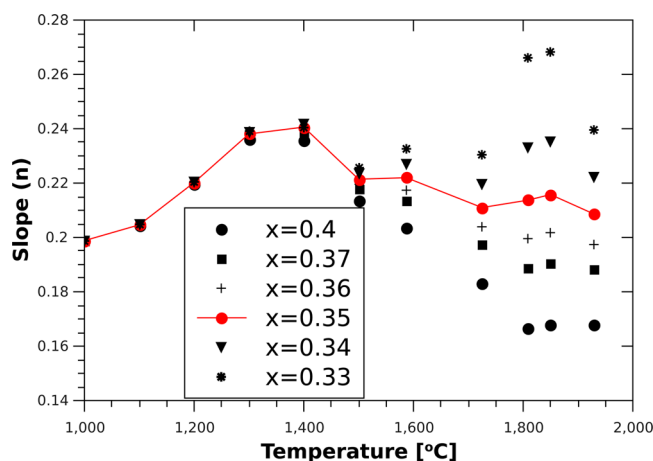
To determine the best value of  $x$ , we plotted the data for a  
155 range of different values of  $x$ . The plots were then fit linearly,  
156 and the variation in slope and the  $R^2$  regression value of each  
157 set of data was compared. 158

The dependency of slope on the temperature is plotted in  
159 Figure 2. For simplicity, we want the value of  $n$  to be constant.  
160 The best choice of  $x$  would therefore be that which gives the  
161 least variation in slope. Comparing the statistics of the range of  
162 slopes obtained for each value of  $x$ , the value of  $x$  that gives the  
163 lowest standard deviation is  $x = 0.35$ . Taking the average of  
164 these slopes to be  $n$  and the standard deviation to be the error,  
165 we get  $n = 0.218 \pm 0.013$ . 166

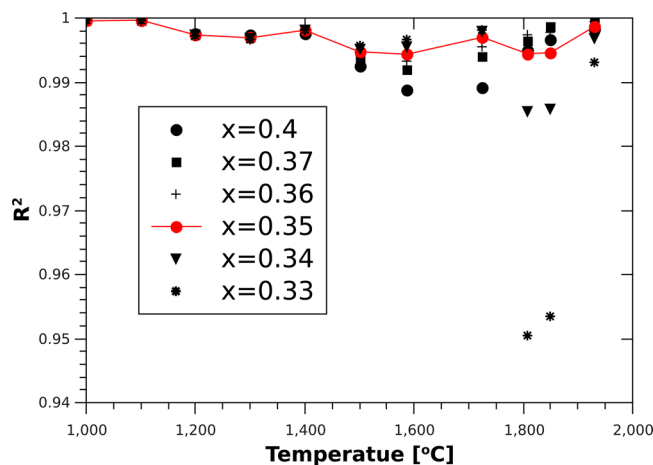
To evaluate each linear fit, the variance in the  $R^2$  regression  
167 value was plotted against temperature. From Figure 3, we can  
168 see that for  $x = 0.33$  the  $R^2$  regression value drops below 0.96 at  
169



**Figure 1.** Isothermal plots of  $\log(\delta/(x - \delta))$  versus  $-\log(P_{O_2})$  with the value of  $x$  set to 0.35. The temperatures plotted are from bottom to top 1000, 1100, 1200, 1300, 1400, 1500, 1587, 1725, 1850, and 1930 °C. The data are taken from Panlener et al.<sup>29</sup> and Zinkevich et al.<sup>24</sup>



**Figure 2.** Slope obtained from a linear fit of  $\log(\delta/(x - \delta))$  versus  $-\log(P_{O_2})$  plotted against temperature for six different values of the parameter  $x$ .



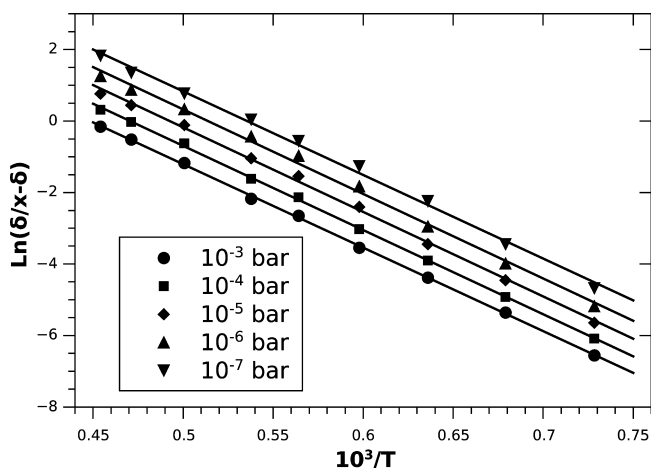
**Figure 3.**  $R^2$  value obtained from a linear fit of  $\log(\delta/(x - \delta))$  versus  $-\log(P_{O_2})$  plotted against temperature for five different values of the parameter  $x$ .

high temperatures. The rest of the values of  $x$  give good linear fits over the range investigated, with  $x = 0.35$  to 0.36 having the best average values, both around  $R^2 = 0.997$ . The value  $x = 0.35$  gave the most consistent slope and is the best fit of the published equilibrium data.

The best fit value of  $x = 0.35$  can now be applied to further analyze the equilibrium data. Taking the natural logarithm of eq 9 allows us to easily extract the difference in activation energies  $\Delta E$ .

$$\ln\left(\frac{\delta}{x - \delta}\right) = \frac{-\Delta E}{RT} + \ln\left(P_{O_2}^n \frac{A_{red}}{A_{ox}}\right) \quad (11)$$

Each set of data plotted in Figure 4 was fit linearly. Taking the average value calculated from the slopes as the activation energy and the standard deviation as the error, we get  $\Delta E = 195.6 \pm 1.2 \text{ kJ mol}^{-1}$ .



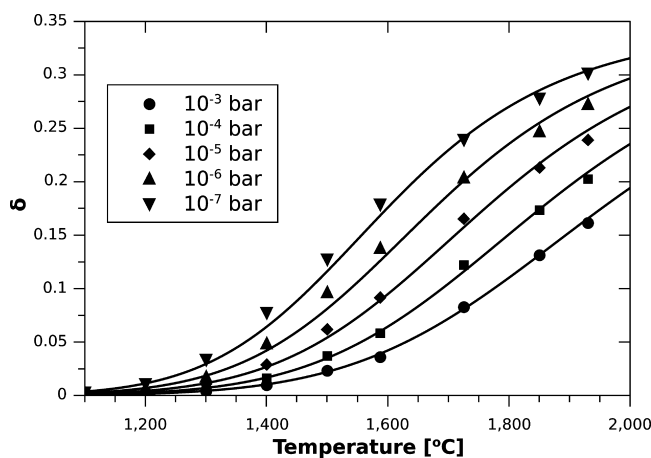
**Figure 4.** A graph of  $\ln(\delta/(x - \delta))$  versus  $10^3/T$  for a range of different pressures. The data are again taken from Panlener et al.<sup>29</sup> and Zinkevich et al.<sup>24</sup> The data were fit linearly, and from the slope of each line we can calculate the difference in activation energies  $\Delta E$ .

We can now use our values of  $x$ ,  $n$ , and  $E$  to get information from the intercepts of Figures 1 and 4. This will allow us to determine the ratio between the frequency factors  $A_{red}/A_{ox}$ . Taking the average of all of the values determined from the linear fit intercepts of Figures 1 and 4 and taking the standard deviation as the error, we get  $A_{red}/A_{ox} = 8700 \pm 800 \text{ bar}^n$ . The units of  $\text{bar}^n$  are from our choice to absorb the constant of proportionality between the oxygen partial pressure and the oxygen gas concentration into  $A_{ox}$ .

$$\left(\frac{\delta}{0.35 - \delta}\right) = 8700 \times P_{O_2}^{-0.217} \exp\left(\frac{-195.6 \text{ kJ mol}^{-1}}{RT}\right) \quad (12)$$

Substituting the above values into eq 9 yields eq 12, which depends only on the oxygen partial pressure and temperature. In Figure 5, we plot the results of the fits along with the original data from Figure 4 on a linear scale. As can be seen, the results of the fit match the original data quite well on a linear scale.

**Reaction Kinetics.** For oxygen to leave  $\text{CeO}_2$ , it must first diffuse to the surface. This diffusion process may conversely be considered as the diffusion of oxygen vacancies. For simplicity, we will consider spherical particles. This means we can use the



**Figure 5.** Plot of the vacancy concentration  $\delta$  versus temperature. The points are the same as Figure 4, plotted with the results of fitting the analytical model to the same data.

203 spherically symmetric diffusion equation, where the solution  
204 depends only on the radial position.

$$\frac{\partial C(T, t, r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} D(C, T) r^2 \frac{\partial C(T, t, r)}{\partial r} \quad (13)$$

206 The boundary condition at the surface of a spherical particle  
207 of radius  $R$  can now be set as our reaction rate formula shown  
208 in eqs 5 and 8. As before, the units could be simplified by  
209 dividing each concentration by the concentration of cerium.

$$\frac{\partial C_R}{\partial t} = (C_m - C_R) A_{\text{red}} \exp\left(\frac{-E_{\text{red}}}{RT}\right) - C_R P_{\text{O}_2}^n A_{\text{ox}} \exp\left(\frac{-E_{\text{ox}}}{RT}\right) \quad (14)$$

211 If we know our diffusion coefficient,  $D$ , and our particle  
212 radius,  $R$ , the problem is a simple partial differential equation in  
213 one spatial dimension. The diffusion coefficient for  $\text{CeO}_2$  can  
214 generally be well-described with an Arrhenius dependence on  
215 temperature.<sup>34,35</sup>

$$D(T) = D_0 \exp\left(\frac{-E_d}{RT}\right) \quad (15)$$

217 As we deviate from stoichiometry and the concentration of  
218 oxygen vacancies increases, the diffusion coefficient will also  
219 increase. Therefore, our complete diffusion coefficient is a  
220 function of both temperature and oxygen vacancy concentra-  
221 tion.<sup>36</sup>

$$D(C, T) = D_0(C) \exp\left(\frac{-E_d(C)}{RT}\right) \quad (16)$$

223 In the temperature range 900–1100 °C and for vacancy  
224 concentrations  $\delta$  in the range 0 to 0.2, Stan et al.<sup>37</sup> found that  
225 both  $D_0(C)$  and the diffusion activation energy  $E_d(C)$  were  
226 well-described by a linear dependence on  $C$ . The temperature  
227 range, however, is too narrow for use in this work. Here we are  
228 dealing with a wide range of temperatures and oxygen partial  
229 pressures, and so a full analytical solution of the diffusion  
230 problem is impractical. We will later simplify the effect of  
231 diffusion by assuming a shrinking core model.

232 To complete the rate equation, the values of  $E_{\text{red}}$  and  $A_{\text{red}}$  or  
233  $E_{\text{ox}}$  and  $A_{\text{ox}}$  need to be determined. During the reduction of

ceria at high temperature, the kinetics are determined by the  
balance between both the oxidation and reduction terms in our  
equation. There are sources that suggest activation energies for  
the reduction reaction,<sup>38–40</sup> although the values vary from  
101.2<sup>39</sup> to 221 kJ mol<sup>-1</sup>.<sup>38</sup> It is also difficult to determine  
exactly what activation energy they have extracted from the data  
due to the combination of oxidation and reduction.

241 Instead, consider the oxidation of oxygen-deficient ceria at  
242 moderate temperatures. At relatively moderate temperatures  
(500–1000 °C), the reduction term should be very small  
relative to the oxidation term due to its much larger activation  
energy ( $E_{\text{red}} - E_{\text{ox}} \approx 196$  kJ mol<sup>-1</sup>). So, at moderate  
temperatures, we can treat the reaction kinetics for a reduced  
sample as only the oxidation term in eq 5, resulting in eq 17.

$$\frac{d\delta}{dt} = -\delta P_{\text{O}_2}^n A_{\text{ox}} \exp\left(\frac{-E_{\text{ox}}}{RT}\right) \quad (17)$$

By examining this reaction, it should be possible to  
determine the remainder of the unknown constants in the  
rate equation.

## EXPERIMENTAL PROCEDURE

In our experiments, we aim to investigate both the backward  
and forward reactions of the equilibrium reaction shown in eq  
1. In other words, when displaced from equilibrium in either  
direction, how quickly does the system return to equilibrium?  
Most importantly, we first wish to investigate the reoxidation  
of cerium because, according to eq 17, this should allow us to  
extract  $E_{\text{ox}}$  and  $A_{\text{ox}}$ .

An apparatus was built by the authors, which allows oxides to  
be heated to high temperatures in a controlled atmosphere. The  
apparatus consists of a vacuum chamber in which the sample is  
placed and a focused Xenon lamp for rapidly heating the  
sample to reaction temperatures. The Xenon lamp uses an  
elliptical mirror to focus 100 W of broadband power into a focal  
point <8 mm in diameter. This allows temperatures up to 1650  
°C to be achieved.

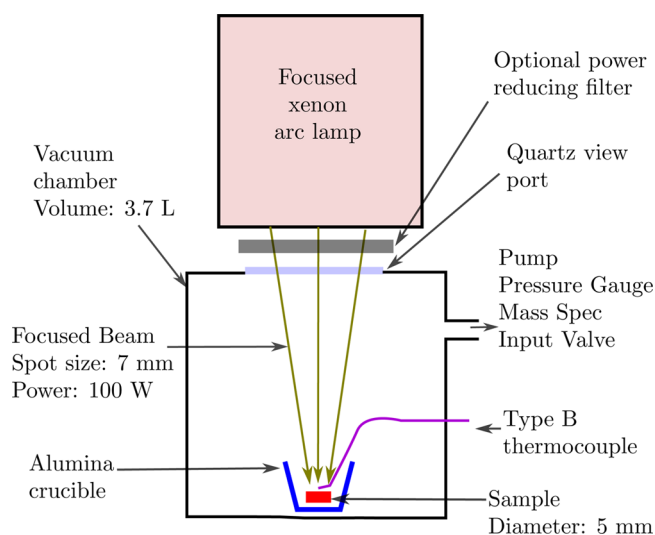
Changes in pressure are measured using a capacitance  
manometer, and the gas composition is monitored using a mass  
spectrometer. Oxygen released from the sample is observed by  
an increase in pressure and an increase in the oxygen signal  
measured by the mass spectrometer. Conversely, oxygen  
absorbed by the sample is accompanied by a drop in pressure  
and a drop in the oxygen signal.

Figure 6 shows a schematic of our apparatus. The type-B  
thermocouple is placed on top of the sample, and the Xenon  
lamp is focused onto the sample and thermocouple. The  
sample holder is an alumina crucible surrounded by another  
layer of alumina to protect the steel chamber from the high  
temperatures.

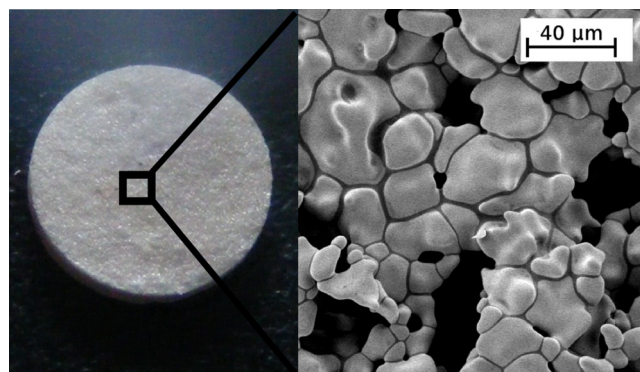
A reduction cycle is started by pumping the chamber down  
to 10<sup>-5</sup> bar and then sealing the chamber off from the pump.  
The lamp is then switched on to heat the sample to high  
temperatures. The changes in sample temperature, gas  
temperature, pressure, and gas composition are recorded.

A reoxidation cycle is conducted by first pumping the  
chamber down to 10<sup>-5</sup> bar; the chamber is then backfilled with  
oxygen to a pressure of  $P_{\text{O}_2} = 1.4 \times 10^{-4}$  bar. This pressure was  
selected to give us a measurable reaction rate at the  
temperatures used for reoxidation (500–1000°C). The sample  
is then heated using the Xenon lamp with the input power





**Figure 6.** Apparatus showing the vacuum chamber, Xenon lamp, sample, thermocouple, and connected instruments.

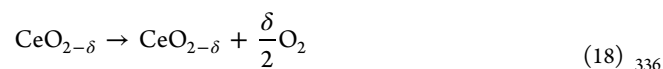


**Figure 7.** Image of a sample with an image taken using a scanning electron microscope showing its porosity.

## EXPERIMENTAL RESULTS

333

As previously described, we will first look at the reoxidation of reduced cerium to determine our constants for eq 16.

334  
335

Typically in these oxidation experiments, the total amount of oxygen absorbed was in the range of  $\delta = 0.06$  to  $0.07$ . Again here,  $\delta$  is a dimensionless number of moles of vacancies per moles of cerium. The variance was thought to come from the reduction step carried out prior to the start of the experiment, and the samples were assumed to be fully reoxidized at the end of the experiment. This is an approximation, as there will still be a number of vacancies present because the reaction has reached equilibrium; however, the concentration of vacancies can be assumed to be small.

The volume of the chamber, changes in pressure, and gas temperature are all known. Therefore, using the formula  $\Delta PV = \Delta nRT$ , the number of moles of oxygen that have been absorbed by the sample can be calculated. For the initial phase of the reaction, the rate-determining feature is the reaction at the surface and not the diffusion through the bulk. Additionally, to make an Arrhenius plot, a varying temperature is needed that happens during the initial stage of the reaction. For this, it is convenient to study the reaction in the region of 0–40% completion, before the temperature starts leveling off. Equation 17 can be rearranged to get a suitable plot for extracting the activation energy  $E_{\text{ox}}$  and frequency factor  $A_{\text{ox}}$ .

$$\ln\left(-\frac{d\delta}{dt}\right) - \ln(\delta P_{\text{O}_2}^n) = \frac{-E_{\text{ox}}}{RT} + \ln(A_{\text{ox}}) \quad (19)$$

This can be thought of as an Arrhenius plot of  $\ln(k)$  versus  $10^3/T$ . The values of  $\delta$  and  $P_{\text{O}_2}$  are calculated from the data obtained from the pressure manometer and mass spectrometer. A number of cycles were conducted. All cycles started at room temperature similar to that shown in Figure 8. The cycles were run for a range of different input powers, with the final temperatures reached in the range 500–1000 °C. We assume that in this range the reaction kinetics are still of the type discussed and should be well-described by eq 19.

The data were analyzed with a regression fit as seen in Figure 9, and the 95% confidence interval was taken as the error in the slope and the intercept. The oxidation activation energy was calculated to be  $E_{\text{ox}} = 36 \pm 4 \text{ kJ mol}^{-1}$ , and the intercept was found to be  $\ln(A_{\text{ox}}) = 4.4 \pm 0.5$ . This intercept value gives the frequency factor  $A_{\text{ox}} = 82 \pm 41 \text{ s}^{-1} \text{ bar}^{-n}$ . This value should

292 reduced by a filter. The changes in temperature, pressure, and  
293 gas composition are again recorded.

294 The background pressure increase due to heating of the  
295 chamber without a sample present was taken into account. In  
296 the case of the reoxidation cycles, the power incident into the  
297 chamber is relatively moderate and the increase in pressure is  
298 negligible.

299 One issue identified with the system is that for the high-  
300 temperature reduction cycles the oxygen given off was seen to  
301 take part in other reactions as the cycle proceeds. This was  
302 observed as a decrease in the oxygen signal from the mass  
303 spectrometer and an increase in the carbon dioxide signal. No  
304 such competing reactions were observed in the reoxidation  
305 cycles. We believe that the high power incident into our  
306 chamber during the reduction cycles is causing reactions with  
307 the chamber walls. For this reason, our system is less accurate  
308 in measuring reduction than oxidation. This is not a big  
309 problem because the main experimental focus is on reoxidation,  
310 and reduction experiments will be used only for comparison  
311 with the model.

312 The samples used are porous pellets of  $\text{CeO}_2$ . They were  
313 prepared by mixing  $\text{CeO}_2$  powder (Sigma-Aldrich: 544841)  
314 with a grain size  $<25 \text{ nm}$  and graphite powder (Sigma-Aldrich:  
315 282863) with a grain size  $<20 \mu\text{m}$ . They were mixed in a  
316 volumetric ratio of three parts graphite to one part ceria. The  
317 powders were thoroughly mixed by placing them in a beaker  
318 and vibrating them in a sonic bath for 15 min. Additionally,  
319 polished ball bearings were placed in the beaker to accelerate  
320 mixing. The mixed powder was then pressed into pellets using a  
321 pellet die and a hydraulic press. The pellets are then annealed at  
322 1000 °C for 3 h to remove the graphite. This was followed by  
323 24 h of annealing at 1500 °C to induce sintering. The sintered  
324 pellets are on average 4.5 mm in diameter and 1 mm in height.  
325 The porosity was calculated by measuring the mass and volume  
326 of the samples to be in the range 60–65% void space, and their  
327 masses were in the range of 28–30 mg (Figure 7).

328 The arc lamp focuses the light into a spot  $\sim 7 \text{ mm}$  in  
329 diameter; therefore, the entire sample fits into the focal point.  
330 For this reason, we believe that the temperature gradients  
331 throughout the sample will be small, and in the analysis, it is  
332 assumed that the sample temperature was uniform.

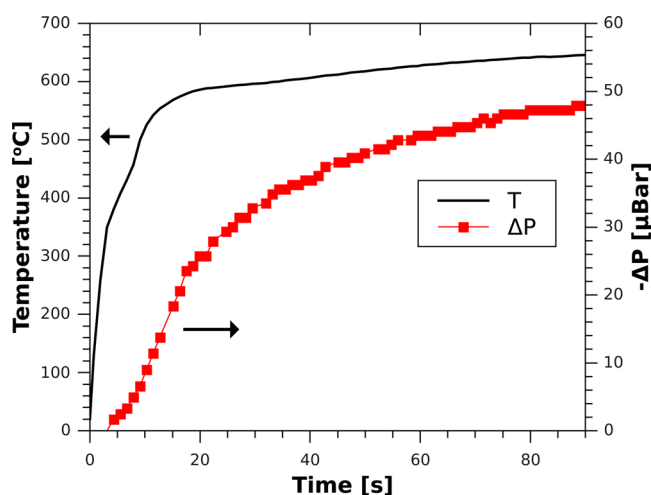


Figure 8. Graph showing sample temperature and the drop in pressure for the reoxidation of a Ceria pellet.

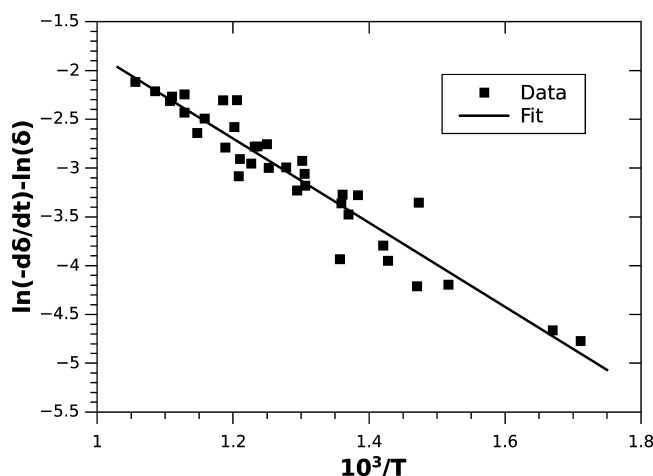


Figure 9. Plot of  $\ln(k)$  versus  $10^3/T$ . These points are from several different scans with the final temperatures reached in the range 500–1000 °C.

depend on the surface to volume ratio. The value of surface-to-volume ratio will change due to sintering during the reduction, so the low precision for the value  $A_{\text{ox}}$  is not surprising. However, the ratio between the frequency factors  $A_{\text{red}}/A_{\text{ox}}$  is a characteristic property of the material and was determined with greater precision.

$E_{\text{red}}$  and  $A_{\text{red}}$  can now be calculated using our values for  $E_{\text{ox}}$ ,  $A_{\text{ox}}$ , and the results from the analysis of equilibrium data for  $\Delta E$  and  $A_{\text{red}}/A_{\text{ox}}$ . In summary, we have the following equation with the values given in Table 1.

$$\frac{d\delta}{dt} = (x - \delta)A_{\text{red}} \exp\left(\frac{-E_{\text{red}}}{RT}\right) - \delta P_{\text{O}_2}^n A_{\text{ox}} \exp\left(\frac{-E_{\text{ox}}}{RT}\right) \quad (20)$$

The oxygen partial pressure is in bar; if another unit is used, the value of  $A_{\text{ox}}$  must be changed accordingly. Remember, the rate equation has been divided by the concentration of cerium to make the concentration terms unitless. Therefore, this rate must be multiplied by the concentration of cerium to get the absolute rate of reaction. The oxidation term in the ranges of temperature, oxygen partial pressure, and vacancy concentration considered in our reoxidation experiment can now be

Table 1. Constants in Equation 20

$x$	0.35
$n$	$0.218 \pm 0.0013$
$\Delta E$	$195.6 \pm 1.2 \text{ kJ mol}^{-1}$
$E_{\text{red}}$	$232 \pm 5 \text{ kJ mol}^{-1}$
$E_{\text{ox}}$	$36 \pm 4 \text{ kJ mol}^{-1}$
$A_{\text{red}}/A_{\text{ox}}$	$8700 \pm 800 \text{ bar}^n$
$A_{\text{red}}$	$720\,000 \pm 360\,000 \text{ s}^{-1}$
$A_{\text{ox}}$	$82 \pm 41 \text{ s}^{-1} \text{ bar}^{-n}$

calculated to be at least four orders of magnitude greater than the reduction term in our rate equation.

**Model versus Experiment.** To test the model, we can compare our reoxidation reactions to ones predicted by the model. The temperatures recorded by the thermocouple were used in a numerical model of the rate. The oxygen partial pressure is set to be the same as the initial value and is reduced proportionally as the reaction proceeds. To account for diffusion in the later stages of the reaction, a shrinking particle model is used. In particular, the case of a small particle in which the surface reaction is the rate-determining step is employed. This assumes that there is a shrinking sphere of vacancies and introduces a restriction on our rate as we proceed.

$$\frac{d\delta}{dt} = \text{rate} \times (1 - \alpha)^{1/3} \quad (21)$$

where rate in eq 21 corresponds to the rate given in eq 20. The fraction-completed  $\alpha$  is the amount of absorbed oxygen divided by the total final absorbed oxygen. This is a simplification of the effect of diffusion; for a full analytical solution, one must solve eqs 13 and 14 on a suitable sized sphere. It is assumed that the reoxidation proceeds to the final fully oxidized state with  $\delta = 0$ . From Figure 10, it can be seen that the experimental results agree well with the model. If the diffusion term is omitted after

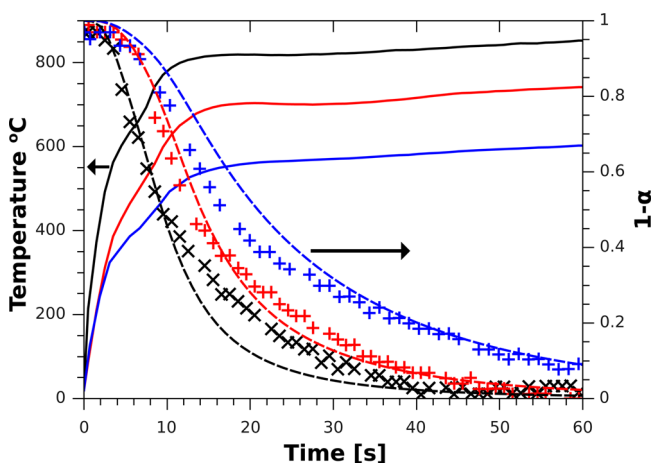
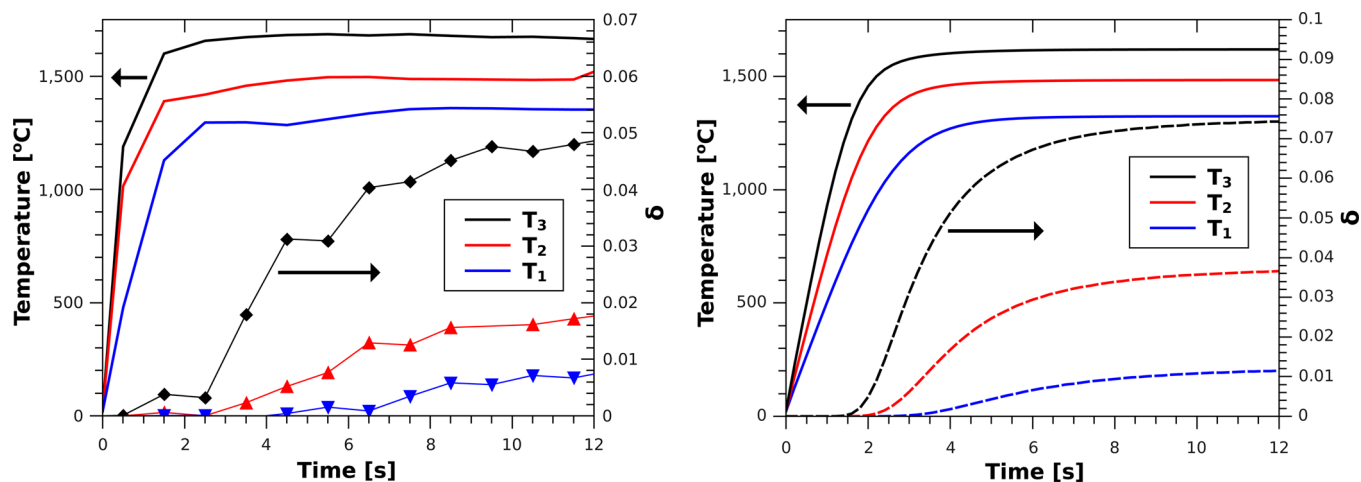


Figure 10. Experimental temperature and the corresponding fraction of remaining oxygen vacancies for three different input powers. The solid lines are the temperature, the crosses are the experimental fraction of remaining oxygen vacancies, and the dashed lines are those predicted by eq 21

the initial stages of the reaction, then the model predicts faster oxidation than was experimentally observed.

The rate of the reduction reaction of  $\text{CeO}_2$  can also be compared with the model. Again, eq 21 is used to model the reaction. In the experiment, the parameters are measured once



**Figure 11.** Left: Experimental temperature and the corresponding measured  $\delta$  for three different input powers. Right: A numerical model with similar temperature curves and the corresponding numerical rates predicted.

every second; however, the reduction reaction proceeds very rapidly, and so our temperature curves have low resolution. For this reason, analytical curves of radiative heating, which are very similar to the ones seen in the experiment, were used in the numerical model. In this case, the value  $\alpha$  is more difficult to determine. As the temperature and oxygen pressure change, so does the equilibrium  $\delta$  (Figure 11). The fraction-completed  $\alpha$  can be defined as the instantaneous value of  $\delta$  divided by the equilibrium value, so to determine  $\alpha$ , we must recalculate both the equilibrium  $\delta$  and the actual  $\delta$  in each iteration of the numerical model. Again, as the reaction proceeds, the oxygen partial pressure in the model increases accordingly, just as it would in the experiment.

The rate curves observed in the experiment have very similar shapes to those predicted by our model. The model predicts a somewhat faster reaction, which could be attributed to the assumption that the entire pellet is uniformly heated. In reality, the bottom of the pellet is heated at a lower rate as the pellet is a porous ceramic, which has poor heat-transfer properties.<sup>27</sup> This will reduce the rate. The final value in the model is that of equilibrium, but in our experiment the final values were all roughly 30% lower than predicted by the model. This could be due to reactions with the chamber walls absorbing oxygen, as described in the experimental procedure. It could also be due to trapped unreacted oxide in our pellets.

## DISCUSSION

The discussed model of the kinetics of the high-temperature reduction and oxidation of cerium dioxide agrees well with the equilibrium and kinetic data presented in this work; however, the model kinetics remain to be tested over a wider range of temperatures and pressures.

**Theoretical Issues.** It should be noted that the activation energy for reduction found here of  $E_{\text{red}} = 232 \pm 5 \text{ kJmol}^{-1}$  is far lower than the overall change in enthalpy  $\Delta H \approx 480 \text{ kJmol}^{-1}$  for ceria reduction.<sup>29</sup> However, it is widely believed that producing an oxygen vacancy at the surface of ceria takes less energy than creating a vacancy in the bulk. The change in enthalpy is then broken up into two parts, the energy change required to produce a vacancy at the surface plus the energy change due to migration of this vacancy to the bulk. In the review by Sauer et al.,<sup>42</sup> a value of  $321 \text{ kJ mol}^{-1}$  is given in table 4 for oxygen vacancy formation at the surface.

These formation energies are still a good deal larger than the activation energy we have found. However, this formation of a surface vacancy could itself be a multi-step process. For example, initially an oxygen surface defect could be formed in which an oxygen molecule is displaced from its usual position; this oxygen molecule could then be removed from the surface more easily. Either of these steps could then be the rate-determining step. The activation energy required to produce a vacancy could then be as low as the value we have found. This low activation energy may also explain the relative ease at which oxygen vacancies can be formed in ceria despite the large enthalpy of formation for bulk vacancies.

The activation energies determined experimentally by other authors for the thermal reduction of cerium are also very low when compared with the enthalpy of formation. A value of  $221 \text{ kJmol}^{-1}$  was obtained by Le Gal and Abanades for the reduction of cerium dioxide doped with zirconium.<sup>38</sup> This is lower than the value found here for pure cerium dioxide, which makes sense, as a higher oxygen yield is obtained when cerium is doped with zirconium, which would imply a lower activation energy. In the work presented by Ramos-Fernandez at The Materials for Energy conference held in Karlsruhe Germany, they found an activation energy for the reduction of pure ceria to be  $236 \text{ kJ mol}^{-1}$ ,<sup>43</sup> which is within the error of the value found in this work.

Different surfaces of ceria will also have different formation energies for oxygen vacancies. This should not affect the bulk thermodynamics but may have an effect on the kinetics. We cannot bring further clarity to this issue as our experiments were carried out with polycrystalline samples. Our values for activation energies are representative of averages over the various facets present in the ceria pellets.

**Model Applications.** This model should be particularly useful in the development and assessment of syn-gas producing reactors based on the ceria redox system. It can easily be coupled to heat flow simulations; one simply needs to introduce a heat source to account for the reaction consuming or producing heat.

$$Q = \frac{d\delta}{dt} \Delta H \quad (22)$$

Here the heat produced is the rate times the change in enthalpy for the reaction, which is known.<sup>29</sup>



504 In the case where dopants are added to ceria to improve the  
505 stability and reaction yields, we should be able to modify our  
506 equation to suit. Both  $\text{ZrO}_2$  and  $\text{HfO}_2$  have been shown to  
507 improve the high-temperature redox properties of  $\text{CeO}_2$ .<sup>9,44–46</sup>  
508 The crystal structure, however, remains unchanged, and so the  
509 same reaction model should still be applicable with a suitable  
510 change in the constants.

511 The model also gives us the boundary condition for the  
512 diffusion equation if the ceria is in an oxygen atmosphere. This  
513 should allow for a more in depth study of the effect of  
514 temperature and composition on the diffusion of oxygen in the  
515 bulk.

## 516 ■ CONCLUSIONS

517 An Arrhenius-type model for the thermal reduction and  
518 oxidation of  $\text{CeO}_2$  in an oxygen atmosphere was developed.  
519 The model was developed by considering the processes  
520 involved in the reactions. By analyzing equilibrium data from  
521 the literature with our model as a template, we were able to fix  
522 the difference between the activation energies of reduction and  
523 oxidation, the oxygen partial pressure dependence, the ratio of  
524 the frequency factors, and the maximum removable oxygen in  
525 this reaction regime. The resulting analytical model of the  
526 equilibrium composition is seen in eq 12. We then examined  
527 the reoxidation of cerium to determine the activation energy  
528 and frequency factor for the reoxidation term in the model.  
529 This fixed the remainder of the constants involved in the  
530 model, which are all listed in Table 1. The model's reaction  
531 kinetics were then compared with novel experimental data. The  
532 experimental results agree well with the model predictions in  
533 the temperature and pressure ranges examined.

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### 537 Notes

538 The authors declare no competing financial interest.

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## 545 ■ NOMENCLATURE

546  $\delta$ , oxygen stoichiometry;  $x$ , maximum  $\delta$ ;  $[\text{O}_{\text{Ce}}]$ , removable  
547 oxygen concentration;  $[\text{O}_{\text{vac}}]$ , oxygen vacancy concentration;  
548  $[\text{O}_{\text{gas}}]$ , oxygen gas concentration;  $[\text{Ce}]$ , concentration of  
549 cerium;  $n$ , oxygen gas power dependency;  $k_{\text{a}}$ , rate constant;  
550  $A_{\text{a}}$ , frequency factor;  $E_{\text{red}}$ , activation energy for reduction;  $E_{\text{ox}}$ ,  
551 activation energy for oxidation;  $P_{\text{O}_2}$ , oxygen partial pressure;  $D$ ,  
552 diffusion coefficient;  $C$ , local vacancy concentration;  $C_{\text{R}}$ ,  
553 boundary vacancy concentration;  $C_{\text{m}}$ , maximum  $C_{\text{R}}$ ;  $\alpha$ , fraction  
554 completed;  $\Delta H$ , change in enthalpy

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