"The Electrical Conductivity of CaO-doped Nonstoichiometric
Cerium Dioxide from 700° to 1500°C"*

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ABSTRACT

The electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 16.0 mole %) was measured over the temperature range 700° - 1500°C and from 1 to 10^{-22} atm of oxygen. All specimens of CaO-doped CeO_2 exhibited mixed conduction. Predominantly ionic conductivity was observed at low temperatures and high oxygen partial pressures. Conversely, high temperatures and lower oxygen partial pressures were dominated by electronic conductivity. CaO-doped CeO_2 exhibited both electronic and ionic conductivity. Two limiting case regions were observed. At low temperatures and high oxygen pressures, the conductivity is predominantly ionic. In this region the conductivity is independent of P_{O_2} and between approximately 1 and 8 mole % CeO is proportioned to mole % CaO.

The following equation for ionic conductivity

THIS DOCUMENT CONFIRMED AS 0 ± 0.5 [mole % CaO] $\exp^{-0.62/kT}$
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DATE 11/6/72

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* Supported by the U.S. Atomic Energy Commission, Division of Research.
This is AEC Report C00-1441-16.

**This paper is based in part on theses submitted in partial fulfillment of the requirements for the Ph.D. degree and M.S. degree, Marquette University, by F. S. Brugner (August 1971) and J. E. Garnier (December 1972), respectively.

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was obtained by fitting the conductivity data in this region to an expression derived on the basis of an oxygen vacancy model. An approximate expression for the diffusion coefficient for oxygen vacancies, $D_{V_o} \approx 3.7 \times 10^{-3} e^{-0.62/kT}$, was calculated from the above expression and the Nernst-Einstein relation.

At high temperatures and low oxygen partial pressures and for lower CaO contents the conductivity is predominantly electronic. In this region σ decreases with increasing CaO addition and the magnitude and P_{O_2} dependence of σ is similar to "pure" CeO_2 . A thermodynamic argument is presented which favors oxygen vacancies as the nonstoichiometric defect in both "pure" and CaO-doped CeO_2 .

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INTRODUCTION

Only a limited number of studies¹⁻⁴ have been reported on the electrical conductivity of CaO-doped nonstoichiometric cerium dioxide. Kevane et al² measured the electrical conductivity as a function of temperature (250° - 1500°C), oxygen pressure ($1 - 10^{-4}$ atm) and CaO content (0.03 - 0.86 % Ca). They reported mixed conduction, electronic and ionic. The electronic conductivity was predominately n-type at elevated temperatures; at lower temperatures p-type behavior was observed. A recent electrical conductivity study of solid electrolytes in air by Meyer and Marincek⁴ indicates that a 15 mole % CaO-doped CeO₂ specimen is highly ionic. Ionic transference measurements in air by Yushina and Pal'guev⁵ confirm the ionic nature of CeO₂ doped with 5-15 mole % CaO in the temperature range 700° - 1100°C.

The solubility of CaO in CeO₂ based on an x-ray study has been reported to be 16 mole % CaO at 1600°C.⁶ Although no thermodynamic study on CaO-doped CeO₂ has been reported, the range of oxygen pressure over which the fluorite structure is stable should be large because CeO_{2-x} is thermodynamically stable⁷⁻⁹ over a wide range of P_{O_2} and temperature. For example, the fluorite structure of CeO_{2-x} is stable to values of P_{O_2} as low as 10^{-20} atm at 1023°C.

The above conductivity studies on CaO-doped CeO₂ have been made over only a rather limited range of oxygen pressures and CaO content. The results of a recent electrical conductivity study¹⁰ on cerium dioxide over a wide range of oxygen pressures (1 to 10^{-21} atm) and temperatures (800° - 1500°C) have been interpreted in terms of a nonstoichiometric defect model involving triply and quadruply ionized cerium interstitials and localized electrons. This defect model was based on a comparison of

the isothermal oxygen pressure dependence of the electrical conductivity and a theoretically derived expression for the conductivity using the law of mass action.

The purpose of this study was to (1) measure the electrical conductivity over a wide range of temperature, oxygen pressure and CaO content and (2) to characterize the electronic and ionic conductivity by a comparison of the data with proposed defect models for CaO-doping and oxygen nonstoichiometry.

THEORY

Based on the results of the previous electrical conductivity and transference studies, CaO-doped cerium dioxide exhibits mixed electronic and ionic conduction.¹⁻⁵ Thus the total electrical conductivity, σ , may be represented as a sum of the electronic conductivity, σ_e , and the ionic conductivity, σ_i . Based on thermodynamic considerations the concentration of electronic and ionic defects in CaO-doped cerium dioxide should be a function of temperature, oxygen partial pressure and CaO content. Expressions for σ_e and σ_i as a function of these variables were derived using simple limiting case models as discussed below.

1. Defect Model for Ionic Conductivity

It is generally assumed that doping CeO_2 with CaO produces oxygen vacancies.² In order to test the oxygen vacancy model a room temperature study¹¹ was made in this laboratory comparing the pycnometric density and calculated values of the density based on lattice parameter data. The results of this study, for specimens in the nonstoichiometric condition with CaO contents between 0.1 and 16 mole %, are shown in Fig. 1. Curves A and B corresponding to Eqs. (1) and (2),* respectively

were calculated assuming calcium ions occupy cerium interstitial sites and the formation of charge-compensating defects which can be oxygen interstitials

*The notation used to identify defects in this paper is the same as used by Kroger.

or cerium vacancies. Curves B and C corresponding to Eqs. (3) and (4), respectively

were calculated assuming calcium ions occupy cerium sites and the formation of charge-compensating defects which can be cerium interstitials or oxygen vacancies. The lattice parameter data used in these calculations is shown in Fig. 2. The data points shown in Fig. 1 correspond to the room temperature pycnometric density measurements made on the CaO-doped specimens used in this conductivity study. The agreement between the experimental data and curve C confirms the existence of oxygen vacancies in CaO-doped CeO_2 .

The simplest model for ionic conduction in CaO-doped CeO_2 is to assume that the ionic conduction occurs by the migration of oxygen vacancies with only one state of ionization, $\text{V}_{\text{O}}^{\text{'\cdot\cdot}}$. For this case the ionic conductivity, σ_{i} , may be represented by the expression

$$\sigma_{\text{i}} = B[\text{V}_{\text{O}}^{\text{'\cdot\cdot}}] e\mu_{\text{V}_{\text{O}}^{\text{'\cdot\cdot}}} \quad (5)$$

where the bracketed term represents the number of a given species divided by the number of sites available for that species, B is a parameter which relates the concentration in site fraction to number/cc, e is the charge on an electron and $\mu_{\text{V}_{\text{O}}^{\text{'\cdot\cdot}}}$ is the mobility of doubly ionized oxygen vacancies. If the oxygen vacancies are isolated point defects randomly distributed and the concentration of nonstoichiometric defects is small, then

$$[\text{V}_{\text{O}}^{\text{'\cdot\cdot}}] = B_1 (\text{mole } \% \text{ CaO}) \quad (6)$$

where B_1 is a parameter which converts the concentration of mole % CaO to

$[V_o^{\bullet\bullet}]$. In addition, if $\mu_{V_o^{\bullet\bullet}}$ is assumed to be a function of temperature only

$$\mu_{V_o^{\bullet\bullet}} = \mu_{V_o^{\bullet\bullet}}' \exp(-E_i/kT) \quad (7)$$

Combining Eqs. (5, 6 and 7) the relation for ionic conductivity is

$$\sigma_i = A(\text{mole \% CaO}) \exp(-E_i/kT) \quad (8)$$

where

$$A = BB_1 \mu_{V_o^{\bullet\bullet}}' e$$

Eq. (8) may be tested in a region near-stoichiometry where the ionic conduction predominates (i.e. $\sigma \approx \sigma_i$) by observing if σ is directly proportional to the CaO content in this region. In this limiting case region σ should also be independent of P_{O_2} .

2. Defect Models for Electronic Conductivity

Brugner¹³ has obtained an expression for the electronic conductivity of CaO-doped cerium dioxide by modifying the equations which have been derived previously for the electronic conductivity, σ_{oe} , of pure nonstoichiometric cerium dioxide.¹⁰

Equations for σ_{oe} have been derived based on a nonstoichiometric defect model involving triply and quadruply ionized cerium interstitials and localized electrons. Over a wide range of oxygen pressures and temperature (e.g. $1 < P_{O_2} < 10^{-7}$ atm at 1500°C and $1 < P_{O_2} < 10^{-12}$ atm at 1200°C) the following defect reaction was assumed to predominate.

where V_i is a vacant interstitial site, Ce_{Ce} and O_o are cerium and oxygen

ions in their normal lattice sites, $\text{Ce}_i^{\cdot\cdot\cdot}$ is a quadruply ionized cerium interstitial, and Ce_{Ce}' is an electron localized at a cerium ion on a normal cerium site. Applying the law of mass action and assuming that the predominant nonstoichiometric defect is $\text{Ce}_i^{\cdot\cdot\cdot}$, Brugner¹³ has shown that the concentration of electrons localized at cerium ions in CaO-doped cerium dioxide may be approximated by the following

$$[\text{Ce}_{\text{Ce}}']_{\text{CaO-doped}} = [\text{Ce}_{\text{Ce}}']_{\text{"pure"CeO}_2} [1 - \xi a] \quad (10)$$

where a is the site fraction of Ca_{Ce}'' on $\text{Ce}_{\text{Ce}}^{\text{x}}$ sites and ξ is a blocking parameter for electrons on $\text{Ce}_{\text{Ce}}^{\text{x}}$ ions which are nearest neighbors of Ca_{Ce}'' ions. The physical basis for this is that since Ca_{Ce}'' has a negative effective charge when it replaces cerium atoms there should be a coulombic interaction between Ca_{Ce}'' and Ce_{Ce}' which would tend to block near neighbor $\text{Ce}_{\text{Ce}}^{\text{x}}$ atoms from accepting localized electrons.

The mobility of electrons may also be affected by CaO-doping. The proposed compositional dependence of the electron mobility may be approximated by the expression¹³

$$\mu_e = (1 - \xi a) \mu_{oe} \quad (11)$$

where μ_{oe} is the electron mobility¹⁴ for "pure" CeO_2 .

Thus according to this model the electronic conductivity of CaO-doped CeO_2 may be approximated by

$$\sigma_e = \sigma_{oe} (1 - \xi a)^2 = \sigma_{oe} (1 - 2\xi a) \quad (12)$$

One of the major criticisms of this derivation is that $\text{Ce}_i^{\cdot\cdot\cdot}$ and $\text{V}_{\text{O}}^{\cdot\cdot}$ are treated as independent experimental variables (i.e. the interdependence of the concentration of $\text{Ce}_i^{\cdot\cdot\cdot}$ and $\text{V}_{\text{O}}^{\cdot\cdot}$ through the thermal disorder constants are ignored in this analysis).

An expression relating $[Ce_i^{\cdot\cdot\cdot}]$ to $[V_o^{\cdot\cdot}]$ may be readily obtained as described below. If Eq. (3) is subtracted from Eq. (4), the following expression is obtained

$$1/2 Ce_i^{\cdot\cdot\cdot} = 1/2 Ce_{Ce}^x + V_o^{\cdot\cdot} . \quad (13)$$

Applying the law of mass action yields

$$K = \frac{[Ce_{Ce}^x]^{1/2} [V_o^{\cdot\cdot}]}{[Ce_i^{\cdot\cdot\cdot}]^{1/2}} . \quad (14)$$

Under near-stoichiometric conditions

$$[Ce_{Ce}^x] \approx 1 ,$$

thus

$$K \approx \frac{[V_o^{\cdot\cdot}]}{[Ce_i^{\cdot\cdot\cdot}]^{1/2}} . \quad (15)$$

Since Eq. (4) is the appropriate defect reaction for the incorporation of CaO in CeO_2 , the free energy change for this reaction is more negative than the defect reaction according to Eq. (3). Thus, the free energy change, ΔG , for the defect reaction described by Eq. (13) is also negative. Since ΔG is negative and

$$K = \exp^{-\Delta G/RT} , \quad (16)$$

$K > 1$. Then according to Eq. (15)

$$[V_o^{\cdot\cdot}] > [Ce_i^{\cdot\cdot\cdot}] ,$$

because $[V_o^{\cdot\cdot}]$ and $[Ce_i^{\cdot\cdot\cdot}]$ are < 1 . On the basis of the above thermodynamic argument it appears that if the addition of CaO to CeO_2 produces oxygen

vacancies then the nonstoichiometric defects in "pure" CeO_2 are oxygen vacancies. Of course this argument would be invalidated if significant defect interaction occurs because of the addition of CaO to CeO_2 as a result of large departures from stoichiometry.

Assuming the oxygen vacancies are doubly ionized, the nonstoichiometric defect reaction in CeO_2 may be characterized by the following reaction

applying the law of mass action to Eq. (17) yields

$$K_1 = \frac{[\text{Ce}_\text{Ce}']^2 [\text{V}_\text{O}^{\bullet\bullet}] P_{\text{O}_2}^{1/2}}{[\text{O}_\text{O}^\times] [\text{Ce}_\text{Ce}^\times]^2} . \quad (18)$$

If the appropriate electroneutrality expression is

$$[\text{Ce}_\text{Ce}'] = 2[\text{V}_\text{O}^{\bullet\bullet}] , \quad (19)$$

and $[\text{O}_\text{O}^\times]$ and $[\text{Ce}_\text{Ce}^\times] \approx 1$ then

$$[\text{Ce}_\text{Ce}'] \propto P_{\text{O}_2}^{-1/6} \quad (20a)$$

or

$$\sigma_e \propto P_{\text{O}_2}^{-1/6} \quad (20b)$$

if μ_e is temperature dependent only.

It should be noted that under isothermal conditions and over a range of oxygen pressures the electrical conductivity of "pure" CeO_2 was observed to be proportional to $P_{\text{O}_2}^{-1/5}$. However, at lower oxygen pressures (i.e.

large departure from stoichiometry) the dependence of σ_e on P_{O_2} involves a more complicated relationship.¹⁰ Thus the above analysis is inconsistent with the behavior of the oxygen pressure dependence of σ , which would seem to imply that either or both the mass action approach or the defect reaction given in Eq. (17) are incorrect.

Greener et al¹⁵ discussed a defect model proposed by Bevan involving a simple divacancy, $(V_O - V_O)^{\cdots\cdots}$, to explain the $P_{O_2}^{-1/5}$ dependence of σ in "pure" CeO_2 . For this defect model the defect reaction may be written

The mass action constant is

$$K_2 = \frac{[Ce_{Ce}']^4 [V_O - V_O]^{\cdots\cdots} P_{O_2}}{[O_O^x]^2 [Ce_{Ce}^x]^4} \quad (22)$$

and if $Ce_{Ce}' = 4[(V_O - V_O)^{\cdots\cdots}]$ and $[O_O^x] = [Ce_{Ce}^x] \approx 1$,

$$[Ce_{Ce}'] = (4K_2)^{1/5} P_{O_2}^{-1/5} . \quad (23)$$

With the addition of CaO to CeO_2 , the electroneutrality relation is

$$2[Ca_{Ce}''] + [Ce_{Ce}'] = 4[(V_O - V_O)^{\cdots\cdots}] \quad (24)$$

for the divacancy model and

$$2[Ca_{Ce}''] + [Ce_{Ce}'] = 2[V_O^{\cdots\cdots}] \quad (25)$$

for the doubly ionized oxygen vacancy model.

Two interesting limiting cases may be readily deduced for the above defect models. At low CaO contents and where the departures from stoichiometry are sufficiently large that

$$[\text{Ce}'_{\text{Ce}}] \gg 2[\text{Ca}''_{\text{Ce}}] \quad (26a)$$

the equations derived for CaO-doped CeO_2 would be identical to those derived for "pure" CeO_2 (i.e. Eqs. (20) and (23)).

However for near-stoichiometric conditions, where the CaO content is sufficiently large that

$$[\text{Ce}'_{\text{Ce}}] \ll 2[\text{Ca}''_{\text{Ce}}], \quad (26b)$$

then the concentration of electron carriers, $[\text{Ce}'_{\text{Ce}}]$, is given by Eqs. (27) and (28) for the divacancy model and the doubly ionized oxygen vacancy model, respectively.

$$[\text{Ce}'_{\text{Ce}}] = \frac{(2K_2)^{1/4}}{[\text{Ca}_{\text{Ce}}'']^{1/4}} P_{\text{O}_2}^{-1/4} \quad (27)$$

$$[\text{Ce}'_{\text{Ce}}] = \frac{K_1^{1/2}}{[\text{Ca}_{\text{Ce}}'']^{1/2}} P_{\text{O}_2}^{-1/4} \quad (28)$$

According to Eqs. (27) and (28) for a given temperature and P_{O_2} , $[\text{Ce}'_{\text{Ce}}]$ should decrease with increasing CaO content. On the basis of these simple limiting case models for CaO-doped CeO_2 the P_{O_2} dependence of σ_e , under isothermal conditions, might be expected to vary between $P_{\text{O}_2}^{-1/4}$ and $P_{\text{O}_2}^{-1/6}$ over a limited region of nonstoichiometry and CaO content. Since $\sigma \propto P_{\text{O}_2}^{-1/5}$ for "pure" CeO_2 over a range of oxygen pressures,¹⁰ it would be expected that both "pure" and CaO-doped CeO_2 should exhibit a similar isothermal dependence of P_{O_2} on σ_e , at least over a limited range of oxygen pressures.

EXPERIMENTAL

Conductivity specimens of CeO_2 doped with CaO (0.1 to 16.0 mole % CaO) were prepared by dry mixing the appropriate proportions of CeO_2 and CaCO_3 powder. The chemical analysis of CeO_2 and CaCO_3 powders are shown in Tables I and II, respectively. These mixtures were calcined for 12 hours at 1000°C in air. The calcined material was ground in an alumina mortar and pestle to an approximate particle size of 20 microns or less. These powders were then pressed into bars 2 in. x 1/4 in. x 1/4 in. with a pressure of 20,000 psi. The bars were placed in an alumina boat and completely covered with CaO doped CeO_2 powder of the same composition to avoid loss of CaO during sintering. A molybdenum wound resistance furnace was used to sinter the bars at 1650°C for 3-1/2 hrs in an argon atmosphere. Conductivity specimens were cut from the sintered bars to an average length of 2 cm. The nominal calcia content, density and the results of the chemical analysis on several of these specimens are shown in Table III. The nominal calcia content specimens, 0.3, 2.0, 5.0 and 7.0 mole % CaO , agree with the results of the x-ray fluorescence and the atomic absorption analysis within the reported experimental error of these analyses $\pm 10\%$. With the exception of the 1 mole % CaO specimen, the nominal values of mole % CaO of all specimens analyzed were within the reported experimental accuracy of the x-ray fluorescence and atomic absorption analysis. Thus, in this study the nominal mole % CaO values will be used to identify the calcia content of each specimen.

The electrical conductivity measurements on the above CaO -doped cerium dioxide specimens as a function of P_{O_2} in the temperature range $700^\circ - 1500^\circ\text{C}$ were made in a molybdenum wound resistance furnace. A standard four-probe

d-c technique was employed for the electrical conductivity measurements. The experimental apparatus employed was essentially the same as that described in an earlier publication.¹⁶ Four-probe conductivity specimens were prepared from sintered bars of CaO-doped CeO_2 by wrapping with 0.01 inch diameter platinum wire. Two current leads were wrapped near the ends of the specimen and two potential leads were wrapped closer to the center with a spacing of approximately 1 cm. An Altair Model C2 constant current source with a continuously variable range from $1\mu\text{A}$ to $50\mu\text{A}$ was used to supply the current. The DC conductivity measurements were found to be independent of the applied field and time in this study. In addition AC measurements in the frequency range 10 - 1000 cps were found to be in agreement with the DC measurements. These results indicate that ohmic behavior was achieved and that polarization was not a problem in these measurements.

Oxygen partial pressures were achieved by means of two methods. For pressures from 1 to 10^{-4} atm, premixed and analyzed O_2 -Ar mixtures at 1 atm total pressure were used in the study. Controlled oxygen partial pressures in the low-pressure region were obtained by introducing known mixtures of CO and CO_2 at 1 atm total pressure. The well-known free energy values for the CO/CO_2 reaction were used to calculate the oxygen partial pressure. A linear flow rate of 0.7 cm/sec was maintained for all gas mixtures used in this investigation to avoid errors arising from thermal diffusion.¹⁷ However, no flow dependence was noted when the flow rate was increased or decreased within 50% of this value. Electrical conductivity measurements were made at various temperatures between 700° and 1500°C for a fixed gas mixture for both increasing and decreasing temperature. Data were taken in 200°C increments, starting at 700°C and proceeding to 1500°C while heating. During cooling from 1400° to 800°C

data was recorded at 200°C intervals. Since the composition of calcia doped nonstoichiometric ceria has a unique value for each CaO content, oxygen partial pressure and temperature, the above technique insured the measurement of equilibrium conductivity because the nonstoichiometric equilibrium state was approached from both higher and lower compositions of oxygen. A sluggish return to equilibrium on cooling in Ar-O₂ mixtures below 900°C while using this technique suggested the isothermal method as a time saving alternative. Isothermal conductivity measurements at 700° and 800°C were made in Ar-O₂ mixtures for decreasing oxygen pressures. For this method the criteria for equilibrium was independence of the measured values of the conductivity with time.

RESULTS AND DISCUSSION

The electrical conductivity of sintered specimens of calcia-doped nonstoichiometric cerium dioxide (0.1 to 16.0 mole % CaO) was measured as a function of temperature (i.e. 700° to 1500°C) and oxygen pressure (1 to 10^{-21} atm). Typical behavior of the conductivity as a function of the reciprocal absolute temperature in Ar-O₂ and CO-CO₂ mixtures is illustrated in Fig. 3 for a nonstoichiometric cerium dioxide specimen doped with 1.0 mole % CaO. The measured values of the conductivity, σ_{meas} , for the sintered specimen have been corrected for porosity using the relation¹⁸

$$\sigma = \sigma_{\text{meas}} \frac{\rho_{\text{theor}}}{\rho_{\text{meas}}} \quad (29)$$

where ρ_{theor} is the theoretical density and ρ_{meas} is the bulk density of the sintered specimen. For all of the CaO doped specimens two distinct types of behavior are observed in Fig. 3. At lower temperatures and high oxygen pressures (i.e. Ar-O₂ mixtures), the conductivity is independent of oxygen partial pressure and exponentially dependent on temperature. At higher temperatures and low oxygen pressures, the conductivity exhibits n-type behavior. Based on the simple limiting case defect models discussed in the theory section, the ionic conductivity should be proportional to mole % CaO and independent of P_{O_2} ; whereas the electronic conductivity of Ca-doped CeO₂ should exhibit a dependence on P_{O_2} similar to "pure" CeO₂. Isothermal plots of $\log \sigma$ vs $\log P_{\text{O}_2}$ were made for each of the CaO-doped specimens to test these simple models.¹³ Typical plots are shown in Figs. 4-6 for 1, 5 and 12 mole % CaO, respectively. For comparative

purposes the conductivity¹⁰ of a "pure" CeO_2 specimen is shown as a dashed line in these figures.

A qualitative explanation of the observed electrical conductivity data may be given in terms of three regions as follows:

- Region I At high temperatures and particularly at low oxygen pressures, the σ of the CaO-doped specimens exhibits a similar P_{O_2} dependence as "pure" CeO_2 except that the magnitude of σ is slightly smaller. The conductivity in this region appears to be predominantly electronic (i.e. $\sigma \approx \sigma_e > \sigma_i$) and is probably controlled by the same nonstoichiometric defects as in "pure" CeO_2 . As the CaO content increases, lower oxygen pressures (i.e. a higher concentration of nonstoichiometric defects) are required to "mask" out the effect of the CaO.
- Region II For low temperatures and high oxygen partial pressures (i.e. near stoichiometric conditions), the conductivity of the CaO-doped specimen is independent of oxygen partial pressure. The σ is also much larger than that of "pure" CeO_2 . Since σ_i is to a first order approximation independent of the oxygen pressure, this observation is consistent with a conduction process which is primarily ionic (i.e. $\sigma \approx \sigma_i > \sigma_e$).
- Region III For all oxygen pressures and temperatures intermediate to regions I and II, the conductivity appears to be mixed, i.e. where σ_e and σ_i are of the same order of magnitude.

As discussed in the theory section, the simple limiting case defect models for electronic conduction predict that the concentration of electronic defects should decrease with increasing CaO content. However, based on the defect model for CaO doping the ionic conductivity is directly proportional

to the CaO content. As a test of these models, isothermal plots were made of $\log \sigma$ vs $\log$ mole % CaO for all of the gas mixtures used in this study.^{11,13} Typical plots of $\log \sigma$ vs $\log$ mole % CaO are shown in Figs. 7, 8 and 9 for atmospheres containing 100% O_2 , 0.1% CO and 48.1% CO, respectively. The same three regions of behavior discussed above may be observed. In region I (i.e. $\sigma \approx \sigma_g$) the conductivity decreases slightly with CaO addition. This region extends to higher CaO compositions and lower temperatures in more reducing gas mixtures (i.e. lower oxygen partial pressures). In region II (i.e. $\sigma \approx \sigma_i$) the slope of $\log \sigma$ vs $\log$ % CaO is approximately one. This region is observed primarily at lower temperatures and higher oxygen pressures. For example, in an atmosphere of 100% O_2 (Fig. 7) this region extends from approximately 1 to 8 mole % CaO in the temperature range 700° - 1100°C, whereas in a strongly reducing atmosphere (48.1% CO Fig. 9) this region is barely detectable at 700°C. At high oxygen pressures, low temperatures and low CaO contents (0.1 and 0.3 mole % CaO Fig. 7) a curvature in the line is observed. This effect is probably due to impurities in CeO_2 . For example, the conductivity for "pure" CeO_2 has been reported¹⁰ to be influenced by impurities in this temperature and oxygen pressure region. Thus, it appears that approximately 1 mole % CaO is required to produce a sufficient number of defects to completely swamp out the effect of impurities in "pure" CeO_2 . Region III is a region of mixed conduction. Another interesting observation from Figs. 7-9 is that at high CaO compositions the conductivity appears to exhibit a maximum with increasing CaO content. This behavior also appears to be relatively independent of temperature and oxygen partial pressure. Similar behavior has been reported for other fluorite oxide systems doped with lower valent cations. Two different models have been used to explain the maximum in σ observed in

CaO-doped ZrO_2 .¹⁹ One model is based on a clustering of defects and the other on synthetic zones of composition. In both of these models the activation energy increases with increasing CaO content. In contrast to the predictions of these models, the activation energy for CaO-doped CeO_2 determined from a plot of $\log \sigma$ vs $1/T$ at 1 atm of O_2 is independent of CaO content. Also in the vicinity of the σ maximum only a very small variation in the magnitude of the conductivity with CaO content is observed. Although the reported solubility⁶ is 16 mole % CaO in air at 1600°C, the dependence of temperature and oxygen pressure on the solubility limits of CaO-doped CeO_2 is not known. Thus the question of whether the concentration of CaO in this region exceeds the solubility of CaO in CeO_2 cannot be easily ascertained. Because of these considerations no attempt has been made to analyze the maximum in the conductivity of CeO_2 doped with CaO.

The qualitative interpretation of the electrical behavior of CaO-doped CeO_2 observed in this study may be summarized as follows. CaO-doped CeO_2 exhibits both electronic and ionic conductivity. Two limiting case regions were observed. At low temperatures and high oxygen pressures, and CaO contents of approximately 1 - 8 mole % CaO, the conductivity is proportional to mole % CaO and is predominately ionic. Whereas at high temperatures and low oxygen partial pressures and lower CaO contents the conductivity is predominately electronic.

The qualitative predictions of the limiting case defect models for electronic conduction (i.e. (i) decrease in σ with CaO addition, (ii) similar magnitude and P_{O_2} dependence as "pure" CeO_2) in CaO-doped CeO_2 appear to be consistent with the observed behavior of the conductivity in this limiting case region. It should be noted that the limiting case

models for oxygen vacancies would be expected to apply only in the oxygen pressure region where $\sigma \propto P_{O_2}^{-1/5}$ in "pure" CeO_2 . However, for oxygen pressures below this region, the conductivity of "pure" and CaO-doped CeO_2 are actually in closer agreement. This implies that the same defects are responsible for the nonstoichiometric behavior in "pure" and CaO-doped CeO_2 . In the theory section the inconsistencies of the previously proposed cerium interstitial defect model for "pure" CeO_2 and CaO-doped CeO_2 have been discussed. The problem with the mass action interpretation of the doubly ionized oxygen vacancy model has also been discussed. In addition information on the transference number should be available in order to determine a more exact dependence of σ_e on temperature, oxygen pressure and CaO content. Because of these considerations no attempt has been made in this paper to quantitatively analyze the conductivity data in terms of the above defect models.

In order to quantitatively analyze the proposed oxygen vacancy model for ionic conductivity

$$\sigma_i = A[\text{mole \% CaO}]e^{-E_i/kT} \quad (8)$$

the conductivity in the region where ionic conductivity predominated was plotted as a function of CaO. These results are shown in Fig. 10 at $P_{O_2} = 1$ atm for $700^\circ - 1000^\circ\text{C}$ and for CaO contents between 1 and 16 mole %. A direct proportionality was observed for specimens with CaO contents between approximately 1 and 8 mole % CaO. The parameter E_i in Eq. (8) was obtained from the plot shown in Fig. 11 of $\log \sigma$ vs $1/T$ at $P_{O_2} = 1$ atm for several different CaO contents. The average value of E_i determined from a least square analysis was 0.62 ± 0.03 eV for compositions from 1.0 to 14.0 mole % CaO. A value of $A = 6.0 \pm 0.5$ was determined by curve fitting

Eq. (8) to the data shown in Fig. 11. Thus if the proposed limiting case defect model for ionic conductivity is correct and ionic conductivity predominates in the composition region, 1 to 8 mole % CaO, (i.e. $t_i \approx 1$), σ_i may be approximated by the relation

$$\sigma_i \approx 6.0 \pm 0.5 [\text{mole \% CaO}] \exp(0.62/kT) . \quad (30)$$

An approximate expression for the diffusion coefficient of oxygen vacancies, D_{V_O} , in CaO-doped CeO_2

$$D_{V_O} \approx 3.7 \times 10^{-3} \exp(0.62/kT) \quad (31)$$

was determined in this study from the above data and the Nernst-Einstein relation. It is interesting to note that the diffusion coefficient for oxygen vacancies in CaO-doped CeO_2 is larger than in CaO-doped ZrO_2 .²⁰

A recent study of oxygen self-diffusion²¹ in ceria-yttria solution at $P_{O_2} = 1$ atm in the temperature range 850° - 1150°C indicates that the activation energy, approximately 20 Kcal/mole, is essentially independent of yttria composition (i.e. for x between 0 and 0.2 in the formula $\text{Ce}_{1-2x}\text{Y}_{2x}\text{O}_{2-x}$). The activation energy obtained in this study (~ 14 Kcal/mole) for diffusion of oxygen vacancies produced by CaO is in relatively good agreement with the self-diffusion of oxygen in $\text{Ce}_{1-2x}\text{Y}_{2x}\text{O}_{2-x}$. It is also interesting to note that the reported²¹ activated energy for oxygen self-diffusion in pure ceria varied from about 24 Kcal/mole in near stoichiometric ceria to about 4 Kcal/mole for $\text{CeO}_{1.8}$. Thus it might be expected that the activation energy for oxygen diffusion in CaO-doped CeO_2 would decrease in the presence of a large concentration of nonstoichiometric defects (i.e. at low oxygen pressures).

A study of transference measurements on CaO-doped CeO_2 has been initiated in this laboratory to determine t_i as a function of temperature, P_{O_2} and CaO content. These data when combined with the above σ data should allow the determination of the T, P_{O_2} and CaO dependence of the electronic and ionic conductivity. The combined results of these studies should permit a more quantitative test of the simple limiting case defect models for ionic and electronic conductivity.

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Table 1

Mass Spectrographic Analysis of CeO_2 (ppmw)

Element ¹	American Potash and Chemical Corporation CeO_2 (code 217.91)
Ca	200
F	30
Fe	10
K	600
Li	20
Mg	10
Na	300
P	200
Pb	10
S	100
Si	20
Th	40
Ti	20
Zr	10

¹ Seventy-three elements were present, most in traces; only major impurities are listed.

Table II

Impurity Analysis of Fisher F.W. 100.091
Certified Reagent CaCO_3

Impurity ¹	Percentage
SO_4	0.009
Ba	0.001
Cl	0.0005
Fe	0.0005
Pb	0.001
Sr	0.0
Mg	0.005
K	0.00

¹0.004% insoluble in HCl and 0.001% insoluble in NH_3OH

Table III
Nominal mole % CaO, Density and Chemical Analysis
of the CaO Content of the
Conductivity Specimens used in this Investigation

Nominal Mole % CaO	XRF ¹ Mole % CaO	AAS ² Mole % CaO	Bulk Density % Theoretical
0.10	--	--	72.2
0.30	0.367	--	72.3
1.00	1.43	--	67.0
2.00	1.82	--	86.5
5.00	4.93	5.10	79.0
7.00	7.30	7.10	71.0
8.00	--	--	88.6
10.00	--	--	83.1
12.00	--	--	71.5
14.00	--	--	82.7
16.00	--	--	100.3

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