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AN INVESTIGATION OF MIXED CONDUCTION IN SOLID ELECTROLYTES

Final Report

Robert A. Rapp

The Ohio State University
Research Foundation
Columbus, Ohio

December 1, 1964 - June 30, 1972

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Report No. COO-1440-23

FINAL

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

1314 KINNEAR RD.
COLUMBUS, OHIO 43212

To U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439
Contract No. AT(11-1)-1440

On AN INVESTIGATION OF MIXED CONDUCTION IN SOLID
ELECTROLYTES

For the period December 1, 1964 - June 30, 1972

Submitted by Robert A. Rapp
Department of Metallurgical Engineering

Date July 26, 1972

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ABSTRACT

Over a period of seven and one-half years, this contract has dealt with a variety of novel experimental approaches and associated theoretical interpretations to establish and understand the nature and magnitude of electronic conduction contributions to solid oxide electrolytes. AC conductivity measurements, DC polarization measurements and open-circuit galvanic cell measurements have dominated the experimental methods, while ZrO_2 , ThO_2 , and several rare earth oxides--each containing one of a variety of aliovalent metallic dopants including hydrogen (protons)--have been the electrolyte materials which were investigated.

Theoretical treatments have been derived to predict the dependences of n-type and p-type electronic conductivities on the dopant concentration. A novel analysis allows the receipt of both the excess electron and positive hole conductivities from the data of a DC polarization measurement. The galvanic voltage expected from bielectrolyte cells has been derived in terms of the ionic and electronic conduction parameters of the two series electrolytes. The interpretation of conduction effected by the presence of two dopants (one metal plus hydrogen) has been made.

In ThO_2 -base electrolytes, the electronic conductivities have been found to depend only upon dopant valence and not the ionic size of the dopant. Finally, potentiostatic kinetic measurements were made to establish the solubility and diffusivity of oxygen in liquid tin and in solid silver.

INTRODUCTION

The research conducted under this contract over the past seven and one-half years has led to some considerable understanding of the nature and magnitudes of electronic conduction parameters in solid oxide electrolytes. This work has been and will continue to be of direct practical interest to the AEC as ThO_2 -base electrolyte cells are used to monitor dissolved oxygen concentrations in the liquid sodium coolant of fast breeder reactors, as well as in more fundamental laboratory studies involving such galvanic cells. This research has led to a number of publications, each of which will be discussed later in the report:

M. K. Lasher and R. A. Rapp, "Mixed Conduction in ThO_2 - Y_2O_3 Solid Solutions," Zeitschrift für Physikalische Chemie 49, (1966) 198.

J. W. Patterson, E. C. Bogren and R. A. Rapp, "Mixed Conduction in $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ Solid Electrolytes," J. Electrochem. Soc. 114, (1967) 752.

R. A. Rapp, "Mixed Conduction in Solid Oxide Electrolytes," Thermodynamics of Nuclear Materials, Vienna Intern. Atomic Energy Agency, (1967) 559.

R. A. Rapp and D. A. Shores, "Solid Electrolyte Galvanic Cells," Ch. 6C, pp. 123-192, Techniques of Metals Research, Vol. IV, (R. A. Rapp, Ed.) Wiley Publ. (1970).

D. A. Shores and R. A. Rapp, "Solid Bielectrolyte Cells for Thermodynamic Measurements," J. Electrochem. Soc. 118, (1971) 1107.

D. A. Shores and R. A. Rapp, "Hydrogen Ion (Proton) Conduction in Thoria-Base Solid Electrolytes," J. Electrochem. Soc. 119, (1972) 300.

T. A. Ramanarayanan and R. A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Tin and Solid Silver and the Diffusivity of Oxygen in Solid Nickel," Metall. Trans., in press. (This research has not been reported previously to the AEC. A copy of the manuscript in press is attached as an Appendix to this final report).

D. H. Primas, D. A. Shores, and R. A. Rapp, "Mixed Conduction in Pure ThO_2 , ThO_2 - Sm_2O_3 , and ThO_2 - La_2O_3 Solid Solutions," manuscript in preparation.

J. M. Macki and R. A. Rapp, "Electrical Conduction in Pure and Doped Dy_2O_3 and Gd_2O_3 ," manuscript in preparation.

In addition to these topics specifically supported by the AEC, the Principal Investigator has conducted related research in allied areas under other sponsorship where he has drawn from the knowledge in point defects and solid state electrochemistry to publish the following papers:

Y. D. Tretyakov and R. A. Rapp, "Nonstoichiometry and Defect Structures in Pure Nickel Oxide and Lithium Ferrite," Trans. Met. Soc. AIME, 245 (1969) 1235.

R. L. Pastorek and R. A. Rapp, "The Solubility and Diffusivity of Oxygen in Copper," Trans. Met. Soc. AIME, 245 (1969) 1711.

C. E. Polson, D. G. Kesterke, T. R. Kato, J. H. Trapp, and R. A. Rapp, "A Conceptual Cell for Electrowinning Liquid Uranium," Electrometallurgy, AIME, Proceedings of Extractive Metallurgy Operating Conference (1968) 122.

G. H. Meier and R. A. Rapp, "Electrical Conductivities and Defect Structures of Pure NiO and Chromium-Doped NiO," Zeitschrift für Physikalische Chemie 54, (1971) 168.

K. E. Oberg, L. M. Friedman, R. Szwarc, W. M. Boorstein, and R. A. Rapp, "The Diffusivity of Oxygen in Liquid Iron from Electrochemical Measurements," J.I.S.I., (May 1972) 359.

K. Oberg, L. Friedman, W. M. Boorstein and R. A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Copper and Liquid Silver," Metall. Trans., in press.

L. Friedman, K. Oberg, W. M. Boorstein and R. A. Rapp, "Mixed Conduction in a Commercial Zirconia 3-4 Wt.% CaO Electrolyte," Metall. Trans., in press.

K. E. Oberg, L. M. Friedman, W. M. Boorstein, and R. A. Rapp, "Electrochemical Deoxidation of Induction-Stirred Copper Melts," Metall. Trans., in press.

R. Szwarc, K. Oberg, and R. A. Rapp, "The Solubility and Diffusivity of Oxygen in Liquid Lead," J. High-Temperature Chemistry, in press.

R. Perkins and R. A. Rapp, "The Concentration-Dependent Diffusion of Chromium in Nickel Oxide," Metall. Trans., in press.

D. W. Short, R. A. Rapp, and J. P. Hirth, "The Influence of Surface Charge and Surface Structure on the Sublimation of Ionic Crystals," J. Chem. Phys., in press.

Y. Agrawal and R. A. Rapp, "The Control of Oxygen Activity in Flowing Argon," manuscript in preparation.

L. Friedman, R. Odle, W. M. Boorstein and R. A. Rapp, "The Electrochemical Deoxidation of Induction-Stirred Lead Melts," manuscript in preparation.

These investigations have resulted in the submission of two patents with government-free license rights. Over the span of the AEC research, at least twenty presentations of this research have been delivered to international, national and local technical meetings, to seminars in other universities, and in industrial and government research laboratories. The Principal Investigator has served as a consultant to AEC programs at National Lead of Ohio (Fernald, Ohio) and at Argonne National Laboratory (to two different groups). As a result of the AEC support, a number of students completed graduate programs in the Department of Metallurgical Engineering:

M. S. Degrees

Mark F. Lasker
Eric C. Bogren

Ph. D. Degrees

John W. Patterson
James M. Macki
Trikur A. Ramanarayanan

Post-Doctorate Research

Dr. J. S. Foster
Dr. D. Primas
Dr. D. A. Shores

Because most of the research conducted under this contract has led to the publication of the results which have already been submitted as reprints in previous reports to the AEC, the format of this final report will follow the following pattern:

- A. Title of Specific Experimental or Theoretical Investigation (or previous publication) and List of Contributing Investigators.
- B. Formal Abstract of the Specific Investigation
- C. Comments with regard to the importance and contribution of the investigation and future work by the students involved following graduation.

1.A. Mixed Conduction ThO_2 and $\text{ThO}_2\text{-Y}_2\text{O}_3$ Solutions, M. F. Lasker and Robert A. Rapp (Z. Phys. Chem. N.F. 49 (1966) 198)

B.

Abstract

A dilute solution model was developed for the prediction of the partial ionic and electronic conductivities, as well as ionic transference numbers, in doped ThO_2 electrolytes. Total conductivity measurements were carried out between 800 to 1100°C for "pure" ThO_2 and $\text{ThO}_2\text{-Y}_2\text{O}_3$ solutions over a wide range of oxygen chemical potentials. Galvanic cell measurements were made to separate the total conductivity into partial ionic and partial electronic conductivities. Although σ_{p} was in agreement with the predictions of the dilute solution theory for all electrolyte compositions, σ_{ion} exhibited a maximum with increasing Y_2O_3 concentration. No significant excess electron conductivity was indicated for any $\text{ThO}_2\text{-Y}_2\text{O}_3$ composition at oxygen partial pressures as low as those for $\text{Cr-Cr}_2\text{O}_3$ equilibrium coexistence. With increasing $\text{YO}_{1.5}$ content in $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolytes, the P_{O_2} range for exclusive ionic conduction is extended to higher P_{O_2} ; although no experimental data are available, the dilute solution theory predicts that the P_{O_2} range for exclusive ionic conduction would also be extended to lower P_{O_2} with increasing Y_2O_3 concentration.

C. In this study, measurements of the total conductivity over a wide range of P_{O_2} were made (for the first time) to separate the total conductivity into ionic and p-type electronic conduction. Furthermore, the theory developed to establish the dopant-concentration-dependence allows the prediction of electronic conduction behavior where direct measurement is essentially impossible.

- 2.A. Mixed Conduction in $\text{Cr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ Solid Electrolytes, John W. Patterson, E. C. Bogren, and Robert A. Rapp (J. Electrochem. Soc. 114 (1967) 559)

B.

Abstract

The d-c polarization technique according to Wagner was applied for the first time at elevated temperatures for the determination of $\sigma_{\ominus}$ and $\sigma_{\oplus}$ in the $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ electrolytes over a range of oxygen activity and temperature. The applicability of the technique and an improved method for data analysis were demonstrated. Experimental difficulties and limitation were discussed. The total conductivity of $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ was determined over a range of oxygen activity and temperature.

C. Since this pioneering application of the d-c polarization method to very high temperature measurements, other investigators have improved the experimental arrangement by the use of electrolyte tubes instead of pills. The new arrangement eliminates the possibility of transfer between electrodes of either oxygen or electrons across the surrounding gas phase. The novel rearrangement of the existing theoretical analysis for this experiment by Patterson allowed the determination of both the p-type and n-type electronic conductivity, even when one contribution is significantly small.

Upon receipt of his M. S. degree from OSU, Eric Bogren and his wife (a registered nurse) spent two years in Ghana on a "peace-corps" type assignment, where Eric taught high school math, chemistry, and physics in a remote village. Eric's present address and position is unknown to the Department.

Dr. John W. Patterson is currently an Associate Professor in Metallurgical Engineering at Iowa State University where he has continued his interest in solid-state electrochemistry research. He has published about a dozen significant papers in this area and has investigated the potential electrolyte materials, Y_2O_3 and HfO_2 . He has introduced a very useful concept of "electrolytic domains" for solid electrolytes and has theoretically examined the activity profiles at steady-state across an electrolyte. He has examined important aspects of solid electrolytes in fuel cell applications.

- 3.A. Mixed Conduction in Solid Oxide Electrolytes, Robert A. Rapp
(Thermodynamics of Nuclear Materials, Vienna International Atomic
Energy Agency (1967) p. 559)

B.

Abstract

At temperatures between 800 and 1100°C electrical conductivity and galvanic cell measurements indicate that over a broad intermediate range of oxygen activity "pure" ThO_2 is an ionic conductor, which becomes a p-type electronic conductor at higher P_{O_2} . These measurements for "pure" ThO_2 are best rationalized by assuming that the ionic defects result from the presence of trace impurities. The P_{O_2} -dependence of a-c conductivity measurements in $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solutions shows a wide P_{O_2} -range of predominant ionic conductivity (σ_{ion}), with significant positive hole contributions ($\sigma_{\oplus}$) at higher oxygen activities. The behavior of $\sigma_{\oplus}$ is consistent with the existence of doubly ionized (un-associated) oxygen vacancies in electrical compensation of trivalent dopant ions. No significant excess electron conductivity contribution ($\sigma_{\ominus}$) was indicated for any $\text{ThO}_2\text{-Y}_2\text{O}_3$ composition at oxygen activities as low as those for $\text{Cr-Cr}_2\text{O}_3$ equilibrium coexistence. A d-c polarization technique was used for the direct measurement of $\sigma_{\oplus}$ and $\sigma_{\ominus}$ in $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ electrolytes. An improved method for the analysis of the data and experimental difficulties of this technique are discussed. A lower limit in P_{O_2} for predominant ionic conduction was reported for each electrolyte.

C. This review pointed out the important part played by conductivity measurements in the study and use of solid electrolytes. Prior to our work, experimentation had centered on the simple measurement of a galvanic cell voltage and the comparison of the measured voltage with that calculated from the Nernst equation. The difference then between the observed and "thermodynamic" voltage was assumed to be a result of electronic conduction in the electrolyte, and an interpretation was given in terms of the Schmalzried analysis of the voltage for a cell with a mixed conducting electrolyte. The erroneous assumption involved in this procedure is that the open-circuit cell measurement is perfect, a highly unlikely occurrence for electrodes at very low P_{O_2} which can easily polarize. The work with $\text{ThO}_2\text{-Y}_2\text{O}_3$ solutions also demonstrated that the defect model proposed for p-type conduction was, in fact, followed.

The work reviewed in this paper, as well as later work on this and other contracts, represents a significant contribution to solid-state electrochemistry. In this research area, the Principal Investigator has introduced new procedures for the measurement and interpretation of defect structures in binary and ternary oxides, for the determination of solubilities and diffusivities of oxygen in solid and liquid metals, for the establishment of p-type and n-type electronic conduction in solid electrolytes. Furthermore, a device has been developed (and

patented) for the control of oxygen activities in flowing or stagnant gas atmospheres. A new process for the electrochemical deoxidation of liquid metals has been discovered (and a patent application filed). This new process offers promise of significant industrial application in the production of "oxygen-free" metals. The latter two processes will be discussed in presentations at a meeting of the International Electrochemical Society in Stockholm, Sweden in September, 1972 and at a NATO summer school on Fast-Ion Transport in Solids in Belgrade, Italy in September, 1972. The Principal Investigator has been named as recipient of a Guggenheim Fellowship for "Studies in Electrochemical Processes," at Laboratoire de Thermodynamique et Physico-Chimie Metallurgiques, Domaine Universitaire, St-Martin-d'Heres (Grenoble), France from September 1972 through July 1973. In 1967, the Principal Investigator was awarded the American Society for Metal's Bradley Stoughton Young Teachers Award.

- 4.A. Solid Electrolyte Galvanic Cells, R. A. Rapp and D. A. Shores, Ch. 6C, pp. 123-192 (Techniques of Metals Research, Vol. IV, (R. A. Rapp, Ed.), Wiley Publ. (1970)

B.

Abstract

In this article, the experimental techniques of solid-state electrochemical measurements were critically reviewed. A comprehensive literature survey and a table of selected values for important oxygen reference electrodes were presented. AC and DC (polarization) conductivity measurements, open-circuit galvanic cell measurements, and potentiostatic, galvanostatic, and coulometric titration methods were reviewed, and the interpretation of such experiments was discussed.

C. Dr. David A. Shores, who performed outstanding research in two years as Post-Doctoral Research Associate on this contract, is presently a Research Metallurgist at the General Electric Metallurgy and Materials Laboratory in Schenectady, New York. Based on the experience gained at Ohio State University, Dr. Shores is presently studying the thermodynamics, kinetics, and electrochemical aspects of hot corrosion of high-temperature alloys at General Electric.

- 5.A. Solid Bielectrolyte Cells for Thermodynamic Measurements, David A. Shores and Robert A. Rapp (J. Electrochem. Soc. 118 (1971) 1107)

B.

Abstract

Galvanic cells utilizing two mixed conducting solid electrolytes in intimate contact with each other, and in which transport occurs by a common ion, have been analyzed. The voltage of such cells depends on the nonmetal (or metal) chemical potential at the interface between the electrolytes. A method for calculating the chemical potential at the interface from steady-state transference conditions has been described and example calculations for a $\text{ThO}_2(\text{Y}_2\text{O}_3)\text{-ZrO}_2(\text{CaO})$ bielectrolyte cell have been presented. Voltages less than the thermodynamic value must be expected for bielectrolyte cells when one or both electrolytes exhibit $t_i < 1$ and their partial electronic conductivities are comparable. The bielectrolyte cell arrangement seems to offer no outstanding advantages for thermodynamic measurements over a single electrolyte cell with a properly chosen reference electrode.

C. The theoretical considerations of this paper resulted as a response to another paper published by other authors in J. Electrochem. Soc. In this other paper, measurements were made with a bielectrolyte cell and an interpretation was given without substantiating theoretical work. These authors concluded (incorrectly) that bielectrolyte cells offered an inherent advantage in open-circuit galvanic cell measurements. In our paper, we analyzed the use of a bielectrolyte cell in general, and interpreted the measurements of the other authors specifically. In one case, their reported measurement must have been incorrect. We pointed out that a bielectrolyte cell is, in fact, inferior to the use of a single electrolyte with a well-chosen reference electrode.

- 6.A. Hydrogen Ion (Proton) Conduction in Thoria-Base Solid Electrolytes,
David A. Shores and Robert A. Rapp (J. Electrochem. Soc. 119 (1972)
300

B.

Abstract

The total conductivities of a series of ThO_2 -base electrolytes were determined over a wide range of oxygen activity in atmospheres of $\text{H}_2/\text{H}_2\text{O}/\text{Ar}$ mixtures. At 1200° and 1400°C and low oxygen activities, a significant conductivity contribution corresponding to hydrogen ion (proton) conduction was found for electrolytes with high dopant contents. The experiments are interpreted in terms of a defect model involving two dopants.

C. A couple of years ago Stotz and Wagner wrote a theory predicting that hydrogen ions, either in the form of protons or negative ions, might dissolve into a highly doped solid electrolyte to a sufficient extent that under the influence of an applied voltage hydrogen ions would make a significant contribution to the electrical conductivity of the electrolyte. These authors predicted the differing dependences of the hydrogen conduction contribution on $\text{P}_{\text{H}_2}/\text{P}_{\text{H}_2\text{O}}$ ratio, upon P_{H_2} , and upon dopant content. Wagner had previously sought to detect the hydrogen solubility and hydrogen conduction in a ZrO_2 -base solid electrolyte. While a very small amount of solubility was detected, no hydrogen conduction contribution was found because the oxygen ion partial conductivity is too high in zirconia. We, therefore, studied ThO_2 -base electrolytes where the oxygen conductivity is an order of magnitude lower. In three different ThO_2 -base systems ($\text{ThO}_2\text{-Y}_2\text{O}_3$, $\text{ThO}_2\text{-La}_2\text{O}_3$, and $\text{ThO}_2\text{-Sm}_2\text{O}_3$) a measurable hydrogen ion conductivity contribution was found at the highest dopant content and the highest temperatures (1200 and 1400°C). The design of a galvanic cell in which the electrolyte would function as a hydrogen probe, however, is not obvious or simple.

7.A. The Diffusivity and Solubility of Oxygen in Liquid Tin and Solid Silver and the Diffusivity of Oxygen in Solid Nickel, T. A.

Ramanarayanan and R. A. Rapp

(This research has not previously been reported to the AEC. The manuscript which is in press is attached as an Appendix to this report)

B.

Abstract

The diffusivity and solubility of oxygen in liquid tin and solid silver in the temperature range of about 750-950°C (1023-1223°K) and the diffusivity of oxygen in solid nickel at 1393°C (1666°K) were determined using the electrochemical cell arrangement of cylindrical geometry:

The diffusivity and solubility of oxygen in liquid tin are given by:

$$D_{\text{O}}(\text{Sn}) = 9.9 \times 10^{-4} \exp\left(\frac{-6,300}{RT}\right) \text{ cm}^2/\text{sec} (=9.9 \times 10^{-8} \exp\left(-\frac{6,300}{RT}\right) \text{ m}^2/\text{s})$$

and

$$N_{\text{O}}^{\text{S}}(\text{Sn}) = 1.3 \times 10^{-5} \exp\left(\frac{-30,000}{RT}\right) \text{ atom percent}$$

The diffusivity and solubility of oxygen in solid silver follow the relations:

$$D_{\text{O}}(\text{Ag}) = 4.9 \times 10^{-3} \exp\left(\frac{-11,600}{RT}\right) \text{ cm}^2/\text{sec} (=4.9 \times 10^{-7} \exp\left(-\frac{11,600}{RT}\right) \text{ m}^2/\text{s})$$

and

$$N_{\text{O}}^{\text{S}}(\text{Ag}) = 7.2 \exp\left(\frac{-11,500}{RT}\right) \text{ atom percent.}$$

The experimental value for the pre-exponential in the expression for $D_{\text{O}}(\text{Ag})$ is lower than the value calculated according to Zener's theory of interstitial diffusion by a factor of 11. The diffusivity of oxygen in solid nickel at 1393°C (1666°K) was found to be $1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ ($1.3 \times 10^{-10} \text{ m}^2/\text{s}$).

C. In this paper the authors introduced a new experimental procedure and interpretation for the potentiostatic determination of the diffusivity or solubility of oxygen in a liquid or solid metal. A time-independent electronic current contribution was subtracted from the total cell current during the transient prior to attainment of steady-state. Furthermore, the experiments were conducted as sufficient undersaturation that the product of the ionic current and the ionic resistance were very small compared to the jump in applied voltage used in the experiment. A derivation is presented for the first time relating an applied voltage to the instantaneous oxygen activities at the electrodes and the instantaneous magnitude of the ionic current flowing. Previous experiments by other authors have not been treated in a valid manner.

Prior to these studies, Mr. Ramanarayanan conducted some unsuccessful experiments in an attempt to measure mixed conduction in fused salts. In these studies, he attempted to use beta-alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) which we only had available in very poor quality crucibles cut from commercial bricks. Pyrex with a Pt/fused salt electrode was also attempted. The beta-alumina crucibles proved to be too porous to contain the fused salt and thus these attempts were discontinued until better electrolyte bodies would become available (which never happened). Very good open-circuit galvanic cell measurements were made with the pyrex electrolyte and the Pt/fused salt electrode, but the electrode was not useful in titration; the exchange rate of sodium ions between the pyrex and fused salt at the platinum was too low. Ultimately then, this series of experiments were also aborted.

Upon receipt of his Ph.D., Dr. Ramanarayanan recently accepted a Post-Doctorate Research Associate position with Professor W. Worrell in the Department of Metallurgical Engineering at the University of Pennsylvania in Philadelphia.

- 8.A. Mixed Conduction in Pure ThO_2 , $\text{ThO}_2\text{-Sm}_2\text{O}_3$, and $\text{ThO}_2\text{-La}_2\text{O}_3$ Solid Solutions, D. H. Primas, D. A. Shores, and R. A. Rapp
(Manuscript in preparation)

B.

Abstract

This study was undertaken to test in some detail the effect of dopant ionic size on the "dopant theory" commonly applied to ionic crystals. In particular, the dopants Sm^{3+} and La^{3+} were used in ThO_2 -solid solutions. Lasker and Rapp's study of $\text{ThO}_2\text{-Y}_2\text{O}_3$ solutions was also available for comparison. Of these dopants, La^{3+} is larger than Th^{4+} , Sm^{3+} is smaller than Th^{4+} and Y^{3+} has about the same ionic radius as Th^{4+} . Conductivity measurements were made between 1000 and 1400°C over a wide range of P_{O_2} . Neither the partial ionic conductivity nor the partial positive hole conductivity exhibited any clear trend with dopant radius. This behavior was in contrast to ZrO_2 solid solutions, in which the ionic conductivity increased monotonously with reduction in ionic radii of the dopants.

C. Following the completion of his Post-Doctorate work at Ohio State University, Dr. Dieter Primas was employed three years as a group leader in Metals Research at Degussa in Frankfurt, W. Germany. Dr. Primas is presently teaching physics and metallurgy at a technical school in Oelde, Germany.

- 9.A. Electrical Conduction in Pure and Doped Dy_2O_3 and Gd_2O_3 , J. M. Macki and R. A. Rapp, (Manuscript in preparation)

B.

Abstract

Pure $\text{GdO}_{1.5}$ exhibits predominant ionic conductivity only over a limit range of P_{O_2} from 800-1000°C. Therefore, pure $\text{GdO}_{1.5}$ would not be a useful solid electrolyte. The doping of $\text{GdO}_{1.5}$ with ThO_2 increases n-type semiconduction and, therefore, excludes the solution as a solid electrolyte. Solutions of CaO in $\text{GdO}_{1.5}$ exhibit a region of exclusive ionic conduction in a range of low P_{O_2} , but p-type semiconduction is significant above $\text{P}_{\text{O}_2} = 10^{-7}$ atm.

Both pure $\text{DyO}_{1.5}$ and CaO -doped $\text{DyO}_{1.5}$ exhibit unorthodox conductivity and no P_{O_2} -range of exclusive ionic conduction. Thoria-doped $\text{DyO}_{1.5}$ is an amphoteric semiconductor with little ionic conduction. These solutions would then not be as useful solid electrolyte materials as the presently used ZrO_2 - and ThO_2 - base solid electrolytes.

C. Upon completion of his Ph.D. program at Ohio State University, Dr. James Macki accepted a position as Research Metallurgist with The Dow Chemical Company, Rocky Flats Division (an AEC installation), Golden, Colorado where he is now a Group Leader in Corrosion.

CONCLUDING REMARKS

Upon the conclusion of this long-standing contract the Principal Investigator, Professor Robert A. Rapp, wishes to express his sincere gratitude to the Atomic Energy Commission and to Dr. Louis Ianniello, the technical monitor, for the receipt of research support funds. He hopes and believes that this AEC research support has resulted in both the accomplishment and interpretation of important research, as well as the instruction and training of some exceptional students and researchers. This support was particularly appreciated because it was initiated at the beginning of Professor Rapp's career at the Ohio State University, i.e., at a critical period when research support must be based more on promise and trust than on proven past performance. Professor Rapp hopes and believes that the research accomplished under this contract will be of value to the mission of the AEC and he offers his services for any further cooperation which the AEC might desire in the future.

APPENDIX I

THE DIFFUSIVITY AND SOLUBILITY OF OXYGEN
IN LIQUID TIN AND SOLID SILVER
AND THE DIFFUSIVITY OF OXYGEN IN
SOLID NICKEL *

by

T. A. Ramanarayanan

and

R. A. Rapp

Department of Metallurgical Engineering

The Ohio State University

Columbus, Ohio

May 1972

* This paper is partly based on a thesis submitted by T. A. Ramanarayanan to the Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The diffusivity and solubility of oxygen in liquid tin and solid silver in the temperature range of about 750-950°C (1023-1223°K) and the diffusivity of oxygen in solid nickel at 1393°C (1666°K) were determined using the electrochemical cell arrangement of cylindrical geometry:

The diffusivity and solubility of oxygen in liquid tin are given by:

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and

$$N_{\text{O}}^{\text{S}}(\text{Sn}) = 1.3 \times 10^5 \exp\left(\frac{-30,000}{RT}\right) \text{ atom percent.}$$

The diffusivity and solubility of oxygen in solid silver follow the relations:

$$D_{\text{O}}(\text{Ag}) = 4.9 \times 10^{-3} \exp\left(\frac{-11,600}{RT}\right) \text{ cm}^2/\text{sec} \quad (= 4.9 \times 10^{-7} \exp\left(\frac{-11,600}{RT}\right) \text{ m}^2/\text{s})$$

and

$$N_{\text{O}}^{\text{S}}(\text{Ag}) = 7.2 \exp\left(\frac{-11,500}{RT}\right) \text{ atom percent.}$$

The experimental value for the pre-exponential in the expression for $D_{\text{O}}(\text{Ag})$ is lower than the value calculated according to Zener's theory of interstitial diffusion by a factor of 11. The diffusivity of oxygen in

solid nickel at 1393°C (1666°K) was found to be $1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$
($1.3 \times 10^{-10} \text{ m}^2/\text{s}$).

INTRODUCTION AND THEORETICAL CONSIDERATIONS

The electrochemical determination of the diffusivity of oxygen in solid metals using a stabilized-zirconia solid-electrolyte cell of cylindrical geometry was first carried out by Rickert and Steiner¹ who determined the diffusivity of oxygen in solid silver. Rickert and El Miligy² extended this technique to determine the diffusivity of oxygen in liquid silver and liquid copper. Oberg et al³⁻⁵ used a similar cell with a modified interpretation to determine the diffusivity and solubility of oxygen in liquid silver, copper and lead, and the diffusivity of oxygen in liquid iron. The $\text{ZrO}_2 + (3-4\% \text{ CaO})$ solid electrolyte used by Oberg et al³⁻⁵ exhibited some significant electronic conduction for which a correction was necessary. In the present work, a commercial-grade $\text{ZrO}_2 + (3-4\% \text{ CaO})$ solid electrolyte tube was used to study the diffusivity and solubility of oxygen in liquid tin and solid silver and the diffusivity of oxygen in solid nickel.

The electrochemical cell used in the present investigation may be represented as:

The activity of oxygen at steady-state in the left-hand electrode may be fixed by applying a pre-selected voltage with the liquid or solid

metal at negative polarity. At any location within the solid electrolyte, the following local equilibrium should hold:

From Eq. (1), for an assumed local equilibrium between oxygen molecules, electrons and ions,

$$\frac{1}{2}\mu_{O_2} + 2\eta_{e^-} = \eta_{O^{2-}} \quad (2)$$

where μ_{O_2} is the chemical potential of oxygen molecules, η_{e^-} is the electro-chemical potential of excess electrons, and $\eta_{O^{2-}}$ is the electrochemical potential of oxygen ions. The electrochemical potential, η_i , of a charged species i , is defined by the relation:

$$\eta_i = \mu_i + z_i F\phi \quad (3)$$

where μ_i is the chemical potential of species, i , z_i its valence and ϕ is the local electrical potential. The partial oxygen ion current in stabilized zirconia is given by ⁶:

$$I'_{ion} = \frac{\sigma_{ion} A}{2F} \left(\frac{\partial \eta_{O^{2-}}}{\partial x} \right) \quad (4)$$

whereby the sign of the ionic current I'_{ion} is fixed by the gradient in electrochemical potential of oxygen ions across the electrolyte, i.e., the sign of I'_{ion} is defined relative to the distance coordinate, not the polarity of any applied voltage.

Upon combining Eqs. (2) and (4),

$$\frac{1}{2} d\mu_{O_2} + 2 d\eta_{e^-} = \frac{2I'_{ion} F}{\sigma_{ion} A} dx \quad (5)$$

Integrating from $x = 0$ to $x = L$

$$\frac{1}{2} \left[\mu''_{O_2} - \mu'_{O_2}(t) \right] + 2 \left[\eta''_{e^-} - \eta'_{e^-} \right] = 2I'_{ion}(t) \Omega_{ion} F \quad (6)$$

where

$$\Omega_{ion} = \frac{1}{A} \int_{x=0}^{x=L} \frac{1}{\sigma_{ion}} dx \quad (7)$$

Combining Eqs. (3) and (6) and noting that for identical Pt lead wires

$$\mu''_{e^-} = \mu'_{e^-},$$

we obtain

$$(\Phi'' - \Phi') = \frac{1}{4F} \left[\mu''_{O_2} - \mu'_{O_2}(t) \right] - I'_{ion}(t) \Omega_{ion} \quad (8)$$

Using the relation,

$$d\mu_{O_2} = RT d \ln P_{O_2} \quad (9)$$

where P_{O_2} is the partial pressure of oxygen and noting that

$(\Phi'' - \Phi')$ is equal to the applied voltage, E_{appl} , Eq. (8) reduces to:

$$E_{appl} = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}(t)} - I'_{ion}(t) \Omega_{ion} \quad (10)$$

At this point it is convenient to replace the ionic current I'_{ion} which is defined relative to a distance coordinate by I_{ion} which will be defined in terms of the voltage applied to the cell. Then

$$E_{appl} = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}(t)} + I_{ion}(t)\Omega_{ion} \quad (10a)$$

whereby the value of E_{appl} of Eq. (10) is considered positive when metal is set at negative polarity. By this convention, the ionic current, I_{ion} , is positive when oxygen is pumped out of the liquid or solid metal. Equations (10) implicitly assume that no other polarization occurs besides concentration (diffusion) polarization in the metal electrode.

For a truly potentiostatic experiment, for which P'_{O_2} of Eq. (10) is held time-independent, $I_{ion}\Omega_{ion}$ must be restricted to values much smaller than E_{appl} throughout the pumping transient so that $P'_{O_2}(t)$ is essentially described by the steady-state ($I_{ion} = 0$) condition

$$E_{appl} = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \quad (11)$$

where P'_{O_2} is the steady-state oxygen pressure in equilibrium with the metal.

The electrochemical cell arrangement for these potentiostatic experiments consisted of a solid electrolyte tube with an external porous platinum electrode (air reference electrode) and

the liquid or solid metal inside the tube. An initial concentration, $C_O(1)$ is established in the liquid or solid metal by applying a pre-selected voltage, $E_{\text{appl}}(1)$ across the solid electrolyte with the metal as the negative electrode. At steady state, when the concentration $C_O(1)$ is attained throughout the metal, a constant electronic current prevails and the ionic current has dropped to zero. The applied voltage is then changed quickly to a higher value, $E_{\text{appl}}(2)$, so that instantaneously a concentration, $C_O(2)$ corresponding to P'_{O_2} of Eq. (11), is established at the metal-solid electrolyte interface. If $I_{\text{ion}}(t)\Omega_{\text{ion}}$ is small relative to E_{appl} (and this requirement was met in the present investigation) then Eq. (11) is essentially satisfied and the diffusion of oxygen atoms out of the metal can be followed by recording the current through the external circuit as a function of time. The mathematical solution to Fick's second law, with the relevant boundary conditions, may be used in order to deduce the diffusivity of oxygen from the recorded current-time plot. Fick's second law for this case may be written as:

$$\left(\frac{\partial C_O}{\partial t}\right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r D_O \frac{\partial C_O}{\partial r}\right) \quad (12)$$

where C_O represents the oxygen concentration in the metal in moles/cm³ (10^6 mol/m³), D_O is the diffusion coefficient of oxygen in the metal in cm²/sec (10^{-4} m²/s), t is the time in seconds and

r is the radius in $\text{cm}(10^{-2} \text{ m})$. For the boundary conditions,

$$C_O = C_O(1), \quad 0 \leq r \leq a, \quad t = 0 \quad \text{and}$$

$$C_O = C_O(2), \quad r = a, \quad t > 0,$$

the solution to Eq. (12) is ⁷

$$\frac{C_O - C_O(1)}{C_O(2) - C_O(1)} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \exp - \frac{D_O \lambda_n^2 t J_0(r, \lambda_n)}{\lambda_n J_1(a, \lambda_n)} \quad (13)$$

where J_0 and J_1 are the Bessel functions of zero and first order, respectively, and λ_n^s are the roots of the Bessel function of zero order. If M_t denotes the quantity of oxygen removed from the cylinder after time t and M_{∞} the corresponding quantity after infinite time, then,

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} \exp - \frac{D_O \lambda_n^2 t}{a^2} \quad (14)$$

with M_{∞} given by:

$$M_{\infty} = \pi a^2 h [C_O(1) - C_O(2)] \quad (15)$$

where h is the height of the cylinder and M_t is given by:

$$M_t = \frac{1}{2F} \int_0^t I_{\text{ion}} dt \quad (16)$$

For sufficiently long times, Eq. (14) becomes,

$$\frac{M_t}{M_{\infty}} = 1 - \frac{4}{\lambda_1^2} \exp - \frac{\lambda_1^2 D_O t}{a^2} \quad (17)$$

where $\lambda_1 = 2.405$, is the first root of the Bessel function of zero order. Substitution of Eqs. (15) and (16) into (17) and differentiation with respect to t yields:

$$I_{\text{ion}} = 8\pi hFD_O \left[C_O(1) - C_O(2) \right] \exp -\frac{(2.405)^2 D_O t}{a^2} \quad (18)$$

Equation (18) may be written in the form:

$$\ln I_{\text{ion}} = \ln B - t/\tau \quad (19)$$

where $B = 8\pi hFD_O \left[C_O(1) - C_O(2) \right]$ and $\tau = \frac{a^2}{D_O (2.405)^2}$.

A plot of $\ln I_{\text{ion}}$ vs. t at long times should give a straight line of slope equal to $-D_O \frac{(2.405)^2}{a^2}$ from which D_O may be calculated.

The intercept is given by,

$$\ln B = \ln 8\pi hFD_O \left[\frac{N_O(1) - N_O(2)}{100 V_M} \right] \quad (20)$$

where N_O is the oxygen concentration in atom percent and V_M is the molar volume of the metal. Because the oxygen concentrations are restricted to low values, one may assume that Henry's law applied. Hence, in view of Eq. (11),

$$\frac{N_O(1)}{N_O(2)} = \exp \left[\frac{2F}{RT} (E_{\text{appl}}(2) - E_{\text{appl}}(1)) \right] \quad (21)$$

By solving Eqs. (20) and (21) simultaneously to eliminate either

$N_{O(1)}$ or $N_{O(2)}$, one can obtain the values of $N_{O(1)}$ and $N_{O(2)}$. The saturation solubility N_O^s is calculated using Sieverts' law, namely,

$$N_O^s = N_{O(1)} \left[\frac{P_{O_2}^s}{P_{O_2(1)}} \right]^{\frac{1}{2}} \quad (22)$$

EXPERIMENTAL EQUIPMENT, MATERIALS AND PROCEDURE

The electrochemical cell arrangement is schematically represented in Fig. 1. The solid electrolyte cell consisted of a Zircoa^{*}, commercial-grade, closed-end, impervious $\text{ZrO}_2 +$ (3 - 4% CaO) solid electrolyte tube. For experiments with liquid tin and solid silver, tubes of dimensions 3/8" O. D. x 9/32" I. D. x 12" length (9.53×10^{-3} m O. D. x 7.14×10^{-3} m I. D. x 0.3 m length) were used. For experiments with solid nickel a tube of 1/4" O. D. x 3/16" I. D. x 12" length (6.35×10^{-3} m O. D. x 4.76×10^{-3} m I. D. x 0.3 m length) was used. The outer wall of the tube was platinized over a height of 2.5" (6.35×10^{-2} m) from the closed-end with fluxed platinum paste (No. 6082) obtained from Engelhard Industries. The paste was thinned with xylene and brushed onto the cleaned solid electrolyte surface. The coated portion was heated gradually to 800°C (1073°K) in a furnace, held at this temperature for one hour and furnace cooled to room temperature. A series of four coatings were applied in this manner. A Pt-wire attached to this porous platinum coating formed the lead for the reference electrode. The metal electrodes were contained on the inside of the tube to a height of approximately 2.5" (6.35×10^{-2} m). The electrical lead wire contacting the metal electrode was slightly

^{*} Zirconium Corporation of America, Solon, Ohio

oxidized chromel (90% Ni - 10% Cr) for liquid tin, Ir for solid silver, and thoriated tungsten (1 wt. % ThO_2) for nickel.

During an experiment, an atmosphere of purified argon was maintained over the surface of the liquid or the solid metal. For experiments with solid silver and solid nickel, the argon was purified by passing it through a tower of magnesium perchlorate, two towers of reduced copper catalyst at 250°C (523°K) and a final magnesium perchlorate tower. For experiments with liquid tin, a further purification of argon gas was carried out by passing it through titanium turnings at 900°C (1173°K).

The furnace was a Marshall Products platinum resistance furnace. Zirconia bricks, which were centrally drilled for entry of the solid electrolyte tube, were used to provide good insulation. In the vertical position the furnace had a constant temperature zone ($\pm 1^\circ\text{C}$) over a 3" length at 1400°C (1673°K). A WHEELCO temperature controller was used to control the temperature in the furnace to $\pm 1^\circ\text{C}$. A Pt/Pt - 10% Rh thermocouple, kept in contact with the solid electrolyte tube, was used to measure the temperature of the liquid or solid metal. A Wenking potentiostat (Model 70 HP10) was used to apply constant voltages to the cell and to measure the current as a function of time. The current was recorded with a Leeds and Northrup Speedomax recorder.

Reagent-grade tin sticks from Mallinckrodt chemical works, reagent-grade silver from G. F. Smith Chemical Co., and #270 carbonyl nickel were used in the experiments.

In the experiments with liquid tin, applied voltages ranging from 1000-1300 mV (1-1.3 V) were used. Experiments were carried out over a temperature range from 748-964°C (1021-1237°K). In making diffusivity measurements in solid silver, the silver was first melted and most of the oxygen was pumped out of it with an applied voltage of + 1.5 volts at 1100°C (1373°K). The furnace was cooled at a rate of 15-20°C per hour until solidification had proceeded from the bottom of the melt to the top. During solidification, the bottom of the metal was kept at about 10°C lower than the top of the metal. After completion of solidification, the cell portion of the tube was adjusted to be in the constant temperature zone of the furnace. Pump-out curves of cell current vs time were recorded using applied voltages in the range from 0-200 mV (0-0.2 V). The experiment was conducted over a temperature range from 763-937°C (1036-1210°K). In the experiments with solid nickel the solidification procedure was similar to that used for silver. Only one pump-out experiment at 1393°C (1666°K) could be conducted, because the thoriated tungsten lead wire could not be kept in contact with solid nickel for long times without oxidation. For the pump-out experiment with nickel, $E_{\text{appl}}(1)$ was equal to 460 mV (0.46 V)

and $E_{\text{appl}}^{(2)}$ was equal to 600 mV (0.6 V).

RESULTS

The experimental data consisted of recorded plots of cell current vs. time. Figure 2 shows the total current and the ionic current as a function of time for liquid tin at 864°C (1137°K).

For liquid tin and solid nickel, considerable time-independent electronic currents were noticed at steady-state and these had to be subtracted from the total currents in order to generate the ionic current vs time plots.³ For the curves of Fig. 2, the initial concentration of oxygen corresponded to an applied voltage of 1.0 V, and the final concentration to an applied voltage of 1.1V. Oxygen saturation (coexistence of Sn and SnO_2) at 864°C (1137°K) would occur at 0.855V. Figure 3 shows two typical $\ln I_{\text{ion}}$ vs time plots for liquid tin, one at 748°C (1021°K) and one at 864°C (1137°K).

At long times, the logarithm of the ionic current becomes a linear function of time. In Fig. 3 and succeeding $\ln I_{\text{ion}}$ vs t plots, discrete points have been taken from the continuous recorded current-time plots at arbitrarily chosen times. The diffusivities and solubilities of oxygen were calculated from slopes and intercepts using Eqs. (18) to (22). Table I lists the diffusivity and solubility values of oxygen in liquid tin obtained by the previously discussed method of interpretation, over the temperature range, $748\text{-}964^{\circ}\text{C}$ ($1021\text{-}1237^{\circ}\text{K}$).

The dissolution of oxygen in liquid tin may be represented by the reaction:

Using a standard state for dissolved oxygen such that the activity of oxygen equals the atom percent of oxygen as the atom percent of oxygen tends to zero, the equilibrium constant, K , for reaction (23) becomes,

$$\ln K = \ln N_{\text{O}} - \frac{1}{2} \ln P_{\text{O}_2} = \ln N_{\text{O}}^s - \frac{1}{2} \ln P_{\text{O}_2}^s \quad (24)$$

with the implicit assumption of Henry's law. Values of $\ln K$ vs $\frac{1}{T}$ and $\ln D_{\text{O}}$ vs $\frac{1}{T}$ are plotted in Figs. 4 and 5, respectively. A least-square analysis of the data leads to the expressions:

$$N_{\text{O}}^s(\text{Sn}) = (1.3^{+0.48}_{-0.35}) \times 10^5 \exp\left(-\frac{30,000 \pm 650}{RT}\right) \text{atom\%} \quad (25)$$

(Whereby the oxygen activity for the coexistence of Sn(l) and $\text{SnO}_2(\text{s})$ was taken as ⁸

$$RT \ln P_{\text{O}_2}^s = \Delta G_{\text{SnO}_2}^{\text{O}} = -143,190 - 3.2 T \ln T - 0.7 \times 10^{-3} T^2 + 2.38 \times 10^5 T^{-1} + 76.58 T$$

and

$$\begin{aligned} D_{\text{O}}(\text{Sn}) &= (9.9^{+7.1}_{-4.1}) 10^{-4} \exp\left(-\frac{1,300 \pm 1200}{RT}\right) \text{cm}^2/\text{sec} \\ &= (9.9^{+7.1}_{-4.1}) 10^{-8} \exp\left(-\frac{6,300 \pm 1200}{RT}\right) \text{m}^2/\text{s} \end{aligned} \quad (26)$$

for the solubility and diffusivity of oxygen in liquid tin in the temperature range, 748-964°C (1021-1237°K). Upon substitution

of Eq. (25) into Eq. (24) and the use of the relation,

$$\Delta G^{\circ} = -RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ} \quad (27)$$

the following expression was obtained for the standard free energy change for the dissolution of one gram of diatomic oxygen into liquid tin:

$$\begin{aligned} \Delta G^{\circ} &= -40,000 + 1,64 T \text{ cal/gm. atom} \\ & (= -167,470 + 6.87 T \text{ J/mol}) \end{aligned} \quad (28)$$

Thus a standard solution enthalpy of -40,000 cal/gm atom (-167,470 J/mol) and a standard solution entropy of -1.64 cal/mol^oK (-6.87 J/mol^oK) were found.

Figure 6 represents a typical plot of cell current vs time for solid silver; the current is all ionic. Figure 7 shows the corresponding $\ln I_{\text{ion}}$ vs t plot; at long times, the curve is linear. Values of the diffusivity and solubility (at $P_{\text{O}_2} = 1 \text{ atm}$) of oxygen in solid silver over a temperature range of 763-937^oC (1036-1210^oK) are presented in Table II. Figures 8 and 9 are plots of $\ln N_{\text{O}}^{\text{s}} (\text{Ag})$ and $\ln D_{\text{O}} (\text{Ag})$ as a function of reciprocal temperature. A least-square analysis of the data leads to the relations:

$$N_{\text{O}}^{\text{s}} (\text{Ag}) = (7.2^{+3.5}_{-2.3}) \exp \left(- \frac{11,500 \pm 860}{RT} \right) \quad (29)$$

atom percent at $P_{\text{O}_2} = 1 \text{ atm}$

and

$$D_O(\text{Ag}) = (4.9^{+3.8}_{-2.1}) \times 10^{-3} \exp\left(-\frac{11,600 \pm 1300}{RT}\right) \text{ cm}^2/\text{sec} \quad (30)$$

$$= (4.9^{+3.8}_{-2.1}) \times 10^{-7} \exp\left(-\frac{11,600 \pm 1300}{RT}\right) \text{ m}^2/\text{s}$$

For the equilibrium,

$$\Delta G^\circ = 11,500 - 3.92 T \text{ cal/gm-atom} \quad (32)$$

$$(\quad = 48,150 - 16.41 T \text{ J/mol})$$

where the activity of oxygen is taken as equal to the atom percent of oxygen as the atom percent of oxygen tends to zero. Thus ΔH° equals 11,500 cal per gram atom (48,150 J/mol) and ΔS° equals + 3.92 cal/ $^\circ\text{K}$ (16.4 J/mol $^\circ\text{K}$).

Figure 10 is a dual plot of total cell current and ionic current vs time for solid nickel at 1393 $^\circ\text{C}$ (1666 $^\circ\text{K}$) and Figure 11 represents the corresponding $\ln I_{\text{ion}}$ vs t plot. From the long time slope of this curve, the diffusivity of oxygen in solid nickel at 1393 $^\circ\text{C}$ (1666 $^\circ\text{K}$) was calculated to be equal to $1.32 \times 10^{-6} \text{ cm}^2/\text{sec}$ ($1.32 \times 10^{-10} \text{ m}^2/\text{s}$).

DISCUSSION

From Eq. (26), the diffusivity of oxygen in liquid tin is found to equal $4.15 \times 10^{-5} \text{ cm}^2/\text{sec}$ ($4.15 \times 10^{-9} \text{ m}^2/\text{s}$) at $T = 1000^\circ\text{K}$ and $7.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ ($7.0 \times 10^{-9} \text{ m}^2/\text{s}$) for $T = 1200^\circ\text{K}$. These values are of the usual order of magnitude for liquid metals. Ma and Swalin⁹ have determined the diffusivities of Al, Zn, Ag, Cu and Ni in liquid tin using a capillary reservoir technique. In liquid tin Al, Zn and Ag have positive relative partial molar enthalpies with values that decrease from Al to Ag. Also in tin, Cu has a slightly negative $\Delta \bar{H}$ and Ni has a large negative $\Delta \bar{H}$. Ma and Swalin observed that for positive values of $\Delta \bar{H}$, the solute diffusivities decrease with decrease in $\Delta \bar{H}$ whereas for negative $\Delta \bar{H}$, the solute diffusivities remain about the same as the self-diffusivity of tin, which is about $10^{-4} \text{ cm}^2/\text{sec}$ ($10^{-8} \text{ m}^2/\text{s}$) at 500°C (773°K). This correlation for negative $\Delta \bar{H}$ does not hold for oxygen in liquid tin. Oxygen has a large negative $\Delta \bar{H}$ (relative to the molecule) and an extremely large negative $\Delta \bar{H}$ (relative to atomic oxygen), but the diffusivity of oxygen in liquid tin is much smaller than the self-diffusion coefficient of tin.

Equation (28) represents the standard free energy of solution of oxygen in liquid tin according to Eq. (23) and may be compared with the value of ΔG° calculated from Alcock and

Belford's¹⁰ extrapolated solubility data, namely,

$$\Delta G^{\circ} = -44,700 + 6.95 T \quad (33)$$

and the value of ΔG° according to Fischer and Ackermann¹¹ namely,

$$\Delta G^{\circ} = -46,060 + 8.01 T \quad (34)$$

The $\ln K$ values according to Equation (28) are only slightly higher than the $\ln K$ values from Equations (33) and (34), as seen in Figure 4. Alcock and Belford have presented three solubility determinations for oxygen in liquid tin at 809°K, 873°K and 973°K. Upon extrapolation of the solubility data from the present experiment according to eq. (25) to the lower temperature range used by Alcock and Belford, the agreement is seen to be good as shown on Table III. Fischer and Ackermann's expression for ΔG° is based upon e.m.f. measurements on the cell: Pt, air | stab. ZrO_2 | Sn(0), electrode. Owing to the low oxygen activities associated with tin melts, small electronic contributions can lead to inaccuracies in open-circuit e.m.f. measurement and the resulting ΔG° values.

As shown in Figures 8 and 9, the diffusivity and solubility of oxygen in solid silver from the present experiment agree well with the diffusivity and solubility data according to

Eichenauer and Muller¹², namely,

$$D_{\text{O}}(\text{Ag}) = 3.66 \times 10^{-3} \exp\left(-\frac{11,000}{RT}\right) \text{cm}^2/\text{sec} \quad (35)$$

$$(\quad = 3.66 \times 10^{-7} \exp\left(-\frac{11,000}{RT}\right) \text{m}^2/\text{s})$$

$$N_{\text{O}}^{\text{s}}(\text{Ag}) = 6.69 \exp\left(-\frac{11,860}{RT}\right) \text{atom percent} \quad (36)$$

Rickert and Steiner¹ obtained for the diffusivity of oxygen in solid silver:

$$D_{\text{O}}(\text{Ag}) = 6.41 \times 10^{-3} \exp\left(-\frac{12,400}{RT}\right) \text{cm}^2/\text{sec} \quad (37)$$

$$(\quad = 6.41 \times 10^{-7} \exp\left(-\frac{12,400}{RT}\right) \text{m}^2/\text{s})$$

Their values are slightly lower than the present experimental values.

Wert and Zener¹³ have given a theoretical description of interstitial diffusion in solid metals. The D_{O} calculated for oxygen diffusion in solid silver using the theory of Wert and Zener equals 5.4×10^{-2} in comparison with the experimental value of 4.9×10^{-3} . The experimental value is thus a factor of 11 smaller than the calculated value. Pastorek and Rapp¹⁴ found a disagreement by a factor of 46 for oxygen diffusion in solid copper. Wert¹⁵ has reported good agreement between theory and experiment for interstitial diffusion in certain b. c. c. lattices. But this agreement is not found for f. c. c. lattices.

The diffusivity of oxygen in solid nickel at 1393°C (1666°K) was found to equal $1.32 \times 10^{-6} \text{ cm}^2/\text{sec}$ ($1.32 \times 10^{-10} \text{ m}^2/\text{s}$) from the present experiment. There are no unambiguous experimental values for D_{O}^{Ni} in the literature with which this value can be compared. Recent unpublished research by Kerr and Rapp¹⁶ provides a value of D_{O}^{Ni} (1393°C) (1666°K) which is a factor of three higher.

SUMMARY AND CONCLUSIONS

The diffusivity and solubility of oxygen in liquid tin and solid silver in the temperature ranges, 748-964°C (1021-1237°K) and 763-937°C (1036-1210°K) respectively were determined using a solid electrolyte technique. The experimentally determined values for the diffusivities and solubilities of oxygen in solid silver agreed with the values according to Eichenauer and Muller¹². The diffusivity of oxygen in solid nickel at 1393°C was found to be $1.32 \times 10^{-6} \text{ cm}^2/\text{sec}$ ($1.32 \times 10^{-10} \text{ m}^2/\text{s}$).

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- Fig. 2 Cell current as a function of time in the potentiostatic experiment with liquid tin at 864°C .
- Fig. 3 Ionic current as a function of time in the potentiostatic diffusion experiment with liquid tin.
- Fig. 4 Equilibrium constant, K , for the dissolution reaction of oxygen in liquid tin as a function of reciprocal temperature.
- Fig. 5 Diffusivity of oxygen in liquid tin as a function of reciprocal temperature.
- Fig. 6 Cell current as a function of time in the potentiostatic experiment with solid silver at 937°C .
- Fig. 7 Ionic current as a function of time in the potentiostatic diffusion experiment with solid silver.
- Fig. 8 Solubility of oxygen in solid silver at $P_{\text{O}_2} = 1 \text{ atm.}$ as a function of reciprocal temperature.
- Fig. 9 Diffusivity of oxygen in solid silver as a function of reciprocal temperature.
- Fig. 10 Cell current as a function of time in the potentiostatic experiment with solid nickel at 1393°C .
- Fig. 11 Ionic current as a function of time in the potentiostatic diffusion experiment with solid nickel.

TABLE I

Solubility and Diffusivity Values for Oxygen in Liquid Tin

Temperature °K	E _{appl} ⁽¹⁾ (V)	E _{appl} ⁽²⁾ (V)	N _O ^s (atom%)	D _O × 10 ⁵ cm ² /sec. *
1021	1.10	1.20	---	4.61
1033	1.00	1.10	0.0497	4.49
1033	1.00	1.10	0.0755	4.11
1137	1.00	1.10	0.1880	6.40
1079	1.00	1.10	0.1091	5.95
1086	1.00	1.10	0.1300	5.91
1086	1.10	1.20	----	5.03
1185	1.10	1.20	----	5.92
1185	1.20	1.30	----	6.26
1237	1.00	1.10	0.7340	9.56
1237	1.00	1.05	0.6050	6.78

*To convert to m²/s, multiply by 10⁻⁴.

TABLE II

Solubility and Diffusivity Values for Oxygen in Solid Silver

Temperature (°K)	$E_{\text{appl}}(1)(V)$	$E_{\text{appl}}(2)(V)$	$N_{\text{O}}^s(\text{atom}\%)$	$D_{\text{O}} \times 10^5$ $\text{cm}^2/\text{sec.}^*$
1036	0.05	0.20	0.0281	1.58
1077	0.05	0.20	0.0306	2.37
1085	0.05	0.15	0.0339	2.39
1118	0.05	0.20	0.0443	2.44
1139	0.05	0.15	0.0457	3.24
1163	0.05	0.15	0.0519	3.25
1203	0	0.15	0.0533	3.79
1210	0.05	0.15	0.0629	3.76
1210	0.05	0.15	0.0619	3.39

*To convert to m^2/s , multiply by 10^{-4}

TABLE III

Comparison of Solubility Values of Alcock and Belford¹⁰ with the
Present Experimental Points

Temperature (°K)	$N_{\text{O}}^s(\text{atom}\%)$	
	Present Data	Alcock and Belford
809	0.0010	0.0013
873	0.0040	0.0041
973	0.0240	0.0210

Fig. 1. Electrochemical cell for diffusion experiments.

Fig. 2. Cell current as a function of time in the potentiostatic experiment with liquid tin at 864°C.

Fig. 3. Ionic current as a function of time in the potentiostatic diffusion experiment with liquid tin.

Fig. 4. Equilibrium constant, K , for the dissolution reaction of oxygen in liquid tin as a function of reciprocal temperature.

Fig. 5. Diffusivity of oxygen in liquid tin as a function of reciprocal temperature.

Fig. 6. Cell current as a function of time in the potentiostatic experiment with solid silver at 937°C.

Fig. 7. Ionic current as a function of time in the potentiostatic diffusion experiment with solid silver.

Fig. 8. Solubility of oxygen in solid silver at $P_{O_2} = 1$ atm. as a function of reciprocal temperature.

Fig. 9. Diffusivity of oxygen in solid silver as a function of reciprocal temperature.

Fig. 10. Cell current as a function of time in the potentiostatic experiment with solid nickel at 1393°C.

Fig. 11. Ionic current as a function of time in the potentiostatic diffusion experiment with solid nickel.