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on

"A STUDY OF THE DEFECT STRUCTURE
OF NONSTOICHIOMETRIC CeO_2 "

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ABSTRACT

The electrical conductivity of sintered specimens of nonstoichiometric $\text{Ce}_{1+y}\text{O}_2$ was measured as a function of temperature from $1000^\circ - 300^\circ\text{C}$ and composition from $0.00214 \leq y \leq 0.0977$. These results were described in terms of a high and low temperature region. Each temperature region was characterized by an exponential dependence on temperature. The temperature of the intersection between the high and low temperature regions for each composition was compared with the composition-temperature dependence of the miscibility gap reported by Brauer and Gingerich. The temperature dependence in the high temperature region was attributed to a change in both the carrier concentration and carrier mobility. An approximate value of the standard enthalpy of formation for the defect reaction

was determined from the temperature dependence of the conductivity in this study and from the temperature dependence of the electron mobility reported in the literature.

The electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 7.0 mole %) was also measured over the temperature range $700^\circ - 1500^\circ\text{C}$ and from 1 to 10^{-22} atm of oxygen. All specimens of CaO-doped CeO_2 exhibited mixed conduction. The electrical conductivity has been rationalized in terms of a defect model involving nonstoichiometric defects (ionized cerium interstitials and localized electrons) and impurity generated defects (doubly ionized oxygen vacancies). Good agreement has been obtained between the theoretically derived relation based on this defect model

$$\sigma = \sigma_{oe} (1 - \bar{\xi}a) + A(\%CaO)\exp(-E_i/kT)$$

and the electrical conductivity data; where, σ_{oe} is the electronic conductivity of nonstoichiometric "pure" CeO_2 and $(1 - \bar{\xi}a)$ is a correction for CaO-doping. The second term in the expression for σ represents the ionic conductivity which is proportional to the oxygen vacancy concentration and mole % CaO.

The diffusion coefficient for oxygen vacancies,

$$D_{V_O} = 1.4 \times 10^{-11} (kT)\exp(-.61/kT)$$

in CaO-doped $Ce_{1+y}O_2$ was also determined from the conductivity study.

Ionic transference measurements employing an emf technique have also been made on a 5 mole % CaO-doped $Ce_{1+y}O_2$ specimen as a function of temperature (710° to 1008°C) and oxygen pressure ($1 - 10^{-22}$ atm).

The thermogravimetric measuring system has been modified to work in a partial vacuum. Departures from stoichiometry as low as $y \sim 2 \times 10^{-4}$ may now be measured with this system. At lower temperatures (800° - 1000°C) near stoichiometry (i.e. $3.5 < y < 3.0$) the following simple isothermal relationship between y and P_{O_2} has been observed

$$y = K P_{O_2}^{-1/5}$$

$\Delta \bar{H}_{O_2}$ has also been shown to be independent of y in this region.

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 both electronic and ionic 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. The standard enthalpies

of formation for the following defect reactions in $\text{Ce}_{1+y}\text{O}_2$ were determined from an analysis of the conductivity data:

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 data for the calculation in the temperature range 800° - 1200°C was selected from the oxygen pressure region where according to the analysis of the conductivity data the predominate defects are electrons localized on normal cerium ions and quadruply ionized cerium interstitials. The calculated electron mobility of $\text{Ce}_{1+y}\text{O}_2$ increases exponentially (i.e. $\mu = \mu_0 e^{-0.14/kT}$) with increasing temperature between 800° and 1200°C. The conduction mechanism is assumed to be a "hopping" type process with an activation energy of 0.14 eV (i.e. under the influence of an electric field the electrons localized at normal cerium ion sites move to adjacent cerium ions). The magnitude of the mobility is of the order $10^{-2} \text{ cm}^2/\text{v-sec}$.

One of the difficulties with the above 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

*Approximate values.

in our laboratories using a vapor transport technique.⁵ 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.^{2,6,7} The result of this study^{8,9} is that the conductivity data obtained on sintered specimens of CeO_2 may be corrected for porosity by using the simple relation

$$\sigma_{\text{normalized}} = \sigma_{\text{measured}} \frac{\rho_{\text{theoretical}}}{\rho_{\text{measured}}} \quad (1)$$

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 $\text{Ce}_{1+y}\text{O}_2$.⁴ In addition, a combined study of the electrical conductivity and ionic transference of calcium doped cerium dioxide was continued 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" $\text{Ce}_{1+y}\text{O}_2$.¹⁰

RESULTS AND DISCUSSION

1. Electrical Property Studies

In the last progress report¹⁰ 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 in the range $0.00214 \leq y \leq 0.0977$ have been measured as a function of temperature from 1000° to 300°C employing an improved experimental measuring technique. The composition of the specimen was fixed by equilibrating the sample in a CO-CO_2 mixture with a known CO/CO_2 ratio at 1000°C . The system was then purged with purified argon and the conductivity was measured using a standard four probe DC technique. A constant current was passed through the sample and the voltage across the inner probes 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 was then measured as a function of temperature. The specimen temperature was changed rapidly by moving the furnace relative to the sample. This procedure reduces the time the specimen was 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. The results of this study are described in a paper submitted for publication¹¹ and in AEC Report C00-1441-13. These results may be summarized as follows. The constant composition data may be

described conveniently in terms of high temperature and low temperature regions. In both temperature regions the conductivity exhibits an exponential dependence on temperature.

$$\sigma = \sigma_0 e^{-Q/kT} \quad (2)$$

In the high temperature region the activation energy increased with increasing values of y (i.e. 0.22 eV at $y = .00214$ to 0.37 eV at $y = .098$). The activation energy, $0.61 \pm .03$ eV, in the low temperature was independent of y .

The temperature of the intersection between the high and low temperature regions for each composition was compared with the composition-temperature dependence of the miscibility gap reported by Brauer and Gingerich.¹² The temperature dependence of the conductivity in the high temperature region was attributed to a change in both the carrier concentration and carrier mobility. An approximate value of the standard enthalpy of formation for the defect reaction

was determined from the temperature dependence of the conductivity in this study and from the temperature dependence of the electron mobility reported in the literature.⁴ Although this is an approximate value of ΔH for the ionization of a triply ionized cerium interstitial it is interesting to note the agreement with the approximate value $\Delta H_c \approx 1.9$ eV (see Eq. (c)) obtained from an analysis of the oxygen pressure dependence of the electrical conductivity.¹³ Another point of interest is that based on the defect analysis presented here for donors involving multiple states of ionization, the activation energy which characterizes the temperature dependence of the electrical conductivity for a fixed composition is much smaller than

the calculated value of the ionization energy of the defect. This observation should also apply to other systems where the donor exhibits multiple states of ionization.

As described in the previous progress reports most of the experimental difficulties with the AC Hall mobility technique have been associated with noise problems.^{3,10} 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.¹⁰ Unfortunately these changes have not reduced the noise level enough to permit the measurement of the Hall voltage of $\text{Ce}_{1+y}\text{O}_2$ specimens. A very low noise level (e.g. $\sim 10^{-8}$ volts) is required because the electron mobility of $\text{Ce}_{1+y}\text{O}_2$ is very small (i.e. $\mu \sim 10^{-2} \text{ cm}^2/\text{v-sec}$). The major source of noise is caused by the rotation of the specimen in the magnetic field. The solution to this problem would be to replace the magnet which is currently used with a magnet having a low inductance. This type of magnet would eliminate the need for rotating the specimen, since the magnetic field could then be varied by driving the magnet with an oscillating current. Professor Seitz of the Electrical Engineering Department has designed and built this double AC Hall mobility measuring system. He is currently trying to obtain financial support for the new magnet which will cost several thousand dollars. If he is successful in this effort an attempt will be made to measure the high temperature Hall mobility of $\text{Ce}_{1+y}\text{O}_2$ 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.

As discussed in the last progress report¹⁰ a combined study on the electrical conductivity of sintered specimens of CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO content was initiated to 1) obtain information on the diffusion coefficient for oxygen vacancies in CeO_2 and 2) to characterize the electronic conductivity of CaO-doped CeO_2 by modifying the proposed nonstoichiometric defect model for "pure" $\text{Ce}_{1+y}\text{O}_2$. The results of this study are described in a paper submitted for publication¹³ and in AEC Report C00-1441-14. These results may be summarized as follows.

The electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 7.0 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. In the CaO content, temperature and oxygen pressure region investigated, the electronic conductivity has been rationalized in terms of a defect model involving nonstoichiometric defects (ionized cerium interstitials and localized electrons) and impurity generated defects (doubly ionized oxygen vacancies). Good agreement has been obtained between the theoretically derived relation

$$\sigma = \sigma_{oe} (1 - \bar{\xi}_a) + A(\% \text{CaO}) \exp(-E_i/kT) \quad (4)$$

and the electrical conductivity data. Where, the electronic conductivity of nonstoichiometric "pure" CeO_2 is σ_{oe} and $(1 - \bar{\xi}a)$ is a correction for CaO-doping. The quantity, $\bar{\xi}$, is related to a geometrical blocking factor associated with the site fraction of Ca^{+2} ions on normal Ce^{+4} ion sites, a. The second term in the above expression for σ represents the ionic conductivity which is proportional to the oxygen vacancy concentration and mole % CaO.

Although the proposed defect model appears to provide a good fit of the conductivity data there are a few problems with this model. For example, there is no simple physical model to explain how $\bar{\xi}$ should vary with CaO content. For the low CaO content specimen (e.g. 1 mole % CaO) another problem is observed at low temperatures $700^\circ - 900^\circ\text{C}$ and oxygen pressures where the actual conductivity data exhibits a greater dependence on P_{O_2} than the simple model predicts. Since this region is characterized by predominantly electronic conductivity this observation would imply that the proposed model for electronic conductivity in this region is overly simplified.

A more subtle problem is the assumption that predominantly ionic conductivity occurs in the region of temperature and P_{O_2} where the total conductivity is observed to be independent of P_{O_2} . If this region of P_{O_2} and temperature occurs where the electronic conductivity is a minimum (i.e. in the transition region between n and p-type conductivity), then the electronic conductivity would be only slightly dependent on P_{O_2} and the total conductivity might appear as if it were independent of P_{O_2} . Thus it is also possible that some p-type behavior may exist at lower temperatures (e.g. $700^\circ - 900^\circ\text{C}$) and higher oxygen pressures (e.g. $1 - 10^{-4}$ atm).

Additional studies that would aid in providing a better understanding of electrical conduction in CaO-doped $\text{Ce}_{1+y}\text{O}_2$ are:

1. Thermodynamic measurements of the oxygen content as a function of temperature and oxygen pressure. This type of data would allow one to test the model for dependence of the electronic carrier concentration $[\text{Ce}'_{\text{Ce}}]$ on P_{O_2} and temperature without the complication of considering the effects of CaO on the electronic mobility.
2. Transference measurements as a function of temperature, P_{O_2} and CaO content when combined with the corresponding σ data should allow the determination of the temperature, P_{O_2} and CaO content dependence of the electronic and ionic conductivity. This type of data will indicate if p-type conductivity is present at low temperatures and high P_{O_2} . It would also permit a test of the simple model for ionic conductivity which assumes that σ_i is independent of P_{O_2} .

An equation for the diffusion coefficient of oxygen vacancies, $D_{\text{V}_\text{O}''}$, in CaO-doped CeO_2 was also determined in this study. The expression

$$D_{\text{V}_\text{O}''} = 1.4 \times 10^{-1} (kT) \exp(-.61/kT) \quad (5)$$

was calculated by combining the above defect model for ionic conductivity, the conductivity data in the region where ionic conductivity was assumed to predominate, and the Nernst-Einstein relation.

B. Thermodynamic Study

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 . The preliminary results of a transference study employing an emf technique on a 2 mole % CaO-doped CeO_2 specimen in the oxygen pressure region 1 to 0.5 atm were discussed in the previous report.¹⁰ The ionic transference number was approximately 0.75 at 845°C and appeared to exhibit a small decrease with increasing temperature up to the maximum temperature investigated, 1050°C.

In the current study, transference measurements on a 5 mole % CaO-doped CeO_2 specimen were made over a wide range of oxygen pressure and temperature. The dependence of the transference number on P_{O_2} is shown in Fig. 1 where isotherms of t_i vs P_{O_2} are plotted. For purposes of discussion it is convenient to describe these results qualitatively in terms of a "high" and a "low" oxygen pressure region. No data is shown between these two regions because there is no simple method available to control the P_{O_2} there. The transference number in the high oxygen pressure region (i.e. $1 - 10^{-4}$ atm) appears to increase slightly with decreasing P_{O_2} to a certain value of P_{O_2} characteristic of each temperature and then decrease with decreasing P_{O_2} . Between 1008° and 804°C, t_i increases with decreasing temperature, at 710°C, however, the value of t_i is slightly smaller than 922°C. These results indicate the presence of some p-type conduction. As shown in Fig. 1, $t_i > 0.8$ at $P_{\text{O}_2} = 1$ atm in the temperature range 710° to 1008°C. Thus, the assumption used in the analysis of the conductivity data of CaO-doped CeO_2 that $t_i = 1$ at $P_{\text{O}_2} = 1$ atm in this range of temperature is slightly in error. In the lower P_{O_2} region, t_i decreases with decreasing P_{O_2} and increasing temperature, these results indicate that n-type behavior is significant in this region. This observation is consistent with the electrical conductivity study on CaO- CeO_2 .¹³

Fig. 1 A plot of the ionic transference number, t_i , as a function of $\log P_{O_2}$ for a 5 mole % CaO-doped CeO_2 specimen.

Future work will be concerned with obtaining similar data on t_i for CeO_2 specimens doped with CaO between 1 and 10 mole %. 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 ionic conductivity and the mobility of oxygen vacancies and 2) characterize the electronic conductivity of CaO -doped CeO_2 by modifying the proposed nonstoichiometric defect model for "pure" $\text{Ce}_{1+y}\text{O}_2$.^{2,13}

As discussed in the previous technical reports^{3,10} a thermogravimetric technique has been used to obtain weight change measurements on $\text{Ce}_{1+y}\text{O}_2$ as a function of oxygen pressure in the temperature range $800^\circ - 1400^\circ\text{C}$.

In this technique the Ar-O_2 and CO-CO_2 gas mixtures are diluted with He and the weight measurements were made at a total pressure of one atmosphere. The sensitivity and reproducibility of the weight measurements limited 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.

At lower temperatures most of the data obtained with this technique was in an oxygen pressure region where the nonstoichiometric defects exhibit more than one state of ionization. At higher temperatures the problem of determining the departure from stoichiometry at the reference state was encountered. Thus, it was not possible, as it was with portions of the electrical conductivity data, to perform a straight forward defect structure analysis involving only a single state of ionization. However,

the thermodynamic data offers in principle a more direct approach to defect structure analysis than the conductivity data since it does not involve a mobility term. Unfortunately, the method of analysis used on the isothermal conductivity data where the nonstoichiometric defect exists in more than one state of ionization cannot be employed. This is because in the thermodynamic analysis it is not possible to derive a simple nonlinear equation, $y = f(y, P_{O_2})$.

An attempt was made to analyze the thermodynamic data using a technique which consisted of solving a system of 12 nonlinear simultaneous equations.³ However, this technique was difficult to employ in its simplest form, and was further complicated by terms necessarily included to account for large departures from stoichiometry and defect interactions.

To circumvent these problems another method of analysis was suggested.¹⁰ This method which included the same defect reactions and assumptions as the above method, employed a combined analysis using both the thermodynamic and conductivity data. This method had the distinct advantage of involving only one nonlinear equation. Unfortunately the technique used for curve fitting diverged frequently as a result of the compound scatter involved in the two sets of data. In addition a recent analysis of the constant conductivity data¹¹ indicates that at least three states of ionization coexist in the oxygen pressure region where $m < 4$ in the relation

$$y \propto P_{O_2}^{-1/m} . \quad (6)$$

In light of these problems it became increasingly more apparent that the measurement of y closer to stoichiometry was necessary in order to obtain a more meaningful defect structure analysis of the thermodynamic data.

With this type of data, analysis similar to that performed on the electrical conductivity and a combined analysis of the conductivity and thermodynamic data, as discussed above, would be possible. In addition the availability of this type of data would permit a more accurate determination of the electron mobility than obtained in a previous study.⁴

As suggested in the previous progress report¹⁰ the following changes were made in the thermogravimetric technique to extend the measuring capabilities to values of $y < 10^{-3}$. The total system pressure was reduced and controlled at 0.1 atm with a cartasian diver manostat and measured with a positive closed end manometric gauge. Voltage stabilization was added to the balance and a new method of calibration and procedure was devised to realize the ultimate sensitivity of the balance. The zero offset on the balance was bypassed and all voltages were measured directly with a high input impedance digital voltmeter. The use of the digital voltmeter permitted the maximum filtering on the balance, which resulted in a reduction of the noise level to about $\pm 1 \mu\text{g}$.

Fig. 2, which is an isothermal plot of $\log y$ vs $\log P_{O_2}$, illustrates how y has been extended closer to stoichiometry (i.e. $10^{-3} < y < 10^{-4}$) for the $800^\circ - 1300^\circ\text{C}$ isotherms. Essentially all of the previous data from $800^\circ - 1200^\circ\text{C}$ has been reproduced with the new measuring technique. For the lower temperature isotherms $800^\circ - 1000^\circ\text{C}$, P_{O_2} was controlled by using only CO-CO_2 gas mixtures. In this case the lower limit of y was determined not by the limitation of the weight measuring system but by the highest value of P_{O_2} that could be obtained with the CO-CO_2 mixtures (i.e. the minimum value of the ratio CO/CO_2 , which was 10^{-3}). The calculated values of y are based on the assumption that $y = 0$ in the reference state

Fig. 2 Isothermal $\log y$ in Ce^{1+y}_0 vs $\log P_0^2$ demonstrating the extension of thermogravimetric data using the improved weight change technique.

(i.e. $P_{O_2} = 0.1$ atm). At higher temperature this assumption is not valid, thus the calculated values of y near stoichiometry which are shown in Fig. 2 are slightly lower than the actual values.

For the new thermodynamic data obtained near stoichiometry, y is proportional to $P_{O_2}^{-1/5}$ in the temperature range $800^\circ - 1000^\circ\text{C}$. This behavior is consistent with the proposed defect model where the predominate defects are quadruply ionized cerium interstitials. Near stoichiometry this model may be represented by the expression

$$K \approx y^5 P_{O_2} \quad (7)$$

where K is the mass action constant for the defect reaction

Values of K between 800° and 1000°C were calculated from Eq. (7) and the appropriate data shown in Fig. 2. Since

$$K \propto e^{\Delta S^\circ/k_e - \Delta H^\circ/kT} \quad (9)$$

a plot of $\log K$ vs $1/T$ was made to determine ΔH° for Eq. (8). These results are shown in Fig. 3. $\Delta H^\circ = 9.65 \pm 0.07$ eV was calculated from the least square slope of the line shown in Fig. 3. It is interesting to note that this value is slightly smaller than the corresponding value, 10.4 eV, obtained from the analysis of the conductivity data.² The temperature dependence of the electron mobility was required in the calculation of ΔH° from the conductivity data. Thus it appears that the activation energy for electron mobility, 0.14 eV, used in that analysis may have been too small a value. The 0.14 eV value was determined by combining the previous thermodynamic and conductivity data.⁴ In the current study the

Fig. 3 Log K vs 1/T from 800° - 1000°C where the bars represent the range in calculated values of K.

analysis of electron mobility will be repeated using the new thermodynamic data. In addition, analysis of thermodynamic data can now be extended to the higher temperature region by using ΔH^0 in Eqs. (7) and (9) to determine the nonstoichiometry in the reference state. And, finally, the defect analysis, where the thermodynamic and conductivity data can be combined, can now be performed since a significant amount of thermodynamic and conductivity data is now available in the same temperature and P_{O_2} region.

In the last technical report,¹⁰ the thermodynamic quantities $\Delta \bar{H}_{O_2}$ and $\Delta \bar{S}_{O_2}$ were calculated as a function of y . It was observed that near stoichiometry

$$\Delta \bar{H}_{O_2} \approx -\Delta H^0 \quad (10)$$

if the assumptions used in deriving the defect model were correct.

Preliminary calculations with the new thermodynamic data close to stoichiometry indicate that $\Delta \bar{H}_{O_2} \approx -9.6$ eV in the temperature range $800^\circ - 1000^\circ\text{C}$ and from $-3.5 \leq \log y \leq -3.0$, in agreement with the above value of $-\Delta H^0$.

A constant value of $\Delta \bar{H}_{O_2}$ independent of y is consistent with the law of mass action approach. In the same composition region $\Delta \bar{S}_{O_2}$ exhibits a linear dependence on $\log y$. This behavior is in qualitative agreement with a simple entropy model for noninteracting randomly distributed point defects. Thus, the preliminary results of the thermodynamic quantities calculated from the new data near stoichiometry are consistent with use of the law of mass action. This analysis will be extended to higher temperatures by correcting the data for stoichiometry and a more rigorous test of the random distribution models will be performed.

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