C00-1441-12

College of Engineering
Marquette University
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MASTER

TECHNICAL PROGRESS REPORT

C00-1441-12

to

THE ATOMIC ENERGY COMMISSION

DIVISION OF RESEARCH

on

"A STUDY OF THE DEFECT STRUCTURE
OF NONSTOICHIOMETRIC CeO_2 "

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September 1970

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ABSTRACT

The electrical conductivity of a single crystal of $\text{Ce}_{1+y}\text{O}_2$ has been measured as a function of temperature and oxygen pressure. For comparative purposes the conductivity data obtained on sintered specimens has been normalized for porosity using the relation

$$\sigma_{\text{normalized}} = \sigma_{\text{measured}} \frac{\rho_{\text{theoretical}}}{\rho_{\text{measured}}}$$

The agreement between the normalized conductivity values and the single crystal data in the temperature range $1200^\circ - 1500^\circ\text{C}$ was excellent.

The electrical conductivity of sintered specimens of CaO-doped CeO_2 have also been measured as a function of temperature and oxygen pressure. At large departures from stoichiometry $\sigma_e > \sigma_i$ and at small departures from stoichiometry $\sigma_i > \sigma_e$. An estimate of the mobility of oxygen vacancies, $6 \times 10^{-5} \text{ cm}^2/\text{volt-sec}$ at 800°C was obtained from this data.

Preliminary data on the ionic transference of a 2 mole % CaO-doped CeO_2 specimen indicates that $t_i \sim 0.75$ at high oxygen pressures (i.e. $\sim 1 \text{ atm}$) in the temperature region 800° to 1050°C .

The compositional dependence of the thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were determined from the thermodynamic data. Near stoichiometry (i.e. $y \sim 0$) $-\Delta\bar{H}_{\text{O}_2} = 10.4 \text{ eV}$ was shown to be equal to the enthalpy of the defect reaction

INTRODUCTION

The purpose of this research program is to determine the defect structure (i.e. the type and concentration of atomic and electronic defects and the equilibrium relationships between these defects and the external variables such as temperature and oxygen pressure) and transport properties of defects in nonstoichiometric oxides from their electrical and thermodynamic behavior. The analysis of the data should also permit the calculation of the energies of formation of the various defect reactions which contribute to the defect structure. In addition, it should be possible to determine whether the law of mass action is applicable or if a more complex statistical thermodynamic treatment is necessary to explain the equilibrium relations between defects in the nonstoichiometric oxides investigated. Studies of this kind also provide information about the mobility of charge carriers in nonstoichiometric oxides, such data has been rather sparse in the literature.

The thermodynamic and electrical property study initiated on nonstoichiometric cerium dioxide, $\text{Ce}_{1+y}\text{O}_2$, has been continued. The literature on the x-ray thermodynamic and electrical property studies on $\text{Ce}_{1+y}\text{O}_2$ has been reviewed previously.^{1,2} In a recent paper by Blumenthal, Lee and Panlener² the results of an electrical conductivity study on sintered specimens of $\text{Ce}_{1+y}\text{O}_2$ over the temperature range 800° to 1500°C and from 1 to 10^{-21} atm of oxygen was described. Based on the agreement between the experimental conductivity data and theoretically derived relations, the nonstoichiometric defect structure of $\text{Ce}_{1+y}\text{O}_2$ was interpreted in terms of a defect structure consisting of triply and quadruply ionized cerium interstitials and localized electrons.

Assuming the electronic conduction mechanism in $\text{Ce}_{1+y}\text{O}_2$ is a "hopping type" process, an experimental activation energy for motion 0.18 eV was calculated from the conductivity data in the temperature and oxygen pressure region where quadruply ionized cerium interstitials predominate.

The electron mobility in nonstoichiometric cerium dioxide, $\text{Ce}_{1+y}\text{O}_2$, was also calculated⁴ by combining electrical conductivity² and thermogravimetric data³ for the temperature and oxygen region where the atomic defect predominates in one state of ionization. The concentration of charge carriers, n , was obtained from the thermodynamic data³ at 100°C intervals between 800° - 1200°C in the oxygen pressure region where quadruply ionized cerium interstitials were assumed to predominate.² The electronic mobility, μ , was then calculated from the relation

$$\sigma = ne\mu \quad (1)$$

by using the values of σ and n corresponding to the same temperature and oxygen partial pressure. The mobility was calculated for two sintered conductivity specimens² of 70 and 85 per cent theoretical density respectively and one arc cast large grain polycrystalline specimen. The result of this analysis may be summarized as follows. The electron mobility of sintered and arc cast CeO_2 conductivity specimens increase exponentially with increasing temperature between 800° and 1200°C. The conduction mechanism is assumed to be a hopping type process (i.e. the electrons localized at normal cerium ion sites move to adjacent cerium ions). The magnitude of the mobility is of the order $10^{-2} \text{ cm}^2/\text{v-sec}$ and the activation energy for the process is 0.14 eV. It should be noted that although the absolute value of μ varies slightly with the density of the sintered conductivity specimens, the activation energies appear to be independent of the density within experimental error in the range of densities investigated.

In this investigation, thermodynamic and electrical property measurements initiated on $\text{Ce}_{1+y}\text{O}_2$ were continued in order to provide additional data which would permit a more detailed analysis of the proposed defect structure model² for $\text{Ce}_{1+y}\text{O}_2$, and a better understanding of electronic transport in $\text{Ce}_{1+y}\text{O}_2$. In addition, a combined study of the electrical conductivity and ionic transference of calcium doped cerium dioxide was initiated in order to obtain information about the mobility of oxygen vacancies and to characterize the electronic conductivity of Ca-doped CeO_2 by modifying the proposed nonstoichiometric defect model for "pure" $\text{Ce}_{1+y}\text{O}_2$.

RESULTS AND DISCUSSION

1. Electrical Property Studies

As described in a previous report⁵ one of the difficulties with the current electrical conductivity studies of $\text{Ce}_{1+y}\text{O}_2$ is that only sintered and polycrystalline specimens have been used. Recently, small single crystals of CeO_2 have been grown in our laboratories using a vapor transport technique.⁶ The electrical conductivity of one of these crystals has been measured as a function of temperature and oxygen pressure using the same experimental technique as described previously.^{2,7,8} The results^{9,10} of this study is shown in Fig. 1 as isothermal plots of $\log \sigma$ vs $\log P_{\text{O}_2}$. The conductivity data^{1,2} obtained on sintered specimens has been normalized for porosity using the relation

$$\sigma_{\text{normalized}} = \sigma_{\text{measured}} \frac{\rho_{\text{theoretical}}}{\rho_{\text{measured}}} \quad (2)$$

Fig. 1 Isothermal plots of $\log \sigma$ vs $\log P_{O_2}$ for single crystal and sintered specimens of $Ce_{1-y}Y_yO_2$. The conductivity of the sintered specimens has been normalized using Eq. (1).

where ρ_{measured} is the density of the sintered specimen and $\rho_{\text{theoretical}}$ is the theoretical density of CeO_2 . For comparative purposes the normalized conductivity values of 70% and 85% dense sintered specimens are also shown in Fig. 1. The agreement between the normalized σ values and the single crystal data in the temperature range $1200^\circ - 1500^\circ\text{C}$ is excellent. Only the data above 1200°C is shown here because the impurities present in the single crystals effect the magnitude of the conductivity below 1200°C particularly at high oxygen pressures.

The reason that the conductivity of the sintered specimens may be corrected for porosity by using such a simple expression as Eq. (2) is that the μ is small ($\mu \sim 10^{-2}$ volt-sec/cm²), thus any additional scattering due to the porosity and grain boundaries is negligible.⁴ An important observation to be made is that the σ of single crystal $\text{Ce}_{1+y}\text{O}_2$ may be calculated by multiplying the σ of sintered specimens by a simple constant (i.e. $\frac{\rho_{\text{theoretical}}}{\rho_{\text{measured}}}$) which is independent of temperature and oxygen pressure. Thus the calculated values of the temperature dependence of the electronic mobility⁴ and the enthalpies of the nonstoichiometric defect reactions² determined from an analysis of the conductivity data on sintered specimens should be correct because the analysis is independent of the state of aggregation of the conductivity specimen used.

In the last progress report³ the preliminary data obtained on the temperature dependence of the constant composition conductivity of $\text{Ce}_{1+y}\text{O}_2$ was discussed. The temperature dependence of the conductivity was attributed to both a change in the concentration of localized electrons, $[\text{Ce}'_{\text{Ce}}]$, and the mobility of these electrons with temperature. In the current study, the electrical conductivity of sintered $\text{Ce}_{1+y}\text{O}_2$ specimens

with fixed values of y have been measured as a function of temperature employing an improved experimental measuring technique. The composition of the specimen is fixed by equilibrating the sample in a CO-CO_2 mixture with a known CO/CO_2 ratio at 1000°C . The system is then purged with purified argon and the conductivity is measured using a standard four probe DC technique. A constant current is passed through the sample and the voltage across the inner probes is monitored as a function of time along with the emf of Pt-Pt-13%Rh thermocouple on a two channel potentiometric solid state recorder.

The conductivity is then measured as a function of temperature. The specimen temperature is changed rapidly by moving the furnace relative to the sample. This procedure reduces the time the specimen is in contact with the purified argon atmosphere and thus reduces the possibility of composition variation due to reaction with oxygen impurities in the inert gas. Typical results of the constant composition σ data obtained in the current study are shown in Fig. 2, where $\log \sigma$ is plotted as a function of $1/T$ for several different values of y .

The conductivity data was corrected for porosity using Eq. (2). The experimental activation energy, ΔE , shown in Fig. 2 was obtained from the well known expression

$$\sigma = \sigma_0 e^{-\Delta E/kT} \quad (3)$$

by use of the least square analysis of the data. The following observation can be made regarding these results:

- a. ΔE is larger than the reported activation energy 0.14 eV for electron transport.⁴

Fig. 2 $\text{Log } \sigma$ vs $1/T$ for three different values of y in $\text{Ce}_{1+y}\text{O}_2$.

- b. ΔE appears to increase with increasing departure from stoichiometry.

These observations are consistent with a defect model involving cerium interstitials which exhibit multiple states of ionization. Thus, for example, for the defect reaction

the concentration of quadruply ionized cerium interstitials, $[\text{Ce}_{\text{i}}^{+4}]$, and localized electrons, $[\text{Ce}_{\text{Ce}}']$, will increase with increasing temperature for a sample with a constant value of y .

Additional constant composition conductivity data will be obtained and an attempt will be made to calculate the temperature dependence of the equilibrium constant, K , for Eq. (4). The value of K will be obtained from the expression¹¹

$$K = \frac{\{[\text{Ce}_{\text{Ce}}'] - 3y\}[\text{Ce}_{\text{Ce}}']}{4y - [\text{Ce}_{\text{Ce}}']} \quad (5)$$

$[\text{Ce}_{\text{Ce}}']$ will be calculated by combining the conductivity data with the mobility data.⁴ The value of y corresponding to the same temperature and oxygen pressure may be obtained from the thermodynamic data.³ The ionization energy corresponding to Eq. (3) will be calculated by combining the temperature dependence of K with the relation

$$K \propto \exp \Delta S / R \exp -\Delta H / RT \quad (6)$$

As described in the previous progress report most of the experimental difficulties with the AC Hall mobility technique have been associated with noise problems. A number of modifications have been made in the

system to reduce these problems. The bucking circuit has been simplified and the mechanical linkage for rotating the specimen has been redesigned. These modifications when completed should reduce the spurious voltages which interfered with measurement of the Hall voltage. When this work is completed high temperature Hall mobility measurements will be made on $\text{Ce}_{1+y}\text{O}_2$ in order to 1) check the temperature dependence of the electron mobility calculated from the thermodynamic and electrical conductivity data,⁴ and 2) test the proposed model for the compositional dependence of the mobility.²

While the analysis of the thermodynamic and electrical conductivity data on "pure" $\text{Ce}_{1+y}\text{O}_2$ provides information about the nonstoichiometric defect structure and electron mobility, information about the mobility of atomic defects (e.g. oxygen vacancies or cerium interstitials) in $\text{Ce}_{1+y}\text{O}_2$ are virtually nonexistent.

According to Kevane et al¹² and Lay¹³, the doping of CeO_2 with CaO produces oxygen vacancies. Preliminary measurements in this laboratory indicate that CaO doped CeO_2 exhibits mixed conduction. Thus, a combined study of the electrical conductivity σ and the ionic transference, t_i , as a function of temperature, oxygen pressure and CaO content was initiated to obtain information on the mobility of oxygen vacancies in CeO_2 .

A brief description of how the mobility of oxygen vacancies, $\mu_{V_O}^{+2}$, may be obtained from this type of data is described below. The ionic conductivity, σ_i , may be determined from the relation

$$\sigma_i = \sigma t_i. \quad (7)$$

If the mechanism responsible for ionic conduction in Ca-doped CeO_2 is the migration of oxygen vacancies, V_O^{+2} , under the influence of an electric field

$$\sigma_i = 1.6 \times 10^4 [V_o^{+2}] \mu_{V_o^{+2}} \quad (8)$$

$[V_o^{+2}]$ is the fraction of vacant oxygen sites and $\mu_{V_o^{+2}}$ is the mobility of an oxygen vacancy. Since,

$$[V_o^{+2}] = \text{mole \% CaO}/200, \quad (9)$$

$\mu_{V_o^{+2}}$ may be readily calculated by combining the experimental data with Eqs. (7), (8) and (9). For dilute solutions of CaO, $\mu_{V_o^{+2}}$ should primarily be dependent on temperature. Thus, to a first approximation σ_i should be proportional to mole % CaO and exponentially dependent on temperature.

Another objective of the CaO-doping study is to characterize the electronic conductivity of Ca-doped CeO_2 by modifying the proposed nonstoichiometric defect model for "pure" $\text{Ce}_{1+y}\text{O}_2$. For "pure" $\text{Ce}_{1+y}\text{O}_2$ in the oxygen pressure and temperature region where the defect reaction

predominates, the simplified electroneutrality relation $[\text{Ce}_i^{+4}] = 4y$ is assumed to be valid. For this case the departure from stoichiometry, y , may be related to P_{O_2} by the following expression^{1,2}

$$K_1 = \frac{512 y^5 P_{\text{O}_2}}{[1 - y(13 - 12\beta)][1 - y(10 - 6\alpha)]^5} \quad (11)$$

and for CaO doped CeO_2 the corresponding relation can be shown to be

$$K = \frac{(4)^4 y^5 P_{\text{O}_2}}{[1 - (13 - 12\beta)y][1 - a - (10 + a - 6\alpha)y]^5 [1 - a/2 - a/2y]^2} \quad (12)$$

where a is a mole fraction of CaO in CeO_2 .

Based on the above defect model, if $a \leq 0.10$, it can be shown that concentration of localized electrons $[Ce'_{Ce}]$ is controlled primarily by the temperature and oxygen pressure and to a first order approximation independent of the CaO content.

The proposed compositional dependence of the electron mobility may be characterized by the expression

$$\mu_e = \mu_o \{ (1 - a) - 4y - 6(1 - \alpha)y - ay \} e^{-\Delta E/kT} \quad (13)$$

This equation was obtained by modifying the proposed μ_e expression for "pure" CeO_2 .^{1,2} To a first order approximation the electron mobility should decrease linearly with increasing CaO content.

The electrical conductivity of sintered specimens of CaO doped CeO_2 have been measured as a function of temperature and oxygen pressure. Typical results of this data are shown in Fig. 3 where $\log \sigma$ is plotted as a function of $\log P_{O_2}$ for a 1 mole % CaO doped specimen. For comparative purposes the conductivity for a "pure" CeO_2 specimen is also shown in Fig. 3.

Two general observations can be made regarding this data.

- a. In the higher oxygen pressure and lower temperature region the σ of the CaO-doped specimen appears to be independent of oxygen pressure. The σ is also much larger than the σ of "pure" CeO_2 in this region. 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 in nature (i.e., $\sigma \sim \sigma_i > \sigma_e$).
- b. In the high temperature region and particularly at low oxygen pressures the σ of the CaO-doped specimen is slightly less than

Fig. 3 Isothermal plots of $\log \sigma$ vs $\log P_{O_2}$ for "pure" CeO₂ and 1.0 mole % CaO-doped CeO₂ sintered specimens. ² All conductivity data has been normalized using Eq. (1).

the σ of "pure" CeO_2 specimens. Thus in this region the electronic conductivity appears to predominate and $\sigma \sim \sigma_e > \sigma_i$. The small decrease in the σ may be attributed to a decrease in the electronic mobility.

An estimate of the oxygen vacancy mobility, $6 \times 10^{-5} \text{ cm}^2/\text{volt-sec}$, at 800°C was obtained using Eqs. (7) and (8) by assuming $\sigma \sim \sigma_i$ at high oxygen pressures. It is interesting to note that the mobility of oxygen vacancies in CaO-doped CeO_2 is larger than in CaO-doped ZrO_2 .¹⁴ Since CaO-doped ZrO_2 has been used as an electrolyte for solid state fuel cells, it appears that CaO-doped CeO_2 could be a better electrolyte if the electronic conductivity at lower oxygen pressure could be suppressed by appropriate doping.

An attempt is currently being made to combine results obtained from the above limiting case conductivity model in order to obtain an expression which will fit the conductivity data of the CaO-doped specimen over the entire temperature and oxygen pressure region investigated. The data to be obtained from the ionic transference measurements should also aid in analysis of the σ data. Additional CaO-doped conductivity data will be obtained to facilitate this analysis.

B. Thermodynamic Study

Transference measurements employing a galvanic cell technique³ were initially undertaken to determine the ionic conductivity in "pure" $\text{Ce}_{1+y}\text{O}_2$ as a function of temperature and oxygen pressure. These measurements were made on sintered CeO_2 specimens in the temperature range $800^\circ - 1050^\circ\text{C}$ and in the oxygen pressure region 1 to 10^{-8} atm. The sintered CeO_2 specimens were prepared from 99.9% and 99.99% purity CeO_2 powder obtained from American Potash and Chemical Corporation.

The results of these measurements may be summarized briefly as follows. The ionic transference number, t_i , decreased with increasing temperatures and decreasing oxygen pressures. The value of t_i also appeared to vary with the purity of the specimen (i.e., the higher purity specimen exhibited less ionic conductivity). These results are consistent with the observed behavior of the electrical conductivity in the temperature and oxygen region corresponding to region I, as reported in the electrical conductivity study on $\text{Ce}_{1+y}\text{O}_2$.^{1,2} The conductivity in this region was interpreted^{1,2} as being influenced by the presence of impurities. Unless higher purity CeO_2 specimens are used to minimize the effect of impurities, it will not be possible to obtain information about the role of "native" defects on the ionic conduction process from ionic transference measurements.

As discussed in the electrical property study, a combined study of the electrical conductivity and the ionic transference as a function of temperature, oxygen pressure, and CaO content was initiated to obtain information on the mobility of oxygen vacancies in CeO_2 . To date transference measurements have been made only on a 2 mole % CaO-doped CeO_2 specimen in the oxygen pressure region I to 0.5 atm. These results are shown in Fig. 4 where the transference number is plotted as a function of temperature between 800° and 1050°C. The ionic transference number is approximately 0.75 at 845°C and appears to exhibit a small decrease with increasing temperature. These results are consistent with the observed electrical conductivity behavior of CaO-doped CeO_2 as described in the electrical property study. Future work will be concerned with obtaining data on t_i over a wide range of temperature, oxygen pressure and CaO

Fig. 4 Ionic transference fraction versus temperature for a 2.0 mole % CaO-doped CeO_2 sintered specimen.

content. A combined analysis (see electrical property study) of the electrical conductivity and ionic transference data on CaO-doped CeO_2 will be employed to 1) determine the temperature and compositional dependence of the mobility of oxygen vacancies and 2) characterize the electronic conductivity of CaO-doped CeO_2 by modifying the proposed non-stoichiometric defect model for "pure" $\text{Ce}_{1+y}\text{O}_2$.

As discussed in the last technical report³ a thermogravimetric technique has been used to obtain weight change measurements of $\text{Ce}_{1+y}\text{O}_2$ as a function of oxygen pressure in the temperature range $800^\circ - 1400^\circ\text{C}$. The sensitivity and reproducibility of the weight measurements limits the measurement of y to the oxygen pressure at a given temperature where $y > 10^{-3}$. Since $y = f(T, P_{\text{O}_2})$ the range of oxygen pressure studied varies with temperature. For example, at 800°C , P_{O_2} was investigated between 10^{-8} and 10^{-20} atm whereas at 1400°C the range of P_{O_2} studied was between 10^{-2} and 10^{-10} atm.

The nonstoichiometric defect structure analysis of the thermodynamic data should in principle be a more direct method than the corresponding analysis of the electrical conductivity data because the electronic mobility is not involved. Unfortunately, the method of analysis, used on the conductivity data where the nonstoichiometric defect exists in more than one state of ionization cannot be employed in the thermodynamic analysis. The reason for this is that when two states of ionization exist it is not possible to derive a simple nonlinear equation, $y = f(y, P_{\text{O}_2})$. In addition, the proposed defect model contains terms to account for large departures from stoichiometry as well as defect interaction parameters both of which further complicate the model. However, if one assumes that two states of ionization predominate and applies all the

equations of the model to a particular thermodynamic state, $y(T, P_{O_2})$, the result is a system of six nonlinear simultaneous equations in seven unknowns. Five of the six equations can be written for one state of ionization.^{1,2} The sixth equation results from the equilibrium of the ionization reaction

where all quantities have been previously defined.^{1,2} If the same set of equations is again applied to another thermodynamic state at the same temperature and with the same two states of ionization predominating, the result is 12 equations in 12 unknowns since the mass action constants are functions of temperature alone and are therefore equivalent.

This method of analysis then consists of solving the system of 12 simultaneous nonlinear equations for proper combinations of data points and averaging the results of the individual solutions. An extension of Newton's method¹⁵ for nonlinear equations is used coupled with a nonlinear interaction technique for initial estimation of the unknown quantities. Unfortunately, the system of equations is extremely "ill-conditioned" and hence their solution is a rather delicate procedure. The analysis of this system of equations is further complicated because the proposed defect model contains terms to account for large departures from stoichiometry as well as defect interaction parameters.

In order to avoid some of these difficulties, a new method of analysis has been attempted. This method employs the same defect reactions and assumptions as the above analysis. The basic difference is that this analysis utilizes both the thermodynamic and electrical conductivity data. For example, for a cerium interstitial defect model involving two states

of ionization, Ce_i^{+3} and Ce_i^{+4} , the following equation was derived using this method of analysis.

$$\sigma^2 + (KC)\sigma = KC^2y + K^2C^2 \quad (15)$$

In Eq. (15),

$$C = 8.0 \times 10^3 \mu_e \quad (16)$$

and K corresponds to the equilibrium constant for Eq. (14) where $n = 3$.

The advantages of this method of analysis over the previously described method are:

- a. Only one equation has to be solved instead of 12 simultaneous equations.
- b. The additional complication associated with incorporating large departures from stoichiometry and the interaction parameters are eliminated in this analysis.
- c. The electronic mobility may be determined directly in this analysis.
- d. Equations may be derived which are based on an electroneutrality equation which involves the nonstoichiometric defect in three different states of ionization.

To date only the data at 800°C has been analyzed using this technique. The results appear to be consistent with the proposed defect model.^{1,2} Unfortunately, this method of analysis also contains problems. The curve fitting technique is difficult if the actual data points are used. This difficulty arises from the compound scatter of the two sets of data and generally results in overweighting certain terms in Eq. (15).

In order to avoid this problem, the thermodynamic and electrical conductivity data will be curve fit with empirical expressions. Calculated quantities from these expressions will then be used to solve Eq. (15).

The analysis of the combined data using Eq. (15) requires the conductivity and thermodynamic data to be available in the same temperature and oxygen pressure region. Thus, a more complete analysis of the data will require additional thermodynamic data near stoichiometry. The thermogravimetric technique will be modified so that weight measurements can be made in a partial vacuum. This alteration in the system should result in an increased sensitivity and reproducibility of the weight measurements.

The compositional dependence of the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ shown in Figs. 5 and 6, respectively were calculated from the thermodynamic data³ (i.e., $y = (T, P_{O_2})$) and the following equations

$$\Delta\bar{G}_{O_2} = RT \ln P_{O_2} \quad (17)$$

$$\Delta\bar{H}_{O_2} = [\partial \ln P_{O_2} / \partial (1/T)]_y = \text{constant} \quad (18)$$

$$\Delta\bar{G}_{O_2} = \Delta\bar{H}_{O_2} - T\Delta\bar{S}_{O_2} \quad (19)$$

Both $-\Delta\bar{H}_{O_2}$ and $-\Delta\bar{S}_{O_2}$ vary as a function of y and exhibit a minimum; this behavior is consistent with a defect model involving a cerium interstitial which may exhibit multiple states of ionization. For example $-\Delta\bar{H}_{O_2}$ which is defined by the reaction

is equal to the enthalpy of the defect reaction

Fig. 5 The relative partial molal enthalpy of oxygen versus composition.

Fig. 6 The relative partial molal entropy of oxygen versus composition.

if Ce_i^{+n} predominates in a single state of ionization and a weighted sum of the appropriate enthalpies if two states of ionization predominate. Thus in the temperature and oxygen pressure near stoichiometry (i.e. $y \approx 0$) the predominate atomic defect is Ce_i^{+4} and $-\Delta\bar{H}_{\text{O}_2} \approx \Delta H_4$. The defect structure analysis of the conductivity data is consistent with this interpretation.^{1,2} It is interesting to note that the minimum value of $-\Delta\bar{H}_{\text{O}_2}$ is 7.9 eV and the estimated value of ΔH_3 from the conductivity analysis^{1,2} is approximately 8.5 eV.

When the aforementioned combined analysis of conductivity and thermodynamic data is completed, these results will be compared with the compositional variations of $\Delta\bar{H}_{\text{O}_2}$ to test the validity of proposed defect structures for $\text{Ce}_{1+y}\text{O}_2$. An attempt will also be made to use these results to explain the compositional dependence of $\Delta\bar{S}_{\text{O}_2}$.

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