

MATERIALS SCIENCE MONOGRAPHS (Advisory Editor: C. Laird)

- Vol. 1 Dynamic Mechanical Analysis of Polymeric Material (Murayama)
- Vol. 2 Laboratory Notes on Electrical and Galvanomagnetic Measurements (Wieder)
- Vol. 3 Electrodeposition of Metal Powders (Călușaru)
- Vol. 4 Sintering — New Developments (Ristić)
- Vol. 5 Defects and Diffusion in Solids. An Introduction (Mrowec)
- Vol. 6 Energy and Ceramics (Vincenzini)
- Vol. 7 Fatigue of Metallic Materials (Klesnil and Lukáš)
- Vol. 8 Synthetic Materials for Electronics (Jakowlew, Szymański and Włosiński)
- Vol. 9 Mechanics of Aerospace Materials (Nice)
- Vol. 10 Reactivity of Solids (Dyrek, Haber and Nowotny)
- Vol. 11 Stone Decay and conservation (Amoroso and Fassina)
- Vol. 12 Metallurgical Aspects of Environmental Failures (Briant)
- Vol. 13 The Use of High-Intensity Ultrasonics (Pušká)
- Vol. 14 Sintering — Theory and Practice (Kolar, Pejovnik and Ristić)
- Vol. 15 Transport in Non-Stoichiometric Compounds (Nowotny)
- Vol. 16 Ceramic Powders (Vincenzini)
- Vol. 17 Ceramics in Surgery (Vincenzini)
- Vol. 18 Intergranular Corrosion of Steels and Alloys (Čihal)
- Vol. 19 Physics of Solid Dielectrics (Bunget and Popescu)
- Vol. 20 The Structure and Properties of Crystal Defects (Paidar and Lejček)
- Vol. 21 Interrelations between Processing, Structure and Properties of Polymeric Materials (Seferis and Theocaris)
- Vol. 22 Atmospheric Deterioration of Technological Materials: A Technoclimatic Atlas (Rychtera)
 - Part A: Africa
 - Part B: Asia (Excluding Soviet Asia), Australia and Oceania
- Vol. 23 Plasma Metallurgy (Dembowský)
- Vol. 24 Fatigue in Materials: Cumulative Damage Processes (Puškár and Golovin)
- Vol. 25 Sintered Metal–Ceramic Composites (Upandhyaya)
- Vol. 26 Frontiers in materials Technologies (Meyers and Inal)
- Vol. 27 Joints with Fillet Welds (Faltus)
- Vol. 28 Reactivity of Solids (Barret and Dufour)
- Vol. 29 Progress in Advanced Materials and Processes: Durability Reliability and Quality Control (Bartelds and Schliekelmann)
- Vol. 30 Non-Ferrous Metals and Alloys (Sedláček)
- Vol. 31 Defect Recognition and Image Processing in III–V Compounds (Fillard)
- Vol. 32 The Si–SiO₂ System (Balk)
- Vol. 33 Perspectives on Biomaterials (Lin and Chao)
- Vol. 34 Silicon Nitride in Electronics (Belyi et al.)
- Vol. 35 High Tech — The Way into the Nineties (Brunsch, Gölden and Herkert)
- Vol. 36 Composite Systems from Natural and Synthetic Polymers (Salmén, de Ruvo, Seferis and Stark)
- Vol. 37 Copper Indium Diselenide for Photovoltaic Applications (Counts, Kazmerski and Wagner)
- Vol. 38 High Tech Ceramics (Vincenzini)
- Vol. 39 Ceramics in Clinical Applications (Vincenzini)
- Vol. 40 Electron Microscopy in Solid State Physics (Bethge and Heydenreich)
- Vol. 41 Looking Ahead for Materials and Processes (De Bossu, Briens and Lissac)
- Vol. 42 Materials Data for Cyclic loading. Parts A–E (Boller and Seeger)
- Vol. 43 Technical Mineralogy and Petrography. Parts A and B (Szymański)
- Vol. 44 Defect Recognition and Image Processing in III–V Compounds II (Weber)
- Vol. 45 Solid State Electrochemistry and its Applications to Sensors and Electronic Devices (Goto)

MATERIALS SCIENCE MONOGRAPHS, 45

SOLID STATE ELECTROCHEMISTRY AND ITS APPLICATIONS TO SENSORS AND ELECTRONIC DEVICES

KAZUHIRO SYLVESTER GOTO

Tokyo Institute of Technology, Tokyo 152, Japan



ELSEVIER

Amsterdam — Oxford — New York — Tokyo 1988

ELSEVIER SCIENCE PUBLISHERS B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
52, Vanderbilt Avenue
New York, NY 10017, U.S.A.

LIBRARY OF CONGRESS
Library of Congress Cataloging-in-Publication Data

Goto, Kazuhiro Sylvester, 1936-

Solid state electrochemistry and its applications to sensors and
electronic devices / Kazuhiro Sylvester Goto.

p. cm. -- (Materials science monographs ; 45)

Bibliography: p.

Includes index.

ISBN 0-444-42912-3 (U.S.) : Dfl.225.00 (Netherlands : est.)

1. Electrochemistry. 2. Oxides. 3. Solid state chemistry.

I. Title. II. Series.

QD553.G73 1988

681'.2--dc19

87-30971

CIP

ISBN 0-444-42912-3 (Vol. 45)

ISBN 0-444-41685-4 (Series)

© Elsevier Science Publishers B.V., 1988

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V./ Science & Technology Division, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Special regulations for readers in the USA — This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publisher.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

Printed in The Netherlands

Dedicated to Harumi Maria

PREFACE

This monograph is based on lecture notes for the course "Physical Chemistry of Oxides at High Temperature" conducted at the Graduate School of the Tokyo Institute of Technology. The course has been taught since 1971.

Three chapters of the original course notes have been left out because the topics presented in them have been adequately covered in other books. Those three chapters were on the crystal and ionic structure of oxides and the nonstoichiometry of oxides in both solid and liquid states.

Every author must feel humble when he thinks about all the help he has received from others. I would like to express my deep thanks to the late Professor Carl Wagner, Professor Wolfgang Pluschkell, and Professor Hermann Schmalzried for their valuable comments and intensive discussions on the contents of the lecture notes.

Gratefully, I acknowledge the assistance of three associates who reviewed the English-language manuscript: Dr. Ken C. Mills, Senior Researcher at the National Physical Laboratory of Great Britain; Dr. George W. Orton, a former professor with the University of Puerto Rico, and Dr. James E. Battles, Senior Researcher of Argonne National Laboratory.

Equally appreciated is the assistance of Mr. S. Ushigome of Tokyo Yogyo Co., Ltd. and Mr. M. Matsuoka of Yamari-Electronite Co., Ltd. for their financial support for typing and art work.

Heartfelt thanks are extended to Professors Sven Eketorp, Zhou Rong-Zhang and Ji Chunlin for affording me the opportunity to present the lectures on the Physical Chemistry of Oxides at High Temperatures to the Royal Institute of Technology in Stockholm in 1972, the Peking University of Iron and Steel Technology in 1979 and the North East University of Technology in Shenyang in 1981.

Many students and colleagues have given either direct or indirect help. I am especially grateful to Professor S. Matoba, my advisor for the Bachelor and Master Degrees at Tohoku University, to Professor G. R. St. Pierre, my advisor at The Ohio State University, and to Professor Y. Matsushita, my advisor for the Doctorate of Engineering at the University of Tokyo. All have been a source

of inspiration to me in conducting my research. In particular, Professor St. Pierre wisely advised me to undertake experimental studies using new solid electrolytes with oxygen anions. This was the beginning of my investigations in the solid state electrochemistry of oxides.

It is a pleasure to acknowledge my gratitude to Professor M. Someno and to Professor S. Haruyama for teaching me the fundamentals of experimental science and electrochemical theory and to Professor R. A. Rapp for coordinating with me the USA-Japan joint work on hot corrosion of alloys.

Essential parts of the research of many former students are included in this monograph. I want to express my thanks to all of them, especially Professors M. Sasabe, M. Kawakami, K. Nagata and Doctors H. Itaya, Y. Ukyo and S. Yamaguchi.

The appendix was prepared by Mr. M. Susa and to him I am very grateful.

I take pleasure in acknowledging the continued encouragement and moral support of my wife, Harumi Maria.

Finally and most sincerely, I am grateful to Miss H. Higuchi and Miss C. Ishikawa for their patience and care in typing the manuscript and to Mr. Zhang Li-Wei for his skillful drawings.

Chapter 1

INTRODUCTION

1.1 THE SCOPE OF THE BOOK

The scope of this book has been restricted to an examination of the electrochemistry of solid and liquid oxides at high temperatures and to its applications in various electronic devices. Electrochemistry is an interdisciplinary subject covering both chemistry and physics. Research in this area has progressed mainly through studies of aqueous solutions and molten salts, both of which have predominantly ionic bonding. In this book, electrochemical theories have been applied to both solid and liquid oxides at high temperatures. The application of the electrochemistry of oxides to various electronic devices, including chemical sensors, is discussed in the later chapters.

In the first part of the book, Chapter 2 to Chapter 5, a discussion of the micromechanisms of electric conduction and diffusion in the oxides is presented. The theoretical relation between conductivity and diffusivity is criticized with experimental results. The transport properties of multicomponent oxide systems are also discussed.

In Chapters 6 and 7, solid state galvanic cells are constructed, based on the transport properties of the oxides discussed in the previous chapters. Various types of solid state galvanic cells used for many thermodynamic studies are introduced.

In Chapters 8 and 9, the overpotential in galvanic cells and its applications to kinetic studies are discussed.

The most successful application of the solid state electrochemistry of oxides is generally considered to be in oxygen sensors. These electronic devices are discussed in Chapters 10 and 11.

Applications of solid oxides in various electronic devices are discussed in Chapters 12 and 13. Gas sensors with semiconductor oxides, humidity sensors, gas sensors with MOS transistors, electrochemical timers, potential memory cell, switching device, display device, and solid state batteries with high energy density are covered in detail.

The first part of the book is designed to give the reader an insight into the micromechanism of transport phenomena of ions

and electrons in solid and liquid oxides. In the second part, various solid state galvanic cells are discussed in relation to the transport properties of oxides. Then, it is demonstrated how these galvanic cells are used for thermodynamic and kinetic studies at high temperatures.

In the last part of the book, many electronic devices using various solid oxides are introduced as examples of the application of solid state electrochemistry to electronic devices.

Solid and liquid oxides of metals are discussed because of their great importance in various fields of industry.

The oxides of metals have long been used by mankind as raw materials for pottery, refractories, cement, and ceramics. Furthermore, oxides are important as the ores from which metals can be extracted.

In contrast to these classic fields of industry, oxides are now being very extensively studied as promising functional materials for a rapidly advancing technology.

This new technology can be classified into the following;

1) the technology of new functional materials, 2) microelectronic technology (LSI, MOS-IC, optoelectrics, laser devices, etc), 3) sensor technology, 4) energy saving and converting technology, 5) life science and biotechnology, 6) robots for factory automation and 7) space or ocean technology.

In these new technologies, the oxides are used as components of the devices. In the following, the author would like to illustrate the importance of the oxides with two examples from industry; one from a classic field and the other from a newly advancing field.

1.2 IMPORTANCE OF OXIDES IN METALLURGY

The art of extraction and refining metals has been developed over the centuries in a wide variety of locations throughout the world. The crust of the earth is composed of the oxides of metals, which have been and will continue to be the original source of most metals.

Table 1.1 shows the oxide ores along with their mineralogical names. This table was made by rearranging the order and eliminating the sulfide ores from Table 1-1 of the excellent textbook, "Unit Processes of Extractive Metallurgy" by R.D. Pehlke⁽¹⁾.

TABLE 1.1

Oxide ores for common metals

Metal	Formula	Name of Mineral
Iron	Fe_3O_4	Magnetite
	Fe_2O_3	Hematite
	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Limonite
Copper	Cu_2O	Cuprite
Aluminum	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Diaspore
	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Gibbsite
	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Kaolinite
Zinc	ZnO	Zincite
	$\text{ZnO} \cdot \text{FeO} \cdot \text{MnO}$	Franklinite
Magnesium	MgO	Magnesite
Tin	SnO_2	Cassiterite
Manganese	MnO_2	Pyrolusite
	MnSiO_3	Rhodonite
Chromium	FeCr_2O_4	Chromite
Titanium	$\text{FeO} \cdot \text{TiO}_2$	Ilmenite
	TiO_2	Rutile
Zirconium	ZrO_2	Baddeleyite
	ZrSiO_4	Zircon
Vanadium	$\text{K}_2\text{O} \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$	Carnotite
Molybdenum	MoO_3	Molybdenite
Tungsten	FeWO_4	Wolframite
	CaWO_4	Scheelite
Beryllium	$3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	Beryl
Uranium	Complex Oxide	Pitchblende

(Rearranged from Table 1-1 of the book by R.D. Pehlke⁽¹⁾)

The modern science of extraction and refining of metals has a relatively short history, spanning less than two centuries. The common principle of the extraction and of the purification of metals is based on selective reduction and oxidation, usually at high temperature. Scientific theories of thermodynamics and kinetics at high temperature have been used to produce metals with precise composition at the lowest cost.

Table 1.1 indicates the importance of oxides in metallurgy. It is evident that many useful metals are produced from oxide ores.

Furthermore, oxides used in refractories and ceramics are also very important in refining metals. This will now be concisely discussed with help of an example of metal refining. Figure 1.1 shows a schematic picture of a modern method of producing steel from the oxide ores in Table 1.1.

In the blast furnace, iron is extracted from the oxide by selective reduction with carbon monoxide gas. The separation of metallic iron is accompanied by the migration of ionic species, and hence electrochemical processes are involved in the blast furnace.

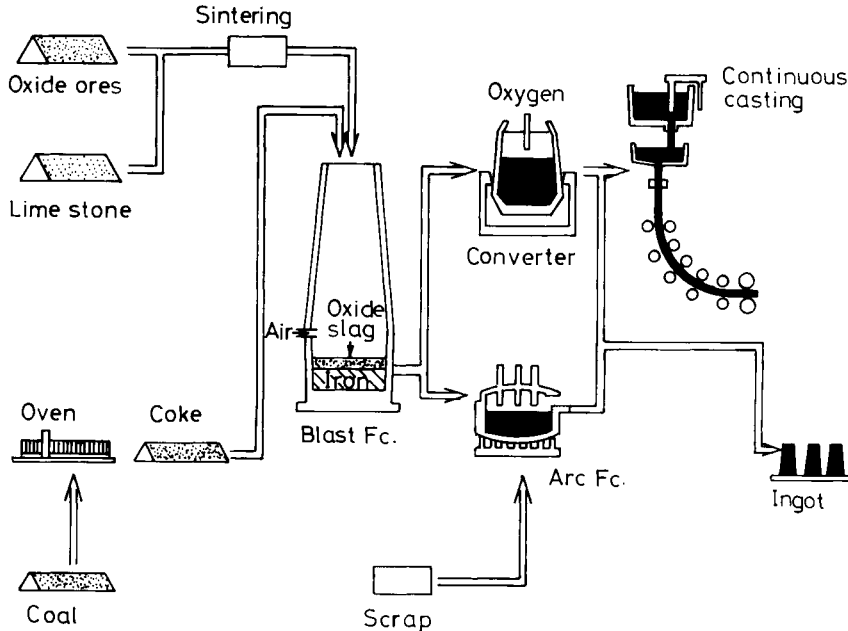


Fig. 1.1 Flow chart of production of steel from iron ores.

The gangue minerals of Al_2O_3 , SiO_2 , MgO , etc. float upwards and are separated from iron melt as a liquid slag. Essential portions of the impurities are removed with the liquid slag. However, the molten iron with a temperature of about 1500°C still contains a significant amount of impurities.

This crude iron is refined by the selective oxidation of impurities in the converter or in the electric arc furnace, as shown in Fig. 1.1. The refined iron is called "steel". The liquid steel is then solidified into convenient shapes for subsequent rolling and forging. Nowadays steel is usually solidified by the continuous casting process or by the traditional mould-casting method.

Refractories for furnaces are made from oxides such as Al_2O_3 , SiO_2 and MgO and their life time is usually controlled by the hot corrosion of liquid slags which are also formed from oxides. As the bonding in both the refractories and the slags is predominantly ionic, hot corrosion is an electrochemical process. One more electrochemical phenomenon in steelmaking is the transfer of impurities between liquid slags and the iron or steel bath. As the slag has an electrolytic nature, the transfer of the impurities is accompanied by charge transfer reactions. This is a phenomenon similar to that observed when electrodes are dipped in aqueous electrolytic solutions.

The present author believes that the applications of electrochemical theories will be helpful in gaining a deeper understanding of natural phenomena taking place during the extraction and refining of metals at high temperature.

More details of iron and steelmaking processes are given in several books listed⁽²⁾⁻⁽¹⁷⁾ at the end of this chapter.

1.3 OXIDES AS FUNCTIONAL ELEMENTS IN MICROELECTRONICS

Metallurgy has a long history spanning thousands of years and it will continue to be very important in the future development of mankind. In a strong contrast to this, we now have several new, rapidly developing fields of technology. Their histories are very short, a few decades at the most.

Among these rapidly-developing technologies, "microelectronics" might be considered the most important. This name of "microelectronics" is used to distinguish the new electronic technology from the classic electrical engineering.

Microelectronics can be defined as a new branch of technology, in which the art and science are being developed in order to produce elegant electronic devices by using new "micro-sized" materials.

Day after day, many electronic materials are being developed. A significant fraction of these new materials are the oxides of metals. Table 1.2 shows examples of solid oxides of metals either being studied or used as electronic materials.

This table was compiled from an encyclopedia of functional materials written by M. Kitada⁽¹⁸⁾ in 1984 and for the sake of brevity only examples of the solid oxides have been included. In fact, the sensor materials alone in Table 1.2 can be sub-divided into another table (Table 1.3). This table was compiled from the proceedings of International Meeting on Chemical Sensors⁽¹⁹⁾

TABLE 1.2

Examples of solid oxides used as electronic materials

Electronic Materials	Solid oxide elements
MATERIALS for IC, MOS-IC, LSI	SiO ₂ in Mo SiO ₂ Si Al ₂ O ₃ as substrate of IC
Magnetic Materials	γ-Fe ₂ O ₃ , BaO-6Fe ₂ O ₃ , MnO-ZnO-Fe ₂ O ₃ MnO-MgO-Fe ₂ O ₃ , YFeO ₃ , YCoO ₃ , Y ₃ Fe ₅ O ₁₂
Optoelectronic Materials	Na ₂ O-B ₂ O ₃ -SiO ₂ , Na ₂ O-Li ₂ O-CaO-SiO ₂ for optical fibres. LiNbO ₃ , LiTaO ₃ , PbTiO ₃ for optical switch.
Sensor Materials	SnO ₂ , In ₂ O ₃ , ZnO, NiO, FeO, BaTiO ₃ for semiconductor gas sensors. ZrO ₂ -MgO, ZrO ₂ -Y ₂ O ₃ for solid electrolyte gas sensors.
Laser Materials	Y ₃ Al ₅ O ₁₂ -Nd ₂ O ₃ , CaWO ₄ , YAlO ₃ , Al ₂ O ₃ -Cr ₂ O ₃ , Phosphate glass doped with Nd ₂ O ₃
Piezoelectric Materials	PbTiO ₃ , PbZrO ₃ , LiNbO ₃ LiTaO ₃
Ceramic superconductors	LiTi ₂ O ₄ , BaPb _{1-x} Bi _x O ₃ , CuO-BaO-Y ₂ O ₃
Condensor Varistor Registor	BaTiO ₃ , CaTiO ₃ , ZnTiO ₃ , SrTiO ₃ , Bi ₂ Ti ₂ O ₅ for condensers. ZnO-Bi ₂ O ₃ for varistor, RuO ₂ for registors.
Others	In ₂ O ₃ -SnO ₂ for transparent conductor. In ₂ O ₃ -Cu ₂ O for solar cell.

TABLE 1.3

Solid oxides used for sensor elements

Sensors	Examples of sensor elements
Thermo-sensors (Thermister)	NTC*: NiO, FeO, CoO, MnO, CoO-Al ₂ O ₃ PTC*: BaTiO ₃
Semiconductor gas sensors	SnO ₂ , In ₂ O ₃ , ZnO, WO ₃ , γ -Fe ₂ O ₃ NiO, CoO, Cr ₂ O ₃ , LaNiO ₃ , BaTiO ₃ TiO ₂ , CoO-MgO
Humidity sensors	Al ₂ O ₃ , P ₂ O ₅ , ZnO-Li ₂ O, NiFe ₂ O ₄ TiO ₂ , MgCr ₂ O ₄ , Fe ₃ O ₄ , ZnO-Cr ₂ O ₃ ZrO ₂ -MgO, SrSnO ₃ , SrTiO ₃
Infrared optical sensors	LiNbO ₃ , LaTaO ₃ , SrTiO ₃ Ba ₂ NaNb ₅ O ₁₅ , LiNbO ₃
Solid electrolyte gas sensors	ZrO ₂ -MgO, ZrO ₂ -Y ₂ O ₃ , ZrO ₂ -CaO, ThO ₂ -Y ₂ O ₃ , Na ₂ O-11Al ₂ O ₃ (β -Al ₂ O ₃) SrO-CeO ₂ -Yb ₂ O ₃ , Bi ₂ O ₃ -MoO ₃ , Na ₃ Zr ₂ Si ₂ PO ₁₂

* NTC and PTC mean negative and positive temperature coefficient of electric resistivity with temperature increase, respectively.

edited by T. Seiyama et al in 1983.

From Tables 1.2 and 1.3, one can see that many kinds of solid oxides are used in integrated circuits, in metal-oxide-semiconductor transistors, in magnetic materials, in optical fibers, in optical switches, in optoelectrical devices, in sensors, in laser generators, and in various other microparts such as piezoelectrics, superconductors, condensers, varistors and transparent conductors.

The oxides used in these applications are produced by sintering, by hot pressing, or by solidification from liquid state. They are often used in the form of thin films, thin wires or ultrafine powders. For such cases, they are produced by physical vapor deposition, by chemical vapor deposition, by ion sputtering, by molecular beam epitaxy, or by combinations of three methods.

Figure 1.2 demonstrates how silicon oxide, SiO₂, is used in microelectronic devices. This "MOS-FET" is a kind of transistor, the abbreviation standing for Metal-Oxide-Semiconductor-Field-

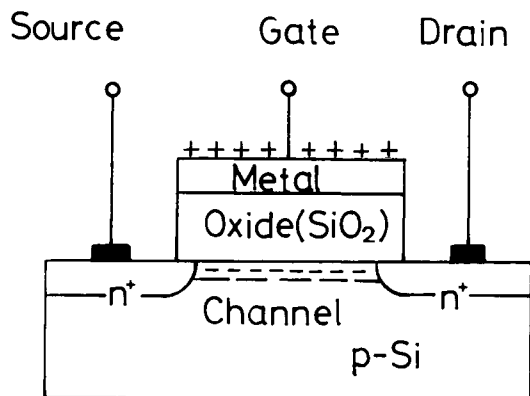


Fig. 1.2. Sectional view of Metal-Oxide-Semiconductor Transistor.

Effect-Transistor⁽²⁰⁾. The current between the source and the drain is controlled by the field of the gate metal through the silica film in this figure. Thus, this transistor can be used for switching and for amplification⁽²⁰⁾.

In Fig. 1.2, Molybdenum or Tungsten is sometimes used as the metal electrode. Thus, the electrochemical reaction appears to take place between the metal electrode and silica layer during heat treatment at 1000°C.

Careful examination of the sectional structure of the integrated circuits reveals various interfaces separating two phases i.e., Al/SiO₂, poly Si/phospho-silicate glass, and Si/SiO₂.

As several steps of heating are involved in the manufacture of the MOS-IC, it is quite natural to expect electrochemical reactions at the interfaces. In fact, Iwata and his coworkers⁽²¹⁾⁻⁽²⁴⁾ have reported experimental results for the reactions occurring at the interfaces in the MOS-Structure using ESCA (Electron Spectroscopy for Chemical Analysis).

Further information⁽²⁵⁾⁻⁽³⁰⁾ on microelectronic devices is given in the reference section at the end of this chapter.

It is the author's belief that an understanding of the electrochemical properties of the oxides used in many kinds of electronic devices could be most helpful in predicting the performance of the devices in service. The rate of the contamination by impurities during processing and the rate of deterioration of the

devices by moisture in use could be related to the electrochemical properties.

References having a close relation to the main subject of the present monograph are given at the end of this chapter.

Rapp and Shores⁽³¹⁾ reviewed the research on Galvanic cells with solid electrolytes in 1970. The book edited by Hladik⁽³²⁾ and one written by Fischer and Janke⁽³³⁾ also include extensive information on solid state electrochemistry at high temperature. In addition to these three monographs, several books have been published on solid state ionics and on super ionic conductors. Among these, the book written by Chandra⁽³⁴⁾ gives the most systematic information on super ionic solids. "Super Ionic Conductors" edited by Mahan and Roth⁽³⁵⁾ also provides an informative documentation of the proceedings of an international meeting. An account of the industrial application of solid electrolytes is covered in the book on chemical sensors⁽¹⁹⁾ edited by Seiyama et al in 1983.

In the following chapters, the electrochemical properties of both solid and liquid oxides are discussed in relation to the electronic and crystal defects in oxides. Then, the solid-state Galvanic cells are applied to thermodynamic and kinetic studies at elevated temperature. Finally, various sensors made of the oxides are introduced and their industrial applications are discussed. A number of electronic devices are also discussed with respect to the electrochemical properties of the oxides.

At the end of the book several problems for discussion and calculation are given for each chapter to help the reader to understand the contents of the chapters from a more critical view point.

REFERENCES TO CHAPTER 1

- (1) R.D. Pehlke, "Unit Processes of Extractive Metallurgy" American Elsevier Publishing Company (1973) New York.
- (2) L.S. Darken and R.W. Gurry, "Physical Chemistry of Metals" McGraw-Hill Book Company, INC. (1953) New York.
- (3) R.G. Ward, "An Introduction to the Physical Chemistry of Iron and Steel Making" Edward Arnold Ltd. (1962) London.
- (4) C. Badsworth, "Physical Chemistry of Iron and Steel Manufac-

- turing" Longmans (1963) London.
- (5) "Die Physikalische Chemie der Eisen-und Stahlerzeugung" compiled by VDEh, Verlag Stahleisen M.B.H. (1964) Düsseldorf.
 - (6) L. von Bogdandy and H.-J. Engell, "Die Reduktion der Eisen-erze" Springer-Verlag (1967) Berlin.
 - (7) O. Kubaschewski, E.L.L. Evans, and C.B. Alcock, "Metallurgical Thermochemistry", Pergamon Press (1967) London.
 - (8) F. Habashi, "Principles of Extractive Metallurgy" Gordon and Breach Science Publishers (1969) New York.
 - (9) Y. Matsushita et al, "Metallurgical Physical-Chemistry" Maruzen Publishing Co. Ltd. (1970) Tokyo (in Japanese).
 - (10) M. Ohtani, "Thermodynamics for Ferrous Metallurgy" Nikkan Kogyo Shinbunsha (1971) Tokyo (in Japanese).
 - (11) F.D. Richardson, "Physical Chemistry of Melts in Metallurgy" Vol.1 and 2, Academic Press (1972) London.
 - (12) D.R. Gaskell, "Introduction to Metallurgical Thermodynamics", McGraw-Hill Book Company (1973) New York.
 - (13) Y. Kawai, "Kinetics in Ferrous Metallurgy", Nikkan Kogyo Shinbunsha (1973) Tokyo (in Japanese).
 - (14) "Kinetics of Metallurgical Processes in Steelmaking" edited by W. Dahl et al, Verlag Stahleisen M.B.H. (1975) Düsseldorf.
 - (15) C.B. Alcock, "Principles of Pyrometallurgy", Academic Press (1976) London.
 - (16) E.T. Turkdogan, "Physical Chemistry of High Temperature Technology" Academic Press (1980) New York.
 - (17) A.K. Biswas, "Principles of Blast Furnace Ironmaking", Cootha Publishing House (1981) Australia.
 - (18) M. Kitada, "An Encyclopedia of Functional Materials" Kyoritsu Shuppansha (1984) Tokyo (in Japanese)
 - (19) "Proceedings of International Meeting on Chemical Sensors" edited by T. Seiyama et al, Elsevier (1983) Tokyo.
 - (20) T. Ito and Y. Ito, "Basic Technology of Integrated Circuit" Shokodo Pub. Co. Ltd. (1983) Tokyo (in Japanese).
 - (21) S. Iwata, N. Yamamoto, N. Kobayashi, T. Terada, and T. Mizutani, IEEE Trans. Electro. Devices, ED-31 (1984) 1174 pp.
 - (22) S. Iwata, Ext. Abstracts of Intern. Conf. on Solid State Devices and Materials, Japan Soc. of Appl. Physics (1984) 15 pp. Kobe, Japan.
 - (23) S. Iwata, A. Ishizaka, and H. Yamamoto, J. of Electrochem. Soc., 126 (1979) 110 pp.
 - (24) S. Iwata, "Many Problems on Reactions and Diffusion in

- Microelectronic Devices", in Text Book on Diffusion (1984) PP. 83-92 organized by Japan Institute of Metals.
- (25) A.S. Grove, "Physics and Technology of Semiconductor Devices" John Wiley and Sons (1967), New York.
 - (26) W.N. Car and J.P. Mize, "MOS/LSI Design and Application", McGraw-Hill (1972), New York.
 - (27) B. Jaffe, W.R. Cook, Jr., and H. Jaffe, "Piezoelectric Ceramics" Academic Press (1971) London.
 - (28) Z.M. Jarzecki, "Oxide Semiconductors" Pergamon Press (1973) Oxford.
 - (29) W. Koechner, "Solid State Laser Engineering" Springer-Verlag (1976) New York.
 - (30) "Semiconductor Optoelectronics" edited by M.A. Herman, John Wiley and Sons (1980) New York.
 - (31) R.A. Rapp and D.A. Shores, in "Physicochemical Measurements in Metal Research" edited by R.A. Rapp, Interscience Publishers (1970) New York.
 - (32) "Physics of Electrolytes" edited by J. Hladik Vol. I and Vol. II, Academic Press (1972) London.
 - (33) W.A. Fischer und D. Janke, "Metallurgische Electrochemie", Springer-Verlag (1975) Düsseldorf.
 - (34) S. Chandra, "Super Ionic Solids"- Principles and Applications, North-Holland (1981) Amsterdam.
 - (35) "Superionic Conductors" edited by G.D. Mahan and W.L. Roth, Plenum Press (1976) New York.

Chapter 2

IONIC AND ELECTRONIC CONDUCTION OF SOLID AND LIQUID OXIDES AND OF OTHER IONIC COMPOUNDS

2.1 DEFINITION OF IONIC AND ELECTRONIC CONDUCTIVITY

In any solid or liquid oxide, an electric current can be conducted by the migration of ionic particles, and electrons and positive holes contained in the oxide.

Usually, the electrical conductivity of materials is denoted as σ and defined by the equation:

$$j = - \sigma \left(\frac{\partial E}{\partial x} \right) \quad (2-1)$$

where j is current density in amperes per square centimeter, E is electrical potential in volts, x is distance in centimeters. Thus the conductivity, σ has the unit of $A/(cm \cdot V)$ or $1/(cm \cdot \Omega)$.

The conductivity as defined by the above equation can be considered to be the sum of the partial conductivities of ions, electrons and positive holes, when these are the migrating species in the oxides. Namely, :

$$\sigma = \sigma_{ion} + \sigma_e + \sigma_p \quad (2-2)$$

where σ_i means the partial conductivity of migrating species i .

According to Eq.(2-1), the absolute value of current density becomes equal to the conductivity, when the potential gradient is unity. Under this condition, Fig.2.1 shows how many particles with a negative charge can cross a plane of 1 cm^2 , perpendicular to the positive potential gradient, in one second.

The distance denoted as $|\mu|$ is the absolute value of the mobility of the charged particles.

The physical meaning of the mobility, μ , can be visualized as the velocity of a charge carrier under unit potential gradient.

Using this mobility, the partial conductivity can be expressed by:

$$\sigma = n_i \cdot |z_i| e \cdot \mu_i \quad (2-3)$$

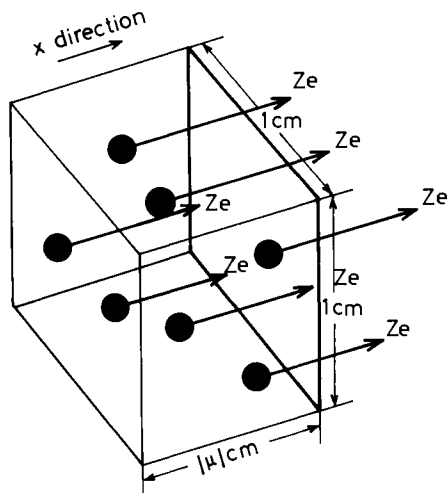


Fig. 2.1. A picture showing how many particles with a negative charge of ze can cross the plane of 1 cm^2 per second.

where n_i is the number of the charge carriers, i , per cm^3 , z_i is its valence, e is the unit charge ($1.60 \times 10^{-19} \text{ A}\cdot\text{sec}$ or coulombs). As σ is always in the units of $\text{A}/(\text{cm}\cdot\text{V})$, the mobility has the unit of $\text{cm}^2/(\text{sec}\cdot\text{V})$.

In many physics books, the absolute mobility, B is often used and thus, the partial conductivity may be alternatively expressed by:

$$\sigma_i = n_i (z_i e)^2 B \quad (2-4)$$

where B is in $\text{cm}^2/(\text{sec}^2\cdot\text{V}\cdot\text{A})$ or $\text{cm}^2/(\text{sec}\cdot\text{Joule})$. Hence B has the physical meaning of the velocity of a particle when a unit force operating upon it.

Fig. 2.2 shows the direction of the current and motion of charged particles in accordance with Eq. (2-1) and to Fig. 2.1.

Inserting Equation (2-3) into (2-2), one obtains:

$$\sigma = n_{\text{ion}} \cdot |z_i| e \cdot \mu_{\text{ion}} + n_e \cdot e \cdot \mu_e + n_p \cdot e \cdot \mu_p \quad (2-5)$$

where the subscripts, ion , e , and p refer to ions (cations and anions), excess electrons, and positive holes contained in oxides,

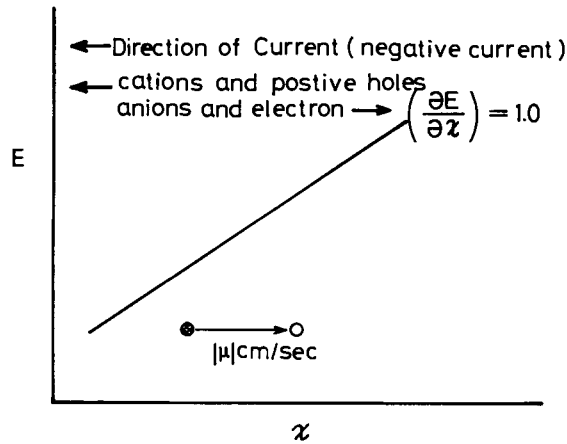


Fig. 2.2. A picture to show directions of motion of charged particles under a positive electrical potential gradient.

respectively.

This equation leads to the definition of ionic and electronic conductivities of oxides. Furthermore, from this equation, one can deduce how the conductivity of the oxides will change with temperature, oxygen pressure, and composition of oxides. In normal circumstances, changes in temperature cause only small changes in n_{ion} , μ_e and μ_p but can produce significant changes in μ_{ion} , n_e and n_p .

An oxide is called an ionic conductor, when the first term of the right hand side of Equation (2-5) is predominant and other terms are negligible.

When the second term is predominant, the oxide is called an n-type semiconductor.

When the last term is predominant, the oxide is called a p-type semiconductor.

Examples of solid oxides with purely ionic conduction are ZrO_2 -15mole%MgO which has a fluorite structure⁽¹⁾ and Na_2O -11mole% Al_2O_3 (beta-alumina) which has a layered structure⁽²⁾. The charge carrier is O^{2-} in the former case and Na^+ in the latter case. The liquid silicate, borate, or phosphate will usually give

cation conduction as long as they do not contain a large quantity of transition metal oxides.

Examples⁽³⁾ of p-type semiconductors are the solid oxides $\text{Fe}_{1-\delta}\text{O}$, NiO , CoO , MnO_2 , and Cr_2O_3 , and examples⁽³⁾ of n-type semiconductors are solid oxides ZnO , CdO , SnO_2 , TiO_2 , and Fe_3O_4 .

2.2 RELATION BETWEEN THE CONDUCTIVITY AND TEMPERATURE AND OXYGEN PRESSURE

The electrical conductivity of an oxide is given as the sum of the partial conductivities in Equation (2-5). Since the mobility and the concentration of the charge carriers are dependent upon temperature and oxygen pressure, the conductivity of the oxide can be expressed as a function of these variables.

2.2.1 Strictly-stoichiometric oxides, and ionic conductors doped with aliovalent ions

The electrical conductivity of this category of oxides is independent of oxygen pressure and is a function of temperature only.

A strictly-stoichiometric oxide can be defined as an oxide containing no electronic defects but only crystal defects. If the oxide is symbolically expressed as " MO " containing M^{2+} and O^{2-} ions, its schematical structure can be depicted as a two-dimensional picture as shown in Fig. 2.3.

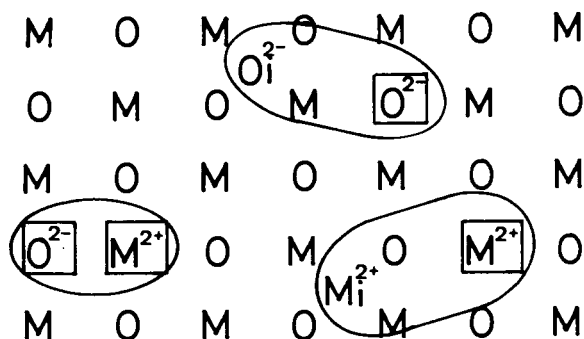


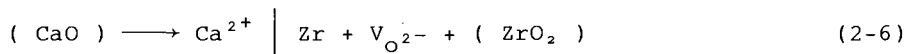
Fig. 2.3. Crystal defects in a strictly-stoichiometric oxide, MO , induced by thermal agitation.

In this figure, M_i^{2+} and O_i^{2-} indicate an interstitial cation and oxygen anion, respectively.

$\boxed{M^{2+}}$ and $\boxed{O^{2-}}$ denote the cation and anion vacancies, respectively.

The crystal defects are produced by thermal agitation only and thus there should be no defects at the absolute zero temperature, according to the third law of thermodynamics. Oxides of this type include K_2O , Li_2O , CaO , BaO , SrO , MgO , SiO_2 , B_2O_3 , Al_2O_3 etc. All of these oxides are white in colour, since the charge transfer band is beyond the ultraviolet range⁽⁴⁾⁽⁵⁾. This is a good indication that the oxides are predominantly ionic conductors.

Another possibility is to produce crystal defects by doping with aliovalent ions. In a solid oxide doped with aliovalent ions, crystal defects must be formed to accommodate the charge differences. As an example of doped solid oxide, Fig. 2.4. shows the fluorite structure of $0.85ZrO_2-0.15CaO$ solid solution. In the figure, an anion defect is shown by a small cube. The valence difference of Ca^{2+} from Zr^{4+} is accommodated according to the following reaction:



where $Ca^{2+} \mid Zr$ denotes a Ca^{2+} cation on a Zr^{4+} lattice site and

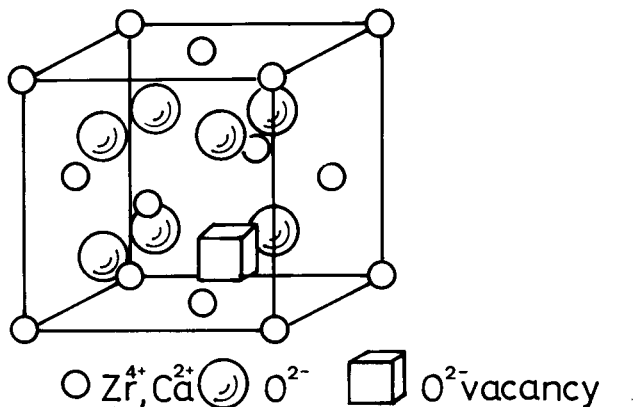


Fig. 2.4. Fluorite structure of ZrO_2 - CaO with O^{2-} vacancy expressed by a small cube.

V_{O_2} - an oxygen vacancy. Thus by dissolution of CaO in ZrO_2 lattice, Zr^{4+} ions are substituted by Ca^{2+} ions and hence an oxygen vacancy must be created for every Ca^{2+} present if electrical neutrality is to be maintained in the lattice.

Consequently, the concentration of crystal defects is controlled by the dopant concentration and is largely unaffected by temperature. In these materials the oxygen anion defects are predominant; the other types of crystal defects are essentially negligible, as can be seen from the following partial conductivities⁽⁶⁾ for $0.85ZrO_2-0.15CaO$ at $1000^\circ C$ under 1 atm of O_2 .

Total electrical conductivity	-----	$4.0 \times 10^{-2}/\Omega \cdot cm$
Oxygen ion conductivity	-----	$4.0 \times 10^{-2}/\Omega \cdot cm$
Zr^{4+} cation conductivity	-----	$1.0 \times 10^{-12}/\Omega \cdot cm$
Ca^{2+} cation conductivity	-----	$1.1 \times 10^{-13}/\Omega \cdot cm$

In order to obtain good ionic conduction, it is necessary to have special arrangements of cations and anions which produce an easy path for the rapid migration of ionic particles. Materials of this category of ionic conductor are sometimes referred as "superionic solids"⁽⁷⁾ or "superionic conductors"⁽⁸⁾. Materials of this type, e.g. superionic solid, will be discussed in the following section, 2.3.

In oxides which contain no electronic defects, the concentration of crystal defects is a function of temperature only and consequently the electrical conductivity of Equation(2-5) can be expressed as follows:

$$\sigma = \sum_{ions}^{all} n_i \cdot |z_i| e \cdot \mu_i^0 \exp\left[-\frac{E_i}{RT}\right] \quad (2-7)$$

where μ_i^0 is the pre-exponential term and E_i is the apparent activation energy of the ionic conduction. The summation Σ is necessary because two or three ionic species are present as charge carriers.

2.2.2 Oxides with p-type semiconduction

One of the characteristics of metals or metallic elements is that the atoms have a tendency to lose electrons and subsequently adopt a stable state with positive charge. Some of these metals

are called transition metals and these metals can easily adopt two or three different states of positive charge, according to the specific energy levels of the electrons. In contrast, oxygen can only adopt the state with a charge of minus two.

Thus, for oxides of transition metals, the ratio of numbers of ions of metal and oxygen is not strictly an integer. In this case, the crystals of oxides should contain excess electrons or positive holes to maintain overall electrical neutrality.

The oxides of transition metals can be classified as either a metal-deficient oxide or a metal-excess oxide. Usually, the former exhibits p-type semiconduction and the latter n-type semiconduction.

Fig. 2.5. shows schematically both crystal and electronic defects in oxides exhibiting p-type semiconduction. In this figure, the cations are M^{2+} with small amount of M^{3+} and the anions are strictly O^{2-} . The trivalent cations, M^{3+} are considered to be equivalent to a M^{2+} plus a positive hole, which is expressed by P in the diagram.

In this figure, there are four positive holes (=four M^{3+}), one cation vacancy, and one interstitial oxygen.

At a constant total pressure and temperature, the equilibrium concentration of positive hole, n_p in Equation(2-5) is determined by the reaction equilibrium of:

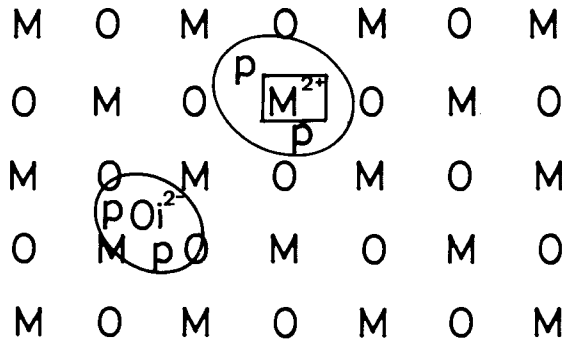
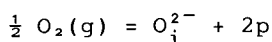
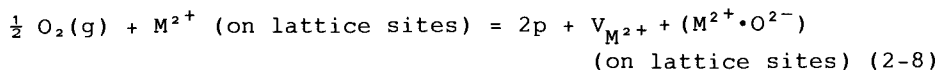


Fig. 2.5. Crystal defects and electronic defects contained in MO with p-type semiconduction.



or



These two reactions can be considered as the chemical dissolution of oxygen gas in an oxide with metal-deficiency.

Inspection of the picture of radii of ionic particles in the book by Pauling⁽⁹⁾, will convince the reader that there is little possibility of oxygen residing in the interstitial positions because of its ionic diameter (2.8 Å). In general, the radii of metal ions are very small.

Therefore, the lower reaction of Equation (2-8) usually determines the number of the positive holes. In this case, the equilibrium constant, K is given by Equation (2-9).

$$K = \frac{[\text{n}_p]^2 [\text{V}_{\text{M}^{2+}}]}{\text{P}_{\text{O}_2}^{\frac{1}{2}}} \quad (2-9)$$

where $[\text{V}_{\text{M}^{2+}}]$ is concentration of cation vacancy, and $[\text{n}_p]$ is concentration of positive holes given in Equation (2-5). If the cation vacancies are predominantly produced only by the reaction given in Equation (2-8), then $[\text{V}_{\text{M}^{2+}}]$ must be equal to $2[\text{n}_p]$ as:

$$[\text{V}_{\text{M}^{2+}}] = 2[\text{n}_p] \quad (2-10)$$

Inserting this relationship into Equation (2-8) and rearranging the terms, one has:

$$[\text{n}_p] = \text{P}_{\text{O}_2}^{\frac{1}{6}} \cdot K^{\frac{1}{3}} \cdot (2)^{-\frac{1}{3}} \quad (2-11)$$

According to a combined statement⁽¹⁰⁾ of 1st and 2nd laws of thermodynamics, one has the relation of:

$$\Delta G^\circ = -RT \ln K (= \Delta H^\circ - T\Delta S^\circ) \quad (2-12)$$

where ΔG° , ΔH° , and ΔS° are standard Gibbs free energy, enthalpy, and entropy changes of the reaction, respectively. R is the gas

constant, T is absolute temperature, and $\ln K$ is natural logarithm of the equilibrium constant. From this equation, the following relationship can be derived:

$$K = \exp\left[-\frac{\Delta H^\circ}{RT}\right] \cdot \exp\left[\frac{\Delta S^\circ}{R}\right] \quad (2-13)$$

Inserting this expression into Equation (2-11) leads to the relationship:

$$[n_p] = p_{O_2}^{\frac{1}{6}} \cdot (2)^{-\frac{1}{3}} \exp\left[\frac{\Delta S^\circ}{3R}\right] \exp\left[\frac{-\Delta H^\circ}{3RT}\right] \quad (2-14)$$

Using this relationship and inserting $\mu_{ion} = 0$ and $n_e = 0$ into Equation (2-5), one obtains:

$$\sigma = \mu_p \cdot p_{O_2}^{\frac{1}{6}} \cdot A \exp\left[\frac{-\Delta H^\circ}{3RT}\right] \quad (2-15)$$

where:

$$A = e \cdot (2)^{-\frac{1}{3}} \cdot \exp\left[\frac{\Delta S^\circ}{3R}\right] \quad (2-16)$$

Equation (2-15) indicates how the electrical conductivity varies with changes in both temperature and oxygen pressure for oxides with p-type semiconductivity. The conductivity increases with an increase of oxygen pressure and of temperature, since ΔH° is usually positive for reaction of Eq. (2-8). However, it can be seen from Equation (2-15) that the mobility of positive holes usually decreases with temperature. The mobility of electrons in semiconductors has been discussed at length in a book by Dekker⁽¹¹⁾. According to Dekker⁽¹¹⁾, no serious error is expected, even if the mobility in metals is used in the following discussion. The mobility of electrons in metallic conductors can be expressed by Equation (2-17):

$$\mu_e = \frac{e}{m} \left(\frac{1}{\tau_i} + aT \right)^{-1} \quad (2-17)$$

where e is unit charge, m is mass of an electron, τ_i is the mean time for successive collisions between an electron and structural imperfections, and "a" in this equation is a material constant.

Since the jump of a positive hole is identical with that of an electron but in the opposite direction, the mobilities of the two

species must be equal. Inserting Equation (2-17) into (2-15), one derives the expression:

$$\sigma = P_{O_2}^{\frac{1}{6}} \cdot \frac{e}{m} \left(\frac{1}{\tau_i} + aT \right)^{-1} A \exp \left[\frac{-\Delta H^\circ}{3RT} \right] \quad (2-18)$$

This relationship shows the dependency of the electrical conductivity of oxides displaying p-type semiconduction upon the temperature and the oxygen pressure.

The change in the pre-exponential term with temperature change is very small compared with that of the exponential term. Thus, the electrical conductivity is nearly proportional to exponential of reciprocal temperature. The slope of the line of $\log \sigma$ versus $(1/T)$ is controlled by enthalpy of the chemical reaction (Equation (2-8)). It can be seen from Equation (2-18) that the electrical conductivity is proportional to the one-sixth power of the oxygen pressure. However, as can be seen by Equation (2-8), this proportionality constant to the one-sixth power is fixed by stoichiometry of the reaction, or in other words, by the valences of the transition metals.

In the above derivation, Equation (2-10) was assumed, however if the concentration of the cation vacancies is constant, then, the electrical conductivity must be proportional to the one-fourth power of oxygen pressure.

If the activities of electronic defects and crystal defects are not proportional to their concentration, due to the formation of complexes, the mass action law of Equation (2-9) is not strictly valid. In this case, Equation (2-18) is valid only for the dilute range of the defects.

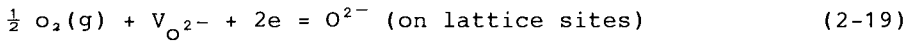
Nevertheless, the theoretical equation, like Equation (2-18) is very helpful to interpret the experimental observations made on many oxides with P-type semiconduction.

The comparison between the theory and the observation is described in detail in the monograph published by Kofstad in 1972⁽³⁾.

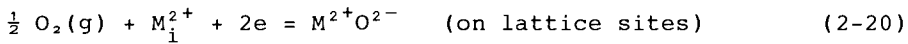
2.2.3 Oxides with n-type semiconduction

This type of oxide contains small amounts of either cations with lower valences or excess electrons, as shown in Fig. 2.6. The combination of a divalent cation and an excess electron is equivalent to monovalent cation.

The equilibrium content of electrons is determined by one of the following reactions:



or:



Realistically, both reactions could occur in oxides, since the radii of cations are relatively small when compared with the radius of O^{2-} anion. However, for cases where Equation (2-19) can be considered to apply the law of mass action, it gives:

$$K' = \frac{1}{p_{\text{O}_2}^{\frac{1}{2}} [\text{V}_{\text{O}^{2-}}] [\text{n}_e]^2} \quad (2-21)$$

Rearranging terms, assuming $[\text{V}_{\text{O}^{2-}}] = 2[\text{n}_e]$, one can have the following equation:

$$[\text{n}_e] = p_{\text{O}_2}^{-\frac{1}{6}} (2)^{-\frac{1}{3}} K'^{-\frac{1}{3}} \quad (2-22)$$

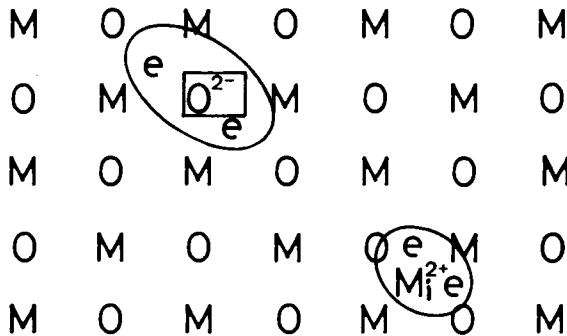


Fig. 2.6. Crystal defects and electronic defects contained in MO with n-type semiconduction.

Adopting a similar procedure to that used in deriving Equations (2-15) or (2-18), the following expression for the electrical conductivity, σ is obtained:

$$\sigma = P_{O_2}^{-\frac{1}{6}} \cdot \frac{e}{m} \left(\frac{1}{\tau'_i} + a'T \right)^{-1} A' \exp\left[\frac{\Delta H^\circ}{3RT}\right] \quad (2-23)$$

where τ'_i , a , A and ΔH° are denoted by primes as they would take on different values to those for p-type and n-type semiconductors.

If one compares Equation (2-23) to (2-18), one can notice that the oxygen-pressure dependency is of the opposite sign. However, the enthalpy of the reaction of Equation (2-8) is usually positive and that of (2-19) negative. Therefore, the temperature dependency is similar in both equations.

In Equation (2-23), the conductivity is dependent upon the oxygen pressure to the power of minus-one-sixth. However, it can change to the power of minus-one-fourth or to other values in the following circumstances:

- a) different stoichiometry in Equation (2-19) or (2-20),
- b) when the assumption of $[V_{O_2}] = 2[n_p]$ is not valid,
- c) when the law of an ideal solution is not valid.

Three theoretical relationships have been obtained to express the electrical conductivity of oxides as functions of temperature and oxygen pressure; Equation (2-7) for ionic conductors, Equation (2-18) for p-type semiconductors and Equation (2-23) for n-type semiconductors.

With the help of these equations, one can judge what type of charge carrier is predominant in the oxide, by measuring the conductivity at various temperatures and oxygen pressures. If the conductivity does not depend upon oxygen pressure, then the oxide is an ionic conductor. However, if the conductivity increases with oxygen pressure, it is a p-type semiconductor. Finally, if the conductivity decreases with the increase of oxygen pressure, it is a n-type semiconductor.

In all cases, the conductivity increases with temperature in proportion to the exponential of the reciprocal temperature.

Thus, one can not deduce the conduction mechanism of an oxide from the temperature dependency alone.

2.3 CLASSIFICATION OF OXIDES, NITRIDES, SULFIDES, SULFATES, AND SUPERIONIC CONDUCTORS ACCORDING TO THE CONDUCTION MECHANISM

There are four different species, which can operate as charge carriers, when a metal oxide is placed in an electric potential gradient. These are metal cations, oxygen anions, excess electrons and positive holes.

The first logical step is to separate the ionic conduction from the electronic conduction. This is then followed by the determination of the transference number of these four species, which is defined by Equation (2-24):

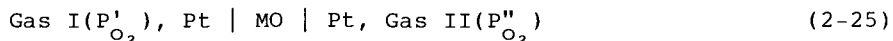
$$t_i = \frac{n_i |z_i| e \mu_i}{\sum_i n_i |z_i| e \mu_i} \quad (2-24)$$

where t_i is the transference number of species, i . The other terms have been defined previously in Equation (2-3).

2.3.1 Experimental method to determine the conduction mechanism

(a) Measurement of the conductivity under various oxygen pressures. According to Equations (2-7), (2-18) and (2-23), one can deduce the predominant conduction mechanism, provided that the conductivity can be determined accurately at various oxygen pressures for a constant temperature. However, one can not determine transference numbers of each species, as defined by Equation (2-24), from the conductivity measurements, alone.

(b) Measurement of the electromotive force of Galvanic cells. When a Galvanic cell is constructed using a pure oxide, MO, as an electrolyte, the measured electromotive force can yield the transference number of ions, t_{ion} :



where the electromotive force, E is given by Equation (2-26):

$$E = t_{ion} \cdot \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \quad (2-26)$$

In this equation, F is Faraday constant and R is gas constant. Platinum is used as the electrode, because it is usually chemically inert even at high temperatures. However, this method is unable to separate the cationic and anionic transference numbers.

(c) Measurement of overpotential through the oxide. When the conduction mechanism of an oxide is predominantly ionic, polarization phenomena take place by the current flow through it. Thus, if a polarization overpotential is observed, it is a good indication that the conduction is predominantly ionic. However, this observation can only give qualitative information on the conduction mechanism.

(d) Electrolysis of oxides. A direct and quantitative determination of the transference number of the species in an oxide can be made by the electrolysis of the oxide.

Fig. 2.7. schematically shows the experimental apparatus for electrolytic decomposition of liquid K_2O-SiO_2 binary solution at high temperature used by Bockris, Kitchner and Davis⁽¹²⁾ in 1952. The method shown in this figure can give the transference number of the ionic species. The changes in the average compositions of the anode and cathode compartments after the current flow are determined by chemical analysis of quenched cell assembly. On the basis of the experimental results⁽¹²⁾ obtained, the transference number of potassium cation is unity in liquid K_2O-SiO_2 .

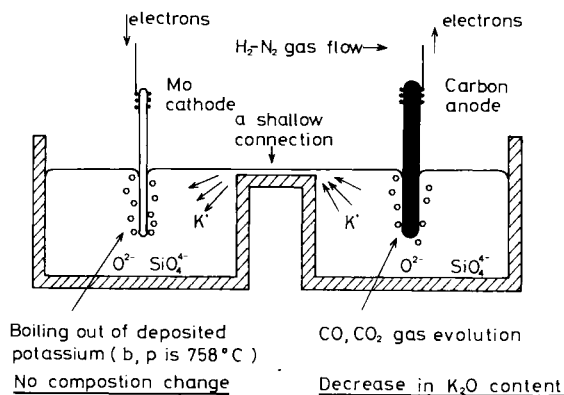


Fig. 2.7. An electrolytic cell to determine cationic and anionic transference numbers from the composition changes in anode and cathode compartments after a given current flow (after Bockris et al. (12)).

solution.

When electrons are supplied to Mo cathode, potassium cations migrate from the anode to the cathode compartment. On the cathode, the deposited potassium metal is boiling out of the melt (because the temperature is above its boiling point) and thus, no composition change is expected. In contrast to this, the K_2O content of the anode compartment decreases, since the O^{2-} anions are continually oxidized at the anode to form carbon monoxide and dioxide gases which are subsequently evolved.

(e) Blocking electrode method. This method can be used to determine the small, partial conductivity values associated with electronic defects in essentially ionic conductors.

The principle of measurement is based upon the residual current passing through an ionic conductor sandwiched by one reversible, (non-polarizable) electrode and one non-reversible (polarizable) electrode as follows:

Reversible electrode (ion sink)	Ionic conductor with a small electronic conduction	Nonreversible electrode

The following is an example of this type of cell:

Pt, Ni, NiO	ZrO ₂ - CaO + O ²⁻ +	a metal with no solubility of oxygen	: : : : :	Vacuum

A constant potential, which is less than the decomposition potential of ZrO₂-CaO, is applied in order to transfer oxygen ions to the Ni/NiO electrode, which is a non-polarizable electrode with respect to oxygen. Since there is no source of oxygen at the "blocking electrode" on the right hand side and as the potential is less than the decomposition potential, the steady current obtained is created by the migration of electronic defects contained in the ZrO₂-CaO electrolyte. According to C. Wagner,⁽¹³⁾
⁽¹⁴⁾ a local equilibrium is assumed by the ions, electrons, and neutral species at any point in the electrolyte. The applied constant potential minus the Ohmic potential drop gives the oxygen pressure difference between the two electrodes.

Wagner⁽¹³⁾⁽¹⁴⁾ postulated that the steady residual current, $I_{\text{resid.}}$ can be expressed as a function of the applied potential, E , of partial conductivity of electrons or positive holes and of a thickness, d in the following manner:

$$I_{\text{resid.}} = \frac{RT}{Fd} \cdot \sigma_p [1 - \exp \frac{F|E|}{RT}] + \frac{RT}{Fd} \cdot \sigma_e [\exp \frac{F|E|}{RT} - 1] \quad (2-27)$$

where σ_p and σ_e are the partial conductivities of positive holes and excess electrons, respectively. Because either σ_p or σ_e will be predominant under a certain conditions of oxygen pressure and temperature, it is customary to simplify Equation (2-27) by including only one exponential term on the right hand side. This method has been used for high temperature measurements by Patterson, Borgen and Rapp⁽¹⁵⁾.

(f) Estimation from tracer diffusivity of ions. When a cation or an anion migrates under an electrical potential gradient, it has to cross a barrier of the Coulomb-static potential of the nearest ions. The same micro-step is necessary for diffusion jumping of a cation (or an anion) in a concentration gradient. Thus, the partial conductivity of an ionic species can be estimated from its tracer diffusivity. The theoretical relation between the partial conductivity and the tracer diffusivity is known as Nernst-Einstein relationship. Since this relationship is very interesting and has considerable scientific significance, it will be fully discussed in detail in the following chapter.

2.3.2 Classification of oxides and other inorganic compounds according to the conduction mechanism

The temperature and oxygen pressure can be accurately controlled in experiments in the ranges of 100°C ~ 1600°C and 10⁰atm ~ 10⁻²atm, respectively. It is for this reason that the conduction mechanism of many inorganic compounds has usually been determined in these ranges of pressure and temperature. In some cases, conduction is a mixture of two or more mechanisms. Therefore, it would not be rigorous to merely classify the compounds by the predominant mechanism alone. Although Table 2.1. gives such a classification, it is necessary to make several remarks about this table. All the examples of p-type, n-type, or

TABLE 2.1

Classification of oxides and other compounds according to conduction mechanism at high temperature.

Classification	Examples of Conductors	Main Charge Carrier	References
p-type Semiconductor	Fe_{1-y}O , NiO , CoO , Cu_2O , MnO_2 , UO_{2+x} Cr_2O_3 , etc.	Positive holes	(3)
n-type Semiconductor	ZnO , CdO , SnO_2 , TiO_2 CeO_2 , Fe_3O_4 , WO_3 V_2O_5 , Nb_2O_5 , $\beta\text{-Ta}_2\text{O}_5$	Excess electrons	(3)
Amphoteric Semiconductor with n- and p-type conduction	MnO , Y_2O_3 , Bi_2O_3 PbO , Sc_2O_3	holes or electrons	(3)
Ionic Conductor	MgO	$\text{Mg}^{2+} (?)$	(16)
	Al_2O_3	$\text{Al}^{3+} (?)$	(16)
	SiO_2	?	(16)
	Spinel MgAl_2O_4	?	(17)
	Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	?	(18)
	Forsterite Mg_2SiO_4	?	(19)
	Liquid PbO-SiO_2	Pb^{2+}	(20)
	Liquid $\text{Li}_2\text{O-SiO}_2$	Li^+	(12)
	Liquid $\text{Na}_2\text{O-SiO}_2$	Na^+	(12)
	Liquid $\text{K}_2\text{O-SiO}_2$	K^+	(12)
	Liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$	Ca^{2+}	
	CaS and CaS-TiS_2	Ca^{2+}	(21)(22)(23)
	SrS and $\text{SrS-Ce}_2\text{S}_3$	$\text{Sr}^{2+} (?)$	(24)
	LiH	?	(25)(26)
	$\text{SrO-CeO}_2\text{-Yb}_2\text{O}_3 (-\text{H}_2\text{O})$	$\text{H}^+ (?)$	(27)(28)
	K_2SO_4	$\text{K}^+ (?)$	(29)
	Na_2SO_4	$\text{Na}^+ (?)$	(30)
	$\text{AlN-Y}_2\text{O}_3$, $\text{AlN-Al}_2\text{O}_3$	$\text{Al}^{3+} (?)$	(31)
	$\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_4$ (called Sialon)	Si^{4+} or Al^{3+}	(32)

TABLE 2.1 Continued.

Classification of oxides and other compounds according to conduction mechanism at high temperature.

Classification	Examples of Conductors	Main Charge Carrier	References
Super Ionic Conductor	ZrO_2 -15mole%CaO	O^{2-}	(1)
	ZrO_2 -15mole%MgO	O^{2-}	(1)
	Na_2O -11 Al_2O_3 (β -Alumina)	Na^+	(2)
	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (called NASICON)	Na^+	(33)
	$\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (called LISICON)	Li^+	(34)
	Glassy Na_2O - B_2O_3 - NaCl - SiO_2	Na^+	(35)
	Glassy AgI - Ag_2MoO_4	Ag^+	(36)
	Glassy AgI - Ag_2O - B_2O_3	Ag^+	(37)
	α -AgI	Ag^+	(7)
	$\text{Ag}_{19}\text{P}_2\text{O}_7\text{I}_{15}$	Ag^+	(7)
	$\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$	Rb^+	(7)
	Li_3N	Li^+	(38)

amphoteric semiconductors were taken from the excellent monograph due to Kofstad⁽³⁾.

Fig. 2.8. gives the relationship between $\log \sigma$ and $\log P_{O_2}$ with NiO which has p-type semiconduction according to Bransky and Tallan⁽³⁹⁾. The conductivity is proportional to $P_{O_2}^{1/4}$ over a wide range of temperatures and oxygen pressures.

In the previous section, only Equations (2-18) and (2-23) have been given for the oxygen pressure dependency of the electrical conductivity. However, in reality, the conductivity can not be interpreted by these two equations alone, as can be seen by the results presented in Fig. 2.8. This is illustrated even more clearly in the results obtained for $Fe_{1-y}O$, which are shown in Fig. 2.9.⁽⁴⁰⁾

In this figure, it can be seen that the conductivity, σ is not proportional to y but to $y(1-3.36y)$. This function was interpreted⁽⁴⁰⁾ as evidence for a hopping-type model for the conductivity and the conductivity was proportional to the product of divalent and trivalent iron ions situated in the octahedral sites.

Fig. 2.10. shows the relation between $\log \sigma$ and $\log P_{O_2}$ for TiO_2 , which exhibits n-type semiconduction according to Blumenthal et al⁽⁴¹⁾. Equation (2-19) can be considered valid in the range where the conductivity is proportional to $P_{O_2}^{-1/6}$. However, in another

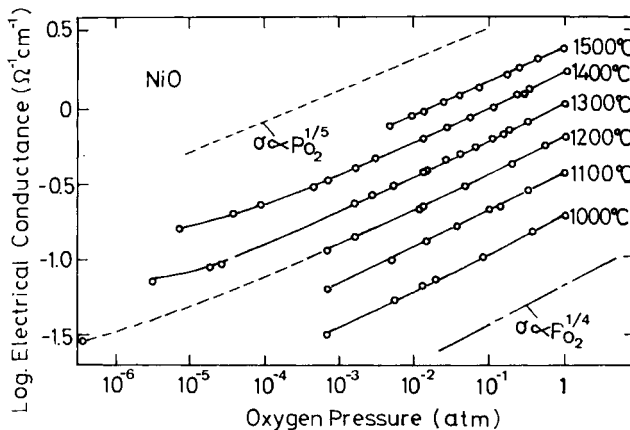


Fig. 2.8. Electronic conductivity of NiO as a function of partial pressure of oxygen (after Bransky and Tallan⁽³⁹⁾).

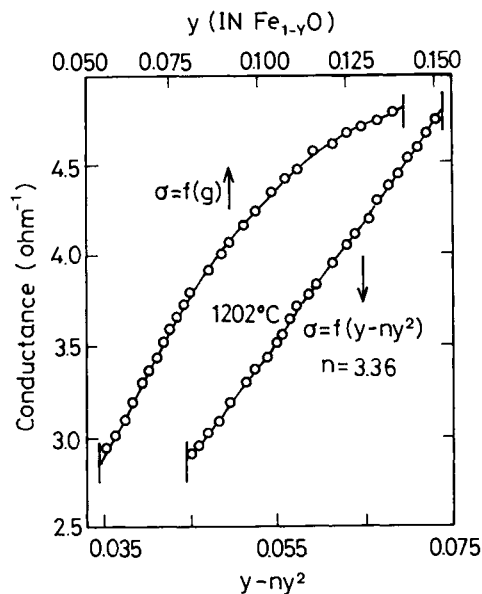


Fig. 2.9. Positive hole conductivity of wüstite as a function of nonstoichiometry at 1202°C (after Neuschütz and Towhidi⁽⁴⁰⁾).

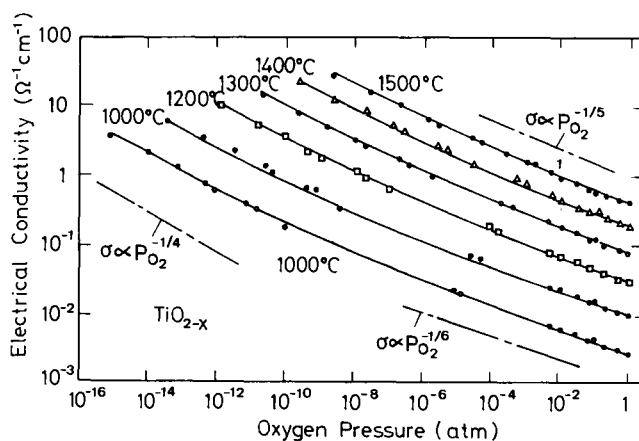
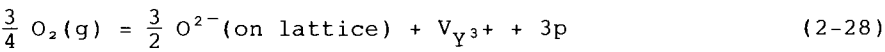


Fig. 2.10. Electric conductivity of single crystal of rutile as a function of oxygen pressure at 1000°C to 1500°C (after Blumenthal et al⁽⁴¹⁾).

range it was also found to be proportional to $P_{O_2}^{-1/4}$ and this has been interpreted as the extrinsic effect of the impurity. More sophisticated interpretations have been proposed to account for the semi-conductivity of oxides but they are considered outside the scope of this monograph.

Fig. 2.11. shows the amphoteric semiconduction of Y_2O_3 , reported by Tallan and Vest⁽⁴²⁾. In the range where p-type semiconduction occurs the results agrees with the prediction of the following theory; the most probable defect formation occurs by the reaction:



If $3[V_{Y^{3+}}] = [n_p]$ is assumed, then Equation (2-29) can be derived:

$$\sigma = [\text{constant}] P_{O_2}^{3/16} \tag{2-29}$$

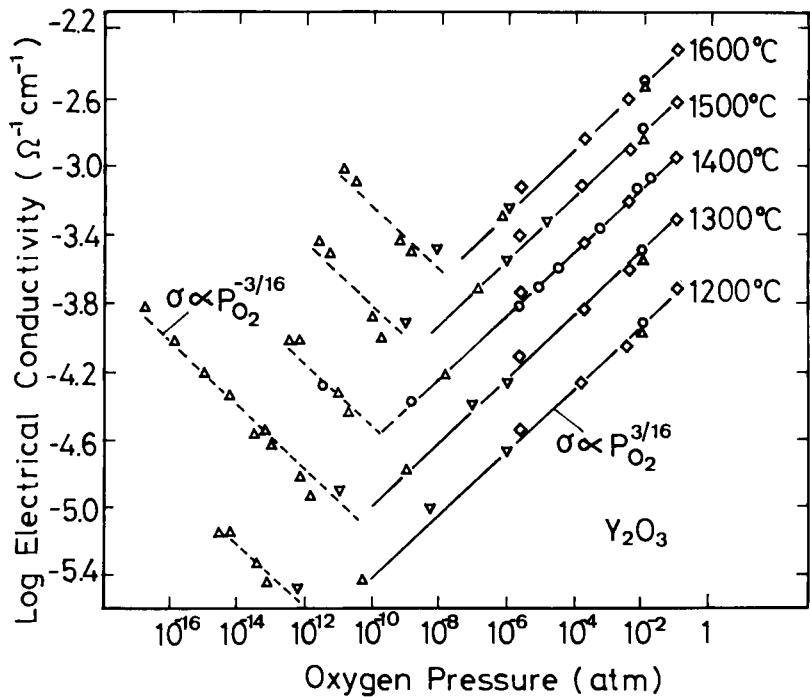


Fig. 2.11. Amphoteric semiconduction of Y_2O_3 as a function of oxygen pressure at 1200°C to 1600°C (after Tallan and Vest⁽⁴²⁾).

The experimental results in Fig. 2.11. can be expressed by the relationship:

$$\sigma = 1.3 \times 10^3 P_{O_2}^{-\frac{3}{16}} \exp[-1.94/kT] \quad (2-30)$$

The agreement of the measured conductivity with the theoretical relationships does not occur in many cases for the solid oxides. Thus, it might be oversimplification to assume that Equations (2-18) or (2-23) are valid for a wide range of oxides. These equations have been given merely as examples of the relationships existing between the electrical conductivity and oxygen pressure.

In Table 2.1, below the "semiconductors", "ionic conductor" and "superionic conductor" are shown.

The difference between these ionic and superionic conductors can be clarified when the following definition for a superionic conductor due to Chandra⁽³⁾ is adopted:

- (1) the crystal bonding is ionic
- (2) the electrical conductivity is comparable with those obtained for liquid electrolytes (in range of 10^{-1} to $10^{-4} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$).
- (3) the transference number of the ion is unity
- (4) the transference number of the electrons or holes is less than 10^{-4} .

The conduction mechanism in superionic conductors occurs by the migration of ionic species and is characterized by very easy movement through "channelled", "layered", or "molten sublattice" structure. Thus, the conduction mechanism of a superionic conductor is distinctly different from that of "ionic conductor" given in Table 2.1.

In the case of "ionic conductor" oxides, the oxygen anions are in the closed packed structure of fcc or hcp, with the cations at the interstitial sites. Thus, the cations are considered to be the charge carriers.

The inclusion of MgO , Al_2O_3 , and SiO_2 in Table 2.1 might be questionable, for the reasons cited in reference⁽¹⁶⁾. However, the intrinsic conductivity at high temperatures, above 1400°C ,

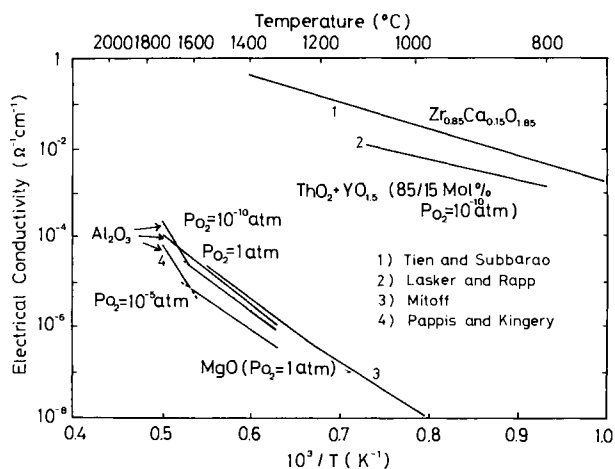


Fig. 2.12. Electrical conductivity as a function of reciprocal temperature for Al_2O_3 , MgO , $\text{ZrO}_2\text{-CaO}$ and $\text{ThO}_2\text{-Y}_2\text{O}_3$. (References (44) to (47))

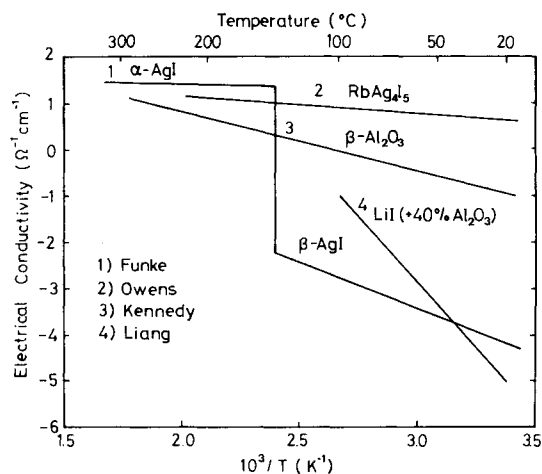


Fig. 2.13. Electrical conductivity of some examples of superionic conductors (48)-(51).

can be attributed to ionic conduction⁽¹⁶⁾. For this reason, they have been included in this table.

The sulfides, sulfates, nitrides, and hydride have also been included because of their potential use in industrial applications. The examples of the conductors given in Table 2.1 were selected on the basis of their good chemical stability and their potential use in industrial applications. This will be further discussed in Chapter 7.

Solid and fused halides have been excluded from Table 2.1 since the conduction mechanism for these materials has been fully reviewed by Klem⁽⁴³⁾.

Fig. 2.12 and 2.13 show the relationship existing between $\log \sigma$ and $[1/T]$ for both ionic conductors of MgO and Al_2O_3 and some superionic conductors, $\text{ZrO}_2\text{-CaO}$, $\text{ThO}_2\text{-Y}_2\text{O}_3$, $\beta\text{-Na}_2\text{O-11Al}_2\text{O}_3$, etc. Figures 2.12 and 2.13 are based on the data given by references (44) to (47) and (48) to (51) respectively.

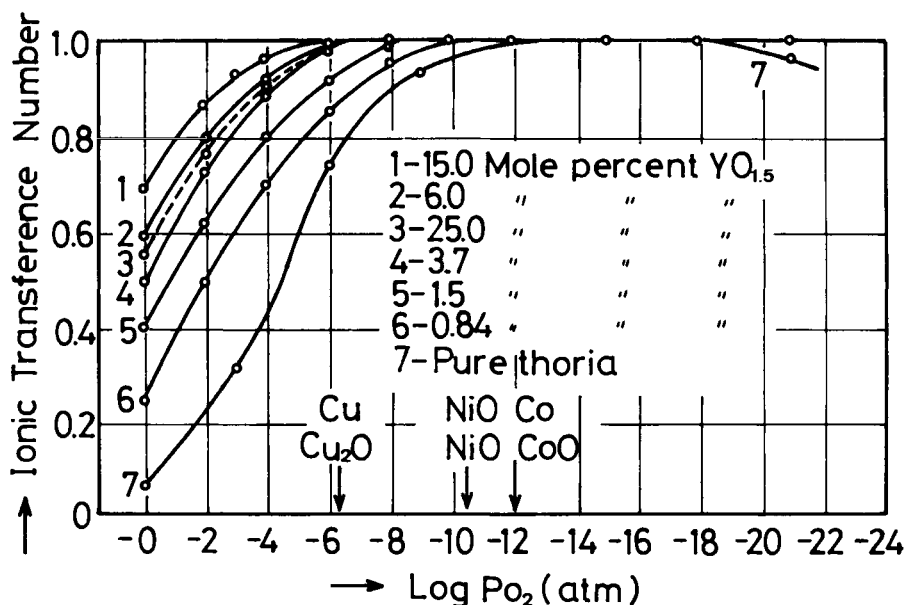


Fig. 2.14. Ionic transference numbers in pure thoria and thoria base solid solutions with yttria as a function of oxygen pressure at 1000°C (after Lasker and Rapp⁽⁴⁵⁾).

However, the superionic conductor is also sometimes amphoteric by nature. As an example, Fig. 2.14 shows the relationship between $\log \sigma$ and $\log P_{O_2}$ at 1000°C as reported by Lasker and Rapp⁽⁴⁵⁾. This solid solution of ThO_2 and Y_2O_3 exhibits p-type semiconduction at the higher oxygen pressures, ionic conduction at the intermediate oxygen pressures, and finally n-type semiconduction (curve 7) at the lower oxygen pressures.

Even with these reservations, Table 2.1 can still be helpful in gaining a perspective understanding on the conduction mechanism occurring in various inorganic compounds, excluding halides.

In summary, in this chapter the various charge carriers available for the electric conduction in oxides of metals have been described and the partial conductivities of the various carriers have been defined.

Secondly, the relationship of the conductivity, with both the temperature and the oxygen pressure has been discussed. Theoretical equations have been derived to express the dependency of electrical conductivity upon temperature and oxygen pressure. Equations (2-7), (2-18) and (2-23) are given as examples of the theoretical relationships. In practice, the situation is complicated by the formations of complexes of electronic defects with crystal defects.

In the last section, the experimental methods used to determine the conduction mechanism of the oxides have been summarized.

Finally, a perspective classification of the oxide and other compounds has been presented on the basis of the predominant mechanism of electric conduction.

REFERENCES TO CHAPTER 2

- (1) K. Kiukkola and C. Wagner, J. Electrochem. Soc., 104 (1957) pp. 379-387.
- (2) Y.F.Y. Tao and J.T. Kummer, J. Inorg. Nucl. Chem., 29 (1967) 2453 pp.
- (3) P. Kofstad, "Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Oxides" Wiley-Interscience, John & Sons Inc., (1972) New York.
- (4) C.J. Ballhausen, "Introduction to Ligand Field Theory" McGraw-Hill Book Co., Inc. (1962) New York.
- (5) C.K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes" Pergamon Press (1962) Oxford.
- (6) B.C.H. Steele, in pp. 3-27 of "Electromotive Force Measurements in High Temperature Systems" edited by C.B. Alcock, Inst. of Mining and Metallurgy (1968) London.
- (7) S. Chandra, "Superionic Solids"- Principles and Applications, North-Holland Pub. Co. (1981) Amsterdam.
- (8) "Superionic Conductors" edited by G.D. Mahan and W.L. Roth, Plenum Press (1976) New York.
- (9) L. Pauling, "The Nature of the Chemical Bond" Cornell University Press (1940) Ithaca, New York.
- (10) L.S. Darken and R.W. Gurry, "Physical Chemistry of Metals" McGraw-Hill Book Co., Inc. (1953) New York.
- (11) A.J. Dekker, "Electrical Engineering Materials" Prentice-Hall, Inc. (1959) New York.
- (12) J.O'M. Bockris, J.A. Kitchner and A.E. Davies, Trans. Faraday Soc., 48 (1952) pp. 536-548.
- (13) C. Wagner, Proceedings of Intern. Comm. Electrochem. Therm. and Kinetics (CITCE), 7th Meeting, Lindau (1955), Butterworth Scientific Publisher (1957) London.
- (14) C. Wagner, Z. Elektrochemie 60 (1956) 4, and 63 (1959) 1027.
- (15) J.W. Patterson, E.C. Borgen and R.A. Rapp, J. Electrochem. Soc., 114 (1967) 752.
- (16) K.S. Goto and W. Pluschkell, "Physics of Electrolytes" vol. II pp. 539-622, edited by J. Hladik, published by Academic Press (1972) London.
- (17) W.A. Fischer and D. Janke, Arch. Eisenhüttenw., 40 (1969) pp. 837-841.
- (18) W.A. Fischer and D. Janke, Arch. Eisenhüttenw., 40 (1969)

- pp. 707-716.
- (19) W. Pluschkell, Arch. Eisenhüttenw., 40 (1969) pp. 401-403.
 - (20) K.S. Goto, "A Review of the Electrolytic Properties of Metallurgical Slags" in Proceedings of Second International Symposium on Metallurgical Slags and Fluxes (1984) Nevada, U.S.A. (edited by H.A. Fine and D.R. Gaskell), MS of AIME.
 - (21) W.L. Worrell, V.B. Tare and F.J. Bruni, "High Temperature Technology", Proc. 3rd Intern. Symp. (1969) 503 pp. published by Butterworth, London.
 - (22) K. Nagata and K.S. Goto, see page 426 of "Metallurgische Elektrochemie" by W.A. Fischer and D. Janke, Verlag Stahleisen m.b.H. (1975) Düsseldorf.
 - (23) A. Egami, T. Onoye and K. Narita, Solid State Ionics 3/4 (1981) 617.
 - (24) E. Banks and R. Ward, J. Electrochem. Soc., 96 (1949) 297.
 - (25) F.E. Pretzel, G.N. Rupert, C.L. Mader, E.K. Storms, G.V. Gritton and C.C. Rushing, J. Phys. Chem. Solids 16 (1960) 10.
 - (26) A. Bergstein, J. Spitz and R. Didier, Czech. J. Phys. B 18 (1968) 538.
 - (27) H. Iwahara, T. Esaka, H. Uchida and N. Maeda, J. Solid State Ionics 3/4 (1981) 359.
 - (28) H. Iwahara, H. Uchida and N. Maeda, J. of Power Source 7 (1982) 293.
 - (29) M. Gauthier and A. Chamberland, J. Electrochem. Soc., 21 (1977) 1579.
 - (30) Y. Saito, T. Maruya, Y. Matsumoto, K. Kobayashi and Y. Yano, 7th Meeting on Solid State Ionics, October (1982) at Tokyo Institute of Technology.
 - (31) M. Yahagi and K.S. Goto, J. Japan Inst. of Metals 47 (1983) 419-425.
 - (32) Y. Ukyo, K.S. Goto and Y. Inomata, J. American Ceramic Soc., 62 (1979) 410-413.
 - (33) H.Y.-P. Hong, Materials Research Bulletin 11 (1976) 173.
 - (34) H.Y.-P. Hong, Materials Research Bulletin 13 (1978) 117.
 - (35) C.A. Levine, "Application of Solid Electrolyte" edited by T. Takahashi and A. Kozawa, published by JEC Press Inc. (1980) 99 pp., Cleveland.
 - (36) T. Minami, K. Matsuda and M. Tanaka, Solid State Ionics, vol. 3/4 (1981) 93.
 - (37) T. Minami, T. Shimizu and M. Tanaka, Abstract Volume of

Solid State Ionics 4th International Conference at Grenoble, France.

- (38) S.G. Bishop, P.J. Ring and P.J. Bray, J. Chem. Phys., 45 (1966) 1525.
- (39) I. Bransky and N.M. Tallan, J. Chem. Phys., 49 (1968) 1243.
- (40) D. Neuschütz and N. Towhidi, Arch. Eisenhüttenwes. 41 (1970) 303.
- (41) R.N. Blumenthal, J. Coburn, J. Baukus and W.M. Hirthe, J. Phys. Chem. Solids., 27 (1966) 643.
- (42) N.M. Tallan and R.W. Vest, J. Amer. Cer. Soc., 49 (1966) 401.
- (43) A. Klem, "Molten Salt Chemistry" pp. 535-606, edited by M. Blander, Interscience Publishers (1964) New York.
- (44) T.Y. Tien and E.C. Subbarao, J. Chem. Phys., 39 (1963) 1041-1047 and J. Am. Ceram. Soc., 46 (1963) 489-492.
- (45) M.F. Lasker and R.A. Rapp, Z. Phys. Chem. 49 (1966) 198-221.
- (46) S.P. Mitoff, J. Chem. Phys., 31 (1959) 1261-1269 and 36 (1962) 1383-1389.
- (47) J. Papis and W.D. Kingery, J. Am. Ceram. Soc., 44 (1961) 459-464.
- (48) K. Funke, Prog. Solid State Chem., 11 (1976) 345 pp.
- (49) B.B. Owens, in "Advances in Electrochem. and Electrochem. Engg" edited by C.W. Tobias, John Wiley (1971) New York.
- (50) J.H. Kennedy, J. Electrochem. Soc., 124 (1977) 865.
- (51) C.C. Liang and L.H. Barnette, J. Electrochem. Soc., 123 (1976) 453 pp.

Chapter 3

RELATION BETWEEN THE CONDUCTIVITY AND DIFFUSIVITY OF IONS
IN OXIDES

3.1 A GENERAL DERIVATION OF NERNST-EINSTEIN RELATION

For many years, it has been known that a close relation between the electrical conductivity of inorganic compounds and the diffusivity of the ions exists. The relation has been called "Nernst-Einstein relation", because it originates from two independent papers, one published by Nernst⁽¹⁾ in 1888 and the other by Einstein⁽²⁾ in 1905.

A concise derivation of this relation proceeds as follows. When an ion with a positive charge of ze is placed in an electrical potential gradient, the force exerted upon it is expressed by:

$$f_x = -ze \left(\frac{\partial E}{\partial x} \right) \quad (3-1)$$

where f_x is the force with x -direction, E is the electrical potential and x is the distance.

When an atom or a molecule is placed in a gradient of its partial molal Gibbs free energy, the equivalent force can be expressed by:

$$f_x = - \frac{1}{N_o} \left(\frac{\partial \bar{G}_i}{\partial x} \right) \quad (3-2)$$

where $\bar{G}_i$ is the partial molal Gibbs free energy of the species, i and N_o is Avogadro's number (6.0222×10^{23} /mole).

The right hand side of Eq. (3-2) is divided by Avogadro's number, because the Gibbs free energy, $\bar{G}_i$ is always given per mole.

Fig. 3.1 shows the direction of forces exerted upon the particles placed in an electrical potential gradient and in a gradient of Gibbs molal free energy.

As given by Eq. (2-4) of the previous chapter, absolute mobility is defined as the net velocity of a particle per unit force of one dyne. Therefore, the velocity is given as:

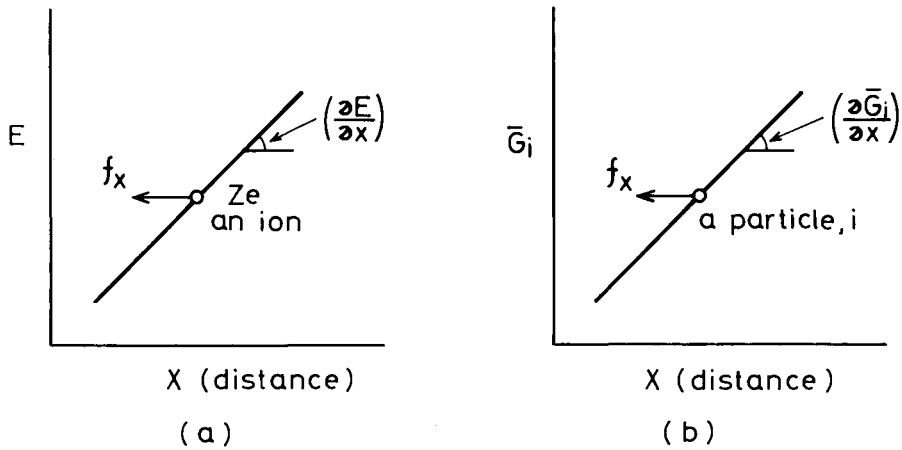


Fig. 3.1. Pictures to show the direction of forces exerted upon an ion with positive charge of ze under an electrical potential gradient (shown by (a)) and upon a particle, i under a gradient of its partial molal Gibbs free energy (shown by (b)).

$$v_x = B_i f_x \quad (3-3)$$

Inserting Eq. (3-1) and Eq. (3-2) into f_x of Eq. (3-3), one can state:

$$v_x = -ze B_i \left(\frac{\partial E}{\partial x} \right) \quad (3-4)$$

and:

$$v_x = -\frac{B_i}{N_o} \left(\frac{\partial \bar{G}_i}{\partial x} \right) \quad (3-5)$$

Because the current density with motion of species, i is the product of v_x and $n_i ze$, it can be given by:

$$j_i = n_i ze v_x \quad (3-6)$$

where n_i is the number of the charge carrier in unit volume/cm³. Inserting Eq. (3-4) into v_x of Eq. (3-6), one has:

$$j_i = - n_i (ze)^2 B_i \left(-\frac{\partial E}{\partial x} \right) \quad (3-7)$$

The comparison of this equation to Eq. (2-1) in the previous chapter gives the partial conductivity as:

$$\sigma_i = B_i (ze)^2 n_i \quad (3-8)$$

This is an important equation which connects diffusivity and electrical conductivity, and thus given in a box.

Parallel to the above procedure for Eq. (3-6) to Eq. (3-8), we should work on Eq. (3-5). According to thermodynamic principles, the partial molal Gibbs free energy is given by:

$$\bar{G}_i = G_i^\circ + RT \ln a_i \quad (3-9)$$

where G_i° is the standard molal Gibbs free energy and a_i is the chemical activity of species, i . If the activity is proportional to the concentration of i , expressed by n_i , the differential of Eq. (3-9) with respect to x yields:

$$\frac{\partial \bar{G}_i}{\partial x} = RT \left(\frac{\partial \ln n_i}{\partial x} \right) = \frac{RT}{n_i} \left(\frac{\partial n_i}{\partial x} \right) \quad (3-10)$$

This relation is strictly valid only in an ideal solution or in dilute solutions, in which the Henry's law is satisfied. In case of diffusion of an isotope, the compound can be considered the ideal solution of the solvent with its isotope.

Inserting Eq. (3-10) into (3-5), one can state:

$$v_x = - kTB_i \frac{1}{n_i} \left(\frac{\partial n_i}{\partial x} \right) \quad (3-11)$$

The number of particles of i per unit time, passing through unit area perpendicular to x -direction is equal to $n_i v_i$ and this quantity is usually called the diffusion flux of species, i , expressed by J_i .

Using Eq. (3-11), one can state:

$$J_i = n_i v_x = - kTB_i \left(\frac{\partial n_i}{\partial x} \right) \quad (3-12)$$

On the other hand, the diffusion flux, J_i is given as follows according to Fick's first law of diffusion:

$$J_i = - D_i^{tr} \left(\frac{\partial n_i}{\partial x} \right) \quad (3-13)$$

where D_i^{tr} means the tracer diffusivity, because we are dealing only with diffusion of the isotope in this chapter.

The comparison between Eq. (3-12) and Eq. (3-13) gives the simple relation:

$$\boxed{kTB_i = D_i^{tr}} \quad (3-14)$$

This is another important relation, called the Einstein relation. By inserting Eq. (3-8) for B_i in this equation, one has:

$$D_i^{tr} = \frac{kT}{(ze)^2 n_i} \sigma_i \quad (3-15)$$

or:

$$\sigma_i = \frac{(ze)^2 n_i}{kT} D_i^{tr} \quad (3-15')$$

This equation of Eq. (3-15) or (3-15') is the Nernst-Einstein relation. With this equation, we can estimate the partial electrical conductivity from the tracer diffusivity or vice versa.

Because the total conductivity is the sum of the partial conductivities according to Eq. (2-2), one can express the total conductivity as:

$$\sigma_{total} = \frac{(ze)^2 n_i}{kT t_i} D_i^{tr} \quad (3-16)$$

where t_i is the transference number defined by Eq. (2-24) or by:

$$t_i \equiv \frac{\sigma_i}{\sigma_{\text{total}}} \quad (2-24')$$

If a radioactive tracer is diffusing with vacancy mechanism, there is a correlation between the directions of the successive jumps of the isotope⁽³⁾. According to Compaan and Haven⁽³⁾, the correlation factor, f , which is sometimes called the Haven ratio, is defined as:

$$D_i^{\text{tr}} = f D_v \quad (3-17)$$

where D_v is self diffusivity of the vacancy.

If the current is carried by migration of vacancies in case of the electrical conduction, the tracer diffusivity in Eq. (3-16) must be replaced by D_v . Therefore, in this case, the Nernst-Einstein equation should include the correlation factor as follows:

$$\sigma_{\text{total}} = \frac{n_i (ze)^2}{k T f t_i} D_i^{\text{tr}} \quad (3-18)$$

The value of f is approximately equal to $1 - (2/z_o)$, where z_o is the number of the nearest neighbors. A rigorous calculation of f was made by Compaan and Haven as given in Table 3.1.

TABLE 3.1

Approximate and rigorously calculated values of f in various lattices. (After Compaan and Haven⁽³⁾).

Lattices	Number of nearest neighbors	$1 - (2/z_o)$	f
Two dimensional			
Square	4	0.5000	0.46705
Hexagonal	6	0.6667	0.56006
Three dimensional			
Diamond	4	0.5000	0.50000
Simple cubic	6	0.6667	0.65549
BCC	8	0.7500	0.72149
FCC	12	0.8333	0.78145

The Nernst-Einstein equation, expressed by Eq. (3-18), is an important theoretical equation, because it has, for a long time, stimulated scientific curiosity about the micromechanism of ionic diffusion and electric conduction of many inorganic compounds. For example, when a compound is composed of a single cation-species and a single anion-species, such as CaO , Al_2O_3 , NaCl , CaS etc, the Nernst-Einstein equation of Eq. (3-18) can be rigorously satisfied.

Thus, the Haven ratio, f can be estimated from the measurements of σ_{total} , D_i^{tr} and t_i . This ratio or correlation factor, f is very helpful in estimating the direction and distance of diffusion jumps of ionic particles.

However, in some cases, the relation is not well satisfied. This implies that the micromechanism of the electric conduction is different from that of the tracer diffusion. This problem will be discussed in the following two sections.

For the derivation of the Nernst-Einstein relation, the velocity of an ionic species is assumed proportional only to the force exerted upon itself (See Eq. (3-5)). However, this should not be assumed for multi-component compounds. This problem will be discussed in Chapter 5.

For a better understanding of the correlation factor, "Diffusion in Solids" by Dr. P.G. Shewmon⁽⁴⁾ is recommended.

3.2 VALIDITY OF NERNST-EINSTEIN RELATION IN SOLID HALIDES AND SOLID OXIDES

The crystal structure of halides of alkali metals is very simple, because larger halogen anions make fcc lattice and cations occupy the octahedral interstitial sites. Thus, the electricity is usually carried by the alkali cations and the diffusion takes place with the vacancy mechanism. Thus, the Nernst-Einstein relation can be expected to be well satisfied.

Mapother, Crooks, and Maurer⁽⁵⁾ worked on this problem and published a paper in 1950. Fig. 3.2 is reproduced from their paper. This figure shows the measured tracer diffusivity of Na^+ cations in solid NaBr versus reciprocal temperature. The curve of a broken line is based on the measured diffusivity and the curve of a solid line is calculated from the measured electrical

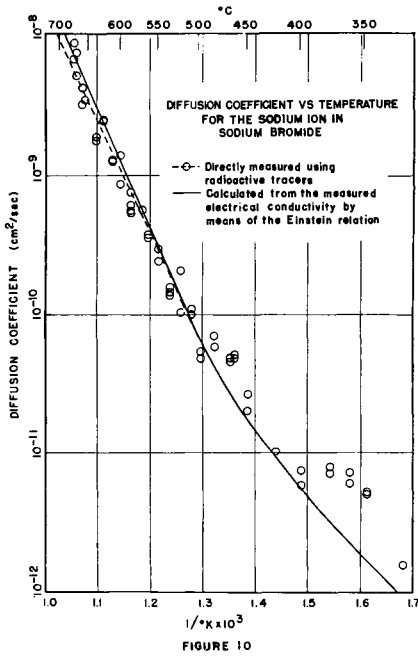


Fig. 3.2. Temperature dependence of cation in NaBr solid. (After Mapother, Crooks and Maurer⁽⁵⁾).

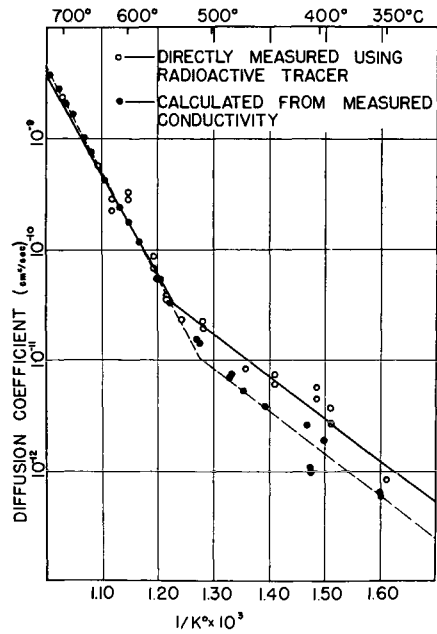


Fig. 3.3. Temperature dependence of tracer diffusivity of Na⁺ in solid NaCl. (After Mapother, Crooks, and Maurer⁽⁵⁾).

conductivity of NaBr. The agreement of the two curves is very good, although the diffusivities measured are slightly larger than those estimated at the lower temperature. This is interpreted⁽⁵⁾ to be the result of the motion of vacancy pairs. The vacancy pairs can aid the diffusion but can not contribute to the electric conduction, because they are electrically neutral. The slight disagreement at the higher temperature is believed to be due to a small contribution of bromine ions to the electric conduction.

Fig. 3.3 shows the comparison⁽⁵⁾ in case of solid NaCl. In the figure, white plots are the tracer diffusivities of Na⁺ and black plots are the diffusivities estimated from the electrical conductivities with the help of the Nernst-Einstein equation. The disagreement at temperatures lower than 500°C is considered due to impurities⁽⁵⁾. In the above calculations for both NaBr and

NaCl, the transference number of Na^+ and its correlation factor were both assumed unity. However, the correlation factor should take the value of 0.78 according to Table 3.1. Nevertheless, the relations shown in Fig. 3.2 and 3.3 are not essentially changed, because the diffusivities are expressed in logarithm.

For the case of solid oxides, Kingery and his coworkers⁽⁶⁾ reported the comparison on ZrO_2 -0.15 mole CaO in 1959, as shown in Fig. 3.4. The white plotts with crosses for magnitude of errors show the measured tracer diffusivities of O^{2-} in fluorite structure of solid solution 0.85 mole ZrO_2 and 0.15 mole CaO. The solid line is the diffusivity of O^{2-} anions estimated from the electrical conductivity. For the estimation, the transference number of O^{2-} is taken as unity (See Table 2.1) and the correlation factor also unity. However, if 0.655 (Table 3.1) is used for f ., the agreement is better in Fig. 3.4.

In older papers, such as references (5) and (6), the correlation factor is sometimes neglected. However, this factor is,

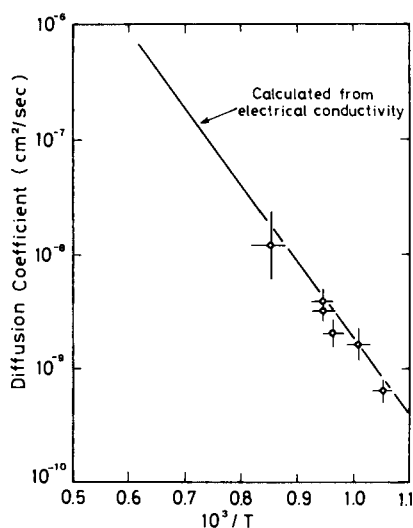


Fig. 3.4. Comparison of measured tracer diffusivity and calculated value according to Nernst-Einstein equation: (After Kingery et al⁽⁶⁾).

recently, more accurately studied with the assumption that the Nernst-Einstein relation should be strictly valid in simple inorganic compounds.

Okazaki⁽⁷⁾⁽⁸⁾ determined the correlation factor of Ag^+ in "average crystals" of $\alpha\text{-Ag}_2\text{S}$, $\alpha\text{-Ag}_2\text{Se}$ and $\alpha\text{-Ag}_2\text{Te}$ in 1967 and 1977. The average structure is equivalent to liquid-like structure. Fig. 3.5 shows the correlation factors as functions of reciprocal temperature. The small correlation factors in Fig. 3.5 have been interpreted by a cooperative motion of Ag^+ for its diffusion, which was proposed by Yokota⁽⁹⁾ as "caterpillar mechanism" of cations in the average structure in 1966.

Meanwhile, the average structure of AgI is given as the cause of superionic conduction as shown in Table 2.1.

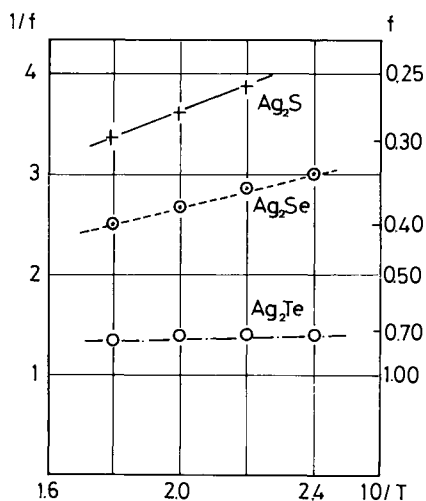


Fig. 3.5. Relation between reciprocal correlation factor and reciprocal absolute temperature on solid Ag_2S , Ag_2Se , and Ag_2Te (After Okazaki⁽⁷⁾⁽⁸⁾).

In concluding this section, let us state that it is plausible that the Nernst-Einstein relation is very valid in simple solid halides and oxides. However, for prudent discussions of this validity, it is always crucial to have accurate measurements on tracer diffusivity, electrical conductivity and transference

number.

3.3 THE VALIDITY IN LIQUID HALIDES AND LIQUID OXIDES

The tracer diffusivities of cations and anions in fused halides have been measured on alkali halides by Bockris and Hooper⁽¹⁰⁾ in 1961 and on Group II chlorides by Bockris, Richards and Narris⁽¹¹⁾ in 1965. Their results are summarized in Table 3.2 and Table 3.3, respectively. Also, Bockris, Richards and Narris⁽¹¹⁾ have made a careful examination of the Nernst-Einstein equation, as shown in Fig. 3.6. The data on PbCl_2 were reported by Perkins et al⁽¹²⁾.

In this figure, the ordinate is the sum of the measured values of $2D_{\text{M}^{2+}}$ and D_{Cl^-} . The abscissa is the product of (RT/F^2) and the measured equivalent conductivity, Λ , defined by:

$$\Lambda \equiv \frac{\sigma_{\text{total}}}{2m_{\text{MCl}_2}} \quad (3-19)$$

where m_{MCl_2} is the number of moles of Group II chlorides per cubic

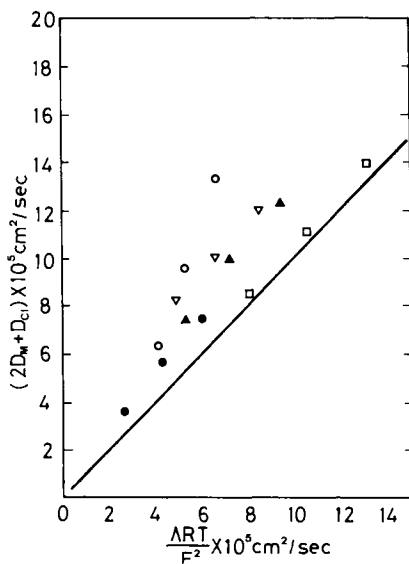


Fig. 3.6. Applicability of Nernst-Einstein equation in liquid divalent metal halides. CaCl_2 , SrCl_2 , BaCl_2 , CdCl_2 , and PbCl_2 . (After Bockris et al⁽¹¹⁾).

TABLE 3.2

Self-diffusion equations for molten halides

$$D = A \exp [-\Delta E/RT] \quad (\text{After Bockris and Hooper(10)}).$$

Salt	tracer	$A \times 10^3$	$\Delta E(\text{cal/mole})$	temp.range($^{\circ}\text{C}$)
NaCl	^{22}Na	3.36	7860 ± 110	830 ~ 990
	^{36}Cl	3.02	8390 ± 40	
RbCl	^{86}Rb	2.51	8010 ± 30	740 ~ 880
	^{36}Cl	1.67	7420 ± 70	
CsCl	^{134}Cs	1.73	7320 ± 50	668 ~ 794
	^{36}Cl	2.46	7820 ± 80	
NaI	^{22}Na	0.63	4030 ± 50	670 ~ 806
	^{131}I	0.43	4420 ± 60	

TABLE 3.3

Energies of activation and pre-exponential factors for self-diffusion in Group I and II chlorides (After Bockris et al (11)).

Molten salt/ tracer	Per-centage mean std. dev. in log ($10^5 \times D^*$)	$10^3 \times D_o^*$ cm^2 sec^{-1}	log ($10^3 \times D_o^*$)	E_D^* , kcal.mole^{-1}	Temp. range, $^{\circ}\text{C}$
NaCl/Na ^{22}	2.59	2.1	2.33 ± 0.05	7.14 ± 0.25	820~1020
NaCl/Cl ^{36}	2.71	1.9	2.28 ± 0.11	7.43 ± 0.84	826~1035
KCl/K ^{42}	1.41	1.8	2.26 ± 0.10	6.88 ± 0.51	798~983
KCl/Cl ^{36}	1.40	1.8	2.26 ± 0.10	7.13 ± 0.49	794~987
CaCl $_2$ /Ca ^{45}	2.68	0.38	1.58 ± 0.12	6.13 ± 0.66	783~1004
CaCl $_2$ /Cl ^{36}	3.08	1.9	2.27 ± 0.18	8.86 ± 0.96	787~1019
SrCl $_2$ /Sr ^{89}	3.38	0.21	1.32 ± 0.16	5.38 ± 0.97	921~1120
SrCl $_2$ /Cl ^{36}	2.36	0.77	1.89 ± 0.12	6.88 ± 0.72	912~1157
BaCl $_2$ /Ba ^{140}	4.03	0.64	1.81 ± 0.21	8.96 ± 1.23	994~1207
BaCl $_2$ /Cl ^{36}	3.34	2.0	2.31 ± 0.16	9.48 ± 1.02	993~1203
CdCl $_2$ /Cd ^{115m}	2.71	1.1	2.04 ± 0.14	6.84 ± 0.62	607~806
CdCl $_2$ /Cl ^{36}	3.98	1.1	2.03 ± 0.21	6.80 ± 1.01	607~802

centimeter. The values on the ordinate should be equal to those of the abscissa, if the correlation factor is unity.

Namely, if one inserts $D_{Ca^{2+}}$ and $D_{Cl^{-}}$ into Eq. (3-18), one can state:

$$2D_{Ca^{2+}} + D_{Cl^{-}} = \frac{\sigma_{total} \cdot kt}{e^2} \left(\frac{t_{Ca^{2+}}}{2n_{Ca^{2+}}} + \frac{t_{Cl^{-}}}{n_{Cl^{-}}} \right) \quad (3-20)$$

Because k is equal to (R/N_0) and e is equal to (F/N_0) , one can rewrite Eq. (3-20) as follows:

$$2D_{Ca^{2+}} + D_{Cl^{-}} = \frac{\sigma_{total} \cdot RTN_0}{F^2} \left(\frac{t_{Ca^{2+}}}{2n_{Ca^{2+}}} + \frac{t_{Cl^{-}}}{n_{Cl^{-}}} \right) \quad (3-21)$$

In fused salts of Group II chlorides, the following relations are satisfied:

$$t_{Ca^{2+}} + t_{Cl^{-}} = 1.0 \quad (\text{Ionic Conductor}) \quad (3-22)$$

$$2n_{Ca^{2+}} + n_{Cl^{-}} = 2N_0 \quad m_{MCl_2} \quad (\text{electric neutrality}) \quad (3-23)$$

Therefore, inserting these relations into Eq. (3-21), one has:

$$2D_{Ca^{2+}} + D_{Cl^{-}} = \frac{RT}{F^2} \frac{\sigma_{total}}{2 \cdot m_{MCl_2}} \quad (3-24)$$

This relation must be satisfied, if the correlation factor is unity with the same micromechanism for the diffusion and the electrical conduction.

In Fig. 3.6, the sum of the measured tracer diffusivities is always larger than the equivalent conductivity multiplied by $(RT/F^2) \times 10^5$.

Table 3.4 shows the comparison made by Bockris and Hooper⁽¹⁰⁾ on tracer diffusivities in fused alkali halides. This table also clearly shows that the measured diffusivities are always significantly larger than those estimated from the electrical conductivity. In the estimation, the correlation factor, f is assumed unity but if the values between 0.6 and 1.0 (See Table 3.1) are assigned for f , the deviation must be enlarged in Fig. 3.6 and in Table 3.4. The reason for the deviations has been extensively

TABLE 3.4

Comparison between self-diffusion constants measured and calculated from conductivity by Nernst-Einstein equation

(After Bockris and Hooper (10)).

salt	temp., °C	cm ² · sec ⁻¹		cm ² · sec ⁻¹				kcal·mole ⁻¹		
		from conductance (D ₊ + D ₋) × 10 ⁻⁴	from tracers (D ₊ + D ₋) × 10 ⁻⁴	% greater than n.e.	calculated D ₊ × 10 ⁻⁴	calculated D ₋ × 10 ⁻⁴	calculated D _p × 10 ⁻⁴	$-\frac{Rd \ln D_+}{d(1/T)}$	$-\frac{Rd \ln D_-}{d(1/T)}$	$-\frac{Rd \ln D_p}{d(1/T)}$
NaCl	838	1.39	1.63	17.0	0.84	0.55	0.12	5.3	5.2	20.4
	977	1.82	2.47	36.0	1.10	0.71	0.32			
RbCl	737	0.75	0.88	17.0	0.40	0.35	0.065	7.0	6.2	12.2
	890	1.17	1.46	24.0	0.64	0.52	0.14			
CsCl	670	0.60	0.73	21.0	0.28	0.31	0.06	7.0	7.5	8.9
	790	0.93	1.15	23.0	0.43	0.49	0.10			
NaI	670	1.05	1.13	8.0	0.68	0.36	0.04	4.9	5.8	variable
	794	1.44	1.47	1.4	0.93	0.51	0.01			

discussed by Bockris and his coworkers⁽¹⁰⁾⁽¹¹⁾. Their interpretation is due to the paired vacancies, which are formed of one cation vacancy and one anion vacancy adjoining each other. The paired vacancies can provide an easy path for simultaneous diffusive movement of a cation and an anion. In the quasi-lattice of ionic melts, the lattice points would be more vacant than in the case of solid halides. Thus, the diffusion via paired vacancies would be more important in the liquid halides. Such displacements of a cation and an anion in a pair will contribute to the diffusion but not to electrical conduction, because the pair is electrically neutral. This is believed to be the reason for the difference between the sum of diffusivities ($D_A^* + D_B^*$) measured and ($D_A + D_B$) estimated from the conductivity. An ionic particle has both possibilities of moving alone into a single vacancy by a jumping and in conjunction with an oppositely charged ion into a paired vacancy by rotation. If the diffusivities with these two micromechanisms are additive, the measured diffusivity can be expressed by:

$$D_A^* = D_{A+} + D_P \quad (3-25)$$

$$D_B^* = D_{B-} + D_P \quad (3-25')$$

With these equations, one can estimate the values of D_P from $(D_A^* + D_B^*)$ and $(D_{A+} + D_{B-})$, because both can be measurable quantities. The estimated diffusivities, D_P due to the vacancy pairs are given in Table 3.4.

The calculation of D_P by Bockris and Hooper shown in Table 3.4 is very significant, because they have quantitatively demonstrated the importance of the vacancy-pair diffusion for ionic diffusion in fused halides.

The validity of Nernst-Einstein relation in the fused oxides can be similarly examined, if the reliable data are available on the tracer diffusivities and on the electrical conductivities. From this view point, 29 pairs of independent measurements have been selected for tracer diffusivities of Na^+ or Ca^{2+} and the electrical conductivities of oxide melts. This was reported by Goto, Sasabe, and Kawakami⁽¹³⁾ in 1977.

The oxide systems are $\text{Na}_2\text{O-GeO}_2$, $\text{Na}_2\text{O-SiO}_2$, CaO-SiO_2 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$. The comparison between the diffusivities of Na^+ or Ca^{2+} , measured and calculated is shown in Fig. 3.7 and Table 3.5. The relative deviation (%) given in Table 3.5 is defined:

$$\left[\frac{D_{\text{measured}} - D_{\text{calculated}}}{D_{\text{calculated}}} \right] \times 100 .$$

In contrast to the fused halides, the diffusivities measured are always smaller than those estimated from the electrical conductivities, as seen in Fig. 3.7.

For the calculation, the correlation factor, f was tentatively assumed to be unity. The transference numbers of Na^+ and Ca^{2+} are assumed unity based upon the review paper by Adachi and Ogino⁽²⁶⁾ and upon the following reports⁽²⁷⁾⁽²⁸⁾. In 1952, Bockris et al⁽²⁷⁾ reported the unit transference number for Li^+ in liquid $\text{Li}_2\text{O-SiO}_2$ and for K^+ in liquid $\text{K}_2\text{O-SiO}_2$ systems. Esin and Kirianov⁽²⁸⁾ have

TABLE 3.5

Tracer diffusivity, measured and calculated from the electrical conductivity
(After Goto, Sasabe and Kawakami⁽¹³⁾).

No.	Composition (Diffusing species)	Temp. (°C)	D _{meas.} (cm ² /sec)	D _{calc.} (cm ² /sec)	relative devia- tion*	Q _d (kcal/mol)	Q _e (kcal/mol)
1	40mol%Na ₂ O-60mol%GeO ₂ (Na ⁺)	1200	3.9×10 ⁻⁵	13.3×10 ⁻⁵	-71	10.5	9.6
2		1100	2.4	7.3	-67		
3		1000	1.7	5.9	-71		
4	30mol%Na ₂ O-70mol%GeO ₂ (Na ⁺)	1200	2.3×10 ⁻⁵	13.3 10 ⁻⁵	-85	14.2	10.5
5		1100	1.2	7.0	-83		
6		1000	0.8	4.7	-83		
7	34wt%Na ₂ O-66wt%SiO ₂ (Na ⁺)	1300	4.4×10 ⁻⁵	9.6×10 ⁻⁵	-54	12.5	11.2
8		1100	2.5	5.6	-55		
9		900	1.1	2.9	-62		
10	24wt%Na ₂ O-76wt%SiO ₂ (Na ⁺)	1300	2.8×10 ⁻⁵	6.7×10 ⁻⁵	-58	16.1	12.5
11		1100	1.3	3.7	-65		
12		900	0.5	1.7	-71		
13	55wt%CaO-45wt%SiO ₂ (Ca ²⁺)	1500	0.9×10 ⁻⁶	7.0×10 ⁻⁶	-87	50±20	35
14	54wt%CaO-46wt%SiO ₂ (Ca ²⁺)	1600	1.8×10 ⁻⁶ _{**}	5.3×10 ⁻⁶	-66	50±20	26
15		1575	1.5	4.7	-68		
16		1550	1.2	4.3	-72		
17	57wt%CaO-43wt%SiO ₂ (Ca ²⁺)	1600	1.8×10 ⁻⁶ _{**}	5.3×10 ⁻⁶	-66	50±20	35
18		1575	1.5	4.7	-68		
19		1500	1.2	4.0	-70		
20	40wt%CaO-40wt%SiO ₂ - 20wt%Al ₂ O ₃ (Ca ²⁺)	1350	3.3×10 ⁻⁷	5.2×10 ⁻⁷	-37	70±20	46
21			3.3		-37	30±15	
22			3.9		-25	50±20	
23		1400	6.8×10 ⁻⁷	9.2×10 ⁻⁷	-26	70±20	46
24			6.2		-33	30±15	
25			6.9		-25	50±20	
26		1450	1.3×10 ⁻⁶	1.6×10 ⁻⁶	-19	70±20	46
27			9.5×10 ⁻⁷		-37	30±15	
28			1.0×10 ⁻⁸		-37	50±20	
29		1500	2.1×10 ⁻⁶	2.6×10 ⁻⁶	-19	70±20	46

Remarks to Table 3.5 : Q_d , Q_e : activation energy for the diffusion and electrical conduction.

* defined by $\left(\frac{D_{\text{meas.}} - D_{\text{calc.}}}{D_{\text{calc.}}}\right) \times 100$

** These values are diffusivities of Ca^{2+} in 55wt%CaO-45wt%SiO₂.

TABLE 3.6
Reference numbers on tracer diffusivities, D^{tr} , on electrical conductivities, σ , and densities, ζ used for the calculation

	D^{tr}	σ	ζ
Na ₂ O-GeO ₂	(14)	(15)	(16)
Na ₂ O-SiO ₂	(17)	(18)	(17)
CaO-SiO ₂	(19)	(20)	(21)
CaO-SiO ₂ -Al ₂ O ₃	(19)(22)(23)(25)	(24)	(21)

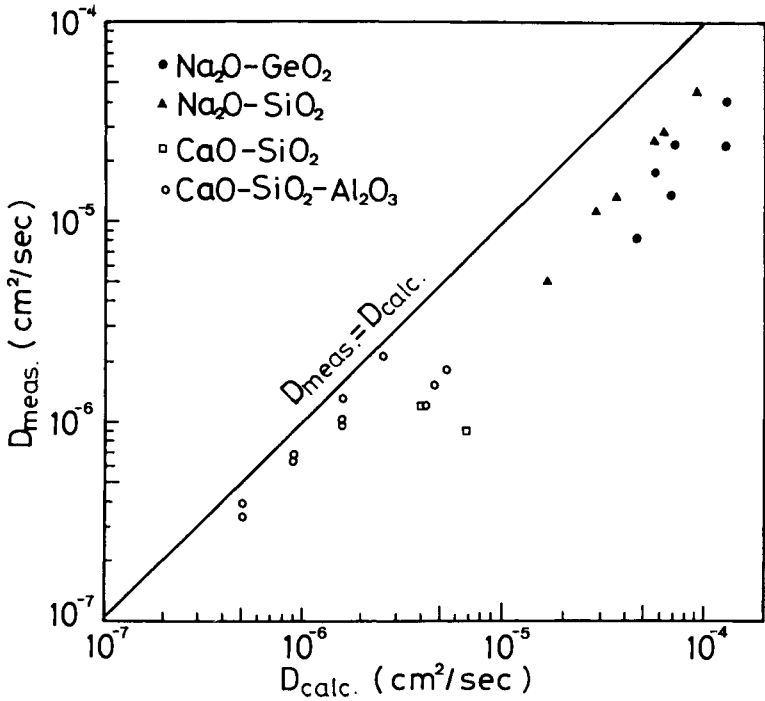


Fig. 3.7. Comparison between tracer diffusivities, measured and calculated from electrical conductivity data using Nernst-Einstein relation.(After Goto, Sasabe and Kawakami⁽¹³⁾).

also reported the unit transference number for Ca^{2+} in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ and CaO-SiO_2 melts.

If the diffusivity measurement suffered from the errors by convection of the fused oxides, the apparent diffusivity would be larger than the true value. Thus, the deviation should be in the opposite direction.

If the electrical conductivity includes the error due to Faradaic impedance of the electrodes dipped in the fused oxides, then the deviation should be again to the opposite direction. Therefore, all the experimental errors discussed above can not be considered as the reason of the deviation.

The probable reason for the deviation would be the small value of the correlation factor, which had been tentatively assumed as unity in the above.

The data plotted in Fig. 3.7 have been replotted as Fig. 3.8 and Fig. 3.9, separately for the four different oxide systems. In the figures, a single line can be drawn for an oxide system regardless of temperature. From the slopes, the correlation factor can be estimated as 0.24 for $\text{Na}_2\text{O-GeO}_2$ system, 0.40 for $\text{Na}_2\text{O-SiO}_2$ system, 0.33 for CaO-SiO_2 system and 0.70 for $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ternary system. These small values of the correlation factors would be reflecting the liquid structure, which is composed of free cations of Na^+ or Ca^{2+} in large silicate or germanate anion polymers.

The small values of the correlation factor are also shown in Fig. 3.5. The "average structure" proposed for silver chalcogenides by Rahlfs⁽²⁹⁾ is very similar to the liquid silicate, because the number of available sites for cations is much larger than that of net cations distributed among large anion polymers. This similarity might be considered as the reason for the small correlation factor for liquid silicate or germanates.

The diffusion by the vacancy-pair mechanism cannot be considered important, because the size of the cations is very small in comparison to the size of large anion polymers in the oxide melts.

Another reason for the deviation, although it may be minor, is the complication of the diffusion due to the multicomponent

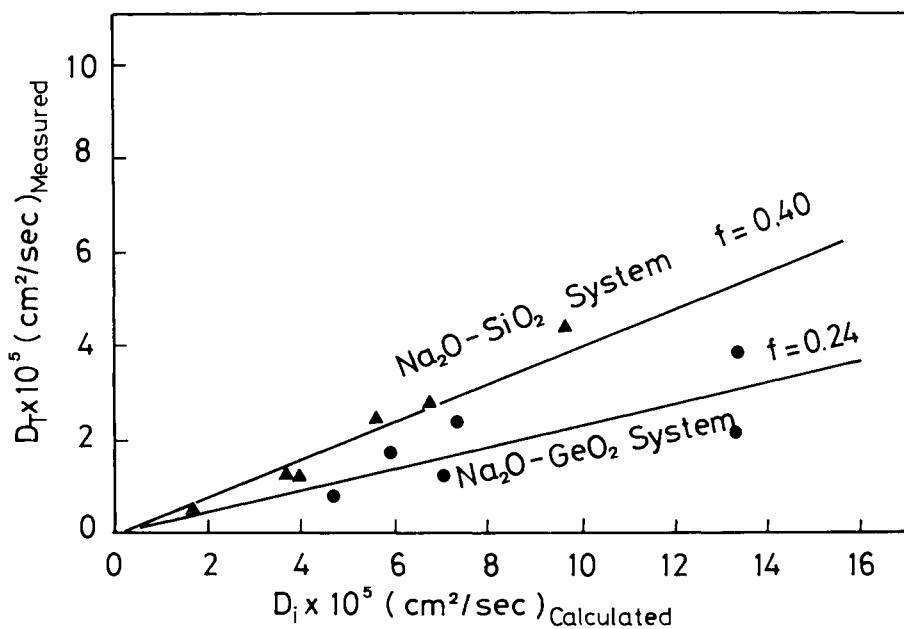


Fig. 3.8. Comparison between diffusivities measured and calculated on liquid $\text{Na}_2\text{O-SiO}_2$ and $\text{Na}_2\text{O-GeO}_2$ binary systems.

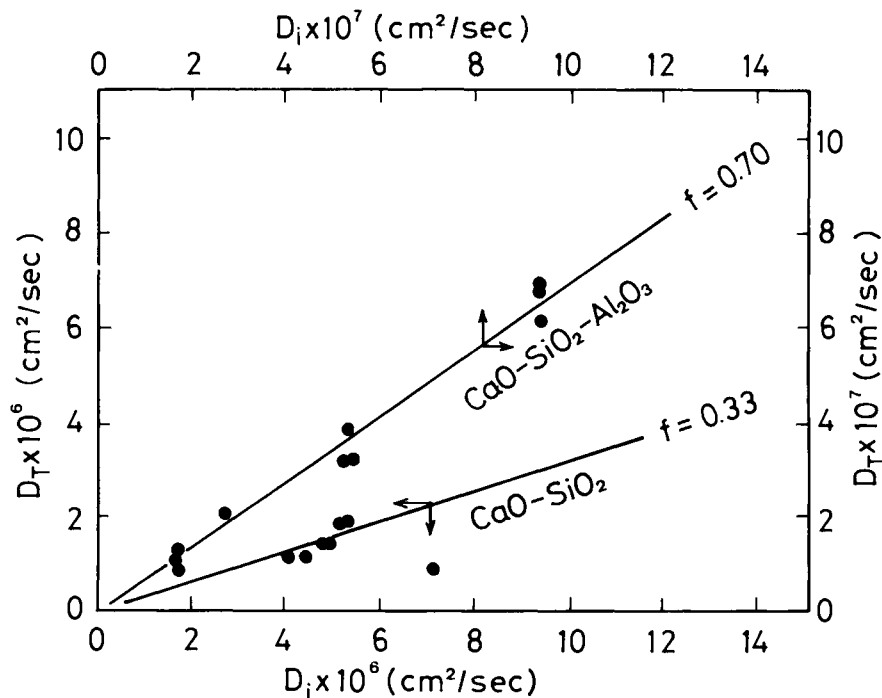


Fig. 3.9. Comparison between diffusivities measured and calculated on liquid CaO-SiO_2 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ systems.

systems. In the multicomponent systems, Equation (3-5) can not be strictly correct. Namely, the velocity of an ionic particle is not only proportional to the force exerted upon itself but also to all the forces exerted upon the other ionic species. In this case, the diffusing velocity of a species should be expressed as the linear equation of the forces. The proportional constants are called "transport coefficients"⁽³⁰⁾⁻⁽³²⁾. This problem will be discussed in Chapter 5 "Transport Properties of Oxide Systems with Multicomponents".

The Nernst-Einstein relation discussed in this chapter is not only helpful to estimate the diffusivity from the electrical conductivity or vice versa, but it is also helpful to have a deeper insight into the micromechanism of the motion of ions.

REFERENCES TO CHAPTER 3

- (1) W. Nernst, Z. phys. Chemie 2(1888) 613 pp.
- (2) A. Einstein, Ann. Physik 17(4)(1905) 549 pp.
- (3) K. Compaan and Y. Haven, Trans. Faraday Soc., 52(1956) 786 pp.
- (4) P.G. Shewmon, "Diffusion in Solids", McGraw-Hill Book Co., (1963) New York.
- (5) D. Mapother, H.N. Crooks, and R.J. Maurer, J. Chem. Phys., 18(1950) 1234 pp.
- (6) W.D. Kingery, J. Pappis, M.E. Doty, and D.C. Hill, J. American Ceramic Soc., 42(1959) pp. 393-398.
- (7) H. Okazaki, J. Phys. Soc. of Japan, 23(1967) pp. 355-360.
- (8) H. Okazaki, J. Phys. Soc. of Japan, 43(1977) pp. 213-221.
- (9) I. Yokota, J. of Phys. Soc. of Japan, 21(1966) 420 pp.
- (10) J.O'M. Bockris and G.W. Hooper, Discussion of Faraday Soc., 32(1961) pp. 218-236.
- (11) J.O'M. Bockris, S.R. Richards, and L. Naris, J. Physical Chemistry, 69(1965) pp. 1627-1637.
- (12) G. Perkins, R.B. Escue, J.F. Lamb and J.W. Wimberley, J. Phys. Chem., 64(1960) 1792 pp.
- (13) K.S. Goto, M. Sasabe and M. Kawakami, Trans. of Iron and Steel Inst. of Japan, 17(1977) pp. 212-214.
- (14) M. Sasabe and K. Kaneko, Tetsu-to-Hagane, 59(1973) 190 pp.
- (15) H. Saito, private communication (1972)
- (16) E.F. Riebling, J. Chem. Phys., 39(1963) 3022 pp.
- (17) Y. Gupta and T.B. King, Trans. Met. Soc. AIME, 239(1967) 1701 pp.
- (18) J.R. Hutchins, dissertation of Sc. Dr, M.I.T., (1959), cited in Ref. (17).
- (19) T. Saito and K. Maruya, J. Japan Inst. Metals, 21(1957) 728 pp.
- (20) Y. Matsushita and K. Mori, Tetsu-to-Hagane, 38(1952) 283 pp.
- (21) R. Kammel and H. Winterhager, Erzmetall., 18(1965) 9 pp.
- (22) H. Towers, M. Paris and J. Chipman, Trans. Met. Soc. AIME, 197(1953) 1455 pp.
- (23) K. Niwa, J. Japan Inst. Metals, 21(1957) 304 pp.
- (24) A.E. Martin and G. Derge, Trans. Met. Soc. AIME, 154(1943) 104 pp.
- (25) H. Towers and J. Chipman, Trans. Met. Soc. AIME, 209(1957) 769 pp.
- (26) A. Adachi and K. Ogino, Yōyūen, 5(1962) 1149 pp.
- (27) J.O'M. Bockris, J.A. Kitchener and A.E. Davies, Trans. Farad.

- Soc., 48(1952) 536 pp.
- (28) O.A. Esin and A.K. Kirianov, *Izv. Akad. Nauk. SSSR Otdel. Tekh. Nauk.*, (1955) No.12, 28.
- (29) P. Rahlfs, *Z. Phys. Chem.*, B31(1936) 157 pp.
- (30) K.S. Goto, H. Schmalzried and K. Nagata, *Tetsu-to-Hagane*, 61 (1975) 2794 pp.
- (31) K.S. Goto, H. Schmalzried and K. Nagata, *Arch. Eisenhüttenw.*, 47(1976) 133 pp.
- (32) K. Nagata and K.S. Goto, *J. Electrochem.*, 1239(1976)1814 pp.

Chapter 4

DIFFUSION OF IONS IN SOLID AND LIQUID OXIDES

4.1 RELATION BETWEEN TRACER DIFFUSIVITY AND INTERDIFFUSIVITY IN OXIDES

Diffusion is a natural phenomenon, by which materials can be homogenized with respect to their compositions. When the shape of materials is defined, the rate of the homogenization can be expressed as a function of diffusivities of elements contained⁽¹⁾. Several kinds of diffusivities or diffusion constants are used, such as tracer diffusivity, self diffusivity, chemical diffusivity, intrinsic diffusivity, and interdiffusivity. These diffusion constants are used, sometimes, without their clear definitions.

In many literatures, the self diffusion constant is used to express tracer diffusivity, neglecting the correlation factor. The chemical diffusion constant is often simply equal to the interdiffusion constant.

Therefore, in this section, the relation among intrinsic diffusivity, tracer diffusivity, and interdiffusivity will be presented.

In 1947, Smigelskas and Kirkendall published a short paper⁽²⁾, in which they reported the velocity of inert markers embeded at the interface of diffusion couples of copper and brass. Since then, the shift of markers caused by the diffusion phenomena is called the "Kirkendall effect". The markers shifted toward the brass side. Later works on a variety of markers in many different alloy systems have confirmed the effect to be quite general⁽³⁾.

The Kirkendall effect has strongly inspired Darken. In 1948, Darken⁽⁴⁾ presented the rigorous relations among interdiffusivity, tracer diffusivity, and intrinsic diffusivity for binary systems. His analysis is also valid for binary oxide systems. In the case of oxide systems, "binary" means the system composed of two kinds of oxide, for example, CaO and MgO. The solid solution of CaO and MgO is composed of ions of Ca^{2+} , Mg^{2+} , and O^{2-} , and thus it can be called a ternary system. However, because of the electric neutrality, it is usually called a binary oxide system. Therefore, the diffusion phenomena in binary oxide systems can be analyzed according to the following Darken's analysis.

According to his analysis, only that motion which is relative to the markers is considered to be directly attributable to diffusion. From this view point, the diffusion flux relative to the external coordination of component 1, J_1 can be expressed by:

$$J_1 = - D_1 \left(\frac{dc_1}{dx} \right) + c_1 v \quad (4-1)$$

where D_1 is the intrinsic diffusivity of component 1 in a binary system of 1 and 2, c_1 is the concentration of component 1, x is the distance parallel to direction of diffusion, and v is the local velocity of the inert marker relative to the external co-ordination.

Eq. (4-1) is very meaningful, because it defines the intrinsic diffusivity and it gives the diffusion flux relative to the external coordination in terms of the diffusivity and local velocity of the marker.

According to conservation of mass, partial differential of concentration with respect to time, t can be given by:

$$\frac{\partial c_1}{\partial t} = - \frac{\partial}{\partial x} (J_1) \quad (4-2)$$

Insertion of Eq. (4-1) to the right hand side of Eq. (4-2) yields:

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \frac{\partial c_1}{\partial x} - c_1 v \right] \quad (4-3)$$

Likewise,

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left[D_2 \frac{\partial c_2}{\partial x} - c_2 v \right] . \quad (4-4)$$

The number of moles of components, 1 and 2 in unit volume, expressed by c is equal to the sum of each concentration as:

$$c = c_1 + c_2 \quad (4-5)$$

Thus, the addition of Eq. (4-3) and (4-4) yields:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \frac{\partial c_1}{\partial x} + D_2 \frac{\partial c_2}{\partial x} - cv \right] \quad (4-6)$$

When the molar volume can be assumed constant during diffusion, the left hand side of Eq. (4-6) becomes zero. Thus, by integration, one has:

$$D_1 \left(\frac{\partial c_1}{\partial x} \right) + D_2 \left(\frac{\partial c_2}{\partial x} \right) - cv = I \quad (4-7)$$

where I is the integration constant.

When the value of x is taken as an infinitely large value ($+\infty$ or $-\infty$), it is clear that the velocity of the marker, and the concentration gradients are all zero because no diffusion takes place at $x = \pm\infty$. Therefore, the integration constant, I must be zero. By rearranging the terms of Eq. (4-7), one has:

$$v = \frac{1}{c} \left[D_1 \left(\frac{\partial c_1}{\partial x} \right) + D_2 \left(\frac{\partial c_2}{\partial x} \right) \right] \quad (4-8)$$

Insertion of Eq. (4-8) to the r.h.s. of Eq. (4-1) gives:

$$J_1 = -D_1 \left(\frac{\partial c_1}{\partial x} \right) + \frac{c_1}{c} \left[D_1 \left(\frac{\partial c_1}{\partial x} \right) + D_2 \left(\frac{\partial c_2}{\partial x} \right) \right] \quad (4-9)$$

The step between Eq. (4-8) and Eq. (4-9) is very important, because it eliminates the velocity of the internal reference frame.

By this method only, the diffusion flux relative to the external reference can be expressed as a function of diffusivities defined by the internal reference (the inert marker in this case). This step will be used again in the following chapter 5.

Meanwhile, the mole fractions of 1 and 2, N_1 and N_2 , respectively are defined by:

$$N_1 \equiv \frac{c_1}{c} \quad (4-10)$$

$$N_2 \equiv \frac{c_2}{c} \quad (4-10')$$

Inserting the mole fractions to Eq. (4-9) and noting $N_1 + N_2 \equiv 1$, one can state:

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x} [(N_2 D_1 + N_1 D_2) \left(\frac{\partial N_1}{\partial x} \right)] \quad (4-11)$$

Before Darken's analysis, the diffusion in binary systems had been expressed by Fick's first and second laws of diffusion with the help of interdiffusivity as follows:

$$J_1 = -\tilde{D}_{1-2} \left(\frac{\partial c_1}{\partial x} \right) \quad \text{----Fick's 1st law} \quad (4-12)$$

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} [\tilde{D}_{1-2} \left(\frac{\partial c_1}{\partial x} \right)] \quad \text{----Fick's 2nd law} \quad (4-13)$$

where $\tilde{D}_{1-2}$ is the interdiffusivity of component 1 and component 2. The wave mark is put on the diffusivity to distinguish the interdiffusivity from intrinsic diffusivity and tracer diffusivity. Dividing both sides of Eq. (4-13) by c , and noting $c_1/c = N_1$, one has:

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x} [\tilde{D}_{1-2} \left(\frac{\partial N_1}{\partial x} \right)] \quad (4-14)$$

From a comparison between Eq. (4-11) and Eq. (4-14), one has the following relation:

$$\tilde{D}_{1-2} = N_2 D_1 + N_1 D_2 \quad (4-15)$$

This equation expresses interdiffusivity as a simple function of intrinsic diffusivities. The interdiffusivity, $\tilde{D}_{1-2}$ can be evaluated by the analysis of Matano on the concentration distribution of the components after diffusion runs.

However, to evaluate both of D_1 and D_2 , one needs one more experimental observation about the local velocity of the inert marker. Namely, by rewriting Eq. (4-8), one has:

$$v = \left[D_1 \left(\frac{\partial c_1/c}{\partial x} \right) + D_2 \left(\frac{\partial c_2/c}{\partial x} \right) \right]$$

$$\begin{aligned}
&= D_1 \left(\frac{\partial N_1}{\partial x} \right) + D_2 \left(\frac{\partial N_2}{\partial x} \right) \\
&= D_1 \left(\frac{\partial N_1}{\partial x} \right) + D_2 \left(\frac{\partial (1-N_1)}{\partial x} \right) \\
&= (D_1 - D_2) \left(\frac{\partial N_1}{\partial x} \right) \tag{4-16}
\end{aligned}$$

In a similar manner, one can state:

$$v = (D_2 - D_1) \frac{\partial N_2}{\partial x} \tag{4-16'}$$

This equation means that the velocity of the shift of the marker is fast when the concentration gradient is large with a large difference in the intrinsic diffusivities. For example, from Eq. (4-15) and Eq. (4-16), Darken has evaluated D_1 and D_2 in Cu-Zn binary alloy at 785°C.

According to the observation by Smigelskas and Kirkendall⁽²⁾,

$v = 1.25 \times 10^{-9}$ cm/sec at $t = 56$ days and 785°C with

$$\left(\frac{\partial N_1}{\partial x} \right) = 0.43/\text{cm}.$$

Thus, from Eq. (4-16), we have:

$$1.25 \times 10^{-9} \text{ (cm/sec)} = (D_{\text{Zn}} - D_{\text{Cu}}) 0.43 \text{ (/cm)}$$

According to the experiment by Rhines and Mehl⁽⁵⁾, the inter-diffusivity is 4.5×10^{-9} cm²/sec at 785°C with the concentration of Zn, $N_{\text{Zn}} = 0.225$. Thus, Eq. (4-15) can be expressed by:

$$4.5 \times 10^{-9} \text{ (cm}^2\text{/sec)} = 0.775 D_{\text{Zn}} + 0.225 D_{\text{Cu}}$$

The solution of the simultaneous equations above gives:

$$D_{\text{Zn}} = 5.1 \times 10^{-9} \text{ cm}^2\text{/sec}$$

$$D_{\text{Cu}} = 2.9 \times 10^{-9} \text{ cm}^2\text{/sec}$$

at 785°C for 0.775 Cu-0.225 Zn alloy. This is an example of how to evaluate the intrinsic diffusivities from the experimental observation.

To derive the relation between tracer diffusivity and intrinsic diffusivity, we can use a similar procedure to the one used to derive the Einstein relation in the previous chapter (see Eq. (3-14)).

The first term of the r.h.s. of Eq. (4-1) can be expressed by $-B_1 c_1 f_1$; namely:

$$J_1 = -B_1 c_1 f_1 + c_1 v \quad (4-17)$$

where B_1 is the absolute mobility, f_1 is the net force exerted upon component 1.

According to Eq. (3-2) of the previous chapter, we have:

$$f_1 = \frac{1}{N_o} \left(\frac{d\bar{G}_1}{dx} \right) \quad (3-2)$$

Inserting this expression of f_1 into Eq. (4-17), and comparing the obtained equation with Eq. (4-1), one can state:

$$D_1 = \frac{B_1 N_1}{N_o} \left(\frac{d\bar{G}_1}{dN_1} \right) \quad (4-18)$$

because:

$$\frac{d\bar{G}_1}{dx} = \left(\frac{d\bar{G}_1}{dN_1} \right) \left(\frac{dN_1}{dx} \right)$$

On the other hand, one has the following thermodynamic definition.

$$d\bar{G}_1 = R T d \ln a_1 \quad \text{with} \quad a_1 = \gamma_1 N_1 \quad (4-19)$$

where a_1 is the activity of component 1 and γ_1 is the activity coefficient with its standard state at the pure condensed state.

Inserting Eq. (4-19) to Eq. (4-18), one has:

$$D_1 = k T B_1 \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right) \quad (4-20)$$

Because of the Einstein relation of $k T B_1 = D_1^{\text{tr}}$, we can state the relation between intrinsic diffusivity and tracer diffusivity as follows:

$$D_1 = D_1^{\text{tr}} \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right) \quad (4-21)$$

We have the following relations according to the Gibbs-Duhem relation:

$$N_1 d \ln \gamma_1 = - N_2 d \ln \gamma_2 \quad (4-22)$$

and:

$$d N_1 = - d N_2, \text{ because } N_1 + N_2 = 1.0 \quad (4-23)$$

Dividing Eq. (4-22) by Eq. (4-23), we have:

$$N_1 \frac{d \ln \gamma_1}{d N_1} = N_2 \frac{d \ln \gamma_2}{d N_2} \quad (4-24)$$

Finally, we can state the following general relation by inserting Eq. (4-21) and Eq. (4-24) to Eq. (4-15);

$$\tilde{D}_{1-2} = (N_1 D_2^{\text{tr}} + N_2 D_1^{\text{tr}}) \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right) \quad (4-25)$$

where D_1^{tr} and D_2^{tr} are tracer diffusivities of components, 1 and 2. With this equation, one can estimate the interdiffusivity for binary systems, when both activity and tracer diffusivities are measured as a function of the composition.

In the case of a dilute solution with a small concentration of component, 2, we can express $N_2 \div 0$ and the Henry's law is valid. Therefore, Eq. (4-25) can be reduced as:

$$\tilde{D}_{1-2} = D_2^{\text{tr}} \quad (4-25')$$

Similarly, Eq. (4-21) can be approximated as:

$$D_1 = D_1^{\text{tr}} \quad (4-21')$$

"Chemical diffusivity" or "component diffusivity" sometimes means interdiffusivity at its dilute range, which is essentially equal to the tracer diffusivity according to Eq. (4-25'). However, we should be very careful about the experimental conditions reported in literatures and ascertain which diffusivity has been measured in each report.

The term "self diffusivity" is often used and this means tracer diffusivity. Self diffusivity must be equal to tracer diffusivity for interstitial diffusion, only because the correlation factor is unity in such a case.

When diffusion is taking place by vacancy mechanism, self diffusivity must be equal to tracer diffusivity divided by the correlation factor according to Eq. (3-17) as follows:

$$D_i^{\text{self}} = D_i^{\text{tr}} / f \quad (3-17)$$

where the self diffusivity of component i is assumed equal to that of vacancy.

4.2 DIFFUSIVITY OF IONS IN SOLID OXIDES

During the 20th century, thousands of papers have been, and will be published on diffusivities of ionic species in both solid and liquid oxides. The measurement of diffusivities started on simple pure oxides. However, in the future, the study of diffusion will be made on more complex oxides, such as superionic conductors, dielectric oxides, magnetic ferrites, optoelectric glass fibers, etc.

The scope of this section and the following section is confined to the presentation of the general rule of diffusion in oxides and some examples of diffusivities as functions of temperature and oxygen pressure.

To supplement these sections, several books with collections of diffusion data will be introduced at the end of the next section.

4.2.1 A general rule of tracer diffusivities of cations and anions in oxides

In solid oxides, tracer diffusivities of cations are usually two or three orders of magnitude larger than tracer diffusivity of oxygen anion. The only exception to this general statement is solid oxides with fluorite crystal structure. According to Pauling's crystal radii⁽⁶⁾, the diameter of an oxygen anion is 2.8Å at room temperature and this is much larger than those of most metal cations. (The only exceptions are K^+ , Rb^+ , Cs^+ , and Ba^{2+}). Therefore, many pure oxides have the closest packed structures of O^{2-} , either in cubic or hexagonal, with metal cations at their interstitial sites⁽⁷⁾.

The interstitial voids in closed packed structure of fcc and hcp are surrounded 1) by four O^{2-} in tetrahedral symmetry or 2) by six O^{2-} in octahedral symmetry. In these closed packed structures, there are two tetrahedral sites and one octahedral site per oxygen ion. The following are four kinds of crystal.

(1) The rock salt structure. Oxygen anions have fcc structure with smaller cations at octahedral interstitial sites. The examples are MgO, CaO, SrO, BaO, CdO, CoO, NiO, FeO, TiO, NbO, and VO.

(2) The corundum (Al_2O_3) structure. This structure is a hexagonal close-packing of oxygen anions with trivalent Al atoms occupying two thirds of the octahedral sites. The examples are α - Al_2O_3 , α - Fe_2O_3 , Cr_2O_3 , Ti_2O_3 , V_2O_3 etc.

(3) The spinel ($MgAl_2O_4$) structure. The oxygen ions are cubic close-packed with metal ions occupying both tetrahedral and octahedral sites. The unit cell consists of 32 oxygen atoms and accordingly contains 32 octahedral and 64 tetrahedral sites. In $MgAl_2O_4$, one half of the octahedral sites are occupied by the Al^{3+} ions while Mg^{2+} ions occupy one eighth of the tetrahedral sites. This kind of spinel is called normal spinel. When eight tetrahedral sites per unit cell are occupied by trivalent cations and the octahedral sites are shared by the trivalent and divalent ions, the structure is termed "inverse spinel". Magnetite, Fe_3O_4 is such a structure.

(4) The fluorite (CaF_2) structure. (see Fig. 2.4.) In this structure, only cations make fcc structure and oxygen anions occupy all tetrahedral sites. Thus, the unit cubic lattice contains eight oxygen and four metal ions. Examples of this structure are ZrO_2 , HfO_2 , CeO_2 , UO_2 , ThO_2 , and PuO_2 . When the positions of

cations and anions are reversed, it is called the antifluorite structure. Li_2O , K_2O , Rb_2O are such structures.

Table 4.1 contains tracer diffusivities of ions composing solid oxides compiled by Oishi and Ando in their review paper on diffusion in oxides⁽⁸⁾. In this table, the tracer diffusivities of cations are usually larger than those of O^{2-} in accordance with the general rule discussed above. The only exceptions are cases of $(\text{Zr}, \text{Ca})\text{O}_{2-x}$, UO_2 , and CeO_2 , all with fluorite structure.

When the general rule is not valid, the reason often appears to be due to the experimental errors caused by impurities and by grain boundaries. When the tracer diffusivity is very small, it is very difficult to determine the intrinsic tracer diffusivity without any effect of impurities, particularly of transition metals.

The extremely large diffusivity of O^{2-} in ZrO_2 stabilized by CaO , MgO , Y_2O_3 etc is the extrinsic diffusivity caused by anion vacancies formed by doping of these aliovalent oxides. However, the large diffusivity of O^{2-} in pure UO_2 is considered to be caused by interstitial O^{2-} anions⁽⁸⁾.

In Table 4.1, the tracer diffusivities are given as a function of absolute temperature at a fixed oxygen pressure, usually in air or in pure oxygen gas.

However, as already demonstrated in Chapter 2, the concentration of crystal and electric defects is also dependent upon oxygen pressure for oxides of transition metals. As shown in the figures of Figs. 2.8,9,10, and 11 in Chapter 2, the electrical conductivities are very dependent upon the oxygen pressure. Therefore, it is a logical assumption that one would find this kind of relation between tracer diffusivity and oxygen pressure on the solid oxides.

In fact, according to the Eyring theory of absolute reaction rate⁽⁴⁰⁾, tracer diffusivity of ions by vacancy mechanism can be expressed as:

$$D_i^{\text{tr}} = \gamma v \lambda^2 [V_{i,\text{ze}}] \exp \left[-\frac{\Delta G^\ddagger}{kT} \right] \quad (4-26)$$

where γ is the probability factor, v is the frequency factor (about 10^{13} in solids), λ is the jump distance ($2-3\text{\AA}$), $[V_{i,\text{ze}}]$ is the concentration of vacancies of ionic species, i with a

TABLE 4.1

Tracer diffusivities of ions in solid oxides (compiled by Y.Oishi and T.Ando⁽⁸⁾).

$$(D = D^0 \exp(-Q/RT))$$

Oxides	Ionic Species	D^0 (cm^2/s)	Q (kcal/mol)	Temperature ($^{\circ}\text{C}$)	References
MgO	Mg (s)	2.49×10^{-1}	79.0	1400-1600	(9)
	Mg (s)	1.2×10^{-5}	36.9	1450-1752	(10)
	O (s)	2.5×10^{-6}	62.4	1300-1750	(11)
CaO	Ca(s,p)	0.4	81	900-1600	(12)
	Ca (s)	3.08×10^{-8}	28.2	1000-1400	(13)
NiO	Ni (s)	4.77×10^{-2}	60.8	1180-1760	(14)
	O (s)	6.2×10^{-4}	57.5	1100-1500	(15)
CoO	Co (p)	2.15×10^{-3}	34.5	800-1350	(16)
	O (s)	50	95	1175-1560	(17)
CdO	O (s)	3.8×10^6	92	630-855	(18)
Fe_{1-x}O	Fe (p)	0.118	29.7	700-1000	(19)
$\alpha\text{-Al}_2\text{O}_3$	Al (p)	28	114	1670-1905	(20)
	O (s)	1.9×10^3	152	1600-1800	(21)
	O (s)	6.3×10^{-8}	57.6	1200-1600	(21)
$\alpha\text{-Fe}_2\text{O}_3$	Fe (p)	1.3×10^6	100.2	950-1050	(22)
	O (p)	1×10^{11}	146	1170-1250	(23)
$\alpha\text{-Cr}_2\text{O}_3$	Cr (p)	0.137	61.1	1045-1550	(24)
	O (p)	15.9	101.0	1100-1450	(25)
MgAl_2O_4	Mg	2×10^2	86		(26)
	O (s)	0.89	105	1432-1740	(27)
NiCr_2O_4	Ni (p)	1.5×10^{-3}	61.4	860-1277	(26)
	Cr (p)	7.4×10^{-1}	72.5	950-1400	(28)
	O (p)	1.7×10^{-2}	65.4	1200-1550	(23)
Fe_3O_4	Fe (s)	6.0×10^5	84.0	850-1075	(29)
BeO	Be (s)	1.27×10^{-3}	64.0	1490-1760	(30)
	Be (s)	1.23×10^{-6}	36.0	1760-2000	(30)
	O (s)	2.95×10^{-5}	68.5	1300-1700	(31)
ZnO	Zn (s)	4.8	73	900-1025	(32)
	O (s)	6.5×10^{11}	165	1100-1300	(33)
(Zr, Ca) O_{2-x}	Zr (p)	3.5×10^{-2}	92.5	1700-2150	(34)
	Ca (p)	4.44×10^{-1}	100.2	1700-2150	(34)
	O(s,p)	1.8×10^{-2}	31.2	800-1097	(35)
$\text{UO}_{2.00}$	U (s)	6.8×10^{-5}	98.3	1620-2010	(36)
	O (p)	0.26	59.3	780-1250	(37)
$\text{UO}_{2.10}$	O (p)	2.7×10^{-4}	21.5	500-800	(38)

TABLE 4.1 Continued.

Oxides	Ionic Species	D^0 (cm^2/s)	Q (kcal/mol)	Temperature ($^{\circ}\text{C}$)	References
CeO_2	O (s)	1.9×10^{-4}	24.8	850-1150	(39)
$\text{CeO}_{1.8}$	O (s)	6.2×10^{-6}	3.6	850-1150	(39)

s : single crystal, p : polly-crystal

charge of ze, $\Delta G^{\ddagger}$ is the free energy for the activated state, and k is the Boltzmann constant.

For example, if the cation vacancies are produced by the reaction of (2-8) in Chapter 2, the concentration of cation vacancies can be expressed by:

$$[V_{M^{2+}}] = (4K)^{\frac{1}{3}} p_{O_2}^{\frac{1}{6}} \quad (4-27)$$

To derive this equation, Eq. (2-10), namely $[n_p] = [V_{M^{2+}}] / 2$, is used.

Inserting Eq. (2-13) in Chapter 2 to Eq. (4-27) and then, to Eq. (4-26), one has the tracer diffusivity as a function of temperature and oxygen pressure as follows:

$$D_{M^{2+}}^{\text{tr}} = A p_{O_2}^{\frac{1}{6}} \exp \left[- \frac{(\Delta H^0/3) + N_o \Delta G^{\ddagger}}{RT} \right] \quad (4-28)$$

where:

$$A = 4\gamma v \lambda^2 \exp \left[\frac{\Delta S^0}{3R} \right] \quad (4-29)$$

Eq. (4-28) tells us that the diffusivity will increase with the increase of oxygen pressure with a power of one sixth.

Also, the apparent activation energy determined by the experiment is composed of enthalpy of the reaction of Eq. (2-8) and Gibbs free energy of the activated state of diffusion jump.

The theoretical equation of Eq. (4-28) is not well satisfied in many solid oxides, because the diffusion is not so simple due to the effect of impurities, grain boundary, nonequilibrium content of crystal defects, etc. Furthermore, the defects are effectively neutral, singly, or doubly charged.

Therefore, only few reports give clear and reliable relations between the diffusivities and oxygen pressure.

Fig. 4.1 was reported in 1953 by Himmel, Mehl and Birchenall (19). As discussed in Chapter 2, when the iron content is decreased (toward the right in Fig. 4.1), the cation vacancy increases its concentration. Thus, the tracer diffusivity of Fe^{2+} would increase. This expectation is satisfied at 983°C and 897°C, but at 800°C, the tracer diffusivity of Fe^{2+} is independent of the iron content. However, this is not clearly interpreted.

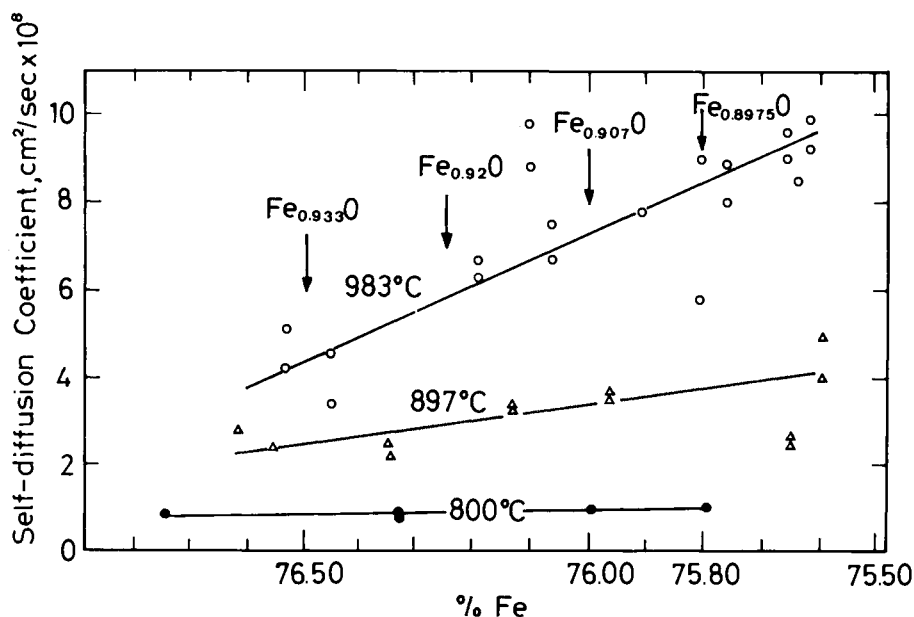


Fig. 4.1. Tracer diffusivity of iron in Wüstite, Fe_xO as a function of iron content in Fe_xO . (after Himmel et al (19)).

Desmarescaux et al⁽⁴¹⁾ proposed in 1965 a linear relation with y^2 of Fe_{1-y}O and $\log D^{\text{tr}}$, which can be interpreted due to vacancy complexes (see Fig. 2.9).

Fig. 4.2 on tracer diffusivity of Co in CoO was reported in 1954 by Carter and Richardson⁽¹⁶⁾. The diffusion constant is proportional to about $P_{\text{O}_2}^{\frac{1}{3}}$ at 1 atm oxygen and to about $P_{\text{O}_2}^{\frac{1}{4}}$ at 10^{-3} atm. This is in agreement with the nonstoichiometry study by Fischer and Tannhauser⁽⁴²⁾. The vacancies are singly charged at a reduced temperature and neutral vacancies make a contribution close to 1 atm O_2 .

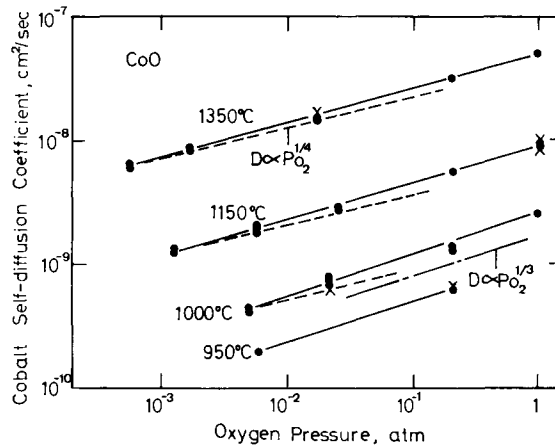


Fig. 4.2. Tracer self-diffusion coefficient of cobalt in CoO as a function of partial pressure of oxygen in the temperature range 950 to 1350°C. (After the results of Carter and Richardson. (16)).

In fact, Kingery, Bowen, and Uhlmann⁽⁴³⁾ have summarized the oxygen pressure dependency, as reproduced here in Fig. 4.3.

Fig. 4.4 is a summary of tracer diffusivities of elements in solid silica reported by the author in 1984⁽⁴⁴⁾ based on a journal, "Diffusion and Defect Data" from Trans. Tech. Pub. Ltd. Fig. 4.5 also gives tracer diffusivities of elements in solid magnesia reported by Nagata, Sata and Goto⁽⁴⁵⁾ in 1982. The reference on data shown in Fig. 4.5 are not given here but they are available in the review paper⁽⁴⁵⁾ by Nagata, Sata, and Goto.

Fig. 4.6 shows the tracer diffusivities of ions in superionic conductors estimated⁽⁴⁴⁾ by the Nernst-Einstein relation of Eq. 3.18 in the previous chapter from the electrical conductivity. In the calculation, the correlation factor and the transference numbers are assumed to be unity. In this figure, CaS is included for a comparison, although it is not a superionic conductor but a typical ionic conductor. By comparing Fig. 4.4, 4.5, and 4.6, one can ascertain that the diffusivities in superionic conductors are significantly larger than those in solid magnesia and silica.

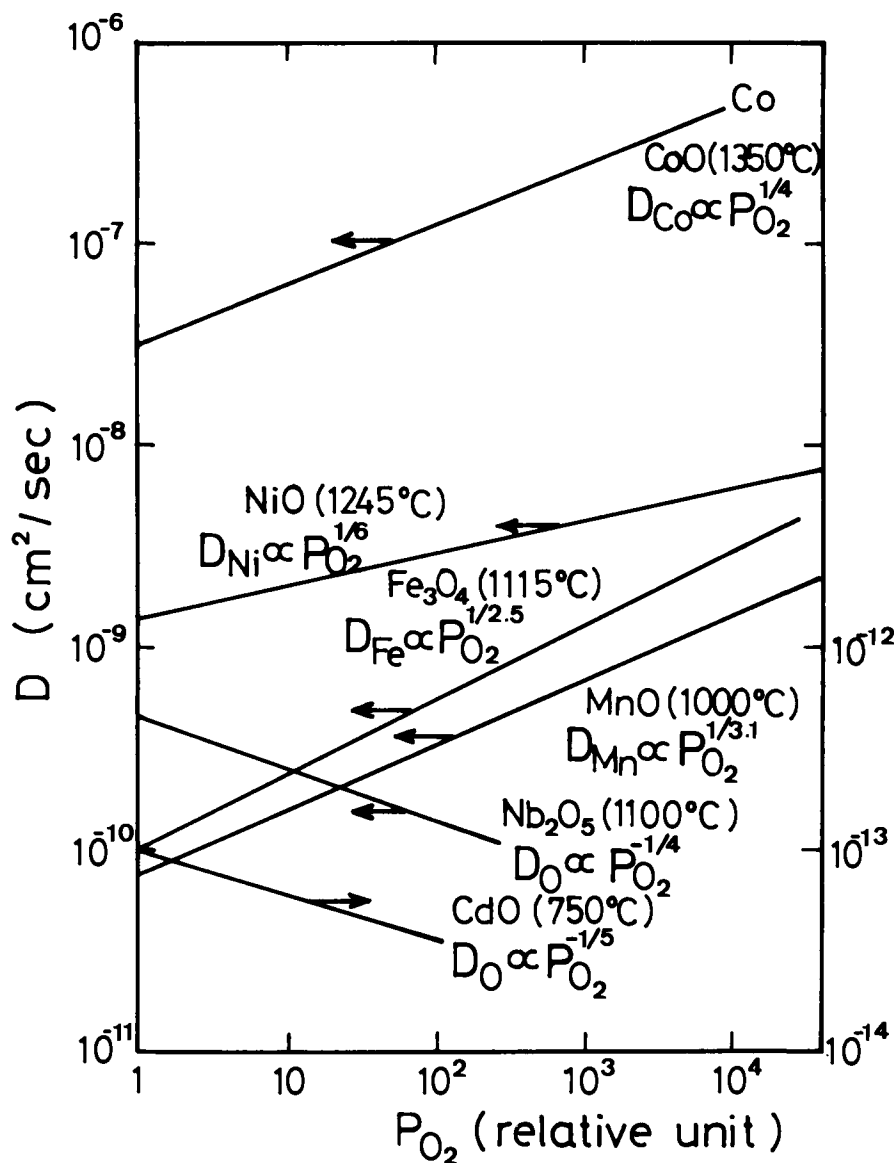


Fig. 4.3. Relation between tracer diffusivities of cations and oxygen anion in pure oxides and oxygen pressures expressed by relative unit. (After Kingery, Bowen and Uhlmann (43)).

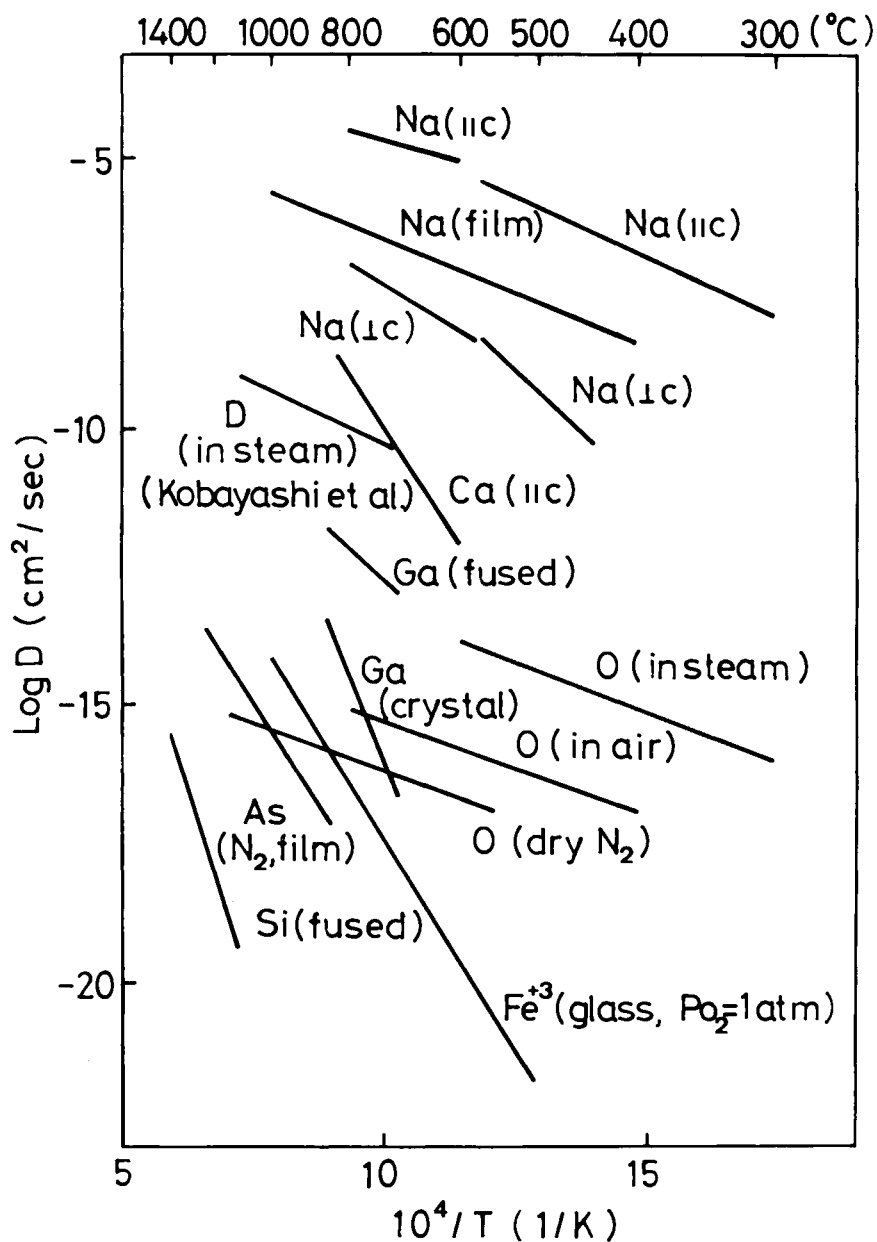


Fig. 4.4. Relation between logarithm of tracer diffusivities in fused, crystal or thin-film silica and reciprocal absolute temperature. (After Goto(44)).

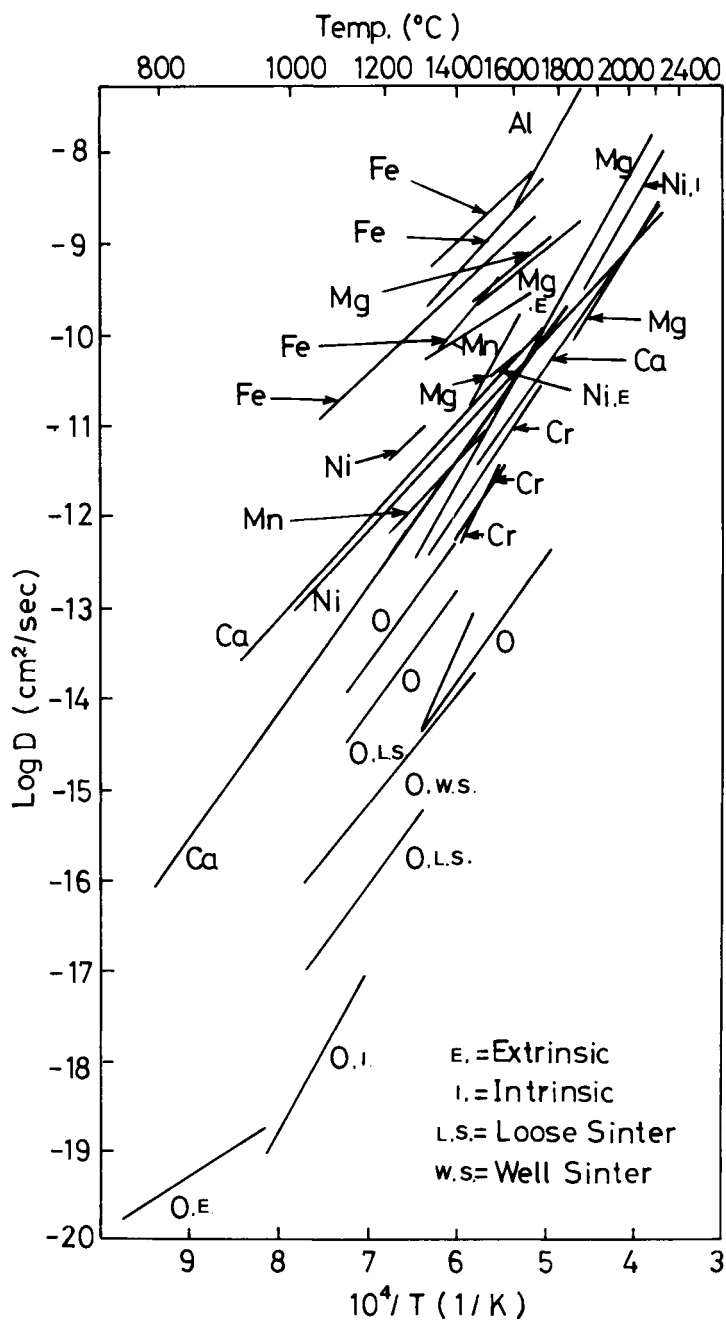


Fig. 4.5. Tracer diffusivities of elements in MgO. (After Nagata, Susa, and Goto.(45)).

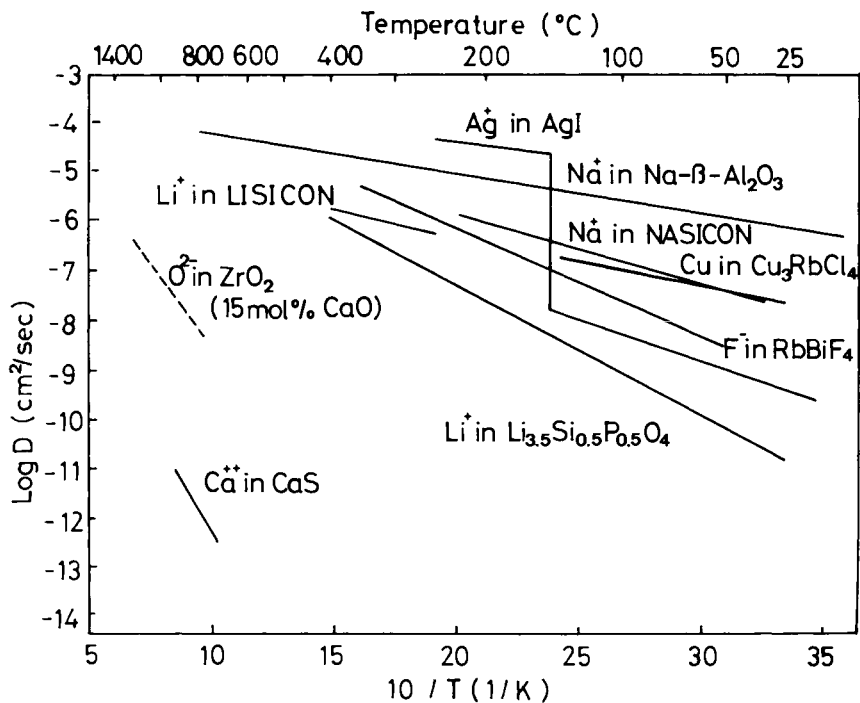


Fig. 4.6. Relation between tracer diffusivities of ions in superionic conductors and reciprocal absolute temperature. (After Goto(44)).

The above are concerned with only tracer diffusivities of ionic species in pure solid oxides. However, at the end of this section, an example of interdiffusivity of solid oxides will be given on $\text{Fe}_{1-\delta}\text{O}$ - MgO binary solid solution. The system of $\text{Fe}_{1-\delta}\text{O}$ and MgO is all proportionally miscible and its nonstoichiometry is well studied by equilibrium experiments. The interdiffusivity in this solid solution has been measured by Ribby and Cutler⁽⁴⁶⁾ in 1965, by Blank and Pask⁽⁴⁷⁾ in 1969, by Soong and Cutler⁽⁴⁸⁾ in 1971 and by N. Sata and K.S. Goto⁽⁴⁹⁾ in 1982.

Fig. 4.7 after Sata and Goto⁽⁴⁹⁾ shows the relation between logarithm interdiffusivity and logarithm oxygen pressure for four different compositions of the solid solution. The interdiffusivity increased as oxygen pressure increased in proportion to $\text{Po}_2^{1/2} \sim \text{Po}_2^{5/2}$, with an increase in content of $\text{Fe}_{1-\delta}\text{O}$ in the solid solution.

This implies that the interdiffusivity is essentially determined by the concentration of the cation vacancies.

Fig. 4.7 shows another interesting feature, that the interdiffusivity is independent of temperature between 1250°C and 1350°C. In wüstite, $\text{Fe}_{1-\delta}\text{O}$, deviation from stoichiometry decreases with an increase in temperature.

A similar tendency also exists in magnesiowüstite solid solution as reported in equilibrium studies by Speidel⁽⁵⁰⁾ and Katsura and Kimura⁽⁵¹⁾. According to these studies, the same diffusivity even at different temperatures can be interpreted to mean that the mobility of the cations increased by a temperature increase would be cancelled by a decrease of the cation vacancies.

Fig. 4.8 shows iso-interdiffusivity lines in the $\text{MgO-FeO-Fe}_2\text{O}_3$ quasi-ternary system at 1300°C, where the open plots are the measured points. The iso-interdiffusivity lines approach a parallel with the FeO-MgO line with an increase in MgO concentration, and a parallel with $\text{FeO-Fe}_2\text{O}_3$ line with an increase in Fe concentration. These results imply that the interdiffusivity depends mainly on the defect concentration at a high concentration of Mg . Also the results suggest that the interdiffusivity becomes remarkably

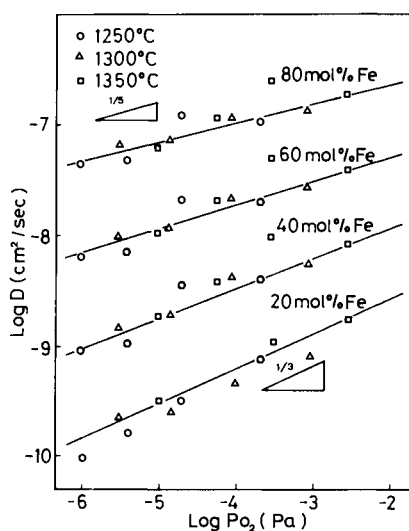


Fig. 4.7. Oxygen pressure dependency of interdiffusivity at 1250°C, 1300°C, and 1350°C and at Fe concentrations 20, 40, 60, and 80 mol%. (After Sata and Goto(49)).

independent of defect concentration at high concentrations of iron, probably because the interaction of defects themselves increases with an increase in iron content.

In this section, only $\text{Fe}_{1-\delta}\text{O}$ -MgO has been presented as an example but similar interdiffusivity studies have been reported on binary systems of MgO-NiO⁽⁵²⁾, MgO-MnO⁽⁵³⁾, and CoO-NiO⁽⁵⁴⁾.

4.3 DIFFUSIVITIES OF IONS IN LIQUID OXIDES

About thirty years ago (1950-1955), radioactive isotopes were widely used to determine tracer diffusivities of elements in many varieties of materials. This isotope technique had also been applied to diffusivity study on liquid oxides. The liquid oxide systems mainly studied are with industrial importance, which is called metallurgical slag.

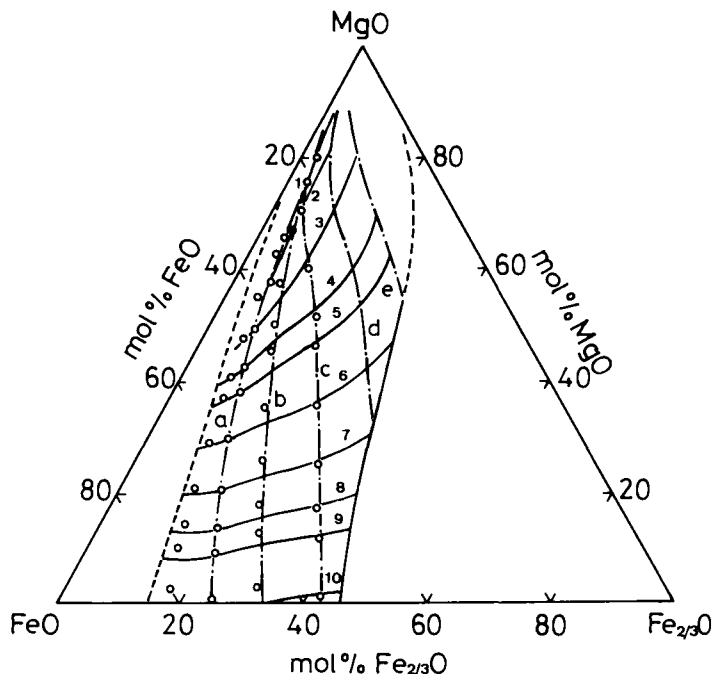


Fig. 4.8. MgO-FeO- $\text{Fe}_{2/3}\text{O}$ quasi-ternary system at 1300°C. Heavy solid lines are iso-interdiffusivities (in cm^2/s) of (1) 1.0×10^{-9} , (2) 2.0×10^{-9} , (3) 4.0×10^{-9} , (4) 7.0×10^{-9} , (5) 1.0×10^{-8} , (6) 2.0×10^{-8} , (7) 4.0×10^{-8} , (8) 7.0×10^{-8} , (9) 1.0×10^{-7} , and (10) 2.0×10^{-7} . Open circles represent measured values. Dash-dot lines are oxygen isobars (in Pa) of Ref. (50): (a) 1.0×10^{-5} , (b) 1.0×10^{-4} , (c) 1.0×10^{-3} , (d) 1.0×10^{-2} , and (e) 1.0×10^{-1} . (After Sata and Goto⁽⁴⁹⁾).

studied are with industrial importance, which is called metallurgical slag.

The fused oxide mixture, called as ironmaking slag, is produced during the reduction of iron ore in a blast furnace. This slag is mainly composed of CaO , SiO_2 , and Al_2O_3 .

Another type of slag, called steelmaking slag, is produced during the refining of crude iron to steel in a basic oxygen converter. The slag is composed of CaO , SiO_2 , and $\text{Fe}_{1-\delta}\text{O}$.

In a review paper on diffusivity of elements, Nagata, Sata and Goto⁽⁴⁵⁾ have collected the diffusivities of elements in fused metallurgical slags, as well as in fused binary and ternary silicates. This paper was published in the Japanese journal, "Tetsu-to-Hagane". This Iron and Steel Institute of Japan publication is widely distributed to major professional libraries throughout the world. The text of the paper is in Japanese but with some detailed English explanations about tables, figures and literature references. Therefore, one can get the information through major libraries in many countries.

The diffusivity data reproduced from this review paper are shown in the following. Fig.4.9 shows a summary of tracer diffusivities of elements in liquid 40wt% CaO -40wt% Al_2O_3 ternary oxide. Fig.4.10 is also a summary of tracer diffusivities in liquid Fe_2O_3 - CaO - SiO_2 system. The composition of the liquid oxide is different for different elements but in the range of 25 to 40 wt% Fe_2O_3 , 30 to 40 wt% CaO and the balance for SiO_2 by charge composition. When the mixture of Fe_2O_3 , CaO , and SiO_2 is melted, some fraction of Fe_2O_3 is reduced to FeO depending upon oxygen pressure and temperature. This must be taken into consideration for interpretation of data in Fig. 4.10.

General features can be observed as follows from Figs. 4.4, 4.6, 4.9, and 4.10, all about tracer diffusivities in oxides;

- (1) The diffusivity of oxygen is smaller than other elements in the solid oxides but it is larger in the liquid oxides. The reason for this would be that oxygen diffuses as oxygen anions, O^{2-} in solid oxides but as diatomic molecules, O_2 in liquid oxides.
- (2) Alkali elements with single positive charges diffuse very rapidly in solid silica (and in silicate melts, though not shown

as figures).⁽⁴⁵⁾

(3) Tracer diffusivity of $\text{Fe}(\text{Fe}^{2+} \text{ and } \text{Fe}^{3+})$ is usually larger than other elements. This is probably caused by many cation vacancies in liquid oxides containing both FeO and Fe_2O_3 .

The relation between tracer diffusivity and oxygen pressure in liquid oxides has been studied by Goto, Kurahashi and Sasabe⁽⁵⁵⁾ in 1977. This study was initiated because of an impact made by Engell and Vygen⁽⁵⁶⁾, who had clearly shown the relation between the electrical conductivity and oxygen pressure on liquid $\text{Fe}_{1-x}\text{O}-\text{CaO}-\text{SiO}_2$ system.

The partial conductivities of electrons and ions had been quantitatively measured as a function of oxygen pressure. This result suggests that the liquid oxide would contain the cation vacancies, although their nature would not be exactly the same with that in solid wustite crystal.

Goto, Kurahashi and Sasabe⁽⁵⁵⁾ have measured tracer diffusivi-

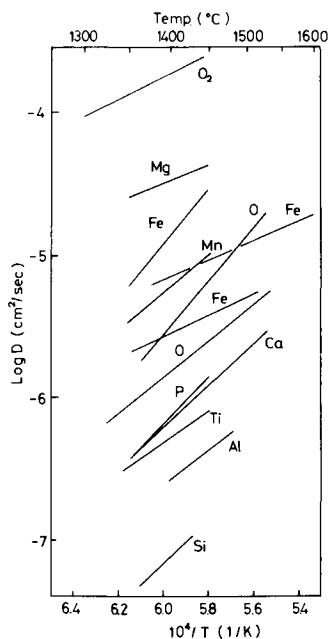


Fig. 4.9. Self-diffusivities of elements in molten slag for blast furnace (40CaO-40SiO₂-20Al₂O₃ (wt%)). (After Nagata, Sata and Goto (45)).

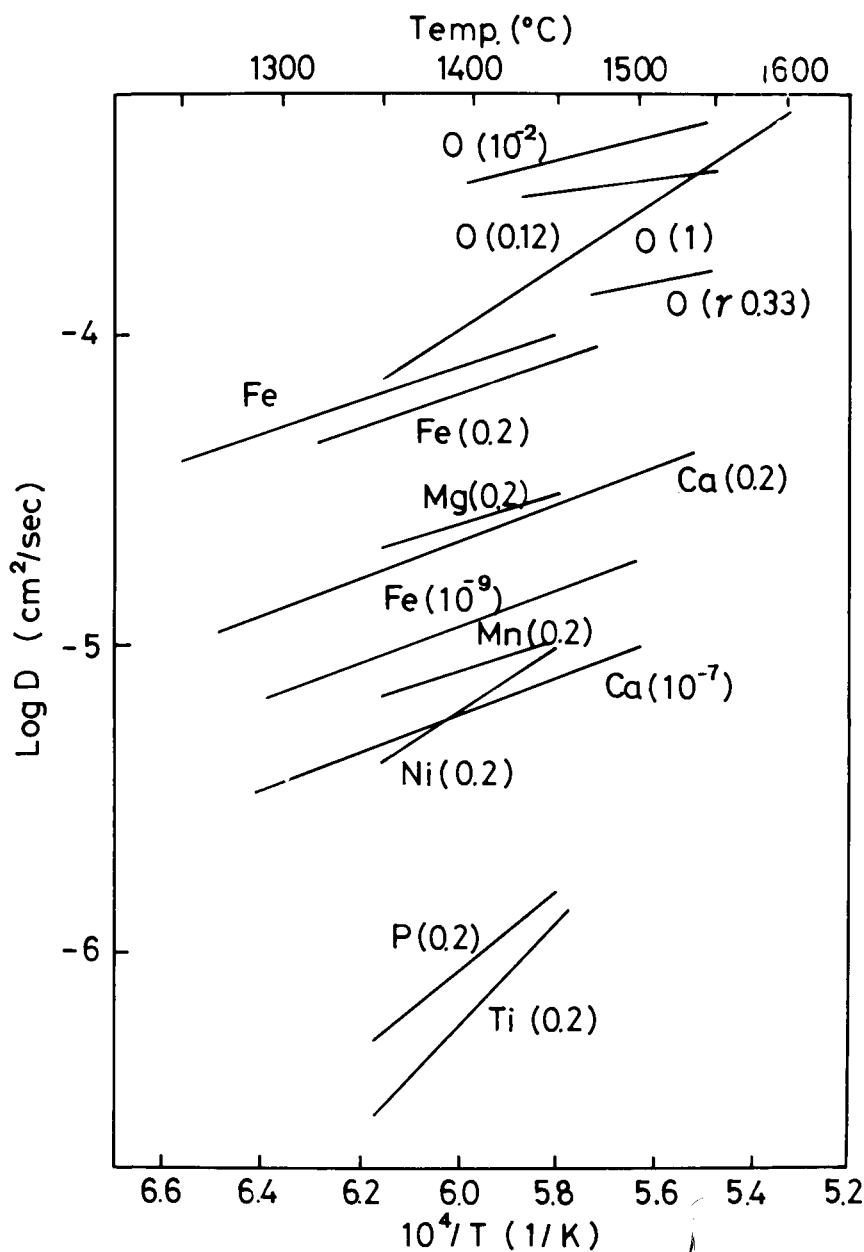


Fig. 4.10. Self-diffusivities of elements in molten slag for steel-making ((25-40) Fe_2O_3 -(30-40) CaO-SiO_2 (wt%)). (Number in () is P_{O_2} (atm) and $\gamma=\text{Fe}^{3+}/\text{T.Fe}$. (After Nagata, Sata and Goto(45)).

ties of both Ca and Fe in liquid $\text{CaO-Fe}_{1-x}\text{O-SiO}_2$ system at 1360°C - 1460°C as a function of oxygen pressure. The initial charge-composition was always fixed at 33wt%CaO-27wt% Fe_2O_3 -40wt% SiO_2 .

Fig. 4.11 shows the relation between logarithm tracer diffusivity and logarithm oxygen pressure. The tracer diffusivities of Fe and Ca were expressed as a function of oxygen pressure and temperature, respectively

$$D_{\text{Fe}}^{\text{tr}} = 0.2 (P_{\text{O}_2})^{\frac{1}{8.5}} \exp \left(- \frac{26,000}{R T} \right)$$

$$D_{\text{Ca}}^{\text{tr}} = 0.1 (P_{\text{O}_2})^{\frac{1}{12.5}} \exp \left(- \frac{28,000}{R T} \right)$$

where D_i^{tr} is given in cm^2/sec and the apparent activation energy in calories. The oxygen pressure dependency of powers of $1/8.5$ and $1/12.5$ is much smaller than those of cations in solid oxides shown in Fig. 4.3. This smaller oxygen-pressure dependency would suggest that the cations in the liquid oxide could diffuse through both kinds of cation vacancies produced by distortion of structure by melting and by redox reaction of Fe^{2+} and Fe^{3+} . In the above, only the tracer diffusivities have been discussed but the inter-diffusivities have been also measured on several liquid oxides.

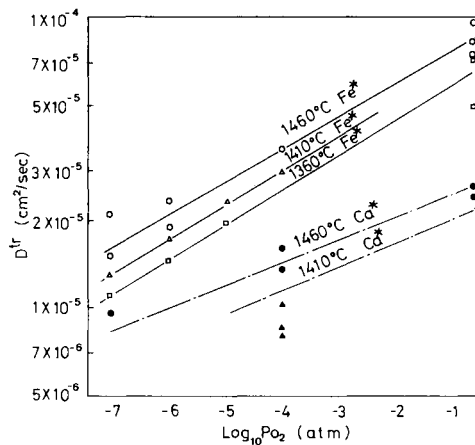


Fig. 4.11. Relation between logarithm of tracer diffusivities of calcium and iron and logarithm of oxygen pressure in liquid $\text{CaO-Fe}_{1-x}\text{O-SiO}_2$ system. (After Goto, Kurahashi and Sasabe(55)).

Table 4.2 summarises fused oxide systems measured for inter-diffusivities and numbers of the reference. The diffusivities have been measured from penetration curves after diffusion runs, from dissolution rates of solid oxides, and from D.C. polarization using the electrochemical method.

TABLE 4.2

Binary or quasi-binary interdiffusivities in fused oxides.

Interdiffusivities	System	Method	Ref.
CaO-SiO ₂	CaO-SiO ₂	from P.C.* of Ca or Si	57
	CaO-SiO ₂ -Al ₂ O ₃	from P.C. of Si; C.P.	58-60
CaO-Al ₂ O ₃	CaO-Al ₂ O ₃	by C.P.**	61
	CaO-Al ₂ O ₃ -MgO	by C.P.	62
CaF ₂ -Al ₂ O ₃	CaF ₂ -Al ₂ O ₃	Dissolution of Al ₂ O ₃	63
Fe _x O-Al ₂ O ₃	Fe _x O	Dissolution of Al ₂ O ₃	64,65
Fe _x O-ZrO ₂	Fe _x O	Dissolution of ZrO ₂ -SiO ₂	66
Na ₂ O-SiO ₂	Na ₂ O-SiO ₂	Dissolution of SiO ₂	67-71
Na ₂ CO ₃ -SiO ₂	Na ₂ CO ₃	Dissolution of SiO ₂	72
SiO ₂ -Bulk	Na ₂ O-SiO ₂ -P ₂ O ₅	from P.C. of Si	73
Na ₂ O, P ₂ O ₅ -Bulk	Na ₂ O-SiO ₂ -P ₂ O ₅	from P.C. of ²⁴ Na and ³² P	74
SiO ₂ -Fe ₂ O ₃	Na ₂ O-SiO ₂ -Fe ₂ O ₃	from P.C. of Fe	75
Na ₂ O, SiO ₂ , Fe _x O-Bulk	Na ₂ O-SiO ₂	Dissolution of iron oxides	76
Fe _x O-Bulk	Na ₂ O-SiO ₂	Dissolution of Fe	77
Na ₂ O, Al ₂ O ₃ -Bulk	Na ₂ O-Al ₂ O ₃ -SiO ₂	from P.C. of Na or Al	78
K ₂ O-SiO ₂	K ₂ O-SiO ₂		68,79
Li ₂ O-SiO ₂	Li ₂ O-SiO ₂	D.C. Polarization	80

* P.C. = Penetration Curves after Diffusion Runs

** C.P. = Chronopotentiometry

In this chapter, the relation among tracer diffusivity, intrinsic diffusivity and interdiffusivity has been discussed according to Darken's paper. In the second section, the diffusivity of ions in solid oxides was presented in relation to crystal structure and oxygen pressure. In the final section, several examples of diffusion data in liquid oxides were presented. Again, the relation to the oxygen pressure was discussed.

The scope of the present chapter is confined to present general characteristics of diffusion of ions in oxides. Therefore, all the data of diffusivity in oxides are not collected. Rather several examples of diffusion data have been presented to show general relations among tracer diffusivity, oxygen pressure and temperature.

At the end of this chapter, some books will be introduced to supplement the diffusion data. First of all, an excellent monograph⁽⁸¹⁾ has been published in 1972 by P. Kofstad, which deals with relations among nonstoichiometry, diffusion and electrical conductivity in oxides. A very comprehensive book⁽⁸²⁾ on chemistry of imperfect crystals has been published by F.A. Kröger in 1973.

A proceedings has been edited in 1982 by J. Nowotny⁽⁸³⁾ on transport in nonstoichiometric compounds. An international technical journal is devoted only to diffusion data and defect data, edited by F.H. Wohlbier⁽⁸⁴⁾. A review paper by M. Iwase and E. Ichise⁽⁸⁵⁾ will be useful as a resource of diffusion data.

REFERENCES TO CHAPTER 4

- 1 J. Crank, "The Mathematics of Diffusion", Clarendon Press, (1975), England.
- 2 A.C. Smigelskas and E.O. Kirkendall, Trans. AIME 171, (1947), 130, and Metals Technology, October, (1946), Technical Paper, TP2071, AIME.
- 3 D. Lazarus, in "Solid State Physics", edited by Seitz and Turnbull, Vol. 10, (1960), Pergamon Press, Inc., 71 pp.
- 4 L. Darken, Trans. AIME, 174, (1948), 184 pp.
- 5 F.N. Rhines and R.F. Mehl, Trans. AIME, 128, (1938), 185 pp.
- 6 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, (1940), Ithaca, N.Y.
- 7 A.F. Wells, "Structural Inorganic Chemistry", Oxford University Press, (1950), London.
- 8 Y. Oishi and T. Ando, Chapter III of "Inorganic Reactions Involving Solids", edited by M. Taniguchi et al, Tokyo University Press, (1975), Tokyo.
- 9 R. Lindner and G.D. Parfitt, J. Chem. Phys., 26, (1957), 182 pp.
- 10 B.C. Harding, D.M. Price and A.J. Mortlock, Phil. Mag., 23, (1971), 399 pp.
- 11 Y. Oishi and W.D. Kingery, J. Chem. Phys., 33, (1960), 905 pp.
- 12 R. Lindner, St. Auströmdal and Å. Åkerström, Acta Chem. Scand., 6, (1952), 468 pp.
- 13 V. Kumar and Y.P. Gupta, J. Phys. Chem. Solids, 30, (1969), 905 pp.
- 14 M.L. Volpe and J. Reddy, J. Chem. Phys., 53, (1970), 1117 pp.
- 15 M. O'Keefe and W.J. Moore, J. Phys. Chem., 65 (1961), 1438 pp and 2277 pp.
- 16 R.E. Carter and F.D. Richardson, Trans. AIME, 200 (1954), 1244 PP. and 203 (1955), 336 pp.
- 17 W.K. Chen and R.A. Jackson, J. Phys. Chem. Solids, 30 (1969), 1309 pp.
- 18 R. Haul and D. Just, J. Appl. Phys., Suppl., 33 (1962), 487 pp.
- 19 L. Himmel, R.F. Mehl and C.E. Birchenall, Trans. AIME, 197 (1953), 822 pp.
- 20 A.E. Paladino and W.D. Kingery, J. Chem. Phys., 37 (1962), 957 pp.
- 21 Y. Oishi and W.D. Kingery, J. Chem. Phys., 33 (1960), 480 pp.
- 22 V.I. Izvekov, N.S. Gorbunov and A.A. Babad-Zakhryapin, Fiz. Meta Metalloved., 14 (1962), 195 pp.
- 23 W.D. Kingery, D.C. Hill and R.P. Nelson, J. Amer. Cer. Soc., 43 (1960), 473 pp.
- 24 W.C. Hagel and A.U. Seybolt, J. Electrochem. Soc., 108 (1961), 1146 pp.
- 25 W.C. Hagel, J. Amer. Cera. Soc., 48 (1965), 70 pp.
- 26 R. Lindner and Å. Åkerström, Z. Phys. Chem., N.F., 18 (1958), 303 pp.
- 27 K. Ando and Y. Oishi, J. Chem. Phys., 61 (1974), 625 pp.
- 28 R. Lindner and Å. Åkerström, Z. Phys. Chem., N.F., 6 (1956), 162 pp.
- 29 S.M. Klotzman, A.N. Timofeev and I.Sh. Trakhtenberg, Phys. Metals Metallogr., 10 (1960), 93 pp.
- 30 S.B. Austerman, J. Nucl. Mat., 14 (1964), 248 pp.
- 31 J.B. Holt, *ibid.*, 11 (1964), 107 pp.
- 32 E.A. Secco and W.J. Moore, J. Chem. Phys., 23 (1955), 1170 pp.
- 33 W.J. Moore and E.L. Williams, Discuss. Faraday Soc., 28 (1959), 86 pp.
- 34 W.H. Rhodes and R.E. Carter, J. Amer. Ceram. Soc., 49 (1966), 244 pp.
- 35 L.A. Simpson and R.E. Carter, *ibid.*, 49 (1966), 139 pp.

- 36 D.K. Reimann and T.S. Lundy, J. Amer. Ceram. Soc., 52 (1969), 511 pp.
- 37 J.F. Marin and P. Contamin, J. Nucl. Mat., 30 (1969), 16 pp.
- 38 P. Contamin, J.J. Bacmann and J.F. Marin, J. Nucl. Mat., 42 (1972), 54 pp.
- 39 B.C.H. Steele and J.M. Floyd, Proc. Brit. Ceram. Soc., 19 (1971), 55 pp.
- 40 S. Glasstone, K.J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co. Inc., (1941), New York.
- 41 Ph. Desmarescaux, J.P. Bocquet and P. Lacombe, Bull. Soc. Chim., France, 15 (1965), 1106 pp.
- 42 B. Fischer and D.S. Tannhauser, J. Chem. Phys., 44 (1966), 1663 pp.
- 43 W.D. Kingery, H.K. Bowen and D.R. Uhlmann, "Introduction to Ceramics", John Wiley & Sons, (1976), New York.
- 44 K.S. Goto, A Lecture Text on "Diffusion in Oxides, Superionic Conductors, etc." published by Japan Institute of Metals as a text book on "Basic Theories and Application of Diffusion" (1984), Sendai, Japan.
- 45 K. Nagata, N. Sata and K.S. Goto, "Diffusivities in Molten Slag, Molten Iron, Steel and Refractories", Tetsu-to-Hagane, 68 (1982), pp. 1694-1705.
- 46 E.B. Ribby and I.B. Cutler, J. Amer. Cer. Soc., 48[2], (1965), pp. 95-99.
- 47 S.L. Blank and J.A. Pask, J. Amer. Cer. Soc., 52[12], (1969), pp. 669-675.
- 48 J.C-K. Soong and I.B. Cutler, J. Solid State Chem., 3 (1971), pp. 134-143.
- 49 N. Sata and K.S. Goto, J. Amer. Cer. Soc., 65[3], (1982), pp. 158-162.
- 50 D.H. Speidel, J. Amer. Cer. Soc., 50[5], (1967), pp.243-248.
- 51 T. Katsura and S. Kimura, Bull. Chem. Soc. of Japan, 38 (1965), pp. 1664-1670.
- 52 H. Schmalzried and J.B. Holt, Z. Phys. Chem., 60 (1968), pp. 220-222.
- 53 J.T. Jones and I.B. Cutler, J. Amer. Cer. Soc., 54[7], (1971), pp. 335-338.
- 54 J.J. Stiglich, Jr., J.B. Cohen and D.H. Whitmore, J. Amer. Cer. Soc., 56[3], (1973), pp. 119-126.
- 55 K.S. Goto, T. Kurahashi and M. Sasabe, Metallurgical Trans., B, 8B (1977), pp. 523-528.
- 56 H.J. Engell and P. Vygen, Ber. Bunsenges., 72 (1968), 5 pp.
- 57 A. Majdic and H. Henning, Ber. Deut. Keram. Ges., 47 (1970), 53 pp.
- 58 N. McCallum and L.R. Barrwtt, Trans. Brit. Ceram. Soc., 51 (1952), 523 pp.
- 59 E.W. Sucov and R.R. Gorman, J. Amer. Ceram. Soc., 48 (1965) 426 pp.
- 60 K. Nagata and K.S. Goto, Ironmaking and Steelmaking, 1 (1977), 23 pp.
- 61 M. Kawakami, K. Nagata and K.S. Goto, Tetsu-to-Hagane, 62 (1976) 23 pp.
- 62 L.N. Barmin, M.I. Zinigrad, A.A. Flyagin, K.K. Zhadanovich, and A.V. Zaitsev, Izv. Vyssh. Uchebn. Zaved. Chern. Metall. 7 (1976), 59 pp.
- 63 A. Mitchell and B. Burel, Met. Trans. B, 1B (1970), 2553 pp.
- 64 R.G. Olsson, T.F. Perzak, and V. Koump, Trans. AIME, 242 (1968) 776 pp.
- 65 H. Kobayashi and T. Oyama, Yogyo-Kyokaishi, 83 (1975), 97 pp.
- 66 H. Kobayashi and T. Oyama, ibid., 82 (1974), 546 pp.

- 67 P.M. Shurygin, L.N. Barmin, and O.A. Yesin, *Izv. Vyssh. Uchebn. Zaved. Chern. Metall.* 5 (1962) 5 pp.
- 68 K. Schewerdtfeger, *J. Phys. Chem.*, 70 (1966), 2131 pp.
- 69 M. Truhlaroua and O. Veprek, *Glastechn. Ber.*, 40 (1967), 257 pp.
- 70 J. Hlavac and H. Nademlynska, *Glass Techn.*, 10 (1969) 54 pp.
- 71 R. Röttenbacher and H. Engelke, *Glastechn. Ber.*, 49 (1976), 257 pp.
- 72 M. Cable and D. Martlew, *Glass Techn.*, 12 (1971), 142 pp.
- 73 J.H. Cleland and D.J. Fray, *Met. Trans. B*, 9B (1978), 539 pp.
- 74 P.O. Perron and H.B. Bell, *Trans. Brit. Ceram. Soc.*, 66 (1967), 347 pp.
- 75 M.L. Pearce and J.F. Beisler, *J. Amer. Ceram. Soc.*, 49 (1966), 547 pp.
- 76 M.P. Borom and J.A. Pask, *J. Amer. Ceram. Soc.*, 51 (1968), 490 pp.
- 77 M. Kosaka and T. Saito, *Reports of Ore Dressing and Refining, Institute of Tohoku Univ.*, 29 (1973), 17 pp.
- 78 K. Hunold and R. Brückner, *Glastech. Ber.*, 53 (1980), 207 pp.
- 79 H.B. May and R. Wollast, *J. Amer. Ceram. Soc.*, 57 (1974), 30 pp.
- 80 M. Kawakami, K. Nagata, and K.S. Goto, *J. Electrochem. Soc.*, 125 (1978), 395 pp.
- 81 P. Kofstad, "Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides", John Wiley & Sons, Inc., (1972), New York.
- 82 F.A. Kröger, "The Chemistry of Imperfect Crystals", Volumes 1.2 and 3, North-Holland Publishing Co., (1973), Amsterdam.
- 83 "Transport in Non-stoichiometric Compounds", edited by J. Nowotny, Elsevier (1982), Amsterdam.
- 84 A periodical journal titled "Diffusion and Defect Data", edited by F.H. Wohlbier and published by Trans. Tech. Publ. Co., Switzerland.
- 85 M. Iwase and E. Ichise, "Diffusion and Nonstoichiometry in Solid Oxides", *Tetsu-to Hagane (J. of Iron & Steel Inst. of Japan)* 72 (1986) 353 pp. and 720 pp.

Chapter 5

TRANSPORT PROPERTIES IN OXIDES WITH MULTICOMPONENTS

5.1 DEFINITION OF TRANSPORT COEFFICIENTS

In previous chapters, the coupling effect of diffusion jumps of different ionic species has been neglected. However, diffusion jumps may take place in multicomponent oxide systems even under temperature gradient. In these cases, two types of coupling effects are expected: first, the interaction among diffusion jumps of many components and secondly, the interaction between heat conduction and diffusion. What, then, is the magnitude of these interactions?

Should the coupling effects be neglected for kinetic processes in multicomponent oxide systems under temperature gradient?

These coupling effects will be discussed in this chapter.

As an example, let us consider the nonisothermal diffusion of ions in a liquid CaO-SiO_2 solution. The diffusion fluxes of elementary ions of Ca^{2+} , Si^{4+} , O^{2-} and the heat flux can be expressed⁽¹⁾ by j_1 , j_2 , j_3 and j_4 .

$$j_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + L_{14}X_4 \quad (5-1)$$

$$j_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 + L_{24}X_4 \quad (5-2)$$

$$j_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 + L_{34}X_4 \quad (5-3)$$

$$j_4 = L_{41}X_1 + L_{42}X_2 + L_{43}X_3 + L_{44}X_4 \quad (5-4)$$

where j_i is the flux relative to an arbitrary internal reference frame, L_{ik} is the transport coefficient and X_i is the generalized force⁽¹⁾.

The driving forces are

$$X_1 = -\frac{d}{dx} [z_1 F\psi + \mu_1(T)] \quad (5-5)$$

$$X_2 = -\frac{d}{dx} [z_2 F\psi + \mu_2(T)] \quad (5-6)$$

$$X_3 = - \frac{d}{dx} [z_3 F \psi + \mu_3(T)] \quad (5-7)$$

$$X_4 = - \frac{d}{dx} [\ln T] \quad (5-8)$$

where z_i represents the valency of the ions, F is Faraday constant, ψ is the local electrical potential in the oxide, μ_i is the chemical potential, T is the local temperature and x is the distance in the direction of diffusion.

The transport coefficients, L_{ik} , are defined by Eqs. (5-1) to (5-4), which are phenomenological linear-equations.

The nondiagonal terms of L_{12} , L_{13} , L_{23} , etc. are the magnitude of the coupling effects among diffusion jumps of the ionic species; Ca^{2+} , Si^{4+} and O^{2-} . The terms of L_{14} , L_{24} and L_{34} are coupling effects between diffusion and heat conduction.

According to Onsager's reciprocal relation⁽¹⁾

$$L_{ik} = L_{ki} \quad (5-9)$$

Furthermore, according to second law of thermodynamics, there are restrictions on L_{ik} ⁽¹⁾

$$L_{ii} \geq 0 \quad \text{and} \quad L_{ii} L_{kk} \geq L_{ik}^2 \quad (5-10)$$

These equations are obtained because the entropy production must be always positive during diffusion phenomenon.

When the driving forces expressed by Eqs. (5-5), (5-6), (5-7) and (5-8) are inserted into Eqs. (5-1) to (5-4), the values of transport coefficient can not be directly evaluated by this means because chemical potentials of ions can never be measurable in principle. The chemical activity of neutral components can be measured but charged species cannot. In thermodynamics, chemical potential is expressed as a function of chemical activity and temperature.

Therefore, to evaluate L_{ik} it is necessary to relate L_{ik} to measurable transport properties such as interdiffusivities, tracer diffusivity, electrical conductivity, transference numbers of ions and heat conductivity⁽²⁾⁽³⁾⁽⁴⁾.

Relations between L_{ik} and the transport properties may be theoretically derived and used to evaluate L_{ik} .

5.2 RELATION BETWEEN TRANSPORT COEFFICIENTS AND MEASURABLE PHYSICAL PROPERTIES

(a) Relation between L_{ik} and $\tilde{D}_{ik}$ under isothermal condition.

Under isothermal condition the heat flux, j_4 , and its driving force, X_4 , are all zero in Eqs. (5-1)~(5-4).

Under this condition, the relations between L_{ik} and interdiffusivities are derived as follows.

The diffusion fluxes of oxide components expressed 10 and 20 in a ternary system of 10-20-30, such as a liquid solution of CaO-SiO₂-Al₂O₃ ternary system at 1500°C, can be expressed by

$$J_{10} = - \tilde{D}_{10-10}^{30} \frac{d c_{10}}{dx} - \tilde{D}_{10-20}^{30} \frac{d c_{20}}{dx} \quad (5-11)$$

$$J_{20} = - \tilde{D}_{20-10}^{30} \frac{d c_{10}}{dx} - \tilde{D}_{20-20}^{30} \frac{d c_{20}}{dx} \quad (5-12)$$

where

$$J_{30} = - (J_{10} + J_{20}) \quad (5-13)$$

Here, $\tilde{D}_{ik}$ is the interdiffusivity and c_{i0} is the concentration of oxide component, i0. For simplicity of discussion, let us assume a constant molar volume during the interdiffusion. Then the Matano interface is immobile and the fluxes expressed by Eqs. (5-11) to (5-13) are given relative to the external references frame.

The interdiffusivity matrices, $\tilde{D}_{ik}$, are measurable quantities, because they can be evaluated⁽⁵⁾⁽⁶⁾ from the concentration distribution curves of 10, 20 and 30 in the diffusion couple after a fixed time of diffusion at a constant temperature.

According to a paper by Darken⁽⁷⁾ in 1948, the diffusion fluxes relative to an external reference can be related to an internal reference by

$$J_i = j_i + c_i v_0 \quad (5-14)$$

where v_0 is the local velocity of the internal reference frame.

Therefore, the diffusion flux of 10 can be given by two expressions which are equal to each other

$$J_{10} = - \sum_{k=1}^0 L_{1k} \frac{d}{dx} (z_k F \psi + RT \ln a_k) + c_1 v_0 \quad (5-14')$$

$$J_{1O} = - \tilde{D}_{1O-1O}^{3O} \frac{d c_{1O}}{dx} - \tilde{D}_{1O-2O}^{3O} \frac{d c_{2O}}{dx} \quad (5-11)$$

where R and a_k in Eq. (5-14') are the gas constant and activity of k , respectively.

Equation (5-14') is obtained by inserting Eqs. (5-5), (5-6) and (5-7) and a similar equation for oxygen anion to the flux equations, similar to Eqs. (5-1) to (5-3). The activity of ions, not a measurable quantity, is expressed by a_k in Eq. (5-14'). Equation (5-11) is again repeated for comparison with Eq. (5-14').

Eq. (5-14') contains inconvenient terms of electrical potential in oxide, ψ , activity of ions, a_k , and local velocity of internal reference frame. These three terms must be eliminated and then one will have relations between L_{ik} and $\tilde{D}_{ik}$.

To eliminate v_0 , one can use Eq. (5-14) with assumption of a constant molar volume

$$J_{1O} + J_{2O} + J_{3O} = 0 \quad (5-13)$$

From Eq. (5-14)

$$v_0 = \frac{-(j_1 + j_2 + j_3)}{c_1 + c_2 + c_3} \quad (5-15)$$

Inserting this expression for v_0 in Eq. (5-14'), one can eliminate the velocity of internal reference frame. This procedure is well explained in Darken's paper⁽⁷⁾ of 1948.

To eliminate electrical potential and activity of ions, C. Wagner's paper⁽⁸⁾ of 1933 provides a very convenient procedure.

To eliminate the electrical potential from Eq. (5-14'), one can use the electroneutrality in any position in the oxide

$$z_1 j_1 + z_2 j_2 + z_3 j_3 - 2 j_{O^{2-}} = 0 \quad (5-16)$$

From this relation, one can have

$$F d\psi = - \frac{\sum_k d\mu_k}{\sum_{i,k} z_i z_k L_{ik}} \quad (5-17)$$

The electrical potential in Eq. (5-14') can be replaced by Eq. (5-17). The equation obtained still includes the chemical potential of ions, which can not be measured.

If local equilibrium prevails in the oxide phase, the chemical potential of a neutral oxide, μ_{iO} is equal to the sum of chemical potential of cation, i and oxygen anion, O^{2-} .

$$\mu_{iO} = \mu_{i^{2+}} + \mu_{O^{2-}} \quad (5-18)$$

or

$$\mu_{i^{2+}} = \mu_{iO} - \mu_{O^{2-}} \quad (5-18')$$

Inserting Eq. (5-18') into μ_i in Eq. (5-14'), one can completely eliminate the chemical potentials of the cations and oxygen anion because the chemical potentials of oxygen anion cancel each other.

The gradient of chemical potential can be converted to the concentration gradient by

$$\frac{d\mu_{iO}}{dx} = \frac{d\mu_{iO}}{dC_{iO}} \cdot \frac{dC_{iO}}{dx} \quad (5-19)$$

where

$$\frac{d\mu_{iO}}{dC_{iO}} = \frac{RT}{C_i} \left(1 + \frac{d \ln \gamma_{iO}}{d \ln N_{iO}} \right) \quad (5-20)$$

In this equation, γ_{iO} is the activity coefficient of a neutral oxide component, iO with Raoult's Standard and N_{iO} is the mole fraction of iO.

The final equation, obtained by the above procedure⁽³⁾, includes only the concentration gradient and the activity coefficients. It can be directly compared to Eq. (5-11) to obtain a relation between L_{ik} and D_{ik}

$$\begin{aligned} \bar{D}_{1O-1O}^{3O} = & -\frac{RT}{C} \left[\frac{C_2 + C_3}{C_1} T_{11} - T_{21} - T_{31} \right. \\ & \left. - \frac{C_1}{C_3} \left(\frac{C_2 + C_3}{C_1} T_{13} - T_{23} - T_{33} \right) \right] \Gamma_{1O} \quad (5-21) \end{aligned}$$

where c is sum of concentration of 1O, 2O and 3O, which are expressed by c_1 , c_2 and c_3 , respectively. Γ_{1O} is the thermodynamic factor of 1O given by

$$\Gamma_{1O} = 1 + \left(\frac{\partial \ln \gamma_{1O}}{\partial \ln N_{1O}} \right)_{N_{2O}/N_{3O}} \quad (5-22)$$

The terms of T_{ik} are given by

$$T_{ik} = L_{ik} - \frac{1}{s} \sum_k^n z_k L_{ik} \sum_i z_i L_{i'k} \quad (5-23)$$

where

$$s \equiv \sum_i^n \sum_k^n z_i z_k L_{ik} \quad (5-24)$$

z_i is the valence of elementary ions.

Three more relations, similar to Eq. (5-21) can be obtained⁽¹⁰⁾ for $\tilde{D}_{10-2O}^{3O}$, $\tilde{D}_{2O-1O}^{3O}$ and $\tilde{D}_{2O-2O}^{3O}$.

Because interdiffusivity matrices, $\tilde{D}_{ik}$ can be measured by the diffusion couple method, it seems possible to evaluate L_{ik} with a help of these four equations. It is impossible, however, because number of unknown terms of L_{ik} is more than four. Therefore, more relations of L_{ik} to measurable physical properties must be derived.

(b) Relation between L_{ik} and electrical conductivity under isothermal conditions. In oxides with predominant ionic conduction, the electrical current is carried by migration of the elementary ions. The current, I is given by

$$I = \sum_i z_i F j_i \quad (5-25)$$

where F is Faraday constant and j_i are the diffusion fluxes of the elementary ions.

The electrical conductivity, expressed by σ , is defined by

$$I = -\sigma \left(\frac{d\psi}{dx} \right) \quad (5-26)$$

The conductivity, σ , is usually measured in a uniform composition so the gradients of chemical potentials of any ionic species are zero.

If one inserts these relationships into the fluxes equations and the equations for j_i are inserted into Eq. (5-25), the conductivity, σ , can be related to L_{ik} by

$$\sigma = F^2 \sum_i \sum_k z_i z_k L_{ik} \quad (5-27)$$

where F is again the Faraday constant.

(c) Relation between L_{ik} and the tracer diffusivity under isothermal conditions. Laity⁽⁹⁾ derived the following relation in 1962:

$$D_i^{tr} = \frac{L_{ii} R T}{c_i} \quad (5-28)$$

where D_i^{tr} is the tracer diffusivity and L_{ii} is a diagonal term of L_{ik} .

(d) Relation between L_{ik} and the Hittorf transference number under isothermal conditions. The Hittorf transference number, H_i^{tr} , of "i"th ionic species relative to "r"th ionic species can be defined by

$$H_i^{tr} \equiv \frac{z_i F}{I} \left(j_i - j_r \frac{c_i}{c_r} \right) \quad (5-29)$$

Inserting the linear flux equations to j_i and j_r , one can easily obtain

$$H_i^{tr} = \frac{z_i}{s} \sum_k z_k \left(L_{ik} - L_{rk} \frac{c_i}{c_r} \right) \quad (5-30)$$

where s is given by Eq. (5-24).

The external transference number, t_i^{ex} , which can be measured relative to the electrodes or the container of oxide solutions as a reference frame, is related to the Hittorf reference number by

$$H_i^{tr} = t_i^{ex} - t_r^{ex} \left(\frac{z_i c_i}{z_r c_r} \right) \quad (5-31)$$

(e) Relation between L_{ik} and heat conductivity under nonisothermal conditions. The heat conductivity is usually measured with uniform composition of oxide solutions under a small temperature gradient so Eq. (5-4) can be simplified to

$$j_4 = -L_{44} \frac{d \ln T}{dx} \quad (5-32)$$

On the other hand, the heat conductivity, λ is defined by

$$j_4 = -\lambda \frac{dT}{dx} \quad (5-33)$$

The comparison of Equations (5-32) and (5-33) gives

$$L_{44} = \lambda T \quad . \quad (5-34)$$

(f) Relation between L_{ik} and coefficient of Soret effect, S under nonisothermal conditions. When a liquid solution of CaO and SiO₂ with initially uniform composition is heated at a given average temperature but with a fixed temperature gradient, the diffusion of components will take place due to the coupling effect by the heat conduction. After a long time, a steady concentration gradient will be established.

The magnitude of the concentration gradient caused by unit temperature gradient is expressed by the coefficient of Soret effect, usually expressed by S , as follows;

$$S \equiv \left(\frac{d \ln N_{\text{CaO}}}{dx} \right) / \left(\frac{dT}{dx} \right) = \frac{d \ln N_{\text{CaO}}}{dT} \quad (5-35)$$

where N_{CaO} is mole fraction of CaO in CaO-SiO₂ solution. The right hand side of Eq. (5-35) can be experimentally determined.

The diffusion flux of Ca^{2+} can be expressed by Eq. (5-1) and equally as well by

$$j_{\text{Ca}^{2+}} = -T_{11} \nabla \mu_{\text{CaO}} - T_{12} \nabla \mu_{\text{SiO}_2} - T_{13} \nabla \ln T \quad . \quad (5-36)$$

Where T_{ik} are defined by Eq. (5-23) and ∇ is differential with respect to distance x . This expression of the flux by T_{ik} , not by L_{ik} , simplifies the discussion on the relation between the Soret coefficient and L_{ik} .

After attaining a steady-state concentration gradient,

$$j_{\text{Ca}^{2+}} = 0 \quad \text{and if} \quad \nabla \mu_i = RT \nabla \ln N_i$$

$$S = -\frac{1}{RT^2} \cdot \frac{T_{13}}{T_{11} - T_{12} \left(\frac{N_{\text{CaO}}}{N_{\text{SiO}_2}} \right)} \quad . \quad (5-37)$$

In the dilute range of CaO, the ration $N_{\text{CaO}}/N_{\text{SiO}_2}$ is nearly zero and thus

$$S = -\frac{1}{RT^2} \cdot \frac{T_{13}}{T_{11}} \quad . \quad (5-38)$$

This equation is valid only for the dilute range.

In the above, the relations between L_{ik} and several measurable properties have been derived. In reference (10) the relation to thermo-electromotive force has been also derived on binary liquid oxide solutions with predominant ionic conduction. It is not given here, because it is discussed in experimental determination of the thermo-electromotive forces on oxide systems with ionic conduction (Section 5.4).

5.3 CALCULATION OF TRANSPORT COEFFICIENTS

The liquid ternary solution of 40wt%CaO-40wt%SiO₂-20wt%Al₂O₃ at 1500°C has industrial importance because it is the main composition of metallurgical slag produced in blast furnaces making pig iron.

In this homogeneous melt, there are four elementary ions, Ca²⁺, Al³⁺, Si⁴⁺ and O²⁻, which are expressed in the following discussion as 1, 2, 3 and 0, respectively.

Under isothermal condition one has four flux equations and 16 unknown L_{ik} . Using Onsager's reciprocal relation of Eq. (5-9), one may reduce the number of these unknown terms to 10.

The number of the unknown coefficients can be further reduced to six with the help of DeGroot and Mazur's relation⁽¹¹⁾ of

$$\sum_{i \text{ or } k}^n L_{ik} = 0 \quad . \quad (5-39)$$

We can therefore calculate all 16 L_{ik} from only 6 physical properties measured experimentally.

For reliable transport properties, three tracer diffusivities, electrical conductivity σ , transference numbers of Ca²⁺ and Al³⁺ have been selected. These properties are given in Table 5.1.

In accordance to the values in Table 5.1, the following values have been assigned to the six properties:

$$\begin{aligned} D_{Ca^{2+}}^{tr} &= 2.1 \times 10^{-6} \text{ cm}^2/\text{sec}, & D_{Al^{3+}}^{tr} &= 6.3 \times 10^{-7} \text{ cm}^2/\text{sec}, \\ D_{Si^{4+}}^{tr} &= 2.3 \times 10^{-7} \text{ cm}^2/\text{sec}, & \sigma &= 0.127 (\Omega \cdot \text{cm})^{-1}, \\ t_{Ca^{2+}}^0 &= 0.95, & t_{Al^{3+}}^0 &= 0.05 \quad (\text{all at } 1500^\circ\text{C}). \end{aligned}$$

Equations (5-27), (5-28), (5-30), (5-9) and (5-39) have been used to estimate the L_{ik} in mol²/cal·sec·cm, which are given in Table 5.2.

TABLE 5.1

Physical properties of 40wt% CaO-40 SiO₂-20 Al₂O₃ melts reported in the literature

	Composition*		Value at 1500°C	Ref.
	CaO (wt%)	SiO ₂ (wt%)		
$D_{Ca^{2+}}^{tr}$	40.32	40.06	2.2×10^{-6} (cm ² /sec)	(12)
	38.5	40.5	2.1×10^{-6}	(13)
	39.8	41.2	2.1×10^{-6}	(14)
	40	40	2.0×10^{-6}	(15)
$D_{Al^{3+}}^{tr}$	38.6	41.3	6.3×10^{-7}	(16)
$D_{Si^{4+}}^{tr}$	38.5	40.5	2.3×10^{-7}	(13)
σ	40.15	40.15	0.144 ($\Omega^{-1}\text{cm}^{-1}$)	(17)
	40	40	0.127	(18)
	38.7	38.9	0.35	(19)
$t_{Ca^{2+}}$	37	45	0.89 at 1550°C	(20)
	38	42	1.0 ~ 0.85 at 1530°C	(21)
$t_{Al^{3+}}$	Larger ratio of Al ₂ O ₃ /CaO		$1 - t_{Ca^{2+}}$	(22)
ρ	39	42	2.796 (g/cm ³)	(23)
	40	40	2.581	(18)

* The content of Al₂O₃ is the balance.

TABLE 5.2

Estimated L_{ik} at 1500°C for a blast furnace slag*

$L_{11} = 1.1 \times 10^{-11}$	$L_{13} = L_{31} = -2.0 \times 10^{-12}$
$L_{22} = 1.8 \times 10^{-12}$	$L_{23} = L_{32} = -5.5 \times 10^{-13}$
$L_{33} = 1.1 \times 10^{-12}$	$L_{10} = L_{01} = -7.1 \times 10^{-13}$
$L_{00} = 5.1 \times 10^{-12}$	$L_{20} = L_{02} = 6.1 \times 10^{-13}$
$L_{12} = L_{21} = -1.9 \times 10^{-12}$	$L_{30} = L_{03} = 1.5 \times 10^{-12}$

* L_{ik} are with mol²/cal·sec·cm .

The estimated L_{ik} in this table satisfy the second law restriction of Eq. (5-10).

When the values of L_{ik} are obtained in this way, one can calculate the interdiffusivities by Eq. (5-21) and the similar relations, even without interdiffusion experiment.

The estimated interdiffusivities, $\tilde{D}_{ik}$, at 1500°C for the fixed average composition of 40wt%CaO-20wt%Al₂O₃-40wt%SiO₂ are

$$\begin{aligned}\tilde{D}_{10-10}^{3O} &= 3.2 \times 10^{-6} \text{ cm}^2/\text{sec} , & \tilde{D}_{10-2O}^{3O} &= -1.08 \times 10^{-6} \text{ cm}^2/\text{sec} , \\ \tilde{D}_{2O-10}^{3O} &= -1.06 \times 10^{-6} \text{ cm}^2/\text{sec} , & \tilde{D}_{2O-2O}^{3O} &= 2.04 \times 10^{-6} \text{ cm}^2/\text{sec} .\end{aligned}$$

For calculation of the interdiffusivities the following values are used from the activity data measured by Chipman's school⁽²⁴⁾;

$$\begin{aligned}\frac{\partial \ln a_{1O}}{\partial N_{1O}} &= 18.52 , & \frac{\partial \ln a_{1O}}{\partial N_{2O}} &= -1.13 , \\ \frac{\partial \ln a_{2O}}{\partial N_{1O}} &= 1.13 , & \frac{\partial \ln a_{2O}}{\partial N_{2O}} &= 12.19 .\end{aligned}$$

In the following section the interdiffusivities here estimated will be compared with direct determinations in interdiffusion experiments.

5.4 MEASUREMENT OF VARIOUS TRANSPORT PROPERTIES

Transport properties such as tracer diffusivity, electrical conductivity, and transference number of ions have been measured usually on pure or binary oxide systems. In such cases, no coupling phenomena will take place. However, the coupling effects, expressed by nondiagonal terms of Eqs. (5-1) to (5-4), must be taken into consideration in multicomponent oxide systems.

Therefore, in this section, several examples are given for direct measurements of transport properties in multicomponent oxide systems both in the solid and liquid states.

(a) Experimental determination of $\tilde{D}_{ik}$ on both iron and steel-making slags under isothermal condition. In 1977, Sugawara, Nagata and Goto⁽²⁵⁾ measured the interdiffusivities on a blast furnace slag composed of CaO, Al₂O₃ and SiO₂ at 1450°C, 1500°C and 1550°C.

Fig. 5.1 shows six charge compositions and three directions of combination of the diffusion-couple elements. The average composition of six charge compositions was 40wt%CaO-20wt%Al₂O₃-40wt%SiO₂.

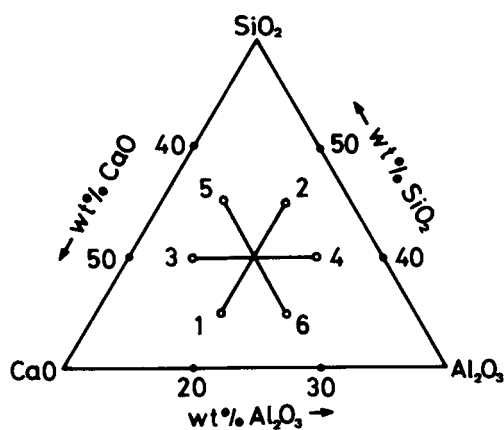


Fig. 5.1. Ternary composition diagram to show compositions of six sample pieces used for three diffusion couples of combinations of 1 and 2, 3 and 4, and 5 and 6 (After Sugawara, Nagata and Goto⁽²⁵⁾).

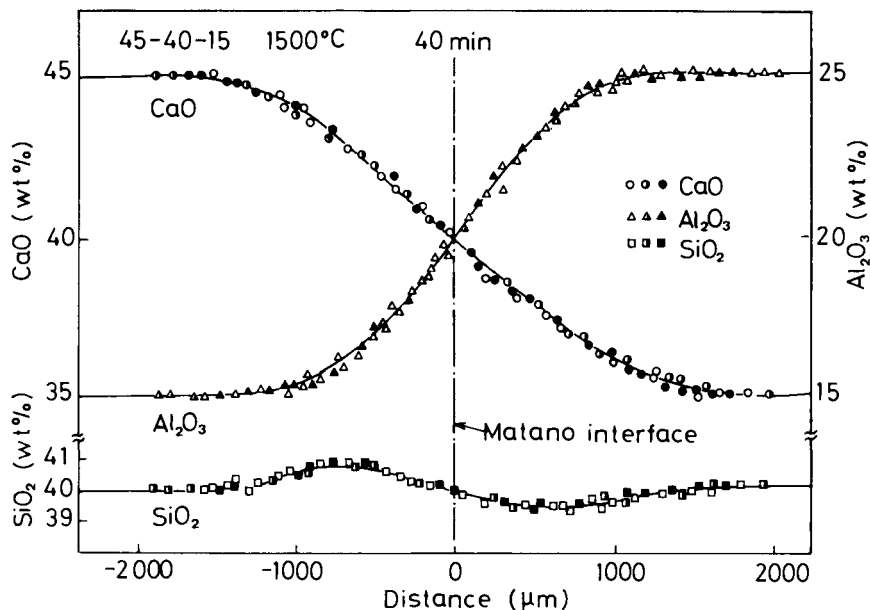


Fig. 5.2. Distribution of contents of CaO, Al₂O₃ and SiO₂ after diffusion run of 40 min. at 1500°C (After Sugawara, Nagata and Goto⁽²⁵⁾).

Penetration curves of the components were measured with an X-ray microprobe analyzer after the diffusion runs at 1450°C, 1500°C or 1550°C.

The total number of successful diffusion runs was 52. Fig. 5.2 gives an example of the penetration curve from three independent diffusion runs at 1500°C. Further, Fig. 5.3 shows the results of 3 diffusion runs for various diffusion times. A slight up-hill diffusion of SiO_2 or Al_2O_3 is taking place due to the coupling effect.

The interdiffusivities were obtained with the Matano interface and Kirkaldy's method⁽⁶⁾:

$$D_{11}^{3\text{O}} = 8.9 \times 10^{-11} \exp\left(-\frac{254,000}{RT}\right) \text{ m}^2/\text{sec}$$

$$D_{12}^{3\text{O}} = -2.5 \times 10^{-11} \exp\left(-\frac{194,000}{RT}\right) \text{ m}^2/\text{sec}$$

$$D_{21}^{3\text{O}} = -4.0 \times 10^{-11} \exp\left(-\frac{178,000}{RT}\right) \text{ m}^2/\text{sec}$$

$$D_{22}^{3\text{O}} = 6.12 \times 10^{-11} \exp\left(-\frac{318,000}{RT}\right) \text{ m}^2/\text{sec}$$

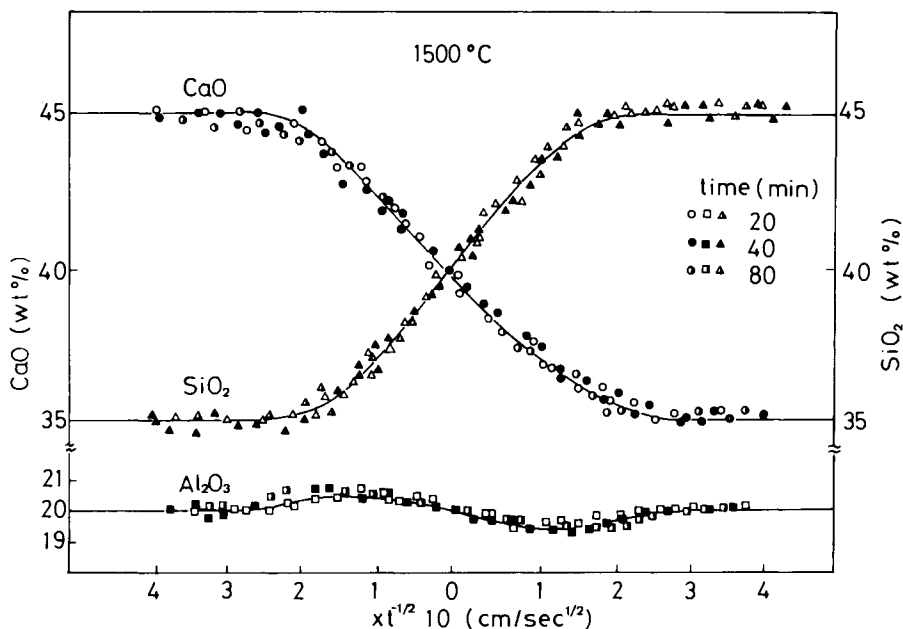


Fig. 5.3. Relation between wt%CaO, SiO_2 and Al_2O_3 and $x/\sqrt{t}$ after diffusion runs of 20, 40 and 80 min. at 1500°C (After Sugawara, Nagata and Goto⁽²⁵⁾).

where the activation energies are given in Joules per mole ($1 \text{ m}^2/\text{sec} = 10^4 \text{ cm}^2/\text{sec}$, $1 \text{ cal} = 4.184 \text{ Joules}$).

Fig. 5.4 gives a comparison between the experimental curves and the estimated ones based upon the D_{ik} values estimated in the previous section. The estimated curves agree very well with the experimental. The agreement in the curves of Al_2O_3 with up-hill diffusion seems not so impressive but it should be noted that the vertical axis for $\text{wt}\%\text{Al}_2\text{O}_3$ is very much expanded.

It therefore seems that the relations between L_{ik} and measurable transport properties, which have been derived in the previous sections, do not include any serious discrepancies.

In 1978, Ukyo and Goto⁽²⁶⁾ made a similar interdiffusion experiment on a steelmaking slag of Fe_2O_3 - CaO - SiO_2 equilibrated with air at 1420°C , 1470°C and 1500°C . About 15% of total ferric content would be converted to ferrous ion under air at 1480°C but the total iron content was expressed as $\text{wt}\%\text{Fe}_2\text{O}_3$.

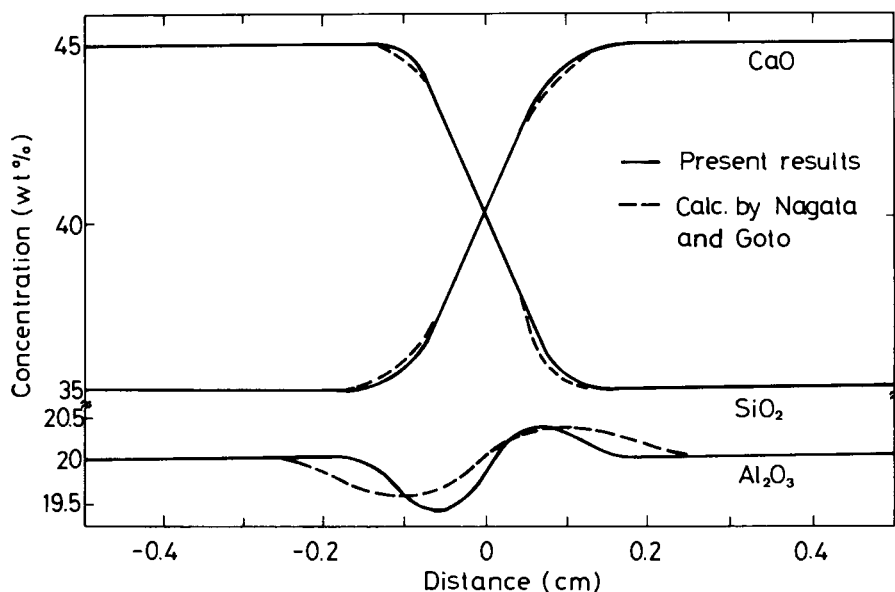


Fig. 5.4. Relations between concentrations of CaO , SiO_2 and Al_2O_3 and distance after diffusion run of 40 min. at 1500°C . The solid lines are experimental results and broken lines are the relations theoretically estimated (After Sugawara, Nagata and Goto⁽²⁵⁾).

Fig. 5.5 is an example of the penetration curves obtained at 1470°C. Two independent runs are plotted on this figure. In a total of 100 diffusion runs, 31 sets of good penetration curves have been successfully obtained. When 1, 2, 3 and 0 mean $\text{Fe}^{3+}(\text{Fe}^{2+})$, Ca^{2+} , Si^{4+} and O^{2-} respectively, the interdiffusivities for the average composition of 20wt% Fe_2O_3 , 35wt% CaO and 45wt% SiO_2 may be expressed as follows:

$$\bar{D}_{10-10}^{3\text{O}} = 3.27 \exp\left(-\frac{50,000}{RT}\right)$$

$$\bar{D}_{10-20}^{3\text{O}} = -11.1 \exp\left(-\frac{55,000}{RT}\right)$$

$$\bar{D}_{20-10}^{3\text{O}} = -8.30 \exp\left(-\frac{56,300}{RT}\right)$$

$$\bar{D}_{20-20}^{3\text{O}} = 11.5 \exp\left(-\frac{56,200}{RT}\right)$$

where $\bar{D}_{ik}$ are given in cm^2/sec , and the activation energies are given in cal/mole.

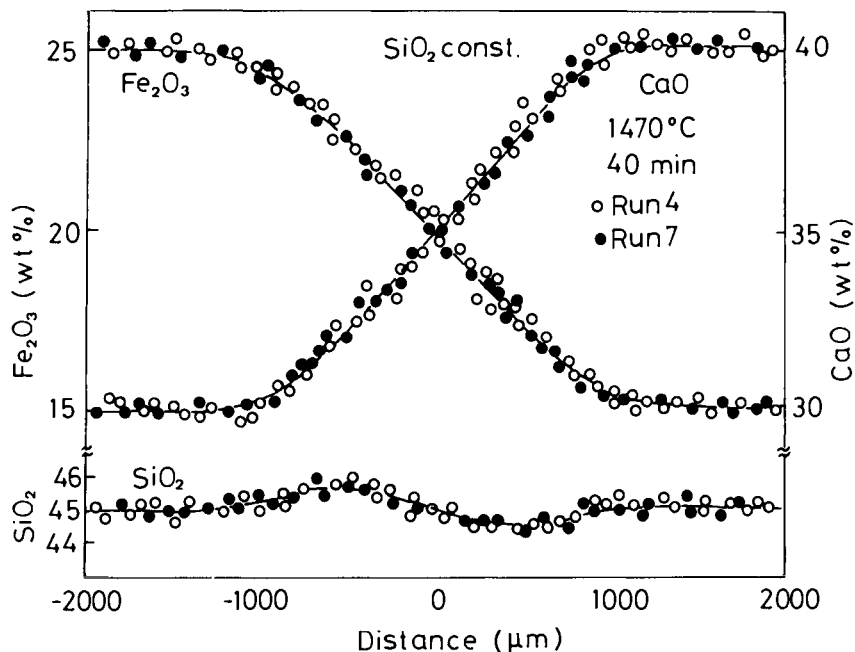


Fig. 5.5. Relation between concentrations of Fe_2O_3 , CaO and SiO_2 and distance after diffusion runs of 40 min. at 1470°C (After Ukyo and Goto⁽²⁶⁾).

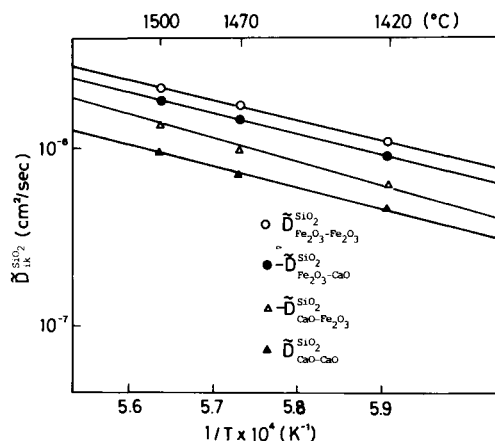


Fig. 5.6. Relation between logarithm of interdiffusivities and reciprocal temperature for ternary system of $\text{Fe}_2\text{O}_3\text{-CaO-SiO}_2$ (After Ukyo and Goto⁽²⁶⁾).

Fig. 5.6 shows the relation between logarithm of the obtained interdiffusivities and reciprocal temperature. Because the cross terms of the interdiffusivities are negative values, logarithm of their absolute values are given in the figure. The obtained result satisfied the second-law restrictions similar to Eq. (5-10).

Because of the highly reactive nature of steelmaking slag, it is not easy to find reliable transport properties in the literature. Therefore, at present, the transport coefficients can not be evaluated.

(b) Thermodiffusion of a solute in multicomponent oxide solution. For simplicity it is desirable to measure the Soret effect in a binary oxide systems in its dilute range, but it is experimentally not easy. Therefore, Ukyo and Goto⁽²⁷⁾ measured the steady-state distribution of a solute in two types of solvent oxides in the liquid state. The two types selected are ternary systems of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ because they are industrially important systems as an iron making slag and a steel making slag, respectively.

Fig. 5.7 shows a dense alumina tube with a small diameter, along which a temperature gradient is maintained during the thermodiffusion experiment. The temperature gradient is controlled by the density of tungsten-wire windings used as the heating element. The diagram at the right is an example of temperature distribution.

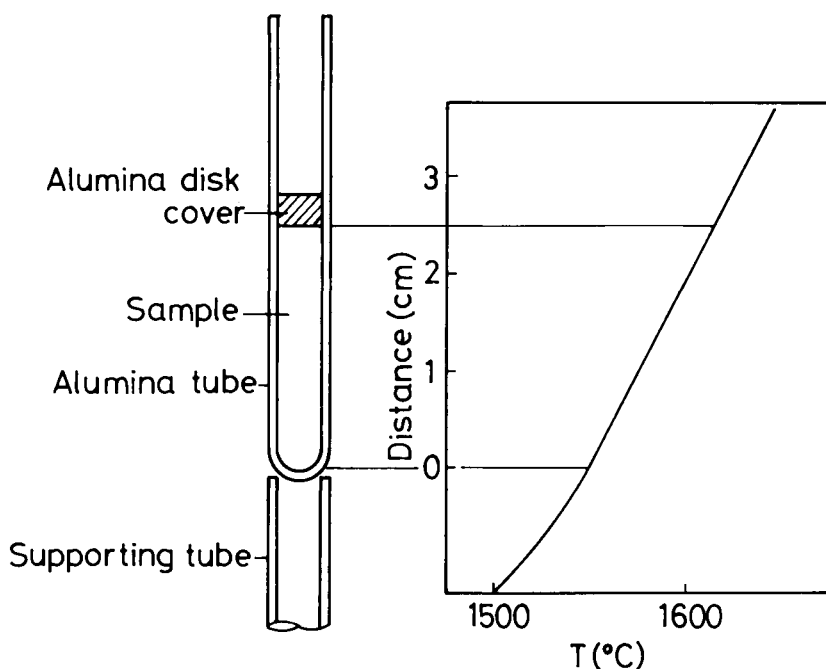


Fig. 5.7. Sectional view of an alumina tube containing a sample slag covered by alumina disk. A constant temperature gradient as shown by the right-hand figure was maintained during a thermodiffusion experiment (After Ukyo and Goto⁽²⁷⁾).

The premelted oxide mixtures have been densely charged in this vertical tube and heated for 18 hours to 40 hours to produce a steady distribution of the solute. After quenching the sample, it was embedded in resin, cut vertically, polished and then analyzed by an X-ray microprobe.

Fig. 5.8 shows the results of two experimental runs, giving the relation between logarithm of wt% of solute, Fe_2O_3 , and local temperature. The composition of the solvent, initially 40wt%CaO-40%SiO₂-20%Al₂O₃, would also change by thermodiffusion but this change was not detected by X-ray microprobe analyzer. Then, the apparent coefficient of the Soret effect can be calculated by

$$S = \frac{d \ln(\text{wt}\%x)}{dT} \quad (5-35')$$

Because the Fe_2O_3 is migrating in the direction of lower temperature, S should take a negative value, i.e. $-1.5 \times 10^{-3}/\text{K}$.

Fig. 5.9 is the summary of the results of thermodiffusion of

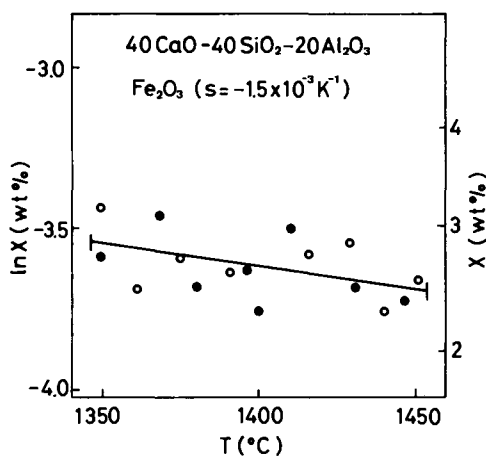


Fig. 5.8. Relation of logarithm wt%Fe₂O₃ and temperature after thermodiffusion experiment in the solvent of 40wt%CaO-40%SiO₂-20%Al₂O₃ (After Ukyo and Goto⁽²⁷⁾).

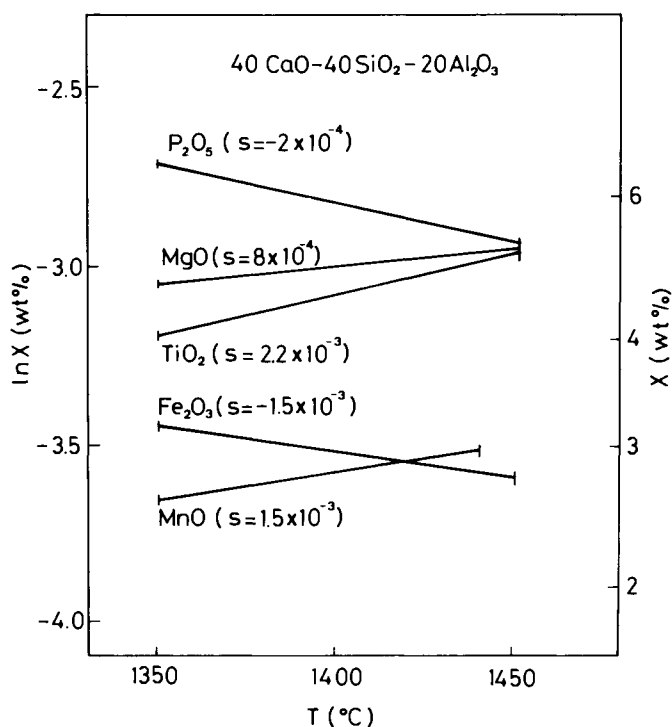


Fig. 5.9. Relation between logarithm wt% of various solute oxides and temperature after thermodiffusion using a solvent slag of 40%CaO-40%SiO₂-20%Al₂O₃ (After Ukyo and Goto⁽²⁷⁾).

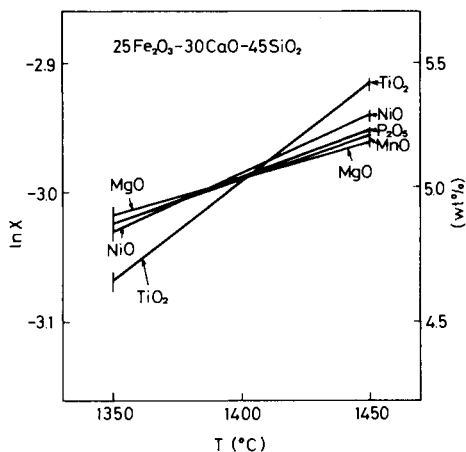


Fig. 5.10. Relation between logarithm wt% of various solute oxides and temperature after thermodiffusion using a solvent slag of $25\text{Fe}_2\text{O}_3\text{-}30\text{CaO-}45\text{SiO}_2$ (After Ukyo and Goto⁽²⁷⁾).

P_2O_5 , MgO , TiO_2 , Fe_2O_3 or MnO as the solute in the slag solvent.

Fig. 5.10 summarizes the results of thermodiffusion of TiO_2 , NiO , P_2O_5 , MnO or MgO in a liquid solvent composed of $25\text{wt}\%\text{Fe}_2\text{O}_3\text{-}30\text{wt}\%\text{CaO-}45\text{wt}\%\text{SiO}_2$.

The initial composition of the solvent would change by thermodiffusion but the change could not be detected by the X-ray microprobe analyzer.

The following table gives the coefficient of Soret effect calculated by Eq. (5-35').

TABLE 5.3

Soret coefficients of several solutes at 1400°C in two solvents of (A) $40\text{wt}\%\text{CaO-}40\text{wt}\%\text{SiO}_2\text{-}20\text{wt}\%\text{Al}_2\text{O}_3$ and (B) $25\text{wt}\%\text{Fe}_2\text{O}_3\text{-}30\text{wt}\%\text{CaO-}45\text{wt}\%\text{SiO}_2$ (After Ukyo and Goto⁽²⁷⁾).

Solute	S in solvent(A)	Solute	S in solvent(B)
P_2O_5	$-2.0 \times 10^{-3} \text{ (K}^{-1}\text{)}$	P_2O_5	$6.8 \times 10^{-4} \text{ (K}^{-1}\text{)}$
Fe_2O_3	-1.5×10^{-3}	TiO_2	1.7×10^{-3}
TiO_2	2.2×10^{-3}	MnO	6.6×10^{-4}
MgO	8.0×10^{-4}	MgO	6.1×10^{-4}
MnO	1.5×10^{-3}	NiO	9.0×10^{-4}

The Soret coefficients in Table 5.3 are not directly helpful in evaluating L_{ik} in Eqs. (5-1) to (5-4) because the systems contain too many components.

Thus, the Soret coefficients have been measured⁽²⁷⁾ by the same method on binary liquid alloys of iron and a solute element.

In this case the tracer diffusivities of solutes and heat conductivity were estimated with reasonable reliability on liquid iron-base alloys. One can now evaluate the magnitude of the coupling effect.

Similarly to Eqs. (5-1) to (5-4), the flux equations for the diffusion of the solute, j_1 and for the heat conduction, j_2 can be expressed by

$$j_1 = -L_{11} \nabla \mu_1 - L_{12} \nabla \ln T \quad (5-40)$$

$$j_2 = -L_{21} \nabla \mu_1 - L_{22} \nabla \ln T \quad (5-41)$$

where ∇ is partial differential with respect to x . The sublattice of iron atoms is taken as the internal reference frame and thus, $j_{Fe} = 0$.

According to Eq. (5-38), the ratio of L_{12}/L_{11} can be given by

$$S \equiv \frac{d \ln N_x}{dT} = -\frac{1}{RT^2} \cdot \frac{L_{12}}{L_{11}} \quad (5-42)$$

where S is Soret effect coefficient and N_x is mole fraction of solute x . Eq. (5-42) is obtained because T_{ik} is equal to L_{ik} for good electron conductors.

The Soret coefficients of P, Si, Ni and Cr, measured and calculated by Eq. (5-42) are given in Table 5.4. Furthermore, one has the relations of

$$L_{11} = \frac{N_x}{RT} D_x^{tr} \quad (5-28')$$

and

$$L_{22} = \lambda T \quad (5-34')$$

Because of Onsager's relation, $L_{12} = L_{21}$, one has three unknowns.

One can therefore calculate all L_{ik} 's. The tracer diffusivities have been estimated by Darken's method⁽⁷⁾ from binary interdiffusivities in the literature.

The heat conductivity is assumed equal to that of pure liquid

TABLE 5.4

Measured Soret coefficients and calculated L_{ik} on liquid Fe-X binary alloys (by Ukyo and Goto⁽²⁷⁾)

Solute	Temp.	S	L_{11}	$L_{12}=L_{21}$	L_{22}
10.1%P	1300	-7.88×10^{-4}	7.3×10^{-11}	2.9×10^{-7}	1.4×10^2
10.1%P	1597	-1.61×10^{-3}	1.5×10^{-10}	1.7×10^{-6}	1.77×10^2
2.98%P	1577	1.43×10^{-3}	4.6×10^{-11}	-4.4×10^{-7}	1.77×10^2
0.99%P	1610	3.78×10^{-3}	1.28×10^{-11}	-3.2×10^{-7}	1.77×10^2
5.0%Si	1590	7.39×10^{-4}	1.37×10^{-10}	-6.6×10^{-7}	1.77×10^2
5.83%Ni	1585	5.70×10^{-4}	1.06×10^{-10}	-6.0×10^{-7}	1.77×10^2
4.0%Cr	1567	4.06×10^{-3}	4.85×10^{-11}	-1.3×10^{-7}	1.77×10^2
wt%	°C	K^{-1}	$\frac{\text{mol}^2}{\text{cal cm sec}}$	$\frac{\text{mol}}{\text{cm sec}}$	$\frac{\text{cal}}{\text{cm sec}}$

iron estimated by Touloukian, Powell and Klements⁽²⁸⁾.

Table 5.4 gives the values of L_{ik} at various average compositions and average temperatures.

The L_{12} or L_{21} in this table gives the magnitudes of coupling of heat conduction and diffusion of the solute elements through the liquid iron alloys. In principle, this kind of measurement seems quite possible for oxide melts if the experimental difficulties are overcome.

(c) Thermo-electromotive force of solid and liquid oxides. No experimental work except Emi and Shimoji⁽²⁹⁾ has been reported on the electromotive force of nonisothermal oxide melts. However, the EMF of thermogalvanic cells with binary solid solutions of oxides have been reported by Fischer⁽³⁰⁾ in 1967 and by Goto, Ito and Someno⁽³³⁾ in 1969 and by others⁽³¹⁾⁽³²⁾⁽³⁴⁾⁻⁽⁴⁰⁾.

The cell studied was

air, Pt(T_1) | ZrO₂-CaO or ThO₂-CaO | Pt(T_2), air .

The charge carrier in the electrolyte is the oxygen anion.

Thus, the EMF can be expressed as⁽¹¹⁾

$$\begin{aligned}
\Delta\psi_t = & \frac{1}{4F} \left[\mu_{O_2}(T_2, P''_{O_2}) - \mu_{O_2}(T_1, P'_{O_2}) \right] \\
& + \frac{1}{2F} \int_{T_1}^{T_2} \left(\bar{S}_{O^{2-}}^{ZrO_2} + \frac{Q_{O^{2-}}^{ZrO_2}}{T} \right) dT \\
& - \frac{1}{F} \int_{T_1}^{T_2} \left(\bar{S}_e^{Pt} + \frac{Q_e^{Pt}}{T} \right) dT
\end{aligned} \tag{5-43}$$

where μ_i is chemical potential of i , $\bar{S}_i^x$ is partial molal entropy of i in substance x , and Q_i^x is heat of transfer of i in substance x (11).

When the quantities in two integrals are assumed independent of temperature, Eq. (5-43) can be simplified to

$$\Delta\psi_t = \frac{1}{4F} \left[\mu_{O_2}(T_2, P''_{O_2}) - \mu_{O_2}(T_1, P'_{O_2}) \right] + \alpha (T_2 - T_1) \tag{5-44}$$

where α is the sum of the partial molal entropies and entropies of transfer. Thus, the coefficient depends on the nature of the oxide solutions and metal electrodes, which have been used for the EMF measurement.

Fig. 5.11 shows the sectional view of a tube of ZrO_2 -base solid solution in a heating furnace with a temperature gradient. Thermo-electromotive force between two electrodes with hot junctions of two thermocouples can be measured as function of the temperature gradient.

Table 5.5 gives the values of the apparent Seebeck coefficients, which are obtained by dividing the measured total potential by temperature difference.

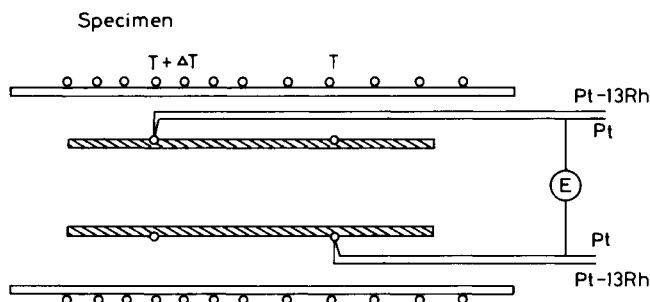


Fig. 5.11. Sectional view of a tube solid electrolyte of ZrO_2 -0.15CaO and of an aluminal tube with dense and loose windings of nichrome wire to produce the temperature gradient (After Goto, Ito and Someno⁽³³⁾).

TABLE 5.5

Comparison of the apparent Seebeck coefficients of ZrO_2 based solid electrolytes and ThO_2 (1 atm = 101.325 kPa)

(Compiled by Goto, Nagata and Ukyo⁽¹⁰⁾)

Investigators	Composition of Electrolyte	ψ (mVK ⁻¹)	T (K)	p (atm)	Ref.
Fischer	0.12 CaO + 0.88 ZrO ₂	-0.43 *	1273	1	(30)
Ruka et al.	0.15 CaO + 0.85 ZrO ₂	-0.44	973 ~ 1573	1	(31)
Stein et al.	0.15 CaO + 0.85 ZrO ₂	-0.26	1473	0.21	(32)
Goto et al.	0.08 CaO + 0.92 ZrO ₂	-0.57	1473	1	(33)
Chebotin et al.	0.15 CaO + 0.85 ZrO ₂	-0.42	1373	1	(34)
		-0.45	1373	0.21	
Pizzini et al.	0.208 CaO + 0.792 ZrO ₂	-0.408	1373	1	(35)
	0.215 CaO + 0.785 ZrO ₂	-0.397	1373	1	
	0.255 CaO + 0.745 ZrO ₂	-0.389	1373	1	
	0.31 CaO + 0.69 ZrO ₂	-0.382	1373	1	
	0.19 Y ₂ O ₃ + 0.81 ZrO ₂	-0.354	1373	1	
Fridman et al.	0.1 Y ₂ O ₃ + 0.9 ZrO ₂	-0.47	1448	0.21	(36)
	0.2 Y ₂ O ₃ + 0.8 ZrO ₂	-0.44	1448	0.21	
	0.3 Y ₂ O ₃ + 0.7 ZrO ₂	-0.43	1448	0.21	
	0.4 Y ₂ O ₃ + 0.6 ZrO ₂	-0.42	1448	0.21	
Volchenkova et al.	0.125 Sc ₂ O ₃ + 0.875 ZrO ₂	-0.4	1273	1	(37)
Fischer and Pieper	0.13 CaO + 0.87 ZrO ₂	-0.3	1373 ~ 1923	0.21	(38)
Alcock et al.	0.15 CaO + 0.85 ZrO ₂	-0.43 ~ -0.41	1300 ~ 1625	1	(39)
Tallan et al.	ThO ₂	-0.2 ~ 1.3	1273	10 ⁻²⁰ ~ 1	(40)

* The value is defined negative when the potential is negative at higher temperature.

Fig. 5.12 is an isoelectromotive force lines diagram reported by Goto, Ito and Someno⁽³³⁾ for isobaric oxygen of 0.21 atm and with different temperatures T_1 and T_2 at the electrodes.

The electromotive force in mV for T_1 and T_2 of ZrO_2 -CaO is shown on the left and for ThO_2 -CaO on the right. The negative electrode was the electrode with higher temperature.

According to this diagram, if there is a temperature difference of 10°C , the EMF would be -5.3 mV for ZrO_2 -CaO solution. Of this $+0.95\text{ mV}$ would be due to $\Delta\psi_{\text{oxide}} + \Delta\psi_{\text{Pt}}$ in the following equation and -6.35 mV to $\Delta\psi_{\text{het}}$, which is caused by the virtual cell reaction:

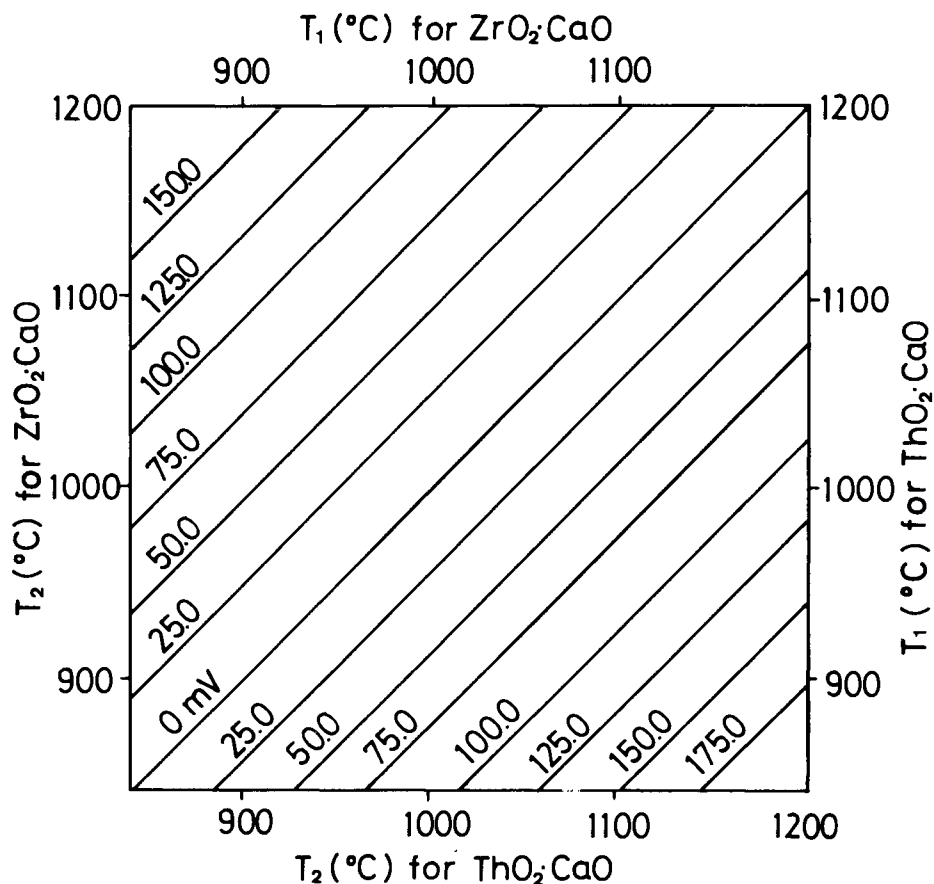


Fig. 5.12. Thermoelectromotive force in milli-Volts of ZrO_2 -0.15CaO tubes and ThO_2 -0.15CaO, when both ends of the tubes are heated at T_1 and T_2 (After Goto, Ito and Someno⁽³³⁾).

$$\Delta\psi_t = \Delta\psi_{\text{het}} + \Delta\psi_{\text{oxide}} + \Delta\psi_{\text{Pt}} \quad (5-45)$$

where $\Delta\psi_t$ is the measurable total potential, $\Delta\psi_{\text{het}}$, the heterogeneous potential due to virtual cell reaction, $\Delta\psi_{\text{oxide}}$, the homogeneous thermal potential of oxide system and $\Delta\psi_{\text{Pt}}$, the homogeneous thermal potential of platinum electrodes⁽⁴¹⁾⁽⁴²⁾.

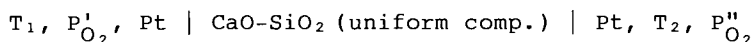
The three terms of the right side of Eq. (5-45) correspond to the three terms of the right side of Eq. (5-43), respectively⁽⁴¹⁾⁽⁴²⁾.

In Eq. (5-43) the difference of chemical potential of oxygen gas at two temperatures can be calculated from thermodynamic data on oxygen gas.

According to measurements made by Cusack and Kendall⁽⁴²⁾, $\Delta\psi_{\text{Pt}}$ is very small, for example, 0.025 micro-Volts/K at 1230°C. This term is therefore neglected in the following discussion.

The absolute thermopotential of the oxide phase itself can then be estimated as shown by lower chain lines in Figs. 5.13 and 5.14. The potentials are negative when the negative electrode is at the higher temperature, according to the international convention. The points plotted in white and black indicate the total measured potential in two independent runs. The temperature is the average temperature of two electrodes and the potential is in mV per degree K.

For the thermopotential measurement in the liquid oxide mixture, the following thermogalvanic cell was constructed by Ukyo and Goto⁽⁴³⁾.



Temperature is different at both electrodes and thus, the thermal diffusion in CaO-SiO₂ melt will take place but initially the composition can be maintained uniform, because the diffusion is usually slow. The initially measurable electromotive force of this type of cell has been fully discussed by Holtan, Mazur and DeGroot⁽⁴¹⁾.

In the liquid solution of CaO-SiO₂, the charge carrier is mainly Ca²⁺ as already discussed in Chapter 3.

The measurable total potential, $\Delta\psi_t$, can therefore be given by

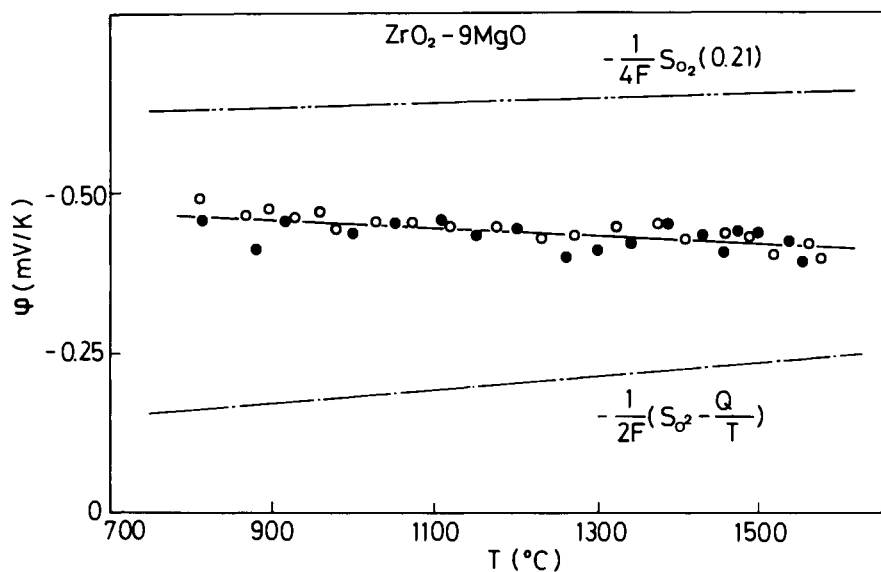


Fig. 5.13. Relation between thermoelectric power of ZrO_2-9MgO and temperature (After Ukyo and Goto⁽⁴³⁾).

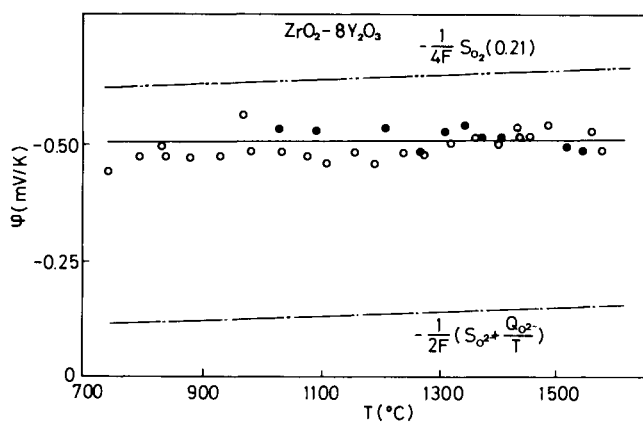


Fig. 5.14. Relation between thermoelectric power of $\text{ZrO}_2-8\text{Y}_2\text{O}_3$ and temperature (After Ukyo and Goto⁽⁴³⁾).

$$\Delta\psi_t = \frac{1}{4F} [\mu_{O_2}(T_2, P_{O_2}'') - \mu_{O_2}(T_1, P_{O_2}')] - \frac{1}{2F} [\mu_{CaO}(T_2) - \mu_{CaO}(T_1)]$$

$$+ \frac{1}{2F} \int_{T_1}^{T_2} \left(\bar{S}_{Ca^{2+}} + \frac{Q_{Ca^{2+}}}{T} \right) dT - \frac{1}{F} \int_{T_1}^{T_2} \left(\bar{S}_e^{Pt} + \frac{Q_e^{Pt}}{T} \right) dT$$

(5-46)

where $\bar{S}_{Ca^{2+}}$ is partial molal entropy of Ca^{2+} in liquid $CaO-SiO_2$ phase and $Q_{Ca^{2+}}$ is its heat of transfer.

The experimental cell with two platinum electrodes dipped in the liquid phase at different temperatures is shown in Fig. 5.15.

The total potential measured for liquid $PbO-25wt\%SiO_2$ is shown in Fig. 5.16 and for liquid $40wt\%CaO-40\%SiO_2-20\%Al_2O_3$ in Fig. 5.17.

From the value of $\Delta\psi_{oxide}$ obtained above it would be possible to evaluate $Q_{Ca^{2+}}$, if the partial molal entropy of Ca^{2+} could be determined. It would therefore be helpful to derive the relation between L_{ik} , defined by Eqs. (5-1) to (5-4), and Q_i .

For this purpose, one should start from a clear definition of heat of transfer often used in thermodiffusion problems.

The heat of transfer of Ca^{2+} ions, Si^{4+} ions and O^{2-} ions are defined by

$$Q_{Ca^{2+}} = \left(\frac{j_4}{j_1} \right) \Delta T = 0, j_2 = j_3 = 0 \quad (5-47)$$

$$Q_{Si^{4+}} = \left(\frac{j_4}{j_2} \right) \Delta T = 0, j_1 = j_3 = 0 \quad (5-48)$$

$$Q_{O^{2-}} = \left(\frac{j_4}{j_3} \right) \Delta T = 0, j_1 = j_2 = 0 \quad (5-49)$$

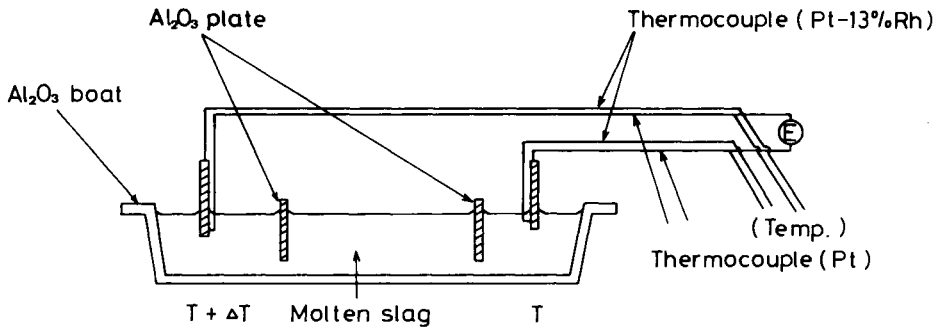


Fig. 5.15. Sectional view of a long alumina boat containing a liquid oxide with temperature gradient along the boat (After Ukyo and Goto⁽⁴³⁾).

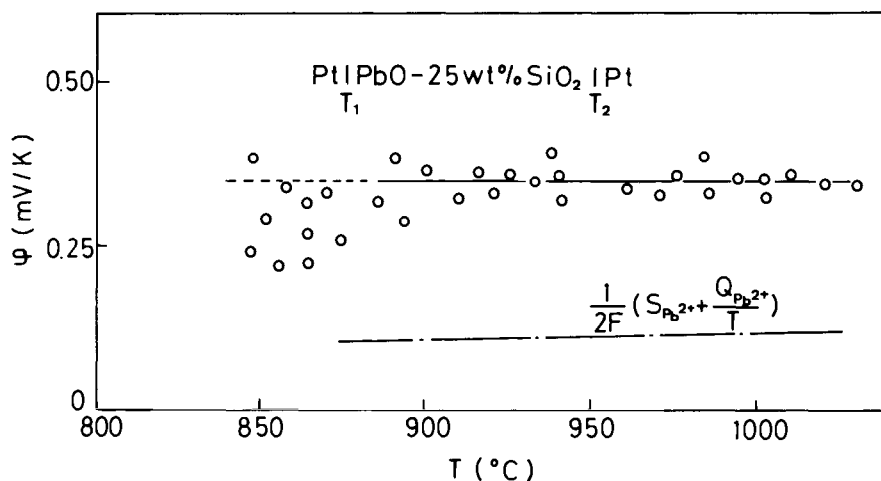


Fig. 5.16. Relation between thermoelectromotive force (mV/K) and temperature for liquid PbO-25wt%SiO₂ (After Ukyo and Goto⁽⁴³⁾).

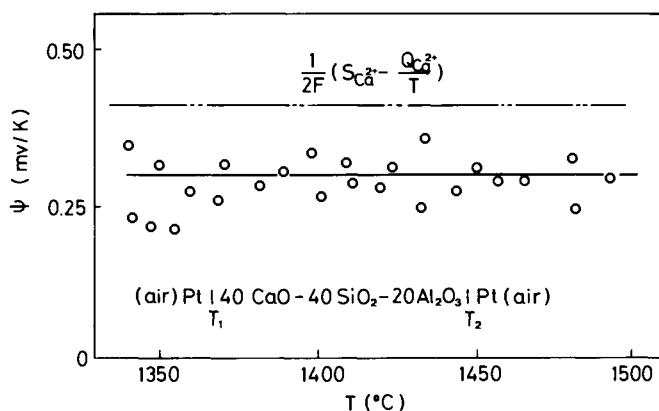


Fig. 5.17. Relation between thermoelectromotive force (mV/K) and temperature for liquid CaO-SiO₂-Al₂O₃ (After Ukyo and Goto⁽⁴³⁾).

where j_1 are given by Eqs. (5-1) to (5-4).

Thus, if one inserts Eqs. (5-1), (5-2), (5-3) and (5-4) to the above three equations, the relation between L_{ik} and Q_i can be obtained as follows;

$$L_{14} = L_{11}Q_1 + L_{21}Q_2 + L_{31}Q_3 \quad (5-50)$$

$$L_{24} = L_{12}Q_1 + L_{22}Q_2 + L_{32}Q_3 \quad (5-51)$$

$$L_{34} = L_{13}Q_1 + L_{23}Q_2 + L_{33}Q_3 \quad (5-52)$$

where $C_1Q_1 + C_2Q_2 + C_3Q_3 = 0$, according to DeGroot and Mazur⁽¹¹⁾.

These relations of Eqs. (5-50) to (5-52) seem, at present, not to be so helpful to evaluate L_{ik} as long as all Q_i s are not known. These relations would have practical meanings, however, if some of heat of transfers of ions will be experimentally measured.

(d) Measurement of heat conductivity of solid and liquid oxides. The heat conductivity is directly related to the transport coefficient by Eq. (5-34).

There are several methods to measure heat conductivity of solid or liquid materials. However, only the "hot wire method" will be explained in this section⁽⁴⁴⁾.

A sectional view of a crucible containing liquid oxide with thin hot platinum wire hung vertically is shown in Fig. 5.18.

When a constant electric current is supplied to the platinum heating wire to generate Joule heat, the rate of temperature rise of the platinum wire is controlled by the rate of heat transfer

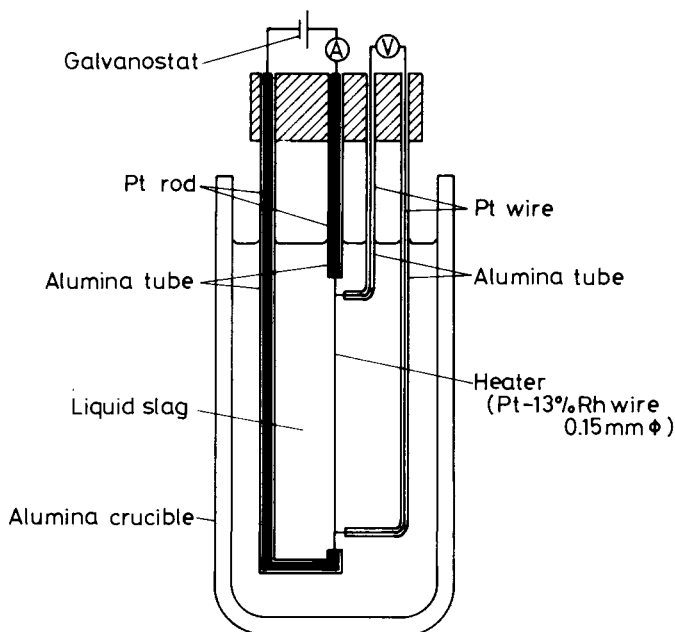


Fig. 5.18. Sectional view of an alumina crucible containing a liquid oxide and a thin platinum wire to measure the heat conductivity of the oxide (After Nagata and Goto⁽⁴⁴⁾).

through the liquid oxide. The temperature rise of the wire may be measured by change in its electrical resistance.

According to Fourier's second law of heat conduction, the change of temperature with time, $\partial T/\partial t$ is given by

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) \quad (5-53)$$

The solution of this differential equation for long times (usually longer than 1 second) gives the relation of

$$\lambda = \frac{q}{4} \cdot \frac{\Delta \ln t}{\Delta T} \quad (5-54)$$

where λ is heat conductivity, q is Joule heat generated by 1 cm of the platinum wire, t is time and T is temperature. Experimentally, the linear relation between $\ln t$ and T is very well satisfied between 1 sec and 30 sec after the flow of the current.

The heat conductivity of solid CaF_2 and liquid CaF_2 with its melting point of about 1420°C is shown in Fig. 5.19. The white points

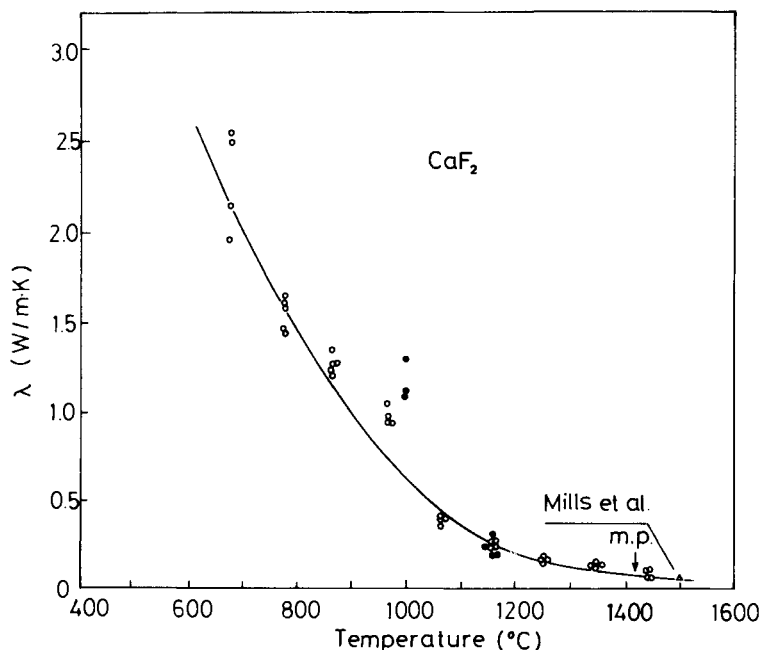


Fig. 5.19. Thermal conductivity of crystalline and liquid CaF_2 as a function of temperature (After Nagata and Goto⁽⁴⁴⁾).

plotted are measured values when the temperature is lowered from the liquid state. The solid points are obtained during reheating of the cell assembly.

The triangular point at 1500°C were obtained by Mills and his coworkers⁽⁴⁵⁾.

Fig. 5.20 shows heat conductivity of $50\text{wt}\%\text{Na}_2\text{O}-50\%\text{SiO}_2$ with melting point or liquidus temperature at about 1070°C . The points with different marks are measurements by independent experimental runs.

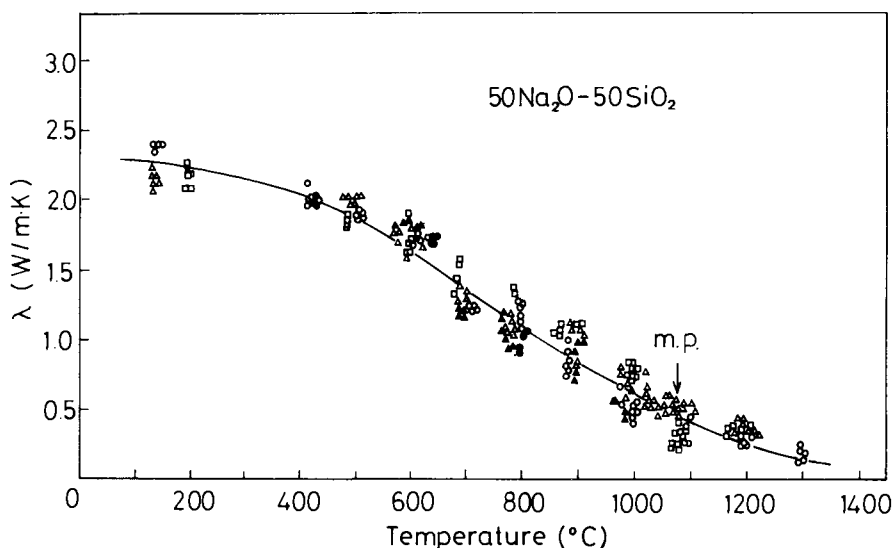


Fig. 5.20. Thermal conductivity of $50\text{wt}\%\text{Na}_2\text{O}-50\%\text{SiO}_2$ in glassy solid state and in liquid state (After Nagata and Goto⁽⁴⁴⁾).

Fig. 5.21 shows the heat conductivity of $33\text{wt}\%\text{Na}_2\text{O}-67\%\text{SiO}_2$ with a melting point of about 860°C .

Fig. 5.22 summarizes heat conductivities measured on the $\text{Na}_2\text{O}-\text{SiO}_2$ binary system with different compositions.

Fig. 5.23 is a summary of heat conductivities in CaO -based systems.

The details of experimental methods and the comparison to the data by other investigators are not given in this section but reference (44) includes these in details with comments on experimental errors.

The value of L_{44} defined by Eq. (5-4) is equal to $T\lambda$, and thus the information on heat conductivity of oxide system would be

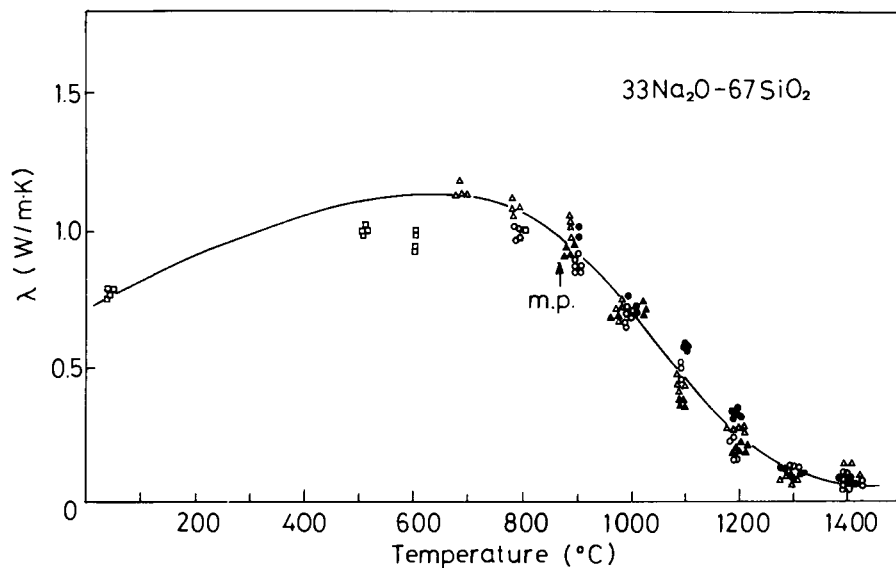


Fig. 5.21. Thermal conductivity of 33wt%Na₂O-67%SiO₂ in glassy solid state and liquid state (After Nagata and Goto⁽⁴⁴⁾).

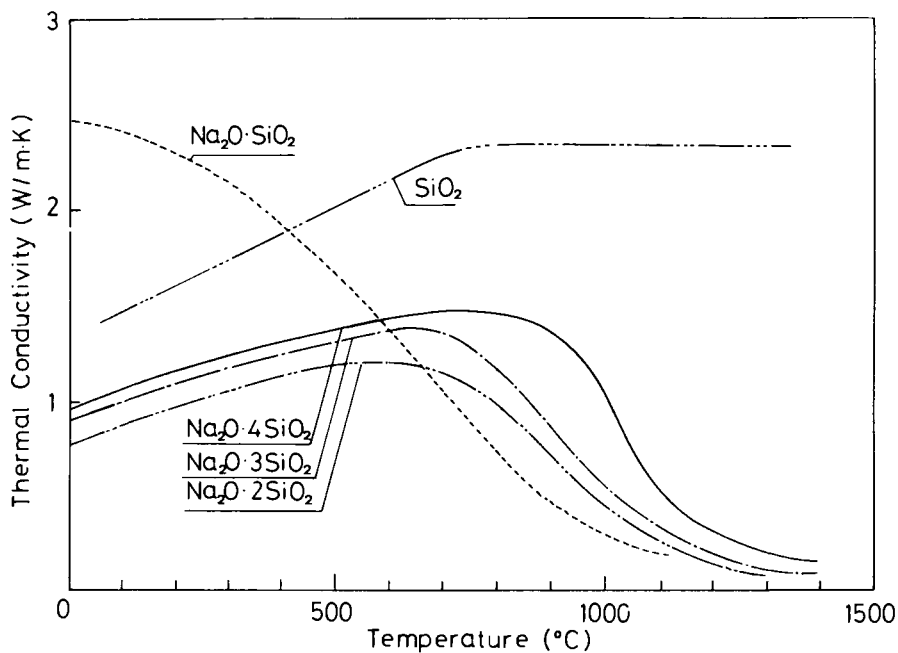


Fig. 5.22. A summary of heat conductivity of Na₂O-SiO₂ mixtures in glassy solid state and liquid state (After Nagata and Goto⁽⁴⁴⁾).

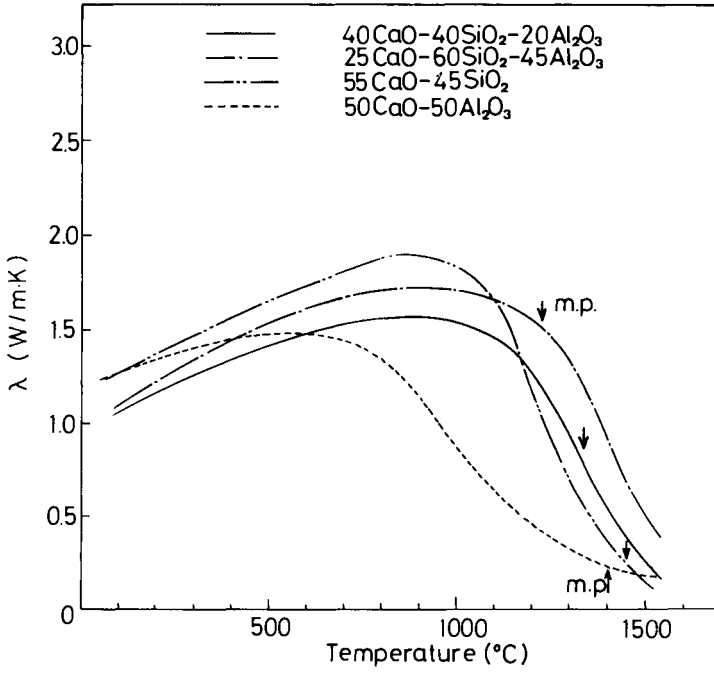


Fig. 5.23. Thermal conductivities of various CaO-based oxide mixtures in glassy solid state and liquid state (After Nagata and Goto⁽⁴⁴⁾).

helpful to estimate all terms of transport coefficients defined by Eqs. (5-1) to (5-4).

REFERENCES TO CHAPTER 5

- (1) I. Prigogine, "Introduction to Thermodynamics of Irreversible Processes", Interscience Publishers, London, (1961).
- (2) K.S. Goto, H. Schmalzried and K. Nagata, *Tetsu-to-Hagane*, 61 (1975), pp. 2794-2804.
- (3) K. Nagata and K.S. Goto, *J. Electrochem. Soc.*, 123 (1976), pp. 1814-1820.
- (4) K.S. Goto, *Proceedings of International Conference on Physical Chemistry and Steelmaking*, Versailles, France, October, (1978).
- (5) H. Fujita and L.J. Gosting, *J. Am. Chem. Soc.*, 78 (1956), p. 1099.
- (6) J.S. Kirkaldy, *J. Phys.*, 35 (1957), p. 435.
- (7) L.S. Darken, *Trans. AIME*, 174 (1948), p. 184.
- (8) C. Wagner, *Z. Physik. Chem.*, B21 (1933), p. 25.
- (9) R.W. Laity, "The Structure and Properties of Ionic Melts", Aberdeen University Press, Aberdeen, (1962).
- (10) K.S. Goto, K. Nagata and Y. Ukyo, *Canadian Metall. Q.*, 20 (1981), pp. 117-127.
- (11) S.R. DeGroot and P. Mazur, "Non-Equilibrium Thermodynamics", North-Holland Pub. Company, Amsterdam, (1969), p. 284, Eq. (272).
- (12) H. Towers, M. Paris and J. Chipman, *J. Met.*, 5 (1953), p. 1455.
- (13) H. Towers and J. Chipman, *ibid.*, 9 (1957), p. 769.
- (14) T. Saito and K. Maruya, *Nippon Kinzoku Gakkaishi*, 21 (1957), p. 728.
- (15) K. Niwa, *ibid.*, 21 (1957), p. 304.
- (16) J. Henderson, L. Yang and G. Derge, *Trans. Met. Soc. AIME*, 221 (1961), p. 56.
- (17) A.E. Martin and G. Derge, *Trans. AIME*, 154 (1943), p. 104.
- (18) R. Kammel and H. Winterhager, *Z. Erzbergbau Metallhüttenw.*, 18 (1965), p. 9.
- (19) M. Kato and S. Minowa, *Tetsu-to-Hagane*, 52 (1966), p. 580.
- (20) O.A. Esin and A.K. Kirianov, *Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk*, 12 (1955), p. 28.
- (21) V.I. Markin, L.A. Schvartsman and S.F. Khokhlov, "Metallugiya i Metallovedenie", *Izdatelystovo Akademiya Nauk SSSR, Moscow*, (1958), p. 23.
- (22) A. Adachi and K. Ogino, *Yoyuen*, 5 (1962), p. 1149 (in Japanese).
- (23) A.G. Thomas and L.R. Barrett, *J. Soc. Glass Technol.*, 40 (1956), 179T.
- (24) J.C. Fulton, N.J. Grant and J. Chipman, *Trans. AIME*, 197 (1953), p. 185;
J.C. Fulton and J. Chipman, *ibid.*, 200 (1954), p. 1136;
F.C. Langenberg and J. Chipman, *Trans. Met. Soc. AIME*, 215 (1959), p. 958;
these are compiled by J.F. Elliot, M. Gleiser and V. Ramakrishna, "Thermochemistry for Steelmaking" Vol. 2, Pergamon Press, London, (1963), pp. 589-593.
- (25) H. Sugawara, K. Nagata and K.S. Goto, *Metall. Trans.*, 8B (1977), pp. 605-612.
- (26) Y. Ukyo and K.S. Goto, *Metall. Trans.*, 12B (1981), pp. 449-454.
- (27) Y. Ukyo and K.S. Goto, *Tetsu-to-Hagane*, 68 (1982), pp. 1971-1980.
- (28) "Thermophysical Properties of Matter" The TPRC. Data Series Vol. 1, edited by Y.S. Touloukian, R.W. Powell and P.G. Klements, Macmillan Corp., (1967).
- (29) T. Emi and M. Shimoji, *Acta Metall.*, 16 (1968), pp. 1098-1100.
- (30) W. Fischer, *Z. Naturforsch.*, A22 (1967), p. 1575.
- (31) R.J. Ruka, J.E. Bauerle and L. Dykstra, *J. Electrochem. Soc.*, 115 (1968), p. 479.
- (32) G. Stein, A. Lecante, M. Guillou and J.C.R. Millet, *Acad. Sci. Paris*, 267 (1968), p. 1660.

- (33) K.S. Goto, T. Ito and M. Someno, *Trans. Met. Soc. AIME*, 245 (1969), p. 1662.
- (34) V.N. Chebotin, S.L. Fridman and S.F. Pal'quev, *Soviet Electrochem.*, 6 (1970), p. 1257.
- (35) S. Pizzini, C. Riccardi, V. Wagner and C. Sinistri, *Z. Naturforsch.*, A25 (1970), p. 559.
- (36) S.L. Fridman, S.F. Pal'quev and V.N. Chebotin, *Soviet Electrochem.*, 5 (1969), p. 325.
- (37) Z.S. Volchenkova, S.F. Pal'quev, S.L. Fridman and N.F. Sizitseva, *Soviet Electrochem.*, 9 (1973), p. 331.
- (38) W.A. Fischer and C. Pieper, *Arch. Eisenhüttenw.*, 44 (1973), p. 251.
- (39) C.B. Alcock, K. Fitzner and K.T. Jacob, *J. Chem. Thermodynamics*, 9 (1977), p. 1011.
- (40) N.M. Tallan and I. Bransky, *J. Electrochem. Soc.*, 118 (1971), p. 345.
- (41) H. Holtan Jr., P. Mazur and S.R. DeGroot, *Physica*, 19 (1953), pp. 1109-1118.
- (42) N. Cusack and P. Kendall, *Proc. Phys. Soc., London*, 72 (1958), p. 898.
- (43) Y. Ukyo and K.S. Goto, *Tetsu-to-Hagane*, 69 (1983), pp. 67-72.
- (44) K. Nagata and K.S. Goto, *Proceedings of Second International Symposium on Metallurgical Slags and Fluxes*, edited by H.A. Fine and D.R. Gaskell, (1984), pp. 875-889, published by Metall. Soc. AIME.
- (45) K.C. Mills, J.S. Powell, J.W. Bryant and B.J. Keene, *Proceedings of First International Symposium on Metallurgical Slags*, Session 7, No. 2 paper, Halifax, Canada, (1980).

Chapter 6

EQUILIBRIUM ELECTROMOTIVE FORCE OF GALVANIC CELLS WITH SOLID ELECTROLYTES OF OXYGEN ANION CONDUCTION

6.1 VIRTUAL CELL REACTION AND ELECTROMOTIVE FORCE

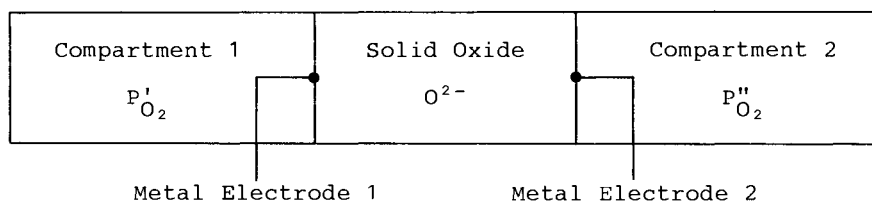
This chapter will discuss anion conduction in solid oxides at high temperature. When the electrical charge is carried through solid electrolyte only by migration of O^{2-} , the virtual cell reactions are usually very simple and observed electromotive forces are in good agreement with the theoretical ones.

In 1957, Kiukkole and C. Wagner⁽¹⁾ successfully demonstrated that ZrO_2 - or ThO_2 -based solid solution with an oxide of aliovalent metals can be used for the Galvanic cells above about $600^\circ C$. After this impressive experiment, hundreds of studies on this type of Galvanic cell have been published all over the world.

A branch of science known as "Solid State Electrochemistry" is believed to have been initiated by this paper of Kiukkole and C. Wagner⁽¹⁾.

In the following section, the physical meaning of the electromotive force is concisely explained and several examples of thermodynamic studies by this type of Galvanic cell are given. During progress of solid state electrochemistry, other types of high temperature Galvanic cells have been also developed with solid electrolytes with non-oxygen conduction. These Galvanic cells will be discussed in next Chapter 7.

When a solid oxide has the ionic conductivity only by migration of oxygen anion, it can be used as the electrolyte in the following Galvanic cell, sometimes called as oxygen concentration cell:



If one considers the above cell as a closed thermodynamic system, the Gibbs free energy change caused by supplying n faradays

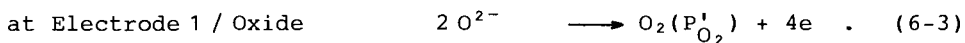
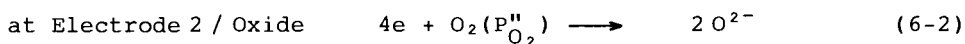
of electrons is equal to the reversible electrical work as long as temperature and total pressure remain constant. Namely,

$$\Delta G = -nFE \quad (6-1)$$

where G is Gibbs free energy, E is the reversible equilibrium electromotive force of the cell, and F is Faraday constant.

The minus sign is given to the right hand side of Eq. (6-1) in accordance to the international convention; "The electromotive force is expressed positive, when the left-hand-side electrode of the cell equation is the negative electrode."

When 4 Faradays of electrons are externally supplied to Metal Electrode 2 and taken out from Metal Electrode 1, the oxygen anion would migrate to the left. Under this condition, the electrochemical reactions at the two interfaces would take place as follows;



Summing up the two equations, one can have the virtual reaction of



Thus, the Gibbs free energy change of the virtual cell reaction is equal to that caused by change in partial pressure of oxygen at a constant temperature and constant total pressure.

$$\Delta G = RT \ln \frac{P'_{O_2}}{P''_{O_2}} \quad (6-5)$$

The combination of Eqs. (6-1) and (6-5) gives

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \quad (6-6)$$

This equation has been satisfied by a great number of experiments using ZrO_2 -CaO, ZrO_2 -MgO, etc. as the solid electrolyte above about 600°C . These types of oxides with oxygen anion conduction are classified as superionic conductors in Table 2.1 of Chapter 2.

However, as discussed in Chapter 2, even superionic conduction would have a certain magnitude of electronic conduction under

extremely lower or higher oxygen pressure. In such case, the amount of transfer of oxygen gas caused by an external current would be decreased by migration of electronic defects in the electrolyte.

Because the ionic transference number is a function of oxygen pressure (see Chapter 2), C. Wagner⁽²⁾ derived the following equation in 1933 for the electromotive force of the Galvanic cell;

$$E = \frac{1}{4F} \int_{\mu_{O_2}'}^{\mu_{O_2}''} t_{ion} d\mu_{O_2} \quad , \quad (6-7)$$

where μ_{O_2}'' and μ_{O_2}' are chemical potential of oxygen at the right and left electrode, respectively and t_{ion} is transference number of oxygen anion. Of course, if the t_{ion} is unity, Eq. (6-7) is reduced to Eq. (6-6).

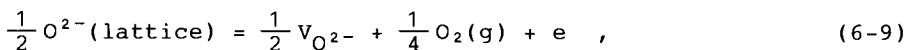
Schmalzried⁽³⁾⁽⁴⁾ has proposed an elegant way to integrate this equation.

The transference number of an ionic species is usually defined by

$$t_{ion} \equiv \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_e + \sigma_p} = \left(1 + \frac{\sigma_e}{\sigma_{ion}} + \frac{\sigma_p}{\sigma_{ion}} \right)^{-1} \quad , \quad (6-8)$$

where σ with the subscript is the partial conductivity of the species of the subscript as given in Chapter 2.

As already given by Eq. (2-6), CaO or MgO is dissolved into ZrO_2 producing very large concentration of oxygen anion vacancies. Because of this large concentration of anion vacancies, the following reaction is believed most probable.



where $V_{O^{2-}}$ is oxygen vacancies and e is excess electrons.

Because $V_{O^{2-}}$ is essentially constant, the equilibrium constant K is defined by

$$K \equiv [P_{O_2}]^{\frac{1}{4}} [n_e] \quad , \quad (6-10)$$

where $[n_e]$ is concentration of excess electrons in the solid electrolyte.

Because the electrical conductivity is proportional to the concentration of charge carriers, the partial conductivity of

electrons, σ_e can be expressed by

$$\sigma_e = \sigma_e^\circ P_{O_2}^{-\frac{1}{4}} \exp\left(-\frac{\Delta H^\circ}{RT}\right) \quad (6-11)$$

where σ_e° is a material constant and its physical meaning has been fully discussed in Chapter 2. The standard enthalpy of the reaction of Eq. (6-9) is expressed ΔH° and included in Eq. (6-11).

Here, Schmalzried has introduced a special oxygen pressure expressed by $P_\ominus$, at which the electronic conductivity becomes exactly equal to the ionic partial conductivity. Inserting this parameter $P_\ominus$ into Eq. (6-11), one can have

$$\sigma_{ion} = \sigma_e^\circ P_\ominus^{-\frac{1}{4}} \exp\left(-\frac{\Delta H^\circ}{RT}\right) \quad (6-12)$$

Dividing Eq. (6-11) by Eq. (6-12), one can have the ratio of σ_e to σ_{ion} in right hand side of Eq. (6-8) as follows;

$$\frac{\sigma_e}{\sigma_{ion}} = \left(\frac{P_{O_2}}{P_\ominus} \right)^{-\frac{1}{4}} \quad (6-13)$$

By the similar procedure, Schmalzried has obtained the relation of

$$\frac{\sigma_p}{\sigma_{ion}} = \left(\frac{P_{O_2}}{P_\oplus} \right)^{\frac{1}{4}} \quad (6-14)$$

where $P_\oplus$ means a special oxygen pressure, at which the partial positive-hole conductivity becomes exactly equal to the partial ionic conductivity. The values of $P_\ominus$ and $P_\oplus$ are functions of temperature and composition of solid electrolytes. Inserting Eqs. (6-13) and (6-14) into right hand side of Eq. (6-8), one can have

$$t_{ion} = \left[1 + \left(\frac{P_{O_2}}{P_\ominus} \right)^{-\frac{1}{4}} + \left(\frac{P_{O_2}}{P_\oplus} \right)^{\frac{1}{4}} \right]^{-1} \quad (6-15)$$

Because $d\mu_{O_2} = RT d\ln P_{O_2}$, inserting Eq. (6-15) to Eq. (6-7) one can integrate it easily as follows;

$$E = \frac{RT}{F} \left[\ln \frac{P_\ominus^{\frac{1}{4}} + P_{O_2}''^{\frac{1}{4}}}{P_\ominus^{\frac{1}{4}} + P_{O_2}'^{\frac{1}{4}}} + \ln \frac{P_\oplus^{\frac{1}{4}} + P_{O_2}'^{\frac{1}{4}}}{P_\oplus^{\frac{1}{4}} + P_{O_2}''^{\frac{1}{4}}} \right] \quad (6-16)$$

This equation gives a theoretical electromotive force for a given P_{O_2}' and P_{O_2}'' at two electrodes, provided that two material constants,

$P_{\ominus}$ and $P_{\oplus}$ are known for the solid electrolyte used.

A few special cases will be discussed;

(a) If the sequence of oxygen pressure is

$$P_{\ominus} \ll P_{\oplus} \ll P'_{O_2} < P''_{O_2} \quad \text{or} \quad P'_{O_2} < P''_{O_2} \ll P_{\ominus} \ll P_{\oplus},$$

E in Eq. (6-16) is zero. In this case, the oxide behaves as a semiconductor without any virtual chemical reaction. It is obvious that the EMF is zero, because it is no longer a Galvanic cell.

(b) If two oxygen pressures P'_{O_2} and P''_{O_2} satisfy the relation of

$$P_{\ominus} \ll P'_{O_2} < P''_{O_2} \ll P_{\oplus},$$

Eq. (6-16) can be reduced to Eq. (6-6).

(c) The condition of

$$P'_{O_2} \ll P_{\ominus} < P''_{O_2} \ll P_{\oplus}$$

gives a constant EMF which depends only on the oxygen pressure of P''_{O_2} ,

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P_{\ominus}}.$$

This relation can be used to determine the value of $P_{\ominus}$ for various solid oxides.

(d) In case of

$$P_{\ominus} \ll P'_{O_2} \ll P_{\oplus} \ll P''_{O_2},$$

the EMF can be given by

$$E = \frac{RT}{4F} \ln \frac{P_{\oplus}}{P'_{O_2}}.$$

This equation can be used to determine the value of $P_{\oplus}$.

(e) The condition

$$P'_{O_2} \ll P_{\ominus} \ll P_{\oplus} \ll P''_{O_2}$$

yields

$$E = \frac{RT}{4F} \ln \frac{P_{\oplus}}{P_{\ominus}}.$$

Fig. 6.1 shows the change of the EMF, when only P'_{O_2} is changed with a fixed P''_{O_2} under the condition $P_{\ominus} \ll P''_{O_2} \ll P_{\oplus}$.

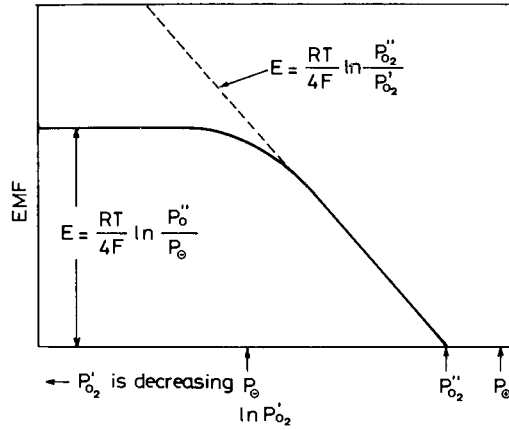


Fig. 6.1. Electromotive force of $P'_{O_2}, Pt | ZrO_2-XO | Pt, P''_{O_2}$ when P'_{O_2} is changed with a fixed P''_{O_2} at $P_Θ \ll P''_{O_2} \ll P_Θ$.

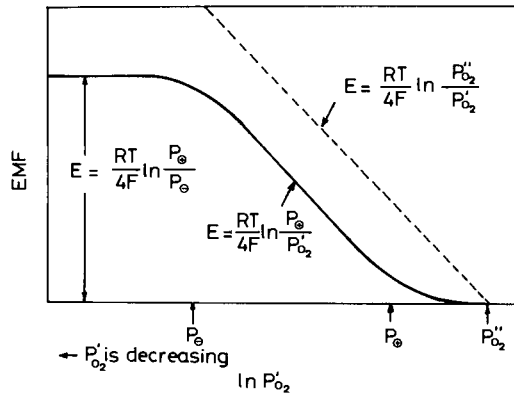
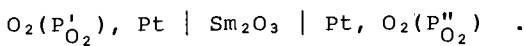


Fig. 6.2. Electromotive force of $P'_{O_2}, Pt | ZrO_2-CaO | Pt, P''_{O_2}$ when P'_{O_2} is changed with a fixed P''_{O_2} at $P_Θ \ll P_Θ \ll P''_{O_2}$.

Fig. 6.2 shows the change of the EMF, when only P'_{O_2} is changed with a fixed P''_{O_2} but under the condition $P_Θ \ll P_Θ \ll P''_{O_2}$.

These two figures satisfy all above special cases of (b) to (f).

Tare and Schmalzried⁽⁵⁾ have measured the EMF of the following Galvanic cell by changing P'_{O_2} with a fixed P''_{O_2} ;

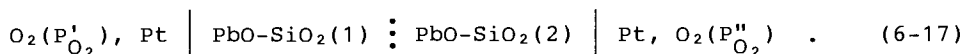


The measured EMF has changed in accordance to that given in Fig. 6.2. Thus, they could calculate the values of $P_{\ominus}$ and $P_{\oplus}$ for solid oxide Sm_2O_3 .

6.2 C. WAGNER'S GENERAL EQUATION OF THE EMF FOR ELECTROLYTES OF MULTI-CHARGE CARRIERS

In the previous section, only the case of simple solid electrolytes has been discussed. The composition of the electrolyte is uniform and the charge is carried by O^{2-} ions with minor carriers of electrons or positive holes.

However, the theoretical EMF is more complicated if the oxide electrolyte has a composition difference. An example is glassy PbO-SiO_2 electrolyte with two different compositions.



The electrolyte is composed of two lead silicate glasses with different compositions (1) and (2).

Possible charge carriers would be Pb^{2+} , Si^{4+} , O^{2-} , excess electron and positive holes. If all of these carriers could have significant contributions to electrical conduction, the virtual cell reaction would be very complicated.

However, let us consider a simple case where the charge is carried predominantly by Pb^{2+} (see Table 2.1 for fused PbO-SiO_2). When 4 faradays of electrons are supplied to the Galvanic cell from the external source, the virtual cell reaction would involve the transfer of one mole of oxygen gas in one direction and the transfer of two moles of PbO in reverse. Thus, the reversible electromotive force is given by

$$E = \frac{RT}{4F} \ln \frac{P''_{\text{O}_2}}{P'_{\text{O}_2}} - \frac{RT}{2F} \ln \frac{a''_{\text{PbO}}}{a'_{\text{PbO}}} \quad (6-18)$$

where a'_{PbO} and a''_{PbO} are the activities of PbO in binary glassy solutions of PbO and SiO_2 with different compositions of (1) and (2), respectively.

If the PbO-SiO_2 electrolyte could be purely an oxygen anion conductor, the virtual cell reaction would involve only the transfer of oxygen gas even with the composition difference. If this could be true, Eq. (6-18) would be reduced to Eq. (6-6).

This means that the value of the second term of Eq. (6-18) depends

on the transference number of Pb^{2+} . Furthermore, if the transference number of Si^{4+} can not be neglected, silicon would be transferred and a third term would be added to Eq. (6-18).

Generally, transference numbers of various charge carriers are functions of oxygen and the composition of the oxide under consideration at a fixed temperature.

C. Wagner⁽⁶⁾ has sliced the electrolyte as shown in Fig. 6.3 to derive a general theoretical equation for electrolytes of multi-charge carriers. He considered the virtual cell reactions between left and right faces of each sliced electrolyte with thickness of dx . The virtual cell reactions of many sliced electrolytes have been summed up and then expressed by integration with respect to distance x . Since the oxygen pressure can be assumed to be a simple function of x , C. Wagner obtained the general equation of the electromotive force, which is valid not only for oxide electrolytes but also for any other salt electrolytes, as follows:

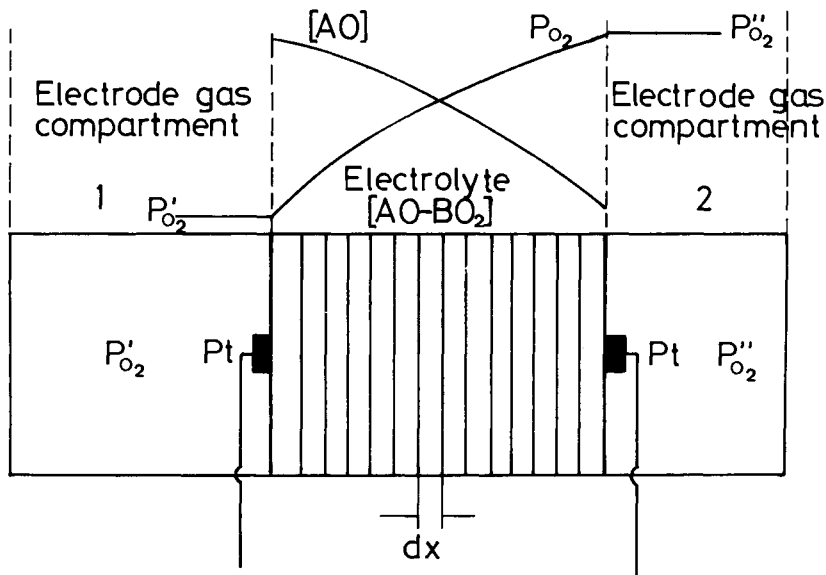


Fig. 6.3. Sliced binary AO-BO_2 oxide electrolyte under gradients of oxygen pressure and concentration of AO (Probable mobile species are A^{2+} , B^{4+} , O^{2-} , electron or positive hole).

$$E = \frac{1}{F} \left[\tilde{\mu}_{[B]}'' - \tilde{\mu}_{[B]}' - \int \sum_{\alpha} t_{\alpha} d\tilde{\mu}_{\alpha,B} - \int t_e d\tilde{\mu}_{[B]} \right] \\ + \frac{1}{F} \left[\sum_{\beta \neq e} \int t_{\beta} d\tilde{\mu}_{A,B} - \int \left(\sum_{\beta \neq e} t_{\beta} \right) d\tilde{\mu}_{A,B} \right] , \quad (6-19)$$

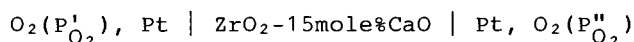
where $\tilde{\mu}_{[B]}$ is the chemical potential per equivalent of the neutral element obtained from an anion, B, by discharging electrons, $\tilde{\mu}_{\alpha,B}$ is the chemical potential per equivalent of a salt (α, B), t_i is the transference number of charge carrier, i , α and β are general symbols for cationic and anionic species, respectively, and A and B are master cation and master anion, respectively.

The only assumption used is local equilibrium at any location in the Galvanic cell. In view of this very general approach, the equation holds for cells with several electrolytes in series contact even with a concentration gradient.

When only a single anionic component is present in the electrolyte, the terms in the second line of Eq. (6-19) cancel each other.

Because Eq. (6-19) seems complicated, the following examples are given for its use.

First, let us apply Eq. (6-19) to the following cell:



The electrolyte, ZrO_2 -CaO has a uniform composition of 15mole%CaO, and the transference number of the oxygen anion is unity. Therefore, the transference numbers are

$$t_{O^{2-}} = 1.0 , \quad t_{Ca^{2+}} = 0 , \quad t_{Zr^{4+}} = 0 .$$

Inserting these numbers to Eq. (6-19) gives

$$E = \frac{1}{F} [\tilde{\mu}_{[O_2]}'' - \tilde{\mu}_{[O_2]}'] .$$

This equation is equal to Eq. (6-6), because

$$\tilde{\mu} = \frac{1}{4} (\mu_{O_2}^{\circ} + RT \ln P_{O_2}) , \quad (6-20)$$

where $\mu_{O_2}^{\circ}$ is the standard chemical potential of oxygen gas per mole.

When the electron transference number can not be neglected, Eq. (6-19) becomes

$$\begin{aligned}
 E &= \frac{1}{F} \left[\tilde{\mu}_{[O_2]}'' - \tilde{\mu}_{[O_2]}' - \frac{1}{4} \int t_e d\mu_{[O_2]} \right] \\
 &= \frac{1}{4F} \int (1 - t_e) d\mu_{[O_2]} \quad . \quad (6-21)
 \end{aligned}$$

This equation (6-21) is equal to Eq. (6-7) because

$$t_{ion} = 1 - t_e \quad .$$

For derivation of Eq. (6-21), Eq. (6-20) is used.

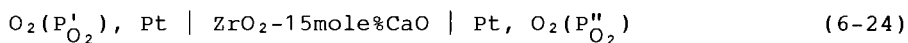
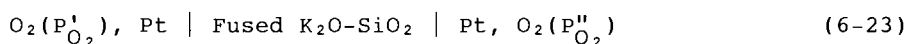
In the case of the Galvanic cell of Eq. (6-17), Eq. (6-19) can be expressed as

$$\begin{aligned}
 E &= \frac{1}{F} \left[\tilde{\mu}_{[O_2]}'' - \tilde{\mu}_{[O_2]}' + \frac{1}{2} \int t_{Pb^{2+}} d\mu_{PbO} + \frac{1}{4} \int t_{Si^{4+}} d\mu_{SiO_2} \right. \\
 &\quad \left. + \frac{1}{4} \int t_e d\mu_{O_2} \right] \quad . \quad (6-22)
 \end{aligned}$$

If the transference number of Pb^{2+} is unity and others are all zero, this equation can be reduced to Eq. (6-18).

The general equation of C. Wagner is very unique in the sense that the theoretical electromotive force can be obtained when transference numbers in the electrolyte are known.

At the end of this section it will be demonstrated, according to Eq. (6-19), that the electromotive force of the following two Galvanic cells is same even with very different charge carriers.



In the above electrolyte of fused K_2O-SiO_2 the potassium K^+ ion is believed as the main charge carrier, so

$$t_{K^+} = 1.0, \quad t_{Si^{4+}} = 0, \quad t_{O^{2-}} = 0, \quad t_e = 0 \quad .$$

When the composition is uniform, $d\mu_{K_2O}$ becomes zero and Eq. (6-19) becomes

$$E = \frac{1}{F} (\tilde{\mu}_{O_2}'' - \tilde{\mu}_{O_2}') = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \quad . \quad (6-6)$$

The EMF of the cell of Eq. (6-24) has been fully discussed in the

above and equal to Eq. (6-6).

By this example, it can be seen that the electromotive force of Galvanic cells is given by Eq. (6-6) as long as the oxide electrolyte has a uniform composition. This is based on the assumption of local equilibrium at any position in the Galvanic cell.

6.3 GALVANIC CELLS WITH SOLID ELECTROLYTES OF OXYGEN ANION CONDUCTION FOR THERMODYNAMIC STUDIES AT HIGH TEMPERATURE

The development of solid electrolytes of ZrO_2 -based or ThO_2 -based anion conductors by Kiukkola and C. Wagner⁽¹⁾ in 1957 made a great contribution to our understanding of solid state electrochemistry at high temperature. They demonstrated that

- (1) the solid solutions of ZrO_2 with MgO , CaO , etc., have extremely good chemical stability even at high temperature,
- (2) the oxygen anion is the predominant charge carrier in a wide temperature and oxygen pressure range, and
- (3) the electrical resistance of the solid electrolytes is very small when they are heated above 600°C .

The above three characteristics are favorable conditions for stable and reversible electromotive forces at high temperature. Condition (1) is needed to avoid any reactions with the electrode materials. Condition (2) is very helpful in simplifying the equation of the theoretical electromotive force as Eq. (6-6). Condition (3) guarantees easy experiments in the sense that the electromotive force measured is very stable even under stray electrical field or under strong electrical noises.

Because of their superior characteristics, these kinds of solid oxide electrolytes have been and will be used by many investigators studying the science of metals and oxides at high-temperature.

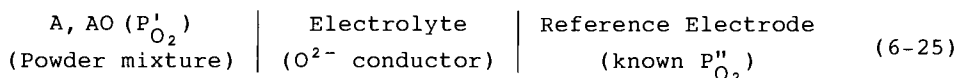
The majority of experimental studies of solid oxides are thermodynamic studies at high temperature. Many hundreds of these thermodynamic studies have been reviewed and documented by three monographs published by Rapp and Shores⁽⁷⁾ in 1970, by Goto and Pluschkell⁽⁸⁾ in 1972, and by Fischer and Janke⁽⁹⁾ in 1975.

Even after 1975, many papers using these electrolytes were published. Kozuka and his coworkers⁽¹¹⁾⁽¹⁴⁾, in particular, have produced a large number of papers using these electrolytes of oxygen-anion conduction.

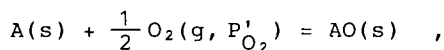
In this section, the author has no intention of making a full documentation of many hundreds of thermodynamic studies. Instead,

the scope of this section is to clarify the principles of thermodynamic measurements by solid state Galvanic cells and to give several examples of the measurements.

(a) Standard free energy of formation of binary and ternary compounds of metal-oxygen system. The following Galvanic cell has been extensively used to determine the standard free energy of formation of binary compounds in metal-oxygen systems:



where A represents a metal and AO is its oxide. In the powder mixture of A and AO, the oxygen pressure is fixed by the reaction equilibrium of



where the standard free energy of formation of a binary compound, AO is defined by

$$\Delta G^\circ \equiv \frac{RT}{2} \ln P'_{\text{O}_2} \quad . \quad (6-26)$$

When the oxygen pressure in the reference electrode is known, the value of P'_{O_2} and ΔG° can be obtained from the measured EMF at a constant temperature after Eq. (6-6).

Fig. 6.4 shows the sectional view of two types of the Galvanic cells made by the author⁽¹⁰⁾ in 1962. The left cell is same structure used in the original work by Kiukkola and C. Wagner⁽¹⁾.

The standard free energy of formation is most accurately known for $\text{Fe}_{1-\delta}\text{O}$ and therefore, the mixture of Fe and $\text{Fe}_{1-\delta}\text{O}$ is usually used as the reference electrode. Once ΔG° is determined for NiO by the cell of (b), then ΔG° for Cu_2O can be determined by the cell of (a), using Ni/NiO mixture as the reference. Temperature of measurements is usually in range of 600°C to 1500°C. The internal resistance of the Galvanic cell becomes too large when temperature is lower than 600°C. The electrolyte itself is very stable even above 2000°C, but the electrode materials used would become unstable at the higher temperature.

By this Galvanic cell, the standard free energies of formation have been measured on NiO, Cu_2O , MnO, SnO, PbO, Cr_2O_3 , MoO_2 , WO_2 ,

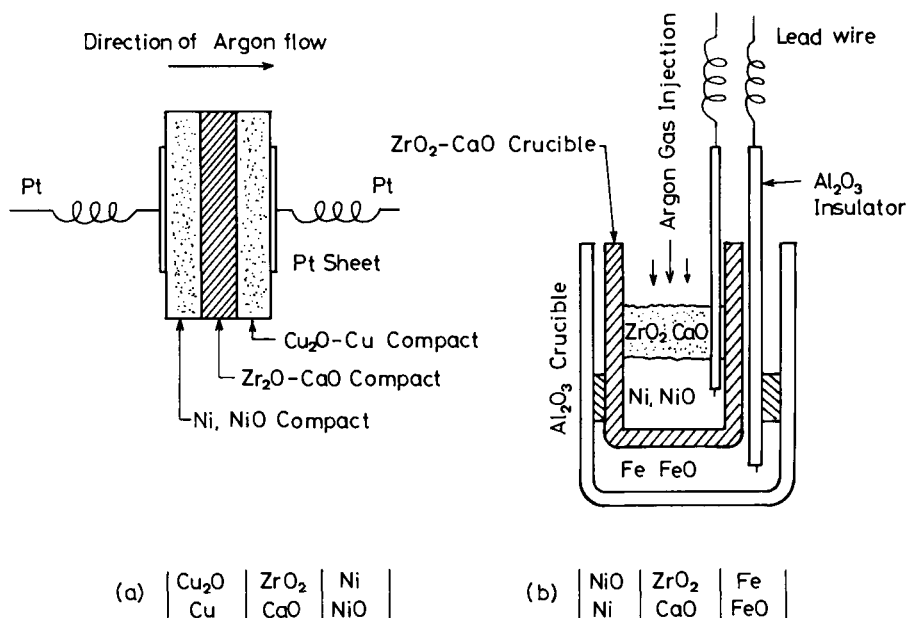
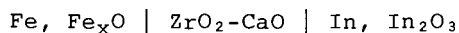


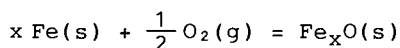
Fig. 6.4. Schematic picture of two types of Galvanic cells to measure standard free energy of formation of metal oxides (After Goto, 1962 (ref. 10)).

$\text{WO}_{2.72}$, WO_3 , ZnO , NbO , NbO_2 , Nb_2O_5 , In_2O_3 and Ga_2O_3 ⁽⁸⁾.

As an example, the results on MoO_2 , WO_2 , In_2O_3 and Ga_2O_3 by Katayama and Kozuka ⁽¹¹⁾ are given below because these compounds are less-common metal oxides. Fig. 6.5 shows the electromotive force measured on Galvanic cell of



at 740°C to 950°C by Katayama and Kozuka ⁽¹¹⁾. The standard Gibbs free energy of formation of Fe_xO is compiled by Chipman ⁽¹²⁾ as follows;



$$\Delta G^\circ = -126400 + 31.2 T \quad (6-27)$$

where ΔG° is in cal/mole, and T is absolute temperature.

Using this equation (6-27) and Eq. (6-26), they obtained the following free energies for various oxides in the temperature

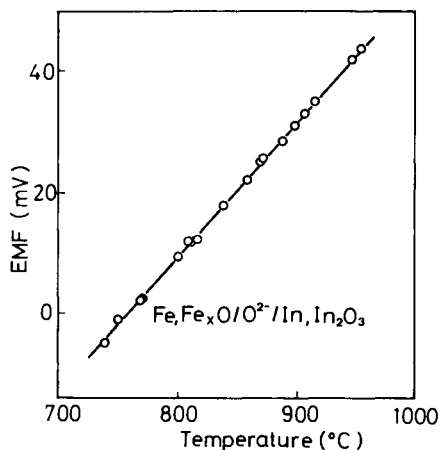


Fig. 6.5. The electromotive force measured on Galvanic cell, $\text{Fe, Fe}_x\text{O} \mid \text{ZrO}_2\text{-CaO} \mid \text{In, In}_2\text{O}_3$ (After Katayama and Kozuka, 1973 (ref. 11)).

range from 700°C to 1100°C in cal/mole;

$$\Delta G^\circ \text{ for } \text{MoO}_2 = -137560 + 40.31 T$$

$$\Delta G^\circ \text{ for } \text{WO}_2 = -136470 + 41.42 T$$

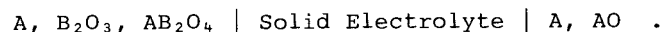
$$\Delta G^\circ \text{ for } \text{In}_2\text{O}_3 = -220600 + 76.8 T$$

$$\Delta G^\circ \text{ for } \text{Ga}_2\text{O}_3 = -261500 + 78.9 T \quad ,$$

where T is absolute temperature.

The values of ΔG° 's have been in good agreement to values determined by other methods.

The standard Gibbs free energies of formation of ternary compounds of metal-oxygen system can be measured by the following Galvanic cell with a three condensed phase equilibrium in an electrode compartment:



On passing two faradays of electricity, one would have the virtual cell reaction of



Because the standard free energy of formation of an interoxide compound is defined by the standard free energy change of Eq. (6-28), one has a simple relation of

$$\Delta G^\circ(\text{for } AB_2O_4) = -2FE \quad , \quad (6-29)$$

where E is the measurable reversible EMF. Many interoxide compounds have been studied by this method.

Fig. 6.6 shows the standard free energies of formation of 10 interoxide compounds reported by Tretjakow and Schmalzried⁽¹³⁾ in 1965. In addition to this figure, Katayama, Kemori and Kozuka⁽¹⁴⁾ measured ΔG° for $CoGa_2O_4$ and $NiGa_2O_4$ in 1979.

(b) Chemical activity measurements on components in alloys and oxide solutions. The chemical activity of the constituents in alloys and oxide solutions can be determined from the following simple relations:

(A-B)alloy, AO | Solid Electrolyte | A, AO (reference)

where

$$E = \frac{RT}{2F} \ln a_A \quad . \quad (6-30)$$

B, (AO-BO₂)solution | Solid Electrolyte | B, BO₂ (reference)

where

$$E = -\frac{RT}{4F} \ln a_{BO_2} \quad . \quad (6-31)$$

In the above equations, a_A and a_{BO_2} are the activity of A and BO₂, respectively, when the standard state is defined at their pure state.

For stable measurements, the free energies of formation of the oxides and the solid electrolyte must satisfy the relation of

$$-\Delta G^\circ \text{ of electrolyte} \gg -\Delta G^\circ \text{ of AO} \gg -\Delta G^\circ \text{ of BO}_2 \quad .$$

It should be borne in mind, however, that since the alloys are always saturated with oxygen, ternary instead of binary solutions are being studied.

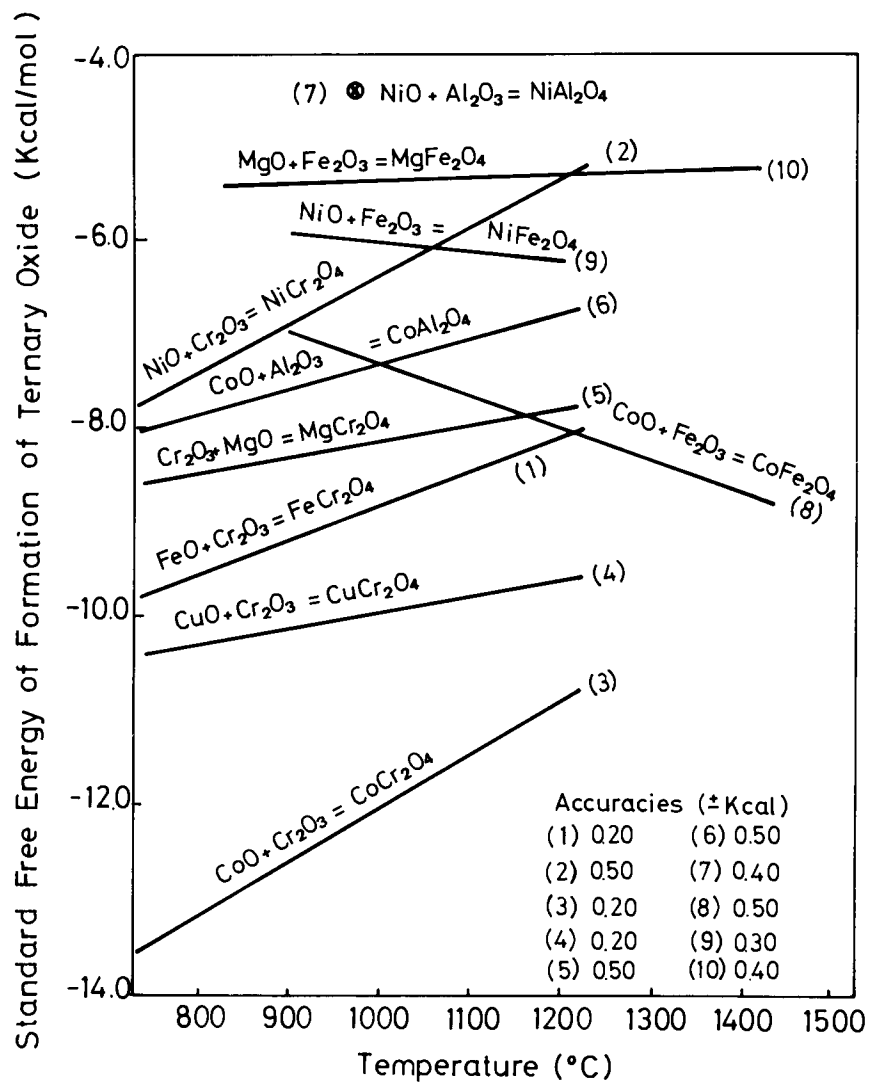


Fig. 6.6. Standard free energies of formation of 10 interoxide compounds (After Tretjakow and Schmalzried, 1965 (ref. 13)).

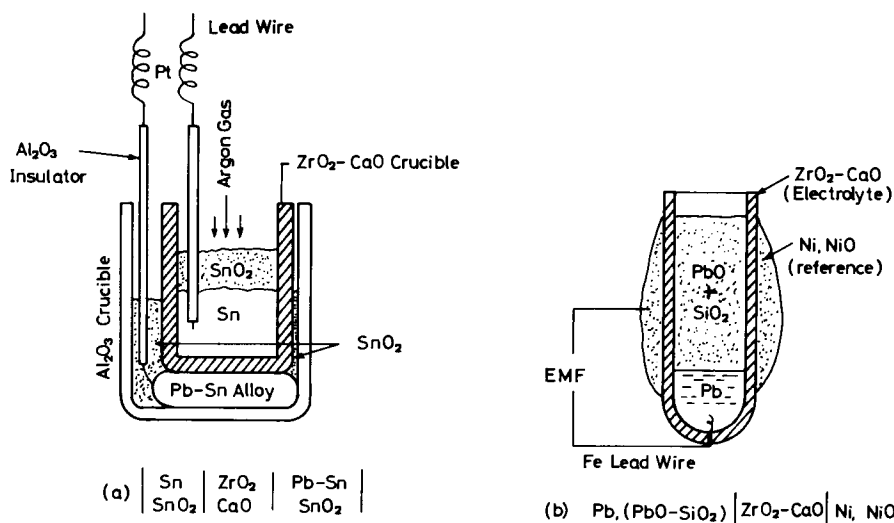


Fig. 6.7. Sectional views of cells (a) to determine activity of Pb (After Goto, 1962 (ref. 10)) and (b) to determine activity of PbO (After Matsushita and Goto, 1966 (ref. 15)).

Fig. 6.7 shows the structure of two Galvanic cells made by the author to measure the activities of Pb in liquid Pb-Sn alloy (a)⁽¹⁰⁾ and of PbO in liquid PbO-SiO₂ solutions (b)⁽¹⁵⁾.

Fig. 6.8 shows how the Galvanic cell is placed in the reaction chamber with a controlled atmosphere. The chamber is inserted in a furnace and heated to a fixed experimental temperature.

The activities of components in the following solid solutions have been measured⁽⁸⁾: Fe-Au, Fe-Pd, Fe-Pt, Fe-Ni, Co-Pd, Pt-Ni, Pd-Ni, Au-Ni, Sn-Fe, Ta-W, Ta-Mo and Nb-Mo. The liquid alloys studied were Sn-Pb, Fe-Cr, Cu-Zn and Ni-Pb⁽⁸⁾.

Liquid solutions of the oxides⁽⁸⁾ studied were SnO-SiO₂ and PbO-SiO₂. Recently, Iwase et al.⁽¹⁶⁾ studied the liquid FeO-CaO-CaF₂ system (1984), Iwase et al.⁽¹⁷⁾ the liquid CaO-CaCl₂-Fe_xO, and Goto, Yamaguchi and Nagata⁽¹⁸⁾ the liquid FeO-Na₂O-SiO₂ system (1984).

Also, the fused PbO-PbF₂ system was studied by Iwase, Okubo and Mori⁽¹⁹⁾ (1979).

The activities of components in the following complex solid solutions have been measured⁽⁸⁾: Fe₃O₄-CoFe₂O₄, Fe₃O₄-MgFe₂O₄,

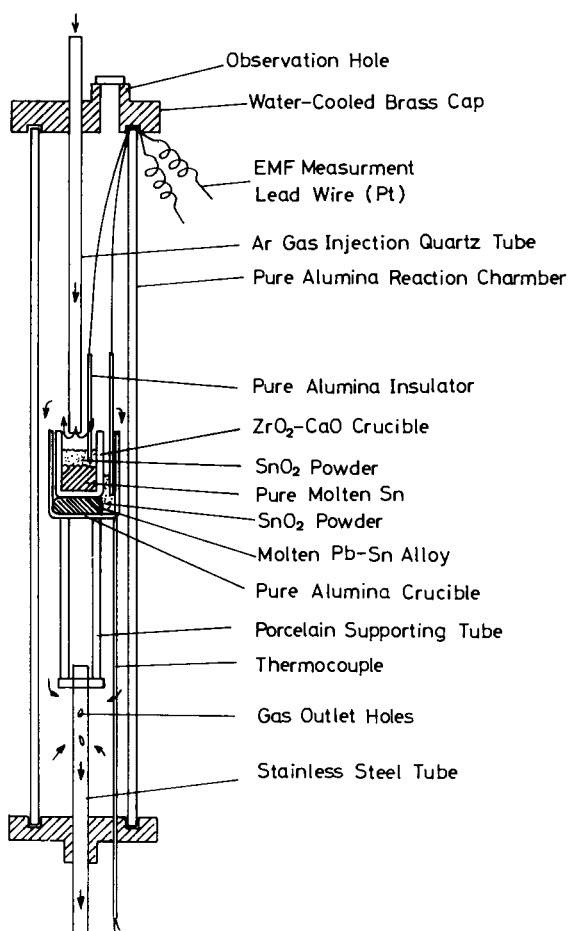


Fig. 6.8. Sectional view of Galvanic cell charged at the center of reaction chamber to be heated (After Goto, 1962 (ref. 10)).

$\text{Fe}_3\text{O}_4\text{-Mn}_3\text{O}_4$, NiO-MgO , NiO-MnO , FeO-MnO , FeO-MgO and CoO-MnO . Recently, Kozuka and his coworkers studied the $\text{Fe}_3\text{O}_4\text{-CuFe}_2\text{O}_4$ ⁽²⁰⁾, $\text{Fe}_3\text{O}_4\text{-NiFe}_2\text{O}_4$ ⁽²¹⁾ and $\text{Fe}_3\text{O}_4\text{-ZnFe}_2\text{O}_4$ ⁽²²⁾ quasi-binary systems.

As an example, Fig. 6.9 shows values for the activity of nickel in Ni-Pt alloys determined by Schwerdtfeger and Muan⁽²³⁾ by two different methods, the EMF method and the $\text{CO-CO}_2\text{-NiO-(Ni+Pt)}$ equilibrium method. The results by the two methods agreed very well as shown by small square and circle plots.

Fig. 6.10 shows the activity of PbO in the liquid PbO-SiO_2 system determined by Matsushita and Goto⁽¹⁵⁾ in 1966.

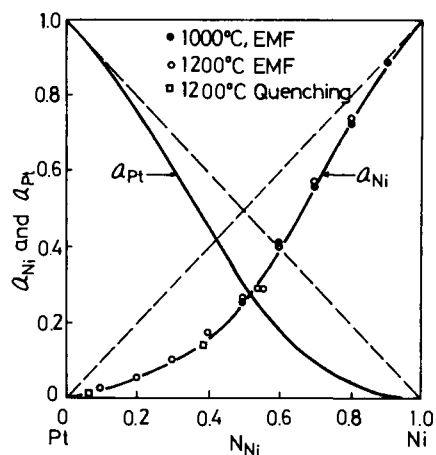


Fig. 6.9. Activity-composition curves for Ni and Pt in Pt-Ni alloys in the temperature range 1000-1200°C. "Quenching" means gas-solid equilibrium method (After Schwerdtfeger and Muan, 1965 (ref. 23)).

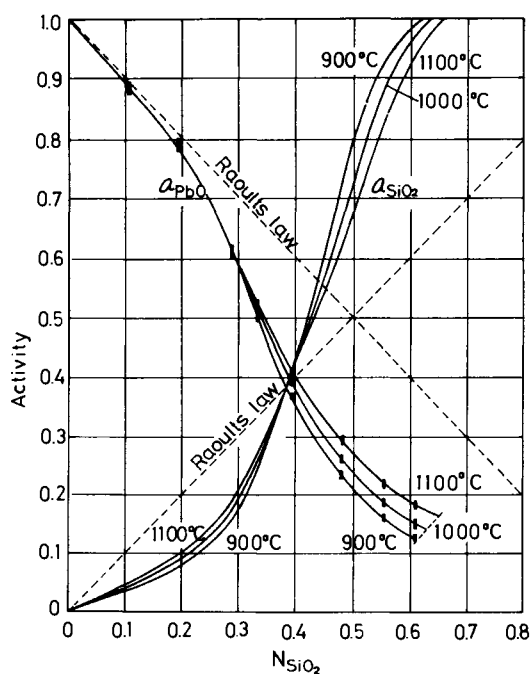


Fig. 6.10. Activity of PbO and SiO₂ in the system PbO-SiO₂ at 900, 1000 and 1100°C (After Matsushita and Goto, 1965 (ref. 15)).

By the above ways the solid electrolytes of ZrO_2 -based solution played an important role in determining thermodynamic properties.

In the following section, a more elegant application will be introduced.

(c) Determination of nonstoichiometric composition of oxides using the solid electrolytes. The deviation of composition of oxides from stoichiometry has been discussed in Chapter 2 in relation to electrical conductivity of oxides. The magnitudes of the deviation on various oxides have been determined usually by chemical analysis, gravimetry or volumetry. However, the solid state Galvanic cell can be used as another method. In this method oxygen is supplied to or removed from one compartment of the oxygen concentration cell by applying a nonequilibrium voltage across the cell. The amount of oxygen transferred through the electrolyte of ZrO_2 -CaO is given by

$$n_{\text{O}} = \frac{I \cdot t}{2F} \quad (6-32)$$

where n_{O} is number of gram-atoms oxygen, I is current, t is time and F is Faraday constant. By this transfer of oxygen, the composition of the condensed phase can be precisely controlled. The equilibrium oxygen pressure in the condensed phase can be determined from the electromotive force after the current is cut off.

This method is called "Coulometric titration". The relation between oxygen pressure and oxygen content in liquid metals has been studied on liquid Cu, Pb and Sn⁽⁸⁾ by this titration method. The nonstoichiometric compositions studied⁽⁸⁾ by the titration were solid $\text{Fe}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$, $\text{Fe}_{3-\delta}\text{O}_4$, $\text{TiO}_{2-\delta}$, $\text{NbO}_{2-\delta}$, $\text{Co}_x\text{Fe}_{3-\delta}\text{O}_4$, $(\text{Mg}, \text{Fe})_{3+\delta}\text{O}_4$ and $\text{LiFe}_5\text{O}_{8-\delta}$.

Fig. 6.11 shows a sectional view of the Galvanic cell used for coulometric titration by Tretjakow and Rapp in 1969⁽²⁴⁾.

Fig. 6.12 shows the relation between $\log \delta$ in solid $\text{N}_{1-\delta}\text{O}$ and logarithm oxygen pressure at 1200°C measured by Sockel and Schmalzried⁽²⁵⁾ in 1968.

For the accurate titration by the cell of Fig. 6.11, Pyrex glass provides a gas tight seal on heating. The sample of transition-metal oxides is not in direct contact with the electrolyte to avoid any interdiffusion between them. Satisfactory performance of the cell is limited by the leakage of oxygen through the container wall.

In Fig. 6.12, the slope of the line corresponds to 1:6, as it

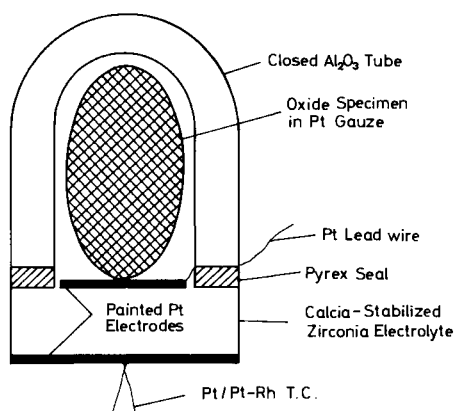
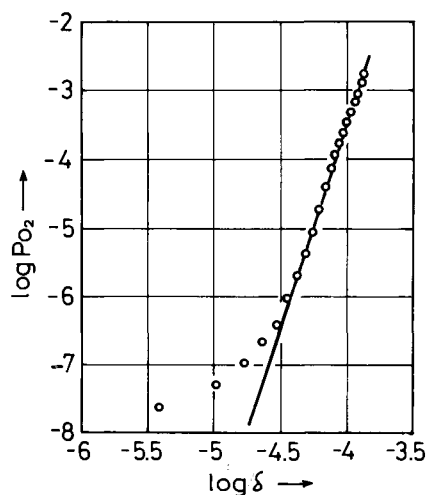


Fig. 6.11. A closed cell for coulometric titration involving an oxide specimen (After Tretjakow and Rapp, 1969 (ref. 24)).



should be, if in nickel oxide the metal vacancies are doubly ionized.

In titration experiments, the current density should not be in excess of about 100 A/cm². This is necessary in order to avoid the possible precipitation of blocking layers at the interfaces between the electrolyte and both electrodes. With very high current density (about 1 A/cm²), blackening of zirconia at the cathode side were sometimes observed⁽⁸⁾, probably due to the partial reduction of ZrO₂.

(d) Oxygen content in liquid metals and alloys. Oxygen dissolved in liquid metals precipitates during solidification as oxide inclusions, which often cause cracking of the metals under stress. Thus, oxygen is usually a very harmful element and should be removed from liquid metals.

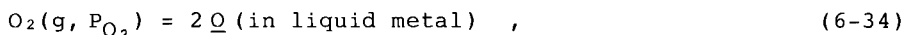
The content of the oxygen in liquid metals can be determined from the electromotive force of the Galvanic cell

Liquid Metal-dissolved $\underline{O}$ | ZrO₂-CaO | Pt, air ,

where

$$E = \frac{RT}{4F} \ln \frac{0.21}{P_{O_2}(\text{in metal})} \quad (6-33)$$

The equilibrium oxygen pressure in a liquid metal is determined by the reaction equilibrium of



where the standard Gibbs free energy of the reaction is defined by

$$\Delta G^\circ = -RT \ln \frac{[\text{wt}\%O]^2}{P_{O_2}} \quad , \quad (6-35)$$

where [wt%O] is the weight percentage of oxygen.

The electromotive force measured can give the oxygen pressure according to Eq. (6-33). Once the oxygen pressure is known, the weight% oxygen can be estimated from Eq. (6-35), when the standard free energy is known as a function of temperature. This is a method to determine the amount of oxygen dissolved in liquid metals.

When the electromotive force is measured and the oxygen content is determined by a vacuum fusion analysis, one can obtain the standard Gibbs free energy of reaction of Eq. (6-34), inserting the values of [wt%O] and P_{O_2} into Eq. (6-35). This is a method to

determine the standard free energy of the reaction.

In many liquid metals, it has been proved that Eqs. (6-33) and (6-35) are both satisfied except in the range of high oxygen concentration, where the activity coefficient of oxygen can not be neglected.

Reference (8) lists a number of liquid metal-oxygen systems, such as Na-O, Mn-O, Fe-O, Fe-O-S, Fe-O-Si, Fe-O-Mn, Fe-O-V, Fe-O-Cr, Fe-O-Co, Fe-O-Ni, Fe-O-Cu, liquid steels, Co-O, Co-O-S, Co-O-Ni, Ni-O, Ni-O-S, Cu-O, Cu-O-Ag, Cu-O-Sn, Cu-O-Co, Cu-O-Ni, Ag-O, Sn-O and Pb-O.

Fig. 6.13 shows the structure of the Galvanic cell dipped in liquid iron at 1600°C to determine the activity of oxygen by Fischer and Ackermann⁽²⁶⁾. Stabilized zirconia is sintered on the outside of the tube to provide a longer life time for the Galvanic cell.

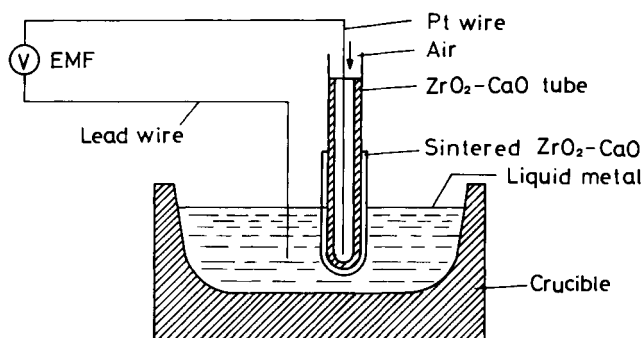


Fig. 6.13. Galvanic cell to determine oxygen activity in liquid iron and alloys at 1600°C. Reference electrode is Pt·Rh/air (After Fischer and Ackermann, 1965 (ref. 26)).

Fig. 6.14⁽²⁶⁾ shows the relation between EMF and weight% oxygen in liquid iron at 1600°C with the reference electrode of Pt·Rh wire with continuously flowing air. The oxygen content on the horizontal axis is determined by the conventional vacuum fusion analysis of the quenched samples.

Fig. 6.15 shows three examples of relations between the EMF of the liquid metal and reference electrode of Pt·Rh/air and the logarithm weight percentage of oxygen, reported by Fischer and Janke⁽²⁷⁾ and Fischer and Ackermann⁽²⁸⁾.

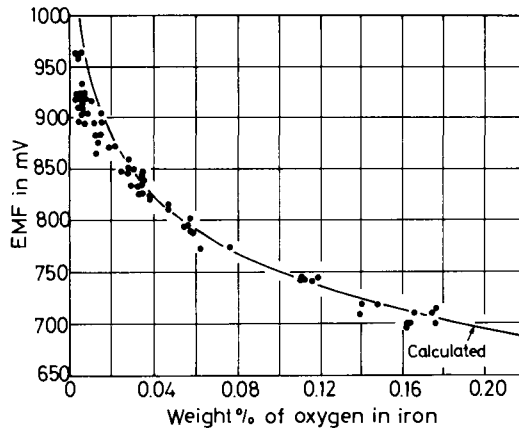


Fig. 6.14. Relation between EMF of cell of Fig. 6.13 and weight%O contained in liquid iron at 1600°C (After Fischer and Ackermann, 1965 (ref. 26)).

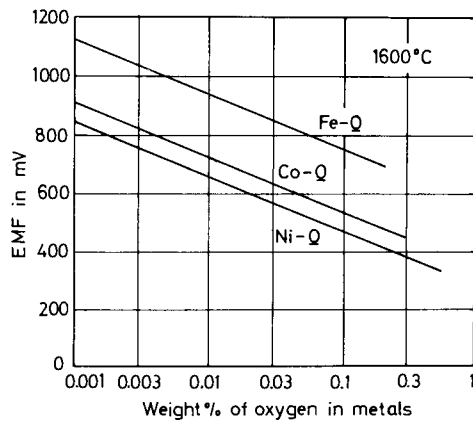


Fig. 6.15. Relation between EMF and weight% of oxygen dissolved in liquid Fe, Co or Ni at 1600°C (After Fischer and Janke, 1970 (ref. 27) for Fe-Q, and after Fischer and Ackermann, 1966 (ref. 28) for Co-Q and Ni-Q).

When the electromotive forces are expressed in volts, the following voltages are reported for the reference electrode of Pt·Rh /air

$E = 0.571 - 0.186 \log[\text{wt}\%O]$	for iron at 1600°C (ref. 27)
$E = 0.345 - 0.186 \log[\text{wt}\%O]$	for Co at 1600°C (ref. 28)
$E = 0.282 - 0.186 \log[\text{wt}\%O]$	for Ni at 1600°C (ref. 28)
$E = 0.258 - 0.146 \log[\text{wt}\%O]$	for Cu at 1200°C (ref. 28)
$E = -0.133 - 0.146 \log[\text{wt}\%O]$	for Ag at 1200°C (ref. 29)
$E = 0.684 - 0.106 \log[\text{wt}\%O]$	for Zn at 800°C (ref. 29)
$E = 0.341 - 0.106 \log[\text{wt}\%O]$	for Pb at 800°C (ref. 29) .

The excellent monograph by Fischer and Janke⁽⁹⁾ includes a very extensive discussion of and comments on these electromotive force with a bibliography of hundreds of papers published up to 1975.

The present author would like to present a supplement by introducing recent studies on oxygen dissolved in liquid metals and alloys by Kozuka and his coworkers as follows: Liquid In-Sb⁽³⁰⁾, Liquid Bi, Sn or Ge⁽³¹⁾, Liquid Cu-Bi⁽³²⁾, Liquid Cu-Sb or Cu-Ge⁽³³⁾, Liquid Cu-Tl⁽³⁴⁾, Liquid Cu-In or Cu-Sn⁽³⁵⁾, Liquid Tl-Te⁽³⁶⁾, Liquid Ce-Se or Cu-Tl⁽³⁷⁾, Liquid Bi-In⁽³⁸⁾, Liquid Pb-Sn⁽³⁹⁾, Liquid Cu-S⁽⁴⁰⁾, Liquid In⁽⁴¹⁾ and Liquid Bi-Pb or Bi-Sb⁽⁴²⁾.

Additional alloy systems have been studied by Kozuka and his coworkers but they are not listed here because these papers of Ref. (30) to Ref. (42) include the references for other systems. In these studies, Kozuka and his coworkers have measured the activity of oxygen as functions of temperature and alloy compositions in a systematic way.

In Eq. (6-35), the standard Gibbs free energy for the dissolution of 1 mole oxygen gas is defined in term of [wt%O] but it should be replaced by the activity for the more precise expression

$$\Delta G^\circ = -RT \ln \frac{a_O^2}{P_{O_2}} \quad , \quad (6-35')$$

where a_O is the activity of dissolved oxygen.

Fig. 6.16 shows the relation between logarithm activity coefficient, $\ln \gamma_O$ and mole fraction of Ge in Cu-Ge alloy, reported by Otsuka, Matsumura and Kozuka⁽³³⁾ in 1982.

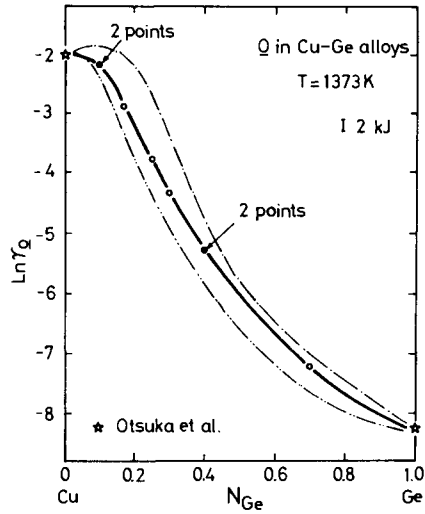


Fig. 6.16. Relation between $\ln \gamma_{\underline{O}}$ and atom fraction of Ge in liquid Cu-Ge-O alloys at 1373K. Two thin curves are estimated from theories (After Otsuka, Matsumura and Kozuka, 1982 (ref. 33)).

In the paper, the activity coefficient is defined by

$$\gamma_{\underline{O}} = \frac{a_{\underline{O}}}{N_{\underline{O}}} \quad (6-36)$$

where $N_{\underline{O}}$ is atom fraction of oxygen in the alloy and oxygen activity is defined by

$$a_{\underline{O}} \equiv \frac{P_{O_2}^{\frac{1}{2}} (\text{in alloy})}{P_{O_2}^{\frac{1}{2}} (\text{at 1 atm})} \quad (6-37)$$

In their study the atomic fraction of oxygen was controlled by coulometric titration.

Fig. 6.17 also shows the relation between logarithm activity coefficient of oxygen and atomic fraction of In in liquid Bi-In alloys reported by Otsuka and Chang⁽³⁸⁾ in 1984.

The definition of activity by Eq. (6-37) is favorable for comparison of effects of different alloys in the concentrated range upon the activity of oxygen as seen in Fig. 6.17. However, when the solvent is always fixed as an element, such as liquid iron, the following treatment is more convenient as long as the dilute range is considered.

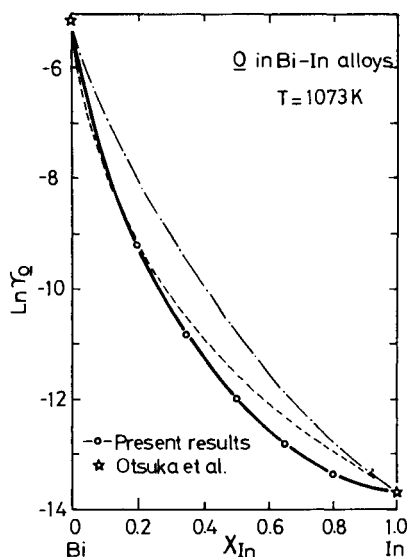


Fig. 6.17. Relation between logarithm activity coefficient of oxygen and atomic fraction of Bi in liquid Bi-In alloys at 1073K with estimated theoretical coefficients shown by two thin curves (After Otsuka and Chang, 1984 (ref. 38)).

In this case, the activity is given by

$$a_O = f_O [\text{wt}\%O] \quad (6-38)$$

where the reference state of the activity is at the infinitely dilute solution of Fe-O binary melt and f_O is the activity coefficient.

According to C. Wagner⁽⁴³⁾, the logarithm of the coefficient, $\log f_O$ can be expanded in the dilute range by a Taylor series as

$$\log f_O = \log f_O^\circ + \frac{\partial \log f_O}{\partial [\%x]} [\%x] + \frac{\partial \log f_O}{\partial [\%y]} [\%y] + \dots \quad (6-38')$$

where $[\%x]$ and $[\%y]$ are weight% of alloying element x and y. Because of the dilute range of x, y and so on, the terms higher than second order are neglected in this equation. The interaction parameter e_O^x is defined by

$$e_O^x = \frac{\partial \log f_O}{\partial [\%x]} \quad (6-39)$$

Thus, by inserting e_O^x , e_O^y , etc. into Eq. (6-38'), one can have

$$\log f_O = \log f_O^\circ + e_O^x [\%x] + e_O^y [\%y] + \dots \quad (6-40)$$

The interaction coefficient, f_O^x , is defined by

$$\log f_O^x \equiv e_O^x [\%x] \quad (6-41)$$

Usually, it is assumed that f_O° is unity in dilute range of Fe-O binary alloys.

Fig. 6.18 shows the relation between this $\log f_O^x$ and weight% of alloying elements in liquid iron at 1600°C, which is reproduced from the monograph of Fischer and Janke⁽⁹⁾. The slope of the lines is equal to the interaction parameter of Eq. (6-39). Table 6.1 gives the interaction parameters for different alloying elements compiled by Fischer and Janke⁽⁹⁾.

The interaction parameters in this table are all determined from the electromotive forces of the Galvanic cells with solid electrolytes.

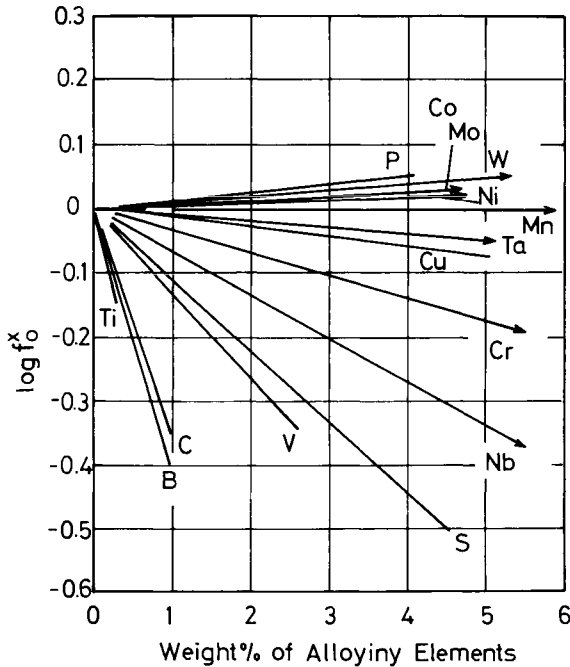


Fig. 6.18. Effects of alloying elements upon activity coefficient of oxygen dissolved in liquid iron at 1600°C determined by using solid electrolytes (Collected by Fischer and Janke, 1975 (ref. 9)).

TABLE 6.1

Interaction parameter for effects of alloying elements upon activity of oxygen in liquid iron at 1600°C (Compiled by Fischer and Janke, 1975 (ref. 9))

Alloying elements	e_O^x Interaction parameter	Valid up to [%x]
Phosphorus	0.014	5
Tungsten	0.011	32
Molybdenum	0.007	23
Cobalt	0.007	40
Nickel	0.006	40
Tantalum	- 0.009	25
Copper	- 0.013	5
Manganese	- 0.028	28
Chromium	- 0.031	18
	- 0.035	18
Niobium	- 0.066	8.5
Sulfur	- 0.104	4.5
	- 0.12	4.5
Vanadium	- 0.13	2.5
Carbon	- 0.36	1
Boron	- 0.40	1.2
Titanium	- 0.45	0.3

The interaction parameter gives the magnitude of the effect of alloying elements upon the activity of oxygen in liquid iron. Generally, when an element has a strong affinity with oxygen, it would decrease the activity of oxygen and the value of the parameter is negatively large.

In this chapter, only a small number of examples has been given for thermodynamic studies with solid electrolytes with purely anion conduction. However, one is convinced that the invention of the reliable electrolyte by Kiukkola and C. Wagner in 1957⁽¹⁾ has ignited the rapid progress of solid state electrochemistry at high temperature. Many types of industrial application of this solid electrolyte will be given in Chapters 10 and 11.

REFERENCES TO CHAPTER 6

- (1) K. Kiukkola and C. Wagner, J. Electrochem. Soc., 104 (1957), pp. 379-387.
- (2) C. Wagner, Z. Physik. Chem., B27 (1933), pp. 25-41.
- (3) H. Schmalzried, Ber. Bunsenges. Phys. Chem., 66 (1962), pp. 572-576.
- (4) H. Schmalzried, Z. Physik. Chem., N. F., 38 (1963), pp. 87-102.
- (5) V.B. Tare and H. Schmalzried, Z. Physik. Chem., N. F., 43 (1964), pp. 30-32.
- (6) C. Wagner in "Advances in Electrochemistry and Electrochemical Engineering", edited by P. Delahay, Vol. 4 (1966), pp. 1-46, published by Interscience Publishers, New York.
- (7) R.A. Rapp and D.A. Shores, "Solid Electrolyte Galvanic Cells" in Part 2 of Volume IV of "Techniques of Metal Research", edited by R.F. Bunshah, Interscience Publishers, New York, (1970).
- (8) K.S. Goto and W. Pluschkell, "Oxygen Concentration Cells", Chapter 13 of "Physics of Electrolytes" Vol. 1 and 2, edited by J. Hladik, Academic Press, London, (1972).
- (9) W.A. Fischer and D. Janke, "Metallurgische Elektrochemie", Verlag Stahleisen, Düsseldorf and Springer-Verlag, Berlin, (1975).
- (10) K.S. Goto, "Electromotive Force Measurements of Metal-Oxygen Systems", Ph. D. Thesis at Ohio State University (1962) with advisorship of Prof. G.R.St. Pierre.
- (11) I. Katayama and Z. Kozuka, Tech. Reports of Osaka Univ., 23 (1973), pp. 411-423.
- (12) J. Chipman, Pure and Appl. Chem., 5 (1962), p. 361.
- (13) J.D. Tretjakow and H. Schmalzried, Ber. Bunsenges. Phys. Chem., 69 (1965), pp. 396-402.
- (14) I. Katayama, N. Kemori and Z. Kozuka, J. Chem. Thermodynamics, 11 (1979), pp. 757-763.
- (15) Y. Matsushita and K.S. Goto, "The Application of Oxygen Concentration Cells with Solid Electrolyte ZrO_2 -CaO to Thermodynamic Research", in Proceedings of a Symposium on Thermodynamics by IAEA and IUPAC, Vienna, (1965), pp. 111-129 of Vol. 1.
- (16) M. Iwase, E. Ichise, N. Yamada and K. Nishida, Trans. ISS of AIME, 4 (1984), pp. 47-53.
- (17) M. Iwase, M. Yamada, E. Ichise and H. Akizuki, Trans. ISS of AIME, 4 (1984), pp. 53-59.
- (18) K.S. Goto, S. Yamaguchi and K. Nagata, Proceedings of 2nd Intern. Symp. on Metall. Slags and Fluxes, edited by H.A. Fine and D.R. Gaskell, Metall. Soc. AIME, (1984), pp. 467-481.
- (19) M. Iwase, N. Okubo and T. Mori, Trans. Japan Inst. Metal, 20 (1979), pp. 383-387.
- (20) I. Katayama, T. Matsuda and Z. Kozuka, Tech. Reports of Osaka Univ., 30 (1980), pp. 385-390.
- (21) I. Katayama, Y. Watanabe and Z. Kozuka, Trans. JIM, 20 (1979), pp. 593-586.
- (22) I. Katayama, J. Shibata, M. Aoki and Z. Kozuka, Trans. JIM, 18 (1977), pp. 743-749.
- (23) K. Schwerdtfeger and A. Muan, Acta Metall., 13 (1965), pp. 509-515.
- (24) J.D. Tretjakow and R.A. Rapp, Trans. Metall. Soc. AIME, 245 (1969), pp. 1235-1241.
- (25) H.G. Sockel and H. Schmalzried, Ber. Bunsenges. Phys. Chem., 72 (1968), pp. 745-754.
- (26) W.A. Fischer and W. Ackermann, Arch. Eisenhüttenw., 36 (1965), p. 643 and p. 695.

- (27) W.A. Fischer and D. Janke, Arch. Eisenhüttenw., 41 (1970), p. 1027.
- (28) W.A. Fischer and W. Ackermann, Arch. Eisenhüttenw., 37 (1966), p. 43.
- (29) W.A. Fischer and W. Ackermann, Arch. Eisenhüttenw., 37 (1966), p. 697.
- (30) S. Otsuka and Z. Kozuka, Metall. Trans. AIME, 12B (1981), pp. 455-459.
- (31) S. Otsuka, T. Sano and Z. Kozuka, Metall. Trans. AIME, 12B (1981), pp. 427-433.
- (32) S. Otsuka, H. Hanaoka and Z. Kozuka, Trans. JIM, 23 (1982), pp. 563-570.
- (33) S. Otsuka, Y. Matsumura and Z. Kozuka, Metall. Trans. AIME, 13B (1982), pp. 77-83.
- (34) S. Otsuka, H. Hanaoka and Z. Kozuka, Trans. JIM, 23 (1982), pp. 70-76.
- (35) S. Otsuka, Y. Matsumura and Z. Kozuka, Trans. JIM, 24 (1983), pp. 829-838.
- (36) S. Otsuka, Y. Kurose and Z. Kozuka, Trans. JIM, 24 (1983), pp. 817-828.
- (37) S. Otsuka, H. Hanaoka and Z. Kozuka, Trans. JIM, 24 (1983), pp. 132-138.
- (38) S. Otsuka and Y.A. Chang, Z. Metallk., 75 (1984), pp. 368-372.
- (39) S. Otsuka, Y. Kurose and Z. Kozuka, Z. Metallk., 75 (1984), pp. 46-52.
- (40) S. Otsuka and Y.A. Chang, Metall. Trans. AIME, 15B (1984), pp. 337-344.
- (41) S. Otsuka, Z. Kozuka and Y.A. Chang, Metall. Trans. AIME, 15B (1984), pp. 329-335.
- (42) S. Otsuka, Y. Kurose and Z. Kozuka, Metall. Trans. AIME, 15B (1984), pp. 141-147.
- (43) C. Wagner, "Thermodynamics of Alloys" Addison-Wesley, Cambridge, Massachusetts, (1952).

Chapter 7

GALVANIC CELLS WITH ELECTROLYTES WITH NON-OXYGEN CONDUCTION

7.1 GALVANIC CELLS WITH SOLID ELECTROLYTES OF CATION CONDUCTION

In the previous chapter, galvanic cells with solid electrolytes of purely oxygen-anion conduction were discussed. The emphasis in this chapter is a discussion of galvanic cells with solid electrolytes of non-oxygen conduction. These electrolytes include halides, such as CaF_2 , PbF_2 , SrF_2 , MgF_2 , and BaCl_2 ; binary or ternary solid oxides with cation conduction, such as $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, MgAl_2O_4 , $4\text{CaO} \cdot \text{P}_2\text{O}_5$, Mg_2SiO_4 , and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; and other ionic compounds, such as CaS , K_2SO_4 , Na_2SO_4 , and AlN .

The scope of the present chapter is confined mostly to the galvanic cells that were not fully discussed by Fischer and Janke⁽¹⁾ in 1975, and by Tretyakov and Kaul⁽²⁾ in 1972. Fischer and Janke⁽¹⁾ gave a comprehensive discussion on solid electrolytes of double oxides, while Tretyakov and Kaul⁽²⁾ discussed solid electrolytes of halides. The details of these two categories of solid electrolytes are, therefore, excluded in the present chapter.

Solid oxides of transition metals, as discussed in Chapter 2, have no ionic conductivity because of easy migration of excess electrons or positive holes. However, solid oxides of non-transition metals have ionic conductivity by nature. This implies that all such oxides can be used as solid electrolytes of Galvanic cells. In reality, this is not true. As already pointed out in Chapter 6, a stable electromotive force can be easily obtained only in the case where the electrolyte is chemically very stable with low electrical resistivity. The so-called "beta-alumina" has recently been very widely studied as such an oxide.

The lamellar crystal structure of beta-alumina, approximate composition of $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, was studied by Beevers and Ross⁽³⁾ already in 1937, and later by other investigators.

In 1967, Yao and Kummer⁽⁴⁾ reported an extensive study on ion exchange and diffusion in solid $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ and demonstrated easy migration of Na^+ even at 300°C - 500°C . As shown in the previous chapter, very reliable electrolyte of ZrO_2 or ThO_2 based solid solutions can be used only above 550°C or 600°C .

In 1967, Kummer and Weber⁽⁵⁾ of Ford Motor Company have

disclosed the invention of a sodium-sulfur battery using beta-alumina as the electrolyte. Their intension was to use this battery for electric cars. These two papers by Yao and Kummer⁽⁴⁾ and Kummer and Weber⁽⁵⁾ have given a strong impact, not only to car engineers, but also to scientists working on physical chemistry at elevated temperature.

The galvanic cell can be expressed as follows:



where liquid sulfur is miscible with liquid Na_2S in wide composition range above 300°C . Thus, the virtual cell reaction can be given by:

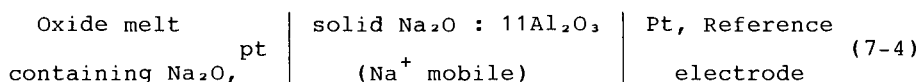


where the Gibbs free energy is given by:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Na}_2\text{S}}}{a_{\text{S}}} \quad (7-3)$$

where ΔG° is the standard Gibbs free energy of reaction of Eq.(7-2), and $a_{\text{Na}_2\text{S}}$ and a_{S} are the activities of sulfur and sodium sulfide in the liquid solution of S and Na_2S , respectively.

When the solid electrolyte of sodium beta-alumina is used in the following galvanic cell, the activity of Na_2O in the oxide melt can be obtained from the electromotive force:



According to Eq. (6-19) of Chapter 6, the electromotive force can be given by

$$E = \frac{RT}{4F} \ln \frac{P''_{\text{O}_2}}{P'_{\text{O}_2}} - \frac{RT}{2F} \ln \frac{a''_{\text{Na}_2\text{O}}}{a'_{\text{Na}_2\text{O}}} \quad (7-5)$$

where R is the gas constant, F is the Faraday constant, P_{O_2} is the oxygen pressure, and $a_{\text{Na}_2\text{O}}$ is the activity of soda. Single prime means at the left-hand-side of the electrode and double prime at the right-hand-side of the electrode.

This galvanic cell has been independently studied by Yokokawa and his coworkers⁽⁶⁾⁻⁽⁸⁾, Elliot and his coworkers⁽⁹⁾⁻⁽¹²⁾ and Froberg and his coworkers⁽¹³⁾.

Later, the present author and his coworkers⁽¹⁴⁾⁻⁽¹⁵⁾ used a very dense beta-alumina and measured the activity of Na_2O up to 1450°C in liquid $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$, and $\text{Na}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ systems.

The $\text{Na}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ ternary system has industrial importance because the system approximates the slag made by soda injection to molten crude iron for the removal of harmful phosphorus.

Fig. 7.1 shows a cross-sectional view of the galvanic cell⁽¹⁴⁾⁽¹⁵⁾. The same oxygen pressure was used at both electrodes to eliminate the first term of the right hand side of Eq. (7-5). The tube of stabilized zirconia with the reference melt of a fixed composition of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Fe}_2\text{O}_3$ is occasionally dipped into the sample melt to know that the oxygen pressure in the reference melt is exactly the same with that in the sample melt. A small quantity of Fe_2O_3 is added to the reference melt to accelerate the attainment of equilibrium between the gas phase and the reference melt. Also, it is necessary to know the activity in the reference melt in advance.

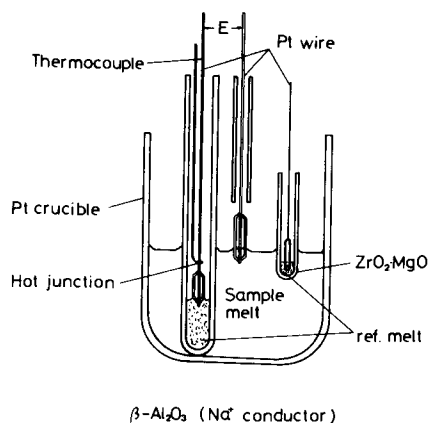
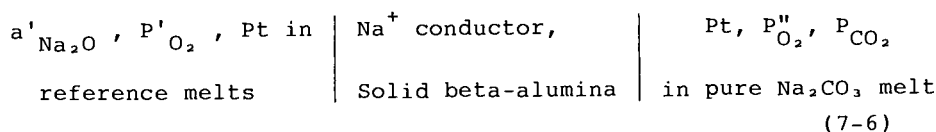


Fig. 7.1. Galvanic cell to measure the activity of Na_2O in sample melts. Third electrode at right hand side is only sometimes dipped to check the equal oxygen pressure in the sample melt and the reference melt. (After Yamaguchi et al (14), 1982).

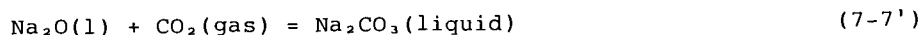
The activity of sodium oxide in the reference melts has been measured by the following galvanic cell:



where the reversible EMF, E , is given by the following equation.

$$E = \frac{\Delta G_f^\circ}{2F} - \frac{RT}{2F} \ln a'_{\text{Na}_2\text{O}} - \frac{RT}{4F} \ln \frac{P''_{\text{O}_2}}{P'_{\text{O}_2}} - \frac{RT}{2F} \ln P_{\text{CO}_2} \quad (7-7)$$

where ΔG_f° means the standard free energy of formation of Na_2CO_3 from CO_2 and Na_2O according to



The values of this free energy change are given in the JANAF tables (16) as 35.184 kcal at 1300 K, 31.915 kcal at 1400 K, 28.692 at 1500 K, and 25.513 kcal at 1600 K.

Fig. 7.2 shows the activity of Na_2O in the reference melts, No.1 and No.2, which have been measured by the above galvanic cell with two electrodes in the separated gas compartments. The composi-

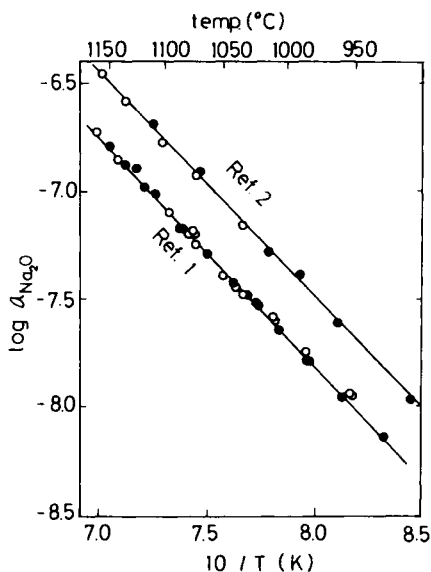


Fig. 7.2. Relation between logarithm activity of Na_2O in two reference melts and reciprocal absolute temperature. (After Yamaguchi and Goto (15), 1984).

tion of the reference melt, No.1 is $0.395\text{Na}_2\text{O}-0.526\text{SiO}_2-0.079\text{Fe}_2\text{O}_3$ by mole ratio and that of No.2 is slightly different from this mole ratio. The plots with different marks (open and closed circles) mean the results with different partial pressure combinations of P_{O_2}' , P_{O_2}'' and P_{CO_2} .

Fig. 7.3 shows the compositions studied on $\text{Na}_2\text{O}-\text{SiO}_2$ binary, $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ binary and $\text{Na}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ ternary systems.

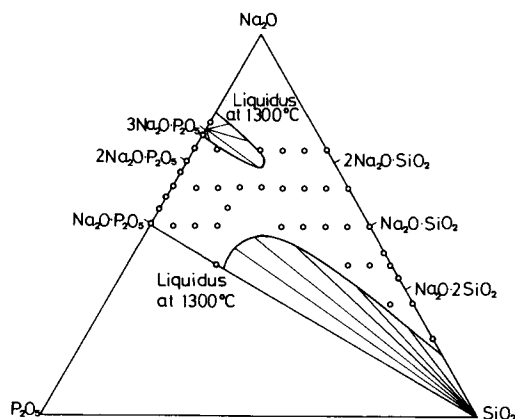


Fig. 7.3. The ternary composition triangle showing the compositions of sample melts to measure the activity of Na_2O . (After Yamaguchi and Goto (15), 1984).

Fig. 7.4 shows the electromotive force measured by the galvanic cell of Fig. 1.1. The open circles and solid circles mean the independent experimental runs on the liquid $\text{Na}_2\text{O}-\text{SiO}_2$ system. From the electromotive force values, one can calculate the activity of Na_2O with its standard state at the pure liquid according to Eq. (7-5), because the activity in the reference melts are known with the galvanic cell of Eq. (7-6).

Fig. 7.5 shows logarithm of the activity of Na_2O in the liquid $\text{Na}_2\text{O}-\text{SiO}_2$ binary system as a function of the reciprocal absolute temperature and composition. In this figure, $x_{\text{Na}_2\text{O}}$ means the mole fraction of Na_2O and the small vertical lines are the liquidus-line temperatures. It can be noted that the activity of Na_2O is extremely small in this binary oxide melt.

Fig. 7.6 shows the activity of Na_2O as a function of composition at 1100, 1300, and 1500°C. The activity of SiO_2 at 1300°C is

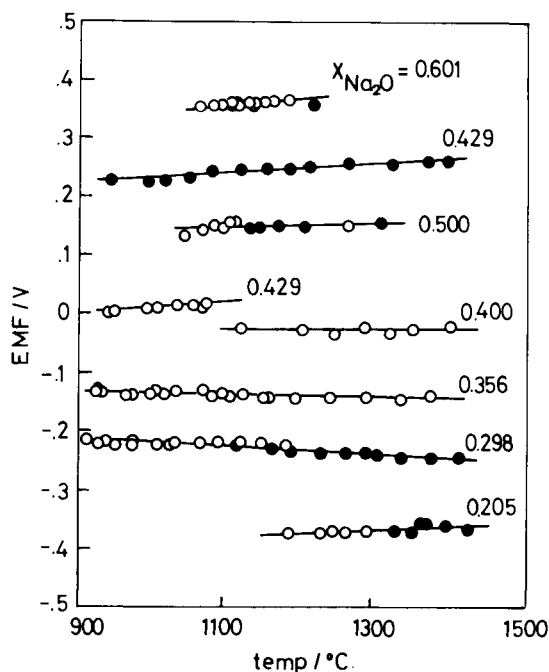


Fig. 7.4. The EMF of the Galvanic cell shown in Fig. 7.1. Different marks mean the different experimental runs. (After Yamaguchi, Imai and Goto (14), 1982).

calculated by Gibbs-Duhem integration.

The results shown in this figure agreed very well with the results of refs. (6) to (8), (9) to (12), (13), and also with the result by Rego, Sigworth, and Philbrook⁽¹⁷⁾, who used the vapor transpiration method on fused oxide mixtures. The good agreement implies that this type of galvanic cell is a reliable experimental method even up to 1450°C. Thus, the same method has been applied to Na₂O-P₂O₅ binary and Na₂O-SiO₂-P₂O₅ ternary systems, on which no activity data have been reported.

Fig. 7.7 shows the activities in Na₂O-P₂O₅ binary melts at 1100, 1200, and 1300°C. At the composition of solid 3Na₂O·P₂O₅ compound, the activities of Na₂O and P₂O₅ are changing step-wisely. The activities of Na₂O in this figure are smaller than those in the Na₂O-SiO₂ binary system shown in Fig. 7.6. This tendency is more clearly shown by the iso-activity line diagrams of Figs. 7.8, 9, and 10, which are for activities of Na₂O, P₂O₅, and SiO₂, respectively.

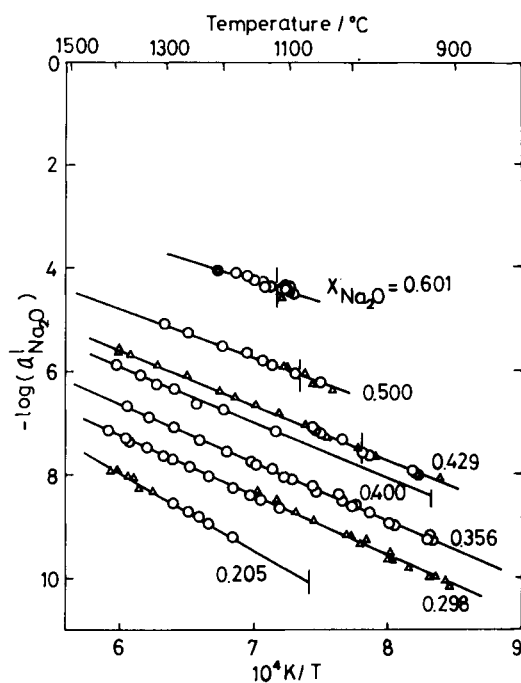


Fig. 7.5. Relation between logarithm activity of Na_2O in the binary melts and reciprocal absolute temperature. (After Yamaguchi, Imai, and Goto (14), 1982).

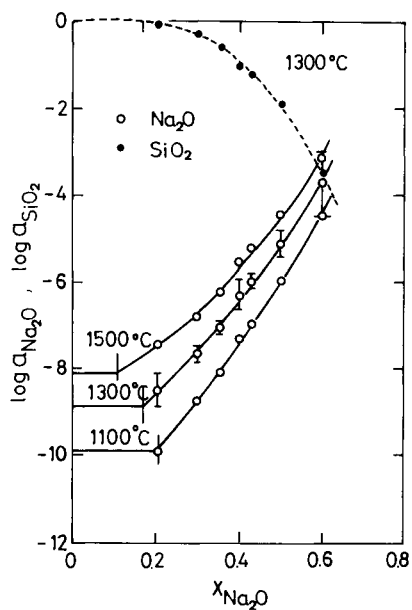


Fig. 7.6. Relation between activities of Na_2O and SiO_2 and mole fraction of Na_2O in Na_2O - SiO_2 binary melts. (After Yamaguchi, Imai and Goto (14), 1982).

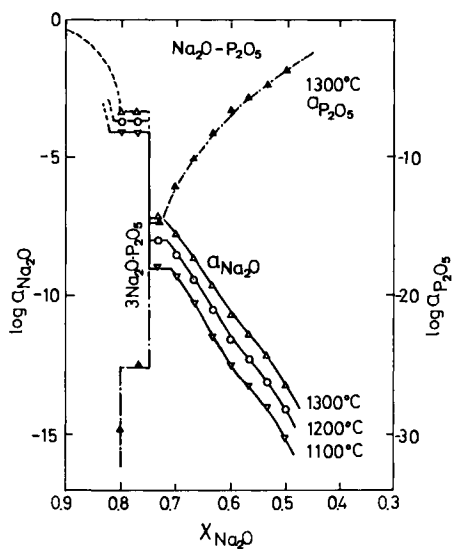


Fig. 7.7. Relation between activities of Na_2O and P_2O_5 and mole fraction of Na_2O in $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ binary melts. (After Yamaguchi and Goto (15), 1984).

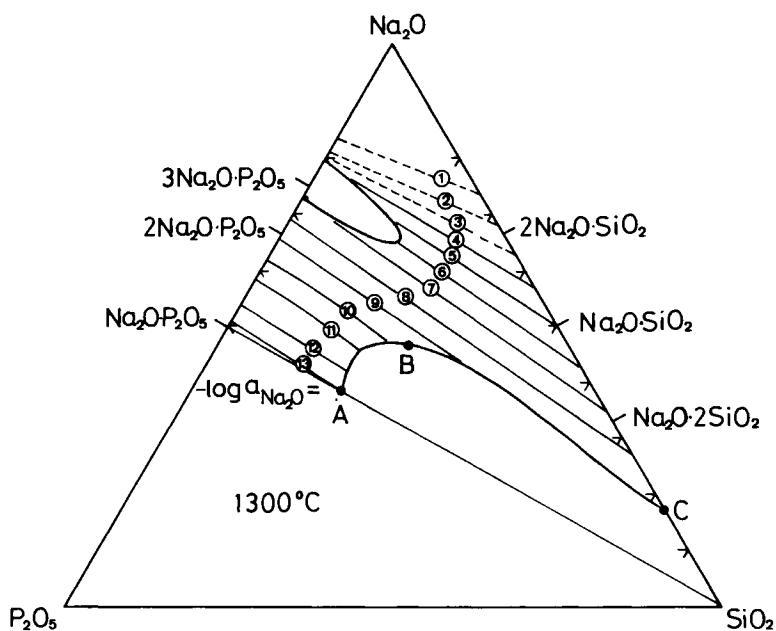


Fig. 7.8. Iso-activity lines of Na_2O on the ternary composition triangle. (After Yamaguchi and Goto (15), 1984).

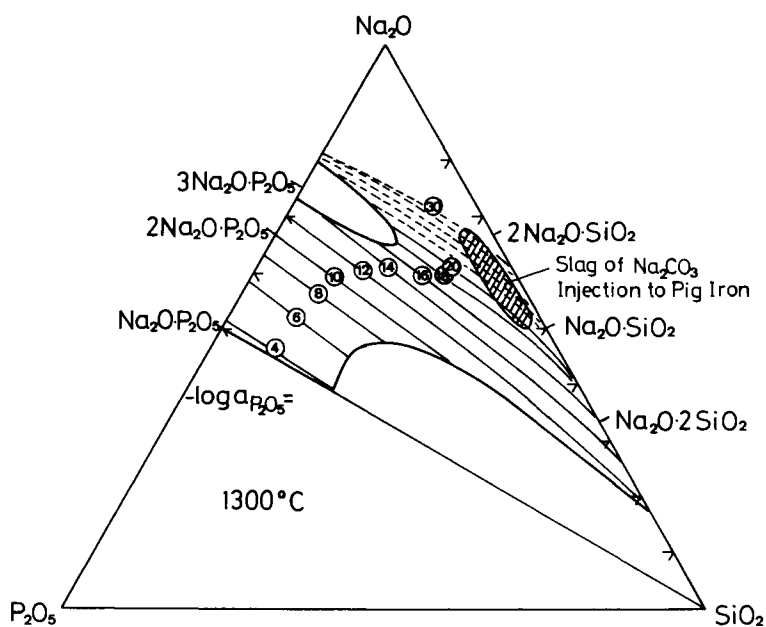


Fig. 7.9. Iso-activity lines of P_2O_5 on the ternary composition triangle. (After Yamaguchi and Goto (15), 1984).

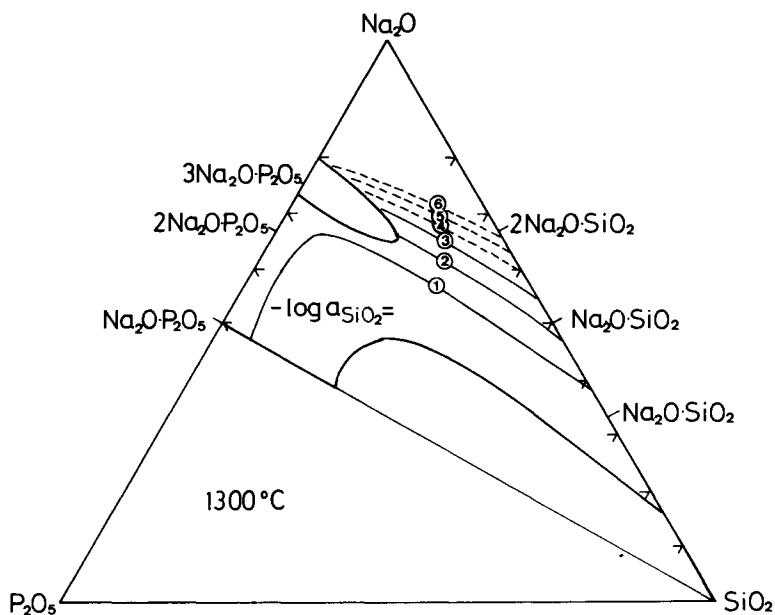


Fig. 7.10. Iso-activity lines of SiO_2 on the ternary composition triangle. (After Yamaguchi and Goto (15), 1984).

The numbers in circles denotes minus logarithm of the activity of the components. (For example, 12 means that the activity of the component is 10^{-12} .) The ellipsoidal area shown in Fig. 7.9 is the composition range of metallurgical slags formed by soda injection to crude iron containing phosphorus and silicon as impurities.

Thermodynamic features of these three diagrams of iso-activity lines are; firstly, the activities of these components are showing extraordinarily negative deviation from Raoult's law, and secondly, the activity of Na_2O is predominantly controlled by the content of P_2O_5 , and not SiO_2 . The former feature would be caused by the mixing of a strongly basic oxide, Na_2O , with two strongly acidic oxides of SiO_2 and P_2O_5 . The latter feature would imply that P_2O_5 is much more acidic than SiO_2 .

Because of these thermodynamic features, the measured activity of Na_2O would not agree with the activity estimated from thermodynamic models, which have been developed for oxide melts with weak interaction among component oxides.

Fig. 7.11 shows a substantial disagreement between the measured and estimated activities in the Na_2O - SiO_2 binary melt at 1300°C . The three models by Toop and Samis⁽¹⁸⁾ (shown as T-S in the figure), by Masson⁽¹⁹⁾, and Yokokawa and Niwa⁽²⁰⁾ (Y-N in Fig. 7.11) are selected for comparison because of their excellent simplicity with good abstractive nature. These models have been successfully

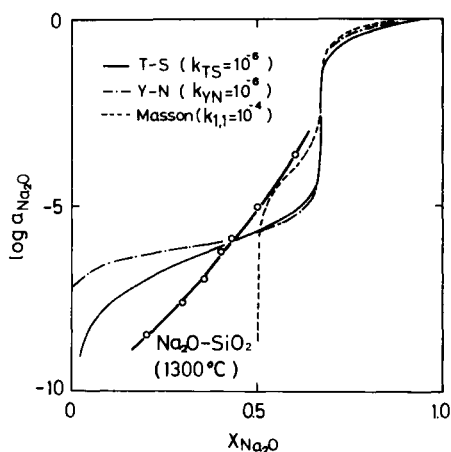


Fig. 7.11. Comparison between the activities of Na_2O in Na_2O - SiO_2 binary melt measured and estimated by models of Toop and Samis, Yokokawa and Niwa, and Masson. (After Yamaguchi and Goto (15), 1984).

applied⁽²¹⁾ with good agreement between the measured and estimated activities in liquid PbO-SiO₂, CaO-SiO₂, FeO-SiO₂, and MnO-SiO₂ binary systems.

The above is an example of galvanic cells with solid electrolytes of purely cation conduction. Some other interoxide compounds also have a homogeneity range with cation vacancies.

Pluschkell and Engell⁽²²⁾ have shown that increased conductivity can be obtained by dissolving excess silica into Mg₂SiO₄, (forsterite). Their results for the conductivity versus mol%SiO₂ in the MgO-SiO₂ binary system is shown in Fig. 7.12.

From this figure, one observes that the compound can be used as a cation conducting electrolyte. The compound, however, should be used at temperatures higher than 1300°C, otherwise it would not be easy to have stable and responceible electromotive forces due to the low conductivity.

In 1969, Pluschkell⁽²³⁾ constructed the galvanic cells of

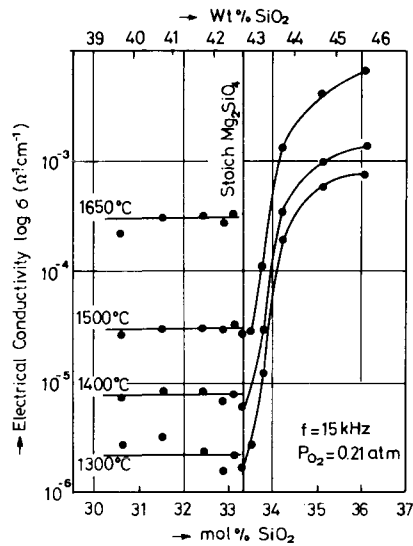
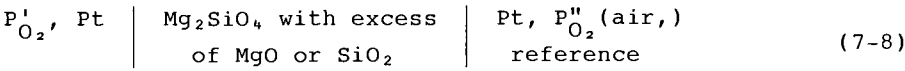


Fig. 7.12. Electrical conductivity of forsterite Mg₂SiO₄. (After Pluschkell and Engell (22), 1968).

It is very important to have a two phase mixture as the electrolyte for simplification of the theoretical electromotive force. When a small quantity of MgO is dispersed in the electrolyte, it would result in an uniform chemical potentials of MgO throughout the electrolyte. This uniformity can also be produced by mixing an excess of SiO₂, yielding a two phase mixture of Mg₂SiO₄ and MgSiO₃ in accordance to the phase diagram.

The theoretical electromotive force can be expressed as follows by applying Eq. (6-19) to the above galvanic cell:

$$E = \frac{RT}{4F} \ln \frac{0.21}{P'_{O_2}} - \frac{1}{2F} \int t_{Mg^{2+}} d\mu_{MgO} - \frac{1}{4F} \int t_{Si^{4+}} d\mu_{SiO_2} \quad (7-9)$$

where $t_{Mg^{2+}}$ and $t_{Si^{4+}}$ are transference numbers of Mg²⁺ and Si⁴⁺ in Mg₂SiO₄-electrolyte.

As long as two phase mixtures are used, both $d\mu_{MgO}$ and $d\mu_{SiO_2}$ would be zero and thus, the theoretical electromotive force would be expressed simply by

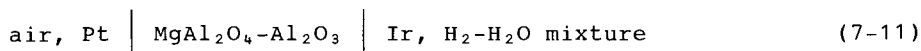
$$E = \frac{RT}{4F} \ln \frac{P''_{O_2} (=0.21)}{P'_{O_2}} \quad (7-10)$$

where 0.21 is the oxygen pressure in air, and P'_{O_2} is the oxygen pressure in the gas mixture in the left-hand-side compartment.

Fig. 7.13, reported by Pluschkell⁽²³⁾, shows good experimental proof on Eq. (7-10).

The deviation at less than 10⁻¹⁰ atm is believed to be caused by the onset of partial electronic conduction. However, this deviation is observed only by mixing an excess of MgO, but not with an excess of SiO₂.

Another good proof of Eq. (7-10) is shown by Fig. 7.14, which was reported by Fischer and Janke⁽²⁴⁾ in 1969. The galvanic cell studied is:



where an excess of Al₂O₃ is added to the solid electrolyte.

The solid lines in the figure are the electromotive forces obtained by using stabilized zirconia as the electrolyte in agreement to Eq. (7-10). The good agreement between theory and experiment as shown in Figs. 7.13 and 14 would support the accuracy of

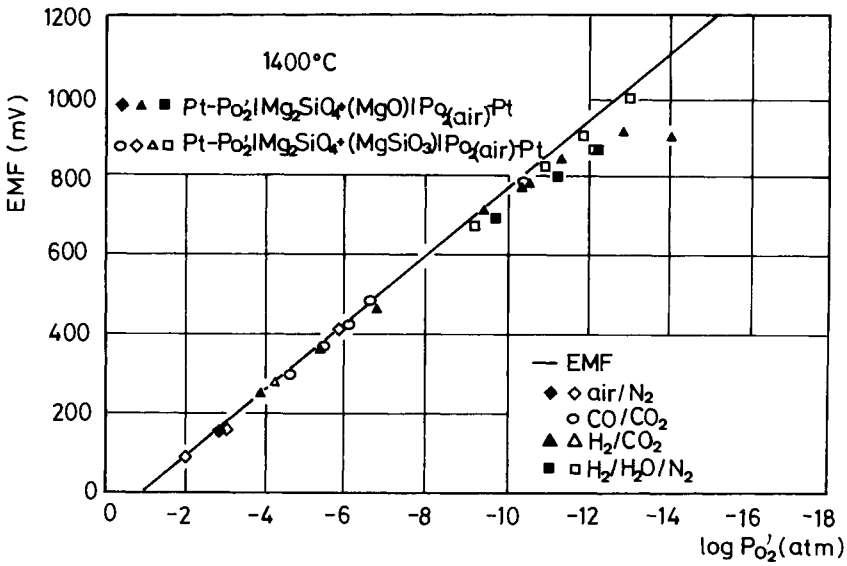


Fig. 7.13. E.M.F. of an oxygen concentration cell with forsterite Mg_2SiO_4 as solid electrolyte. (After Pluschkell (23), 1969).

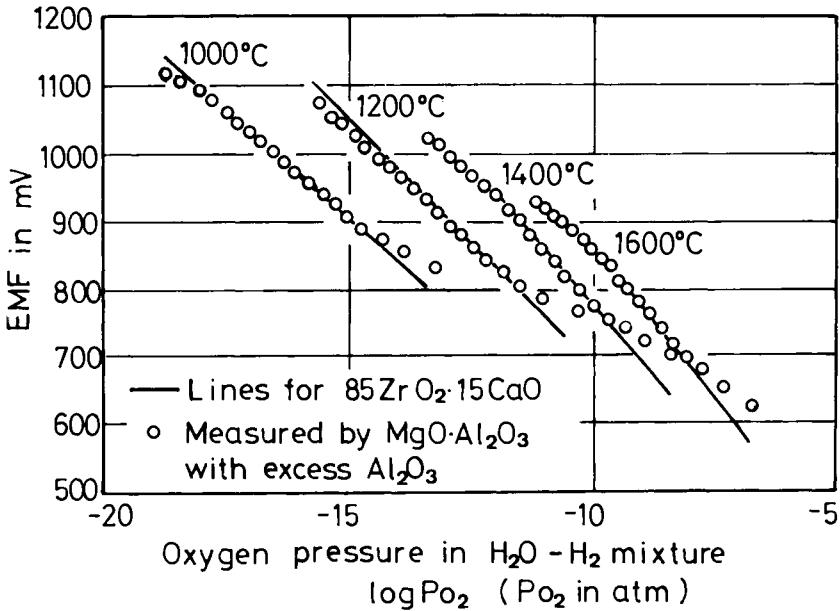
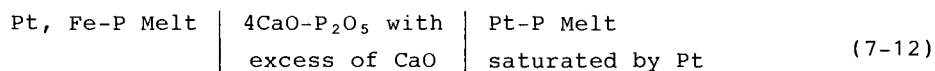


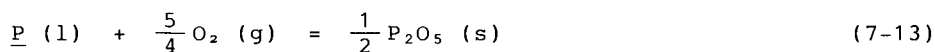
Fig. 7.14. Relation between E.M.F. of galvanic cell of air | $MgAl_2O_4$ | Ir, H_2-H_2O mixture. (After Fischer and Janke (24), 1969).

the older publication by Fischer, Janke, and Engell⁽²⁵⁾ in 1966. Their intension was to determine the activity of phosphorus in iron-phosphorus binary melts at 1650°C. The galvanic cell is shown by Fig. 7.15 and expressed by



The liquid oxide covering the Fe-P and Pt-P melts as shown in Fig. 7.15 can provide a good protection against oxidation of the metallic melt by atmospheric gas.

The equilibrium oxygen pressures in both metallic melts is fixed by the reaction of



where the equilibrium constant, K , is defined by

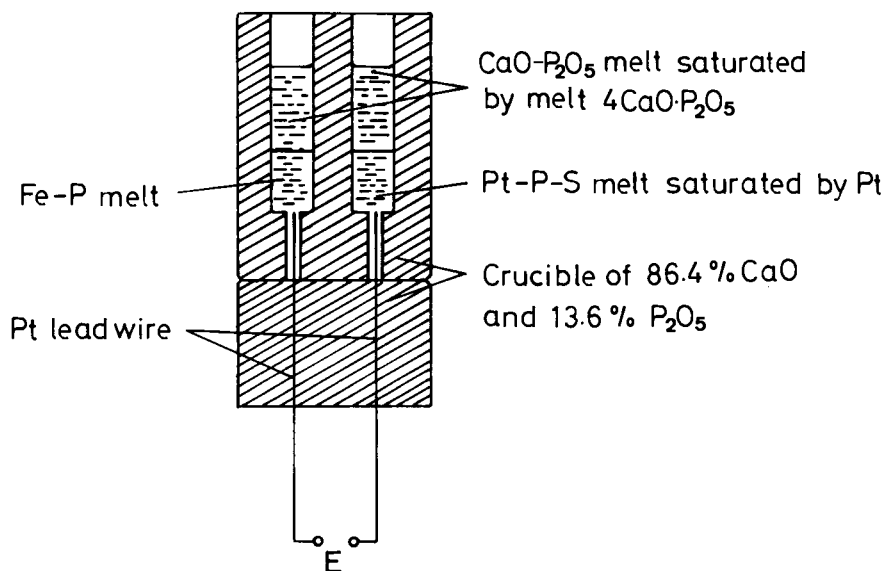


Fig. 7.15. Structure of galvanic cell with solid electrolyte of $4\text{CaO} \cdot \text{P}_2\text{O}_5$ to measure the activity of P in Fe-P melts. (After Fischer, Janke and Engell (25), 1966).

$$K = \frac{a_{P_2O_5}^{\frac{1}{2}}}{a_P^{\frac{5}{4}} P_{O_2}} \quad (7-14)$$

or

$$P_{O_2}^{\frac{5}{4}} = a_{P_2O_5}^{\frac{1}{2}} / [a_P \cdot K] \quad (7-15)$$

Inserting this expression to P_{O_2}' and P_{O_2}'' in Eq. (7-10), one can have

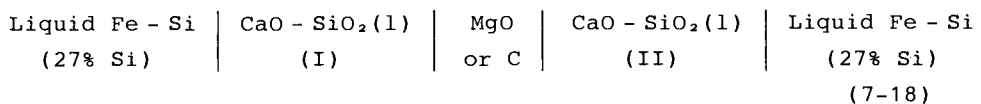
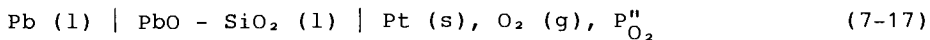
$$E = \frac{RT}{5F} \ln \frac{a_P(\text{in Fe-P})}{a_P(\text{in Pt-P})} \quad (7-16)$$

where K and $a_{P_2O_5}$ are canceled out, because they are the same value on both sides.

When the standard state of the activity is taken at a fixed composition of phosphorus in the Pt-P melt saturated by Pt, the activity of phosphorus in liquid iron can be obtained from the electromotive force according to Eq. (7-16).

Fig. 7.16 shows the activity of phosphorus in liquid Fe-P alloys at 1650°C with its standard state at infinitely dilute solution expressed by mole fraction of phosphorus. The deviation from Henry's law becomes significantly large at larger than 0.04 mole fraction.

As discussed in Chapter 2, liquid oxides containing no transition metal oxides are usually good cationic conductors. The liquid electrolytes $Na_2O-B_2O_3$, $CaO-SiO_2$, $FeO-SiO_2$, $PbO-SiO_2$, $PbO-B_2O_3$, and $CaO-Al_2O_3-SiO_2$ have been used from relatively old times. Experimental difficulties with these electrolytes have been discussed by Goto and Pluschkell⁽²⁶⁾ in details. Therefore, only two examples of galvanic cells are given below:



The cell of Eq. (7-17) has been used to obtain the activity of PbO in liquid $PbO-SiO_2$ system by several investigators; Bockris and

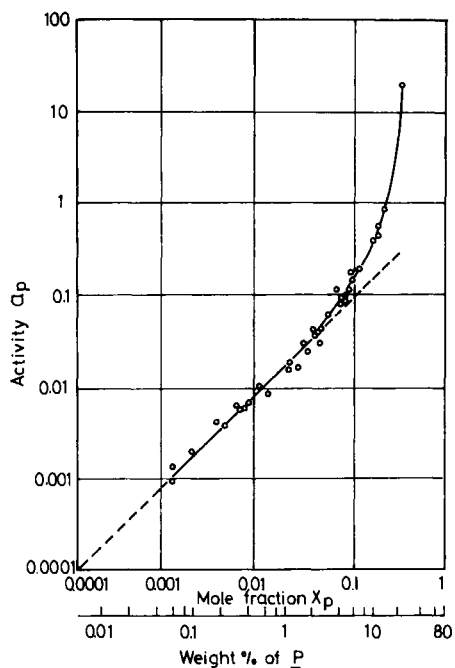


Fig. 7.16. Relation between activity of P in Fe-P binary melt at 1650°C and mole fraction of P. (After Fischer, Janke and Engell (25), 1966).

Mellors (1956)⁽²⁷⁾, Esin et al (1957)⁽²⁸⁾, Sridhar and Jeffes (1967)⁽²⁹⁾, Ito and Yanagase (1960)⁽³⁰⁾, Lepinskikh and Esin (1961)⁽³¹⁾ and Ranford and Flengas (1965)⁽³²⁾.

Using a similar procedure from Eq. (7-13) to Eq. (7-16), one can obtain the electromotive force of the above cell of Eq. (7-17) as

$$E = \frac{RT}{2F} \ln \frac{(P_{O_2}^{\prime\prime})^{\frac{1}{2}}}{a_{PbO}} - \frac{\Delta G^{\circ}}{2F} \quad (7-19)$$

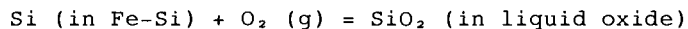
where $P_{O_2}^{\prime\prime}$ is the oxygen pressure in the reference electrode, a_{PbO} is the activity of PbO in the oxide melt used as electrolyte, and ΔG° is the standard Gibbs free energy of formation for pure liquid PbO. The lower galvanic cell of Eq. (7-18) is more complicated, because two liquid oxides with different compositions are separated by solid magnesia or carbon. In 1969, Sanbongi and Omori⁽³³⁾ exploited this type of galvanic cell to determine the activity of

silica in the oxide melts.

If the two oxide melts are directly contacting through a bridge with a capillary, the theoretical electromotive force can be expressed, again by using Eq. (6-19):

$$E = \frac{RT}{4f} \ln \frac{P_{O_2}''}{P_{O_2}'} - \frac{1}{2F} \int t_{Ca^{2+}} d\mu_{CaO} - \frac{1}{4F} \int t_{Si^{4+}} d\mu_{SiO_2} \quad (7-20)$$

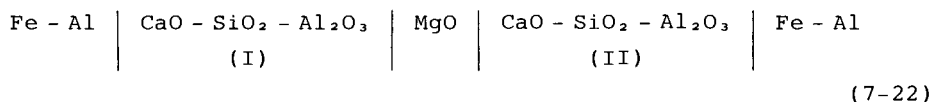
Because the two oxide melts are separated by solid MgO or solid carbon, these would be no net transfer of CaO or SiO₂, and therefore, the two integral terms can be neglected. This is a questionable assumption. Let us, however, accept this assumption. Then, the oxygen pressure at the interface between liquid Fe-Si and oxide melts can be fixed by



Thus, the oxygen pressure can be expressed as a function of the activity of SiO_2 and the equilibrium constant. Here, the activity of silicon is the same for both electrodes. Inserting this expression into Eq. (7-20), one can have

$$E = \frac{RT}{4F} \ln \frac{a_{\text{SiO}_2}(\text{at II})}{a_{\text{SiO}_2}(\text{at I})} \quad (7-21)$$

Also, Sanbongi and Omori⁽³³⁾ attempted to obtain a determination of the activity of Al_2O_3 in liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, using the galvanic cell of



where the electromotive force would be given by the following expression with the same logics of the above case:

$$E = \frac{RT}{6F} \ln \frac{a_{\text{Al}_2\text{O}_3}(\text{at II})}{a_{\text{Al}_2\text{O}_3}(\text{at I})} \quad (7-23)$$

Here, $a_{\text{Al}_2\text{O}_3}$ alternates the activity of Al_2O_3 . This experimental principle proposed by Sanbongi and Omori⁽³³⁾ was very much stimulating, because it was very difficult to obtain the activities

of SiO_2 and Al_2O_3 by other methods. One ambiguity was the physico-chemical role of the separating wall of MgO or carbon.

7.2 GALVANIC CELLS WITH SOLID ELECTROLYTES OF SULFIDES, SULFATES, AND NITRIDES

Galvanic cells with electrolytes of solid halides were extensively discussed by Tretyakov and Kaul⁽²⁾ in 1972. A monograph on molten salts was edited by Blander⁽³⁴⁾ in 1964. Only a few papers, therefore, will be introduced on halide electrolytes at the end of this section. Instead, this section will discuss only the less common electrolytes, such as sulfides, sulfates, nitrides, and oxides with proton conduction.

Solid sulfides of alkali metals or alkali earth metals would have predominant ionic conduction at elevated temperature because they are believed not to contain any electronic defects. In 1969, Worrell, Tare, and Bruni⁽³⁵⁾ published a stimulating paper indicating the range of purely ionic conduction of solid CaS . The paper by Worrell et al⁽³⁵⁾ was the first work where by the range of purely ionic conduction was clearly shown for solid CaS . Later, Nagata and Goto⁽³⁶⁾ attempted to make a more accurate determination of the conduction range as a function of the sulfur pressure and temperature. Their results are shown in Fig. 7.17.

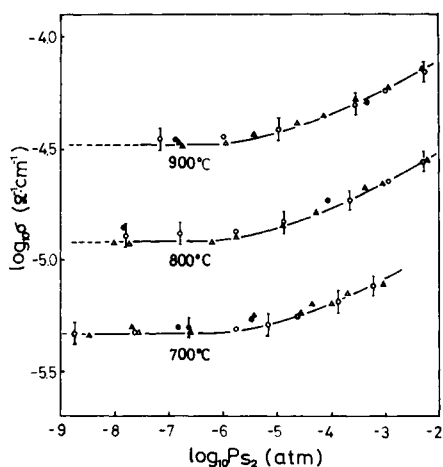
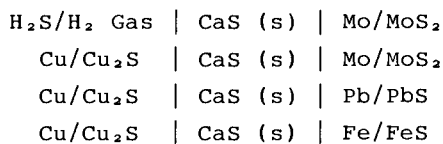


Fig. 7.17. The relation of specific conductivity to sulfur pressure; o:specimen 7, measured at a pressure attained from lower side; ●:specimen 7, from higher side; Δ:specimen 6, from lower side; ▲:specimen 6, from higher side. (After Nagata and Goto (36), 1974).

Further, Nagata and Goto⁽³⁶⁾ constructed the following galvanic cells using CaS as the solid electrolytes:

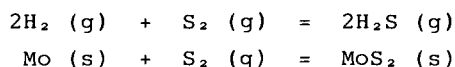


The theoretical electromotive force can be expressed by

$$E = \frac{RT}{4F} \ln \frac{P_{S_2}''}{P_{S_2}'} \quad (7-24)$$

where P_{S_2}' and P_{S_2}'' are the equilibrium sulfur pressures at the left and right side electrodes, respectively.

Because the equilibrium sulfur pressures can be obtained from the Gibbs free energies of the following reactions, one can calculate the theoretical electromotive forces for the above four galvanic cells as a function of temperature. The standard Gibbs free energy for the reactions



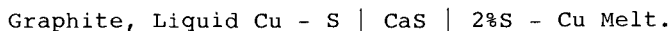
is given, respectively, by these equations

$$\Delta G^\circ = -RT \ln \frac{P_{\text{H}_2\text{S}}^2}{P_{\text{H}_2}^2 \cdot P_{\text{S}_2}}$$

$$\Delta G^\circ = +RT \ln P_{\text{S}_2}.$$

A comparison between the theoretical and measured electromotive forces is shown in Fig. 7.18. The solid lines are the theoretical electromotive forces according to Eq. (7-24).

On the other hand, Fischer and Janke⁽¹⁾ constructed the galvanic cell of



The right electrode is the reference electrode and the sulfur content of the left electrode of Cu - S melt is changed. The equilibrium electromotive forces as measured by this cell are shown

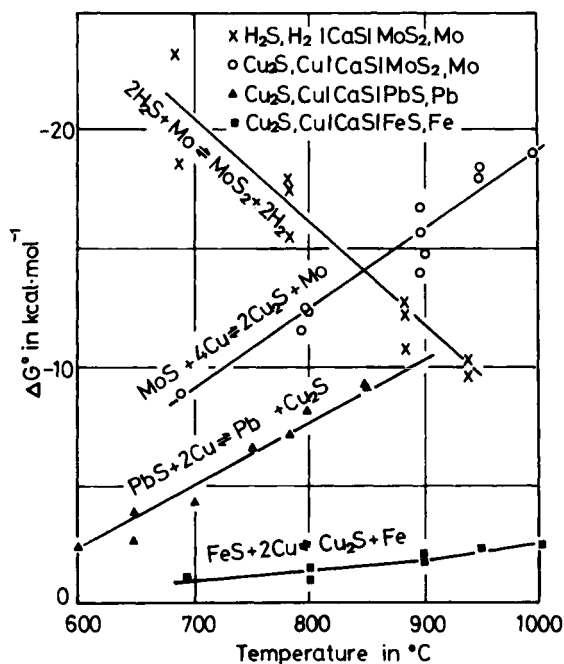
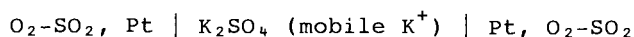


Fig. 7.18. Comparison between the standard Gibbs free energy of exchange reactions of various sulfides calculated from thermodynamic data (shown by solid lines) and from the electromotive forces of the galvanic cells with solid electrolyte of CaS. (After Nagata and Goto (36), 1974).

by Fig. 7.19. The broken line is the theoretical electromotive force.

Other types of less common solid electrolytes will be discussed in the followings with the possible applications of solid electrolytes to chemical sensors for industrial uses.

Under high oxygen pressure, sulfates of alkali metals are thermodynamically stable even at high temperature. In 1977, Gauthier and Chamberland⁽³⁷⁾ used solid K_2SO_4 as the electrolyte for a galvanic cell of



When 2 faradays of electrons are supplied to the left electrode and taken out from the right electrode, the electrode reactions would

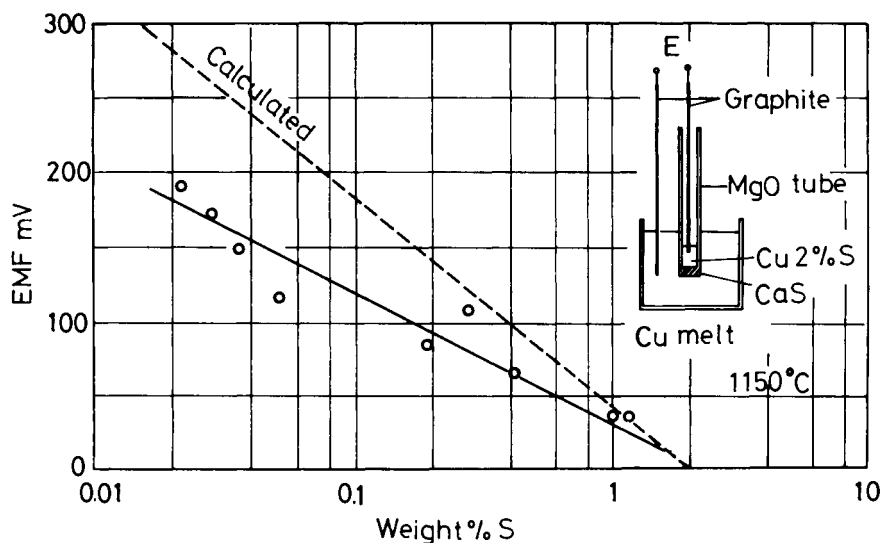
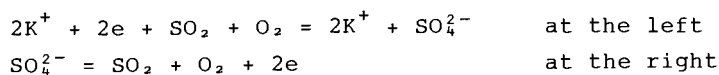
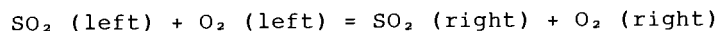


Fig. 7.19. Relation between the electromotive force and weight % of sulfur contained in liquid copper. Solid CaS is used as electrolyte with reference electrode of Cu-2%S melt at 1150°C. (After Fischer and Janke (1), 1975).

be



Summing the two reactions, one can have the virtual reaction of



Therefore, the theoretical electromotive force can be given by

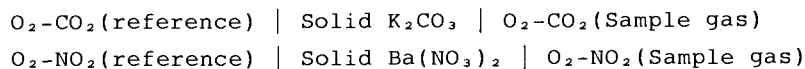
$$E = \frac{RT}{2F} \ln \frac{P_{O_2}''}{P_{O_2}'} + \frac{RT}{2F} \ln \frac{P_{SO_2}''}{P_{SO_2}'} \quad (7-25)$$

where P_i are the partial pressures of gas species of i and single and double primes mean the left and right electrodes, respectively.

When a small quantity of SO_2 is contained in nearly pure oxygen gas, the first term of the right hand side of Eq. (7-25) can be neglected. In such a case, the electromotive force can be deter-

mined only by the difference in partial pressure of sulfur dioxide. As shown in Fig. 7.20, Gauthier and Chamberland⁽³⁷⁾ have proved this theoretical equation (Eq. (7-25)) by the experiments at 820°C. The agreement between the theory and the experiment is excellent.

Furthermore, Gauthier and Chamberland have worked on the following two types of galvanic cells:



The former was operated at 726°C and the latter at 481°C. The electromotive force was proportional to the logarithm of the partial pressure of CO₂ or NO₂ in sample gases. The response time was short and sensitive to change in the gas composition.

Their study is very valuable because the principle of chemical sensors for SO₂, CO₂, or NO₂ has been clearly proven to be

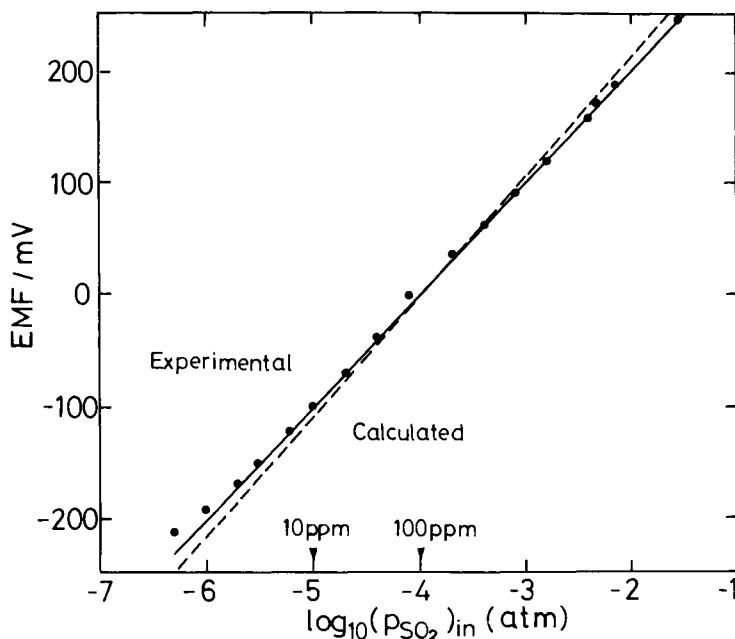


Fig. 7.20. Plot of EMF versus logarithm of the SO₂ partial pressure expressed in atmospheres. A concentration of 100 ppm SO₂ in air was circulated in the reference compartment. Temperature, 820°C; flow rate, 100cm³/min in both compartments. The dashed curve represents the calculated slope 2.3 RT/2F. (After Gauthier and Chamberland (37), 1977).

reliable as long as the galvanic cell is operated under high oxygen pressure and below the melting points of the electrolytes. The chemical sensors will be used for industrial applications.

In 1981, Iwahara and his coworkers⁽³⁸⁾⁽³⁹⁾ invented a solid oxide electrolyte with predominant proton conduction at 700°C to 1000°C. The electrolyte is SrCeO_3 doped with Yb_2O_3 , Sc_2O_3 or MgO . This type of oxide electrolytes is very attractive because of the chemical stability. The cell assembly shown in Fig. 7.21 was used to determine the transference number of H^+ in the electrolyte. A direct current was externally supplied to transfer H_2O gas from the wet air to the dry air. The content of water vapor transferred to dry air was analyzed at the gas exit of the assembly. The transference number of H^+ was calculated to be about 0.99 at 700°C, 0.95 at 800°C, and 0.84 at 1000°C. Although the migration mechanism of H^+ is not known, Iwahara and his coworkers⁽³⁸⁾⁽³⁹⁾⁽⁴⁰⁾ constructed the following galvanic cell

Pure H_2 (reference)	$\text{SrCeO}_3\text{-Yb}_2\text{O}_3$	Inert gas + H_2
$\text{O}_2\text{-H}_2\text{O}$ (reference)	$\text{SrCeO}_3\text{-Yb}_2\text{O}_3$	$\text{O}_2\text{-H}_2\text{O}$ (Sample)

When the transference number of H^+ is unity, the theoretical electromotive forces are given by the following equations for the

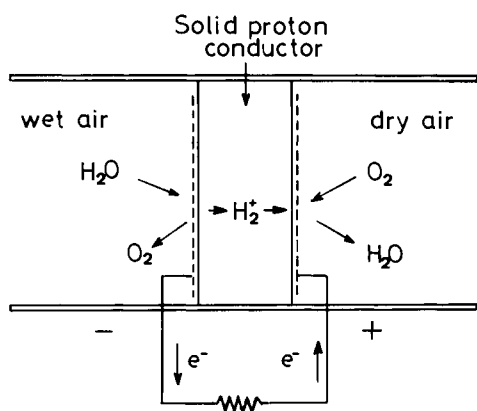


Fig. 7.21. A cell assembly to probe proton conduction in SrO-CeO_2 doped with Sc_2O_3 . (After Iwahara and his coworkers (38), 1981).

former and latter cells, respectively:

$$E = \frac{RT}{2F} \ln \frac{P''_{H_2}}{P'_i} \quad (7-26)$$

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_i} + \frac{RT}{2F} \ln \frac{P''_{H_2O}}{P'_i} \quad (7-27)$$

where P_i is the partial pressure of gas species of i , and single and double primes mean at the left and right electrodes, respectively.

Fig. 7.22 shows the relation between the electromotive force of the former cell and hydrogen pressure in the sample gas (a mixture of an inert gas and hydrogen) at 600°C and 800°C. The measured electromotive forces are smaller than the theoretical values because of the partial electronic conduction.

Other solid electrolytes of proton conduction are hydrogen uranyl phosphate tetrahydrate⁽⁴²⁾, potassium dihydrogen orthophosphate⁽⁴³⁾, zirconium oxide-hydroxide⁽⁴⁴⁾, anhydrous potassium

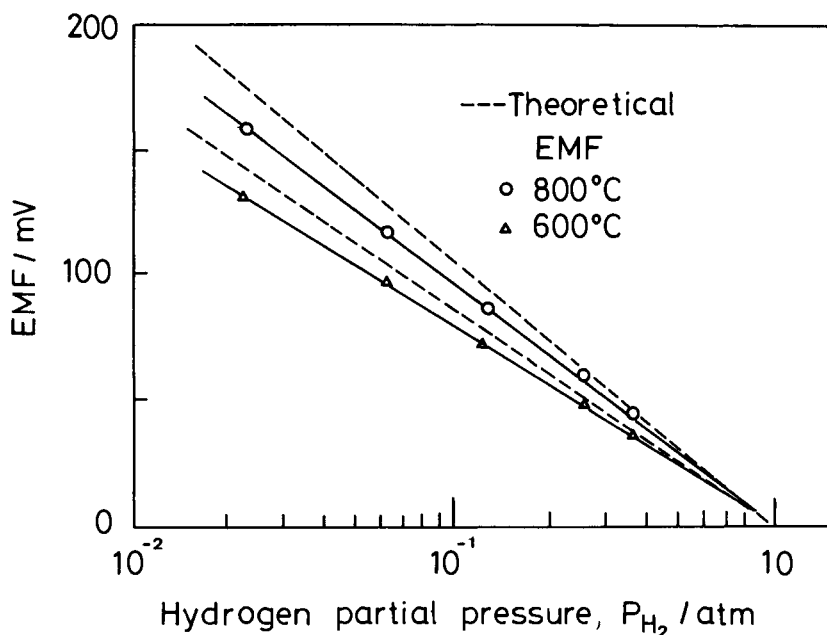


Fig. 7.22. Relation between the EMF and partial pressure of hydrogen in inert gas at 600°C and 800°C. The standard electrode is pure hydrogen gas of 1 atm. (After Iwahara and his coworkers (39), 1982).

hydroxide, or hydrogen substituted beta alumina.

Also, Gee and Fray have used solid CaH_2 as the solid electrolyte of the galvanic cell to measure the hydrogen content in liquid aluminum and its alloys⁽⁴⁵⁾.

The experimental results are generally promising, but very careful handling is needed for these complex compounds with less chemical stability.

In 1975, Fischer and Schuh⁽⁴⁶⁾ reported an interesting experiment to measure the nitrogen activity in liquid iron by the galvanic cell of

$\text{Ir/Al (reference)} \mid \text{Solid AlN} \mid \text{Liquid Fe-N at } 1600^\circ\text{C}$

Although the thermodynamic stability of AlN is questionable, this work by Fischer and Schuh⁽⁴⁶⁾ suggested that aluminum nitride can be used as a solid electrolyte. Later in 1981, Fischer, Doren and Janke⁽⁴⁷⁾ demonstrated the oxidation of AlN in liquid iron. Thus, the electromotive force is essentially determined by the oxygen pressure in liquid iron.

In 1983, Yahagi and Goto⁽⁴⁸⁾ doped solid AlN with Al_2O_3 or Y_2O_3 to accelerate the sintering rate of the electrolyte and also to increase the ionic conductivity. The following galvanic cell was constructed:

$\text{Liquid pure Al (reference)} \mid \text{AlN-Y}_2\text{O}_3 \mid \text{Liquid Fe-Al}$

where the theoretical electromotive force is given by

$$E = -\frac{RT}{3F} \ln a_{\text{Al}} \quad (7-28)$$

In this equation, a_{Al} means the activity of aluminum in the liquid Fe-Al alloy at the right side electrode.

The relationship between the electromotive force and temperature for various mole fractions of Al in liquid Fe-Al alloys is shown in Fig. 7.23. The activity of aluminum in Fe-Al binary alloys was determined⁽⁴⁸⁾. Also, they obtained the stability ranges for the three phases solid Al_2O_3 , solid AlN and liquid Fe-O-N ternary alloy at 1600°C . These results are given in Fig. 7.24. In this figure, the vertical axis is the logarithm of [wt%O] and the

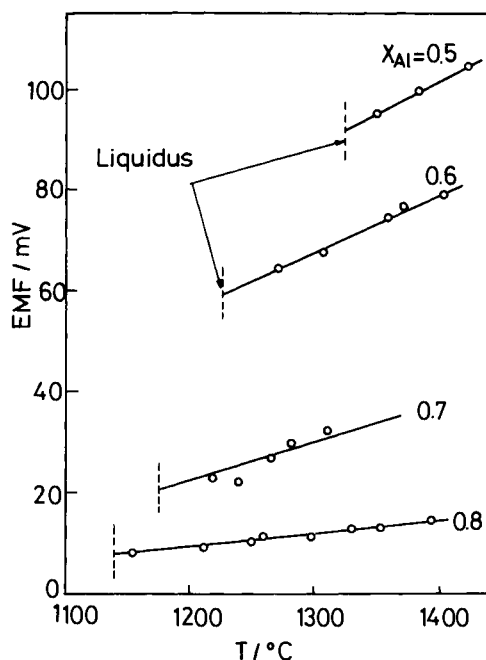


Fig. 7.23. Electromotive forces of galvanic cell : Liq. Al | Solid AlN | Fe-Al(l) as a function of temperature for various mole fractions of Al in liquid Fe-Al solutions. (After Yahagi and Goto (48), 1983).

horizontal axis is the logarithm of [%N]. The boundaries of the stability ranges are shifted when the aluminum content in liquid iron is changed. The small areas indicated by a, b, and c identify the conditions at the end of the normal steel refining, after the deoxidation of steel, and after the strongest deoxidation, respectively.

From this stability diagram, one can understand that solid AlN would be converted to Al_2O_3 , as soon as it is dipped in usual molten steels. Once it is converted to Al_2O_3 , the galvanic cell would become an oxygen concentration cell. Therefore, the nitrogen activity can not be determined. This is an example to demonstrate that one should always be very careful about the chemical stability of any electrolytes; otherwise one can not know the correct theoretical electromotive forces.

Another class of widely used solid electrolytes is the halides,

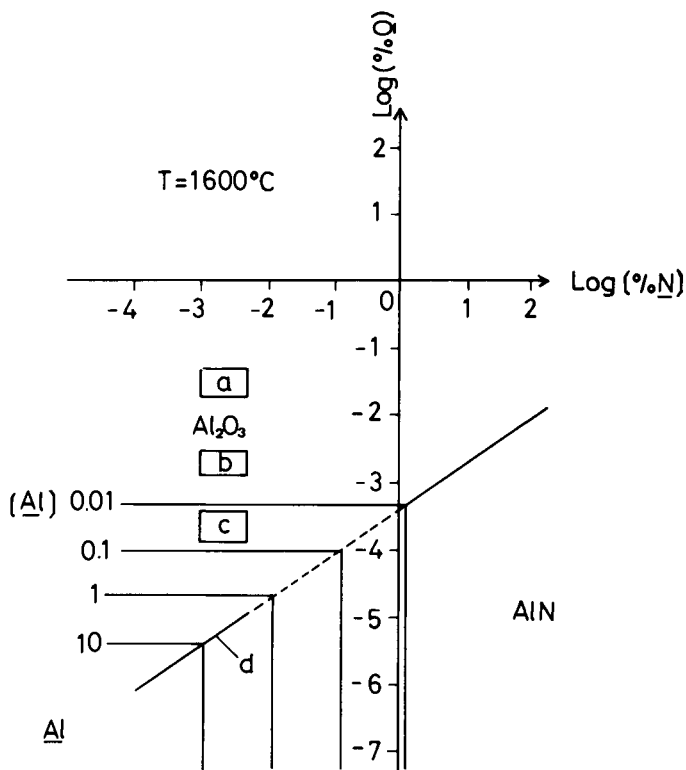


Fig. 7.24. Stability ranges of AlN, Al_2O_3 , and Fe-Al melt at 1600°C . Vertical axis is $\text{Log (wt\%O)}$ and horizontal axis is $\text{Log (wt\%N)}$ in liquid iron at 1600°C . The stable ranges of AlN and Al_2O_3 change with change of Aluminum content in liquid iron. (After Yahagi and Goto (48), 1983).

such as CaF_2 , PbF_2 , SrF_2 , MgF_2 , and BaCl_2 . Because Tretyakov and Kaul⁽²⁾ have already presented an excellent review on solid halides, only examples of galvanic cells are given in the following discussion with appropriate references. In 1957, as a first attempt, Ure⁽⁴⁹⁾ was able to determine the unit transference number of F^- in solid CaF_2 from diffusion experiments.

Stimulated by this paper⁽⁴⁹⁾, Heus and Egan⁽⁵⁰⁾ and Lofgren and McIver⁽⁵¹⁾ have independently published, in 1966, reports on the following types of galvanic cells:

Mg, MgF_2	CaF_2	Th, ThF_4
Th, ThF_4	CaF_2	Al, AlF_3
U, Uf_4	CaF_2	Al, AlF_3
Th, ThF_4	CaF_2	Ni, NiF_2

The electromotive forces have satisfied the theoretical relation of

$$E = \frac{RT}{2F} \ln \frac{P''_{F_2}}{P'_{F_2}} \quad (7-29)$$

where P''_{F_2} and P'_{F_2} are the partial pressures of fluorine gas at the right- and left-hand side electrodes, respectively.

Also, the following galvanic cells have been successfully studied by Kiukkola and Wagner⁽⁵²⁾ in 1957, Berg and Schmalzried⁽⁵³⁾ in 1961, Taylor and Schmalzried⁽⁵⁴⁾ in 1964, Egan et al⁽⁵⁵⁾ in 1962 and Egan⁽⁵⁶⁾ in 1966:

Pb(s.l) | PbCl₂(+KCl) | PbS, Ag₂S | Ag
 Pt, O₂(g) | PbSiO₃, Pb₂SiO₄ | PbF₂ | PbSiO₃, SiO₂ | Pt, O₂(g)
 Pt, O₂(g) | SrO | SrF₂ | SrTiO₃, TiO₂ | Pt, O₂(g)
 Pt, O₂(g) | MgO | MgF₂ | MgAl₂O₄, Al₂O₃ | Pt, O₂(g)
 Ce, CeCl₃ | BaCl₂ | AgCl + NaCl | Ag
 Ni, NiCl₂ | BaCl₂ | AgCl + NaCl | Ag

For the above galvanic cells with solid electrolytes of halides, one should be very careful about the chemical stability of the halides because they are generally unstable in oxygen or in contact with solid oxides. Also, it is very important to decrease the internal resistance of the galvanic cells for good reproducibility of the electromotive forces.

The measurements are limited to relatively low temperatures because of the low melting points for the halides. Thus, the electrode reactions are sometimes very slow. Nevertheless, solid halides are also very promising electrolytes for elegant experiments on thermodynamics and reaction kinetics at elevated temperature.

7.3 ELECTROCHEMICAL KNUDSEN CELL WITH SOLID ELECTROLYTE OF AgI

In the last section of the present chapter, an interesting idea will be introduced that combines a Knudsen effusion cell with a solid electrolyte. This new technique was invented by Ratchford and Richert⁽⁵⁷⁾ in 1962, and has been used with a mass spectrometer by Detry et al. in 1967⁽⁵⁸⁾, and in 1971⁽⁵⁹⁾, to determine the thermodynamic properties of sulfur and selenium vapors, respectively.

To aid in understanding the principle of this elegant experiment

by Ratchford and Richert, it seems helpful to start with an explanation on oxygen analysis by "diffusion-limited current".

Fig. 7.25 shows a schematic diagram of the oxygen sensors developed by Saji et al⁽⁶⁰⁾. The cathode compartment has a small opening. When the electrical potential is applied between two electrodes and gradually increased, the direct current through the stabilized zirconia will be naturally increased. The current would be controlled by the diffusion rate of oxygen gas through the small opening. Therefore, once a steady state is established for the diffusion, the current would become a constant value. The direction of the direct current should be such that oxygen gas will be pumped out from the cathode compartment. Otherwise, no steady state would be established for diffusion of oxygen gas through the opening.

Fig. 7.26 shows the experimental relations between the direct current and the potential at various oxygen contents in the gas outside the opening. Saji et al⁽⁶⁰⁾ determined the calibration curve of the diffusion-limited current at various oxygen contents in the outside gas of 1 atm. This principle of the oxygen analysis is sometimes very convenient, because the calibration curve is approximately proportional to the volume percentages of oxygen gas.

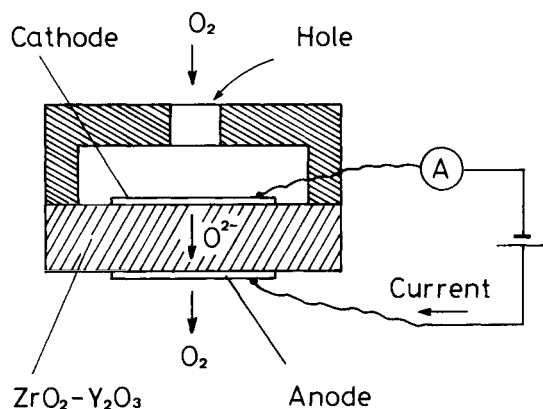


Fig. 7.25. Cell assembly to determine oxygen content in high temperature gases from the diffusion-limited current through the solid electrolyte of yttria stabilized zirconia. The current is limited by steady state diffusion of oxygen through a small opening. (After Saji et al (60), 1977).

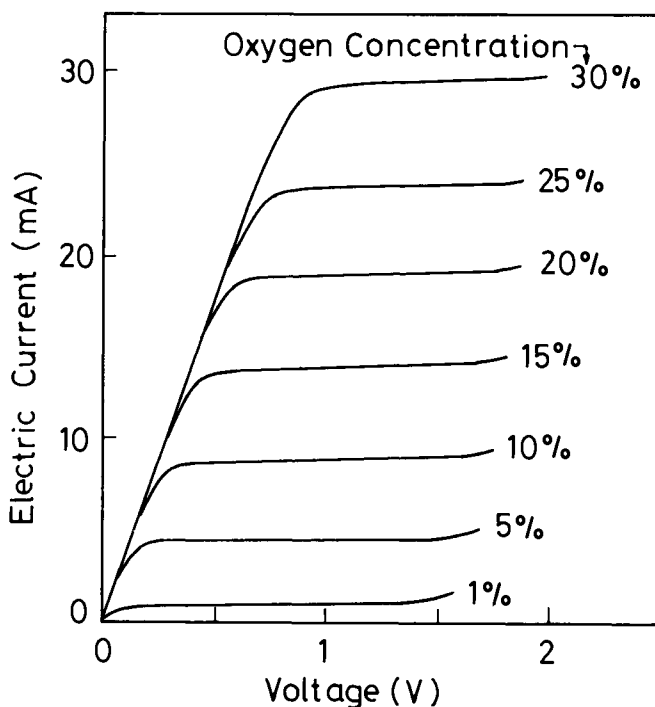
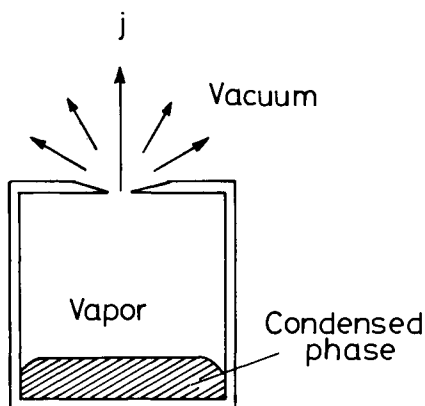


Fig. 7.26. Relation between electric current and potential applied to the cell assembly of Fig. 7.25. The constant currents are the diffusion limited currents. The oxygen concentrations are expressed by volumetric percentages. (After Saji et al (60), 1977).

The equilibrium electromotive force of the oxygen concentration cell is proportional to the logarithm of the oxygen pressure, as discussed in Chapter 6. It is, therefore, convenient to know the oxygen pressure in a wide range with low oxygen pressure but not accurate enough in a narrow range with oxygen pressure close to 1 atm.

When the pressure on the outside is reduced and a source of vapors is placed in the compartment, it becomes a "Knudsen effusion cell". A schematic diagram of the Knudsen cell is shown in Fig. 7.27. This cell was first invented by Knudsen⁽⁶¹⁾ in 1909 and has been, and will be, used in a great number of experiments to determine the vapor pressure of condensed phases.

The most important condition of Knudsen cell is that the diameter of the small opening must be smaller than the mean free path of the molecules in the equilibrium vapor of the condensed phase.



$$j = \frac{P}{\sqrt{2\pi MRT}}$$

Fig. 7.27. Schematic picture of Knudsen cell. Vapor molecules are effusing from a small opening and its diameter should be much smaller than the mean free path of the vapor in the cell. The equation gives the effusion rate per unit area of the opening. (After Knudsen (61), 1909).

When this condition is satisfied, the inside of the cell is always filled by the equilibrium vapor of the condensed phase. Under this condition, the rate of the effusion of the vapor through the small opening can be obtained according to the kinetic theory of gas molecules by

$$j = \frac{P}{\sqrt{2\pi MRT}} \quad (7-30)$$

where j is the rate of effusion per unit area of the opening in mole/cm².sec, P is the vapor pressure in the cell, M is molecular weight of the vapor, R is gas constant and T is absolute temperature. The rate of the effusion is usually known from the total weight change of the Knudsen cell during a fixed time at a constant temperature. Also, it can be known from the weight of the deposit onto a target plate with a certain geometry. When the molecular

weight is known, the equilibrium vapor pressure can be calculated from Eq. (7-30). When a single vapor species is predominant in the Knudsen cell, the vapor pressure can be straight forward calculated by Eq. (7-30).

However, when the vapor phase is a mixture of various molecular species, additional information is necessary. Examples of such case are vapors of sulfur or of selenium. This can be achieved by combining a Knudsen cell with a solid state galvanic cell, thus forming an electrochemical Knudsen cell, and then combining the electrochemical Knudsen cell with a mass spectrometer.

Fig. 7.28 shows a schematic view of the electrochemical Knudsen cell invented by Ratchford and Richert⁽⁵⁷⁾ in 1962. The bottom of the Knudsen cell is composed of two galvanic cells with a solid electrolyte of AgI.

The theoretical electromotive force can be expressed by

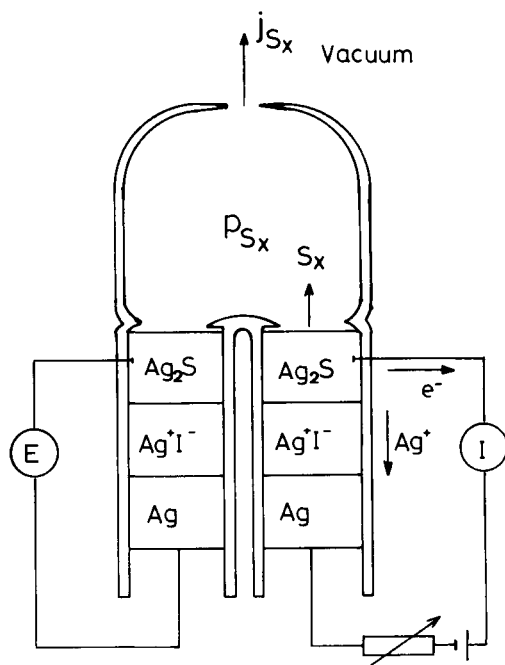
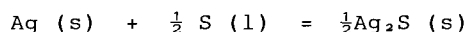


Fig. 7.28. A schematic representation of the electrochemical Knudsen cell. The left cell assembly is used to determine the chemical potential of sulfur in silver sulfide. The right cell assembly is used to control evaporation rate of sulfur by current density. (After Ratchford and Richert (57), 1966).

$$E = \frac{RT}{F} \ln a_{\text{Ag}} (\text{in Ag}_2\text{S}) \quad (7-31)$$

where a_{Ag} is the activity of silver in solid electrode of Ag_2S , which is a good electronic conductor with a small range of homogeneity. Because local equilibrium can be easily attained in the Ag_2S electrode, one can expect the equilibrium of



Thus, Eq. (7-31) can be equally well expressed by

$$E = - \frac{RT}{F} \ln a_{\text{S}}^{\frac{1}{2}} + E^\circ \quad (7-31')$$

where the standard state for the activity of sulfur is taken at pure liquid sulfur. E° means the electromotive force when the Ag_2S electrode is in equilibrium to pure liquid sulfur. The verification of Eq. (7-31) or (7-31') has been shown by experiments between 200°C and 450°C by previous investigators.

The two solid state galvanic cells with equal construction have two different tasks. The left-hand side cell shown in Fig. 7.28 is used to obtain the activity of sulfur by Eq. (7-31'), which is assumed to be uniform in both Ag_2S electrodes. The right-hand side cell is used to supply or to remove sulfur from the Ag_2S electrodes. Also, the rate of total effusion can be obtained when the steady state current is attained at a fixed activity of sulfur in the Ag_2S electrode.

The probable vapor species of sulfur would be S_2 , S_3 , S_4 , S_5 , S_6 , S_7 and S_8 .

The stationary current, i , divided by the cross-section area of the opening, q , yields the summation of the effusion rate, such as

$$\frac{i}{q} = \sum_{x=2}^{\text{all}} \frac{P_{\text{S}_x} (2Fx)}{\sqrt{2\pi M_{\text{S}_x}} \frac{RT}{F}} \quad (7-32)$$

where x is 2,3,4, etc.

The vapor pressures of the various molecules can not be separately determined by this electrochemicals Knudsen cell. However, the advantage of this technique is that one can continuously measure

the total effusion rates at various sulfur activities in the solid Ag_2S electrode.

The vapor pressures of the various vapor species can be separately measured when this electrochemical Knudsen cell is combined with a mass spectrometer. This was done for the first time by Detry et al⁽⁵⁸⁾ in 1967.

The intensity, $I_{\text{S}_x}^+$, of the S_x molecules detected usually consists of two parts; the first part derives from the primary S_x molecules and the second part from the fragments of larger molecules by collisions with electrons.

The former can be related to the partial pressure of S_x in the Knudsen cell by the equation

$$P_{\text{S}_x} = \frac{(I_{\text{S}_x}^+)^{\text{prim}} T}{A_{\text{S}_x}} \quad (7-33)$$

where A_{S_x} is the sensitivity of the mass spectrometer for S_x molecules. On the other hand, the following reaction can be assumed to be in equilibrium in the Knudsen cell:



Where the equilibrium constant, K , is defined by

$$K = \frac{P_{\text{S}_x}}{a_{\text{S}}^x} \quad (7-35)$$

Thus, by rearranging the terms,

$$P_{\text{S}_x} = K a_{\text{S}}^x \quad (7-36)$$

With Eq. (7-31'), one can express the activity of sulfur as a function of E and E° . inserting this function of E and E° into Eq. (7-36), one obtains

$$P_{\text{S}_x} = K \exp \left(\frac{2xF(E^\circ - E)}{RT} \right) \quad (7-37)$$

Again inserting this expression to Eq. (7-33), the following relation is obtained:

$$(I_{S_x}^+)_{\text{prim.}} = \frac{A_{S_x}}{T} \cdot K \cdot \exp \left(\frac{2xF(E^\circ - E)}{RT} \right) \quad (7-38)$$

The logarithm of this equation yields

$$\log (I_{S_x}^+)_{\text{prim.}} = \left(\frac{2xF(E^\circ - E)}{RT} \right) + \log \left[\frac{A_{S_x}}{T} \cdot K \right] \quad (7-38')$$

This equation tells us that the logarithm of the ion intensity would be proportional to E , that is, the measurable electromotive force of the left-hand side of the galvanic cell shown in Fig. 7.28.

The proportionality constant should be $2xF$. The results obtained by Detry et al⁽⁵⁸⁾ on the vapor species of sulfur are shown in Fig. 7.29. In this figure, the right vertical axis gives the total steady state current, (i/q) , of Eq. (7-32), and the top curve with closed circles is the measured currents in Amperes per cm^2 . The increase of the electromotive force on the horizontal axis

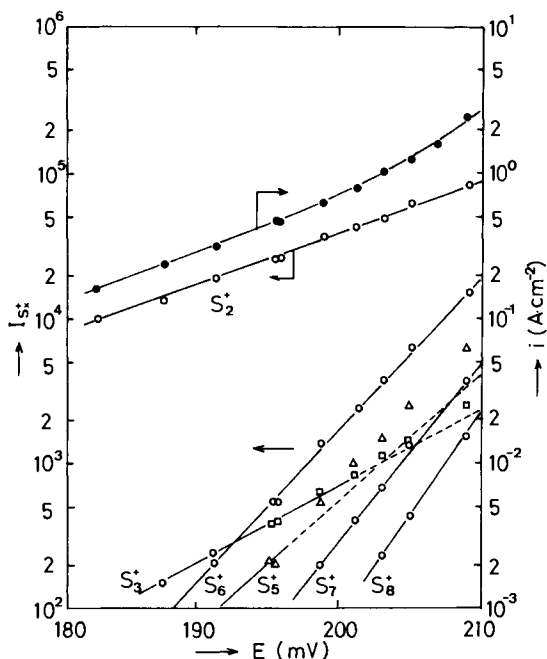


Fig. 7.29. Ion intensities $I_{S_x}^+$ for the S_x molecules (in arbitrary units) and the total current density, as a function of the e.m.f., E , at 300°C . (After Detry et al (58), 1967).

means the increase of the sulfur activity in Ag_2S electrode. The slopes of the six lines for the ion intensities are nearly equal to $2xF$, satisfying Eq. (7-38').

For conversion of the ion intensities to partial pressures for S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , and S_8 , one must first know the sensitivity of the mass spectrometer, i.e., A_{S_x} in Eq. (7-33).

At potentials lower than 190mV (Fig. 7.29), it can be assumed that the predominant vapor species is S_2 and all others can be neglected. With Eq. (7-32), one can obtain P_{S_2} from the measured value of (i/q) , neglecting all other vapor species. Once P_{S_2} is known, this value and the measured ion intensity, $I_{\text{S}_2^+}$, can be inserted in Eq. (7-33) to obtain A_{S_2} . When the following two assumptions can be used, the pressures of other species can be easily obtained using only Eq. (7-33):

- 1) The value of A_{S_2} would be nearly the same for all other vapor species of sulfur.
- 2) The number of ions produced by fragmentation would be relatively small in comparison to the number of ions from primary molecules.

The two assumptions are likely to be valid only in special cases. Table 7.1 shows the standard enthalpies and entropies of reactions

TABLE 7.1.

Standard enthalpies and entropies of reactions with gaseous sulfur molecules. (After Detry et al (58), 1967).

Reaction	Temperature °K	ΔH_T° kcal/mol	ΔS_T°
$2\text{S}(\text{rh}) \rightarrow \text{S}_2(\text{g})$	460-670	28.08 ± 0.35	32.6
$2\text{S}_3(\text{g}) \rightarrow 3\text{S}_2(\text{g})$	566-669	26.6 ± 2.0	$(37.6 \pm 3.0)^*$
$\text{S}_4(\text{g}) \rightarrow 2\text{S}_2(\text{g})$	615	28.2 ± 2.0	$(36.7 \pm 2.5)^*$
$2\text{S}_5(\text{g}) \rightarrow 5\text{S}_2(\text{g})$	565-620	95.5 ± 4.0	$(111.4 \pm 8.0)^*$
$3/4\text{S}_8(\text{g}) \rightarrow \text{S}_6(\text{g})$	435-625	6.26 ± 0.33	7.6 ± 0.3
$7/8\text{S}_8(\text{g}) \rightarrow \text{S}_7(\text{g})$	435-625	5.77 ± 0.31	7.2 ± 4.2
$\text{S}_8(\text{g}) \rightarrow 4\text{S}_2(\text{g})$	460-625	96.8 ± 2.2	110.2 ± 4.2

*Calculated values from statistical mechanical formulae.

involving gaseous sulfur molecules reported by Detry et al⁽⁵⁸⁾.

The experimental details and the results on vapor species of selenium are well given in a review paper by Richert⁽⁶²⁾.

At the end of the present Chapter, an unique idea developed by Richert and his coworkers has been introduced. This idea is a fantasy in experimental methodology because their intention is elegantly to combine a Knudsen cell, galvanic cells, and a mass spectrometer. By this combination, they could measure thermodynamic properties of complex gas phases containing various polymers.

REFERENCES TO CHAPTER 7

- 1 W.A. Fischer and D. Janke, *Metallurgische Elektrochemie*, Verlag Stahleisen, Düsseldorf and Springer-Verlag, Berlin, 1975.
- 2 Y.D. Tretyakov and A.R. Kaul, *Electrochemical Cells with Non-Oxygen Conductivity*, Chapter 14 of *Physics of Electrolytes*, edited by J. Hladik, Academic Press, London, 1972.
- 3 C.A. Beevers and M.A. Ross, *Z. für Kristallogr.*, 97(1937) p.59.
- 4 T. Yao and J.T. Kummer, *J. inorg. nucl. Chem.*, 29(1967) 2453.
- 5 J.T. Kummer and N. Weber, *Proceedings of Power Sources Conference* (1967) 21, 37.
- 6 M. Itoh, S. Saito and T. Yokokawa, *J. Chem. Thermodynamics* 8 (1976) 339.
- 7 S. Kohsaka, S. Sato and T. Yokokawa, *ibid.*, 10(1978) 117.
- 8 S. Kohsaka, S. Sato and T. Yokokawa, *ibid.*, 11(1979) 547.
- 9 W.W. Liang and J.F. Elliott, *J. Electrochem. Soc.*, 123(1976) pp. 617-620.
- 10 W.W. Liang, H.K. Bowen and J.F. Elliott, *Proceedings of Metals-Slag-Gas Reactions and Processes*, Ed. by Z.A. Foroulis and W.W. Smeltzer, *Electrochem. Soc.* (1975) pp. 608-614.
- 11 D.A. Neudorf and J.F. Elliott, *Metallurgical Trans. B*, 11 B (1980) pp. 607-614.
- 12 D.H. Deyong and J.F. Elliott, *Proceedings of Chemical Metallurgy-A Tribute to Carl Wagner* (1982) AIME, Chicago.
- 13 M.G. Froberg, E.C. Caune and M.L. Kapoor, *Arch. Eisenhüttenw.* 44 (1973) 585.
- 14 S. Yamaguchi, A. Imai, and K.S. Goto, *Scandinavian J. of Metall.*, 11 (1982) 263-264.
- 15 S. Yamaguchi and K.S. Goto, *Scandinavian J. of Metall.*, 13 (1984) 129-136.
- 16 D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 1971.
- 17 D.N. Rego, G.K. Sigworth and W.O. Philbrook, *Proc. of JAPAN-USA Seminar on Science of Iron- and Steelmaking*, 1983, Kyoto, pp. 87-94.
- 18 G.W. Toop and C.S. Samis, *Trans. TSM-AIME* 224 (1962) 878.
- 19 C.R. Masson, *Proceedings of Royal Soc.*, A 287 (1965) 201.
- 20 T. Yokokawa and K. Niwa, *Trans. of Japan Inst. of Metals* 10 (1969) pp. 3.
- 21 D.R. Gaskell, *Canadian Metallurgical Quarterly* 20 (1981) pp. 3-19.
- 22 W. Pluschkell and H. -J. Engell, *Ber. Deu. Keram. Ges.*, 45 (1968) 388-394.
- 23 W. Pluschkell, *Arch. Eisenhüttenw.*, 40(1969) 401-403.
- 24 W.A. Fischer and D. Janke, *Arch. Eisenhüttenw.*, 40(1969) 837.
- 25 W.A. Fischer, D. Janke and H.-J. Engell, *Arch. Eisenhüttenw.*, 37 (1966) 853.
- 26 K.S. Goto and W. Pluschkell, *Oxygen Concentration Cells*, Chapter 13 of *"Physics of Electrolytes"*, edited by J. Hladik, Academic Press, London, 1972.
- 27 J. O'M. Bockris and G.W. Mellors, *J. Phys. Chem.*, 60 (1956) 1321-1328.
- 28 O.A. Esin, I.T. Sryvalin, and V.V. Khlynov, *Zh. neorg. Khim.*, 2(1957) 2429-2435 and *Russ. J. of inorg. Chem.*, 2(1957) 237-248.
- 29 R. Sridhar and J.H.E. Jeffes, *Trans. Inst. Min. Metall.*, 76 (1967) 44-60.
- 30 H. Ito and T. Yanagase, *Trans. Japan Inst. Metals*, 1(1960) 115-120.
- 31 B.M. Lepinskikh and O.A. Esin, *Zh. neorg. Khim.*, 6(1961) 1223-

- 1224 and Russ. J. of inorg. Chem. 6 (1961) 625-627.
- 32 R.E. Ranford and S.N. Flengas, Can. J. Chem., 43(1965) 2879-2887.
- 33 K. Sanbongi and Y. Omori, Science Reports of Res. Inst., Tohoku Univ. A 11(1959) 244-263 and 339-359, and A 13(1961) 174-182 and 238-246.
- 34 Molten Salt Chemistry, edited by M. Blander, John Wiley & Sons, Inc., 1964, New York.
- 35 W.L. Worrel, V.B. Tare, and F. J. Bruni, High Temperature Technology, Proc. 3rd Intern. Symp. Asimolar, California, 1967, London, Butterworth 1969, 503 pp.
- 36 K. Nagata and K.S. Goto, presented at Committee on Physical Chemistry of VDEh, Düsseldorf, Oct. 1972 and Metallurgical Trans. 5 (1974) 899.
- 37 M. Gauthier and A. Chamberland, J. Electrochem. Soc., 124 (1977) 1579.
- 38 H. Iwahara, T. Esaka, H. Uchida and N. Maeda, J. Solid State Ionics, 3/4, 359 (1981).
- 39 H. Iwahara, H. Uchida, and N. Maeda, J. Power Sources, 7, 293 (1982).
- 40 J. Kondo, H. Uchida, K. Maeda, and H. Iwahara, 7th Meeting on Solid State Ionics, October 21, 22 (1982) at Tokyo Institute of Technology, Japan.
- 41 S.B. Lyon and D.J. Fray, Solid State Ionics 9 & 10 (1983) 1295-1298.
- 42 G. Pérez, S. Vilminot, W. Granier, L. Cot, C. Lucat, J.M. Réau and J. Portier. Mat. Res. Bull. 15 (1980) 587.
- 43 J.M. Réau, C. Lucat, J. Portier, P. Hagenmuller, L. Cot and S. Vilminot, Mat. Res. Bull. 13 (1978) 877.
- 44 S. Vilminot, G. Pérez, W. Granier and L. Cot, Solid State Ionics 125 (1981) 87.
- 45 R. Gee and D.J. Fray, Metall. Trans. 9B (1978) 427.
- 46 W.A. Fischer and B. Schuh, Arch. Eisenhüttenw., 46 (1975) 101-104.
- 47 W.A. Fischer, H. Doren and D. Janke, Arch. Eisenhüttenw., 52 (1981) 91-98.
- 48 M. Yahagi and K.S. Goto, J. Japan Inst. Metals, 47 (1983) 419-425.
- 49 R.W. Ure, J. chem. Phys. 26 (1957) 1363.
- 50 R.J. Heus and J.J. Egan, Z. phys. Chem., 49 (1966) 38.
- 51 N.L. Lofgren and E.J. McIver, U.K.A.E.A., A.E.R.E.R 5169 (1966) 17.
- 52 K. Kiukkola and C. Wagner, J. Electrochem. Soc., 104 (1957) 379.
- 53 R. Berg and H. Schmalzried, Z. phys. Chem., B38 (1961) 295.
- 54 R.W. Taylor and H. Schmalzried, J. phys. Chem., 68 (1964) 2444.
- 55 J.J. Egan, W. Mcloy and J. Bracher, in "Thermodynamics of Nuclear Materials" (1962) 163 pp. I.A.E.A. Vienna.
- 56 J.J. Egan, in "Thermodynamics" Vol.1 (1966) 157 pp. I.A.E.A., Vienna.
- 57 R.J. Ratchford and H. Richert, Z. Electrochem., 66 (1966) 497.
- 58 D. Detry, J. Drowast, P. Goldfinger, H. Keller, and H. Richert, Z. phys. Chem., 55 (1967) 314.
- 59 D. Detry, J. Drowast, P. Goldfinger, H. Keller, and H. Richert, Z. phys. Chem., 75 (1971) 273.
- 60 K. Saji, T. Takeuchi, and I. Igarashi, 8th Annual Meeting on Chemistry and Related Area, Chubu District of Japan (1977) October.
- 61 M. Knudsen, Ann. phys., Leipzig, 29 (1909) 179.
- 62 H. Richert, "Electrochemical Knudsen Cells for Investigating

the Thermodynamics of Vapors", Chapter 12 of "Physics of Electrolytes" edited by J. Hladik, Academic Press (1972) London.

Chapter 8

OVERPOTENTIAL AT INTERFACE BETWEEN A METAL AND AN OXIDE WITH IONIC CONDUCTION

8.1 DIRECT CURRENT OVERPOTENTIAL AND FARADAIC IMPEDANCE INDUCED BY DIFFUSION OR CHARGE TRANSFER REACTION

In the previous two chapters the equilibrium electromotive force was discussed for Galvanic cells with solid electrolytes. However when an electric current is supplied from the external source to the Galvanic cell, the overpotential is induced at the electrodes. In the present chapter it is first explained why the overpotential is induced. In the second section the application of the overpotential is presented to determine the diffusion constant of oxygen dissolved in solid and liquid metals. After these discussions the reader will be convinced that the local equilibrium prevails at the interface between a metal electrode and a solid electrolyte at high temperature. When the local equilibrium prevails at the interface, valuable information can be obtained on concentration distribution of the reactants and the reaction products in a reacting system. In the final section of this chapter the use of the Galvanic cells is introduced for several cases of heterogeneous reactions at high temperature.

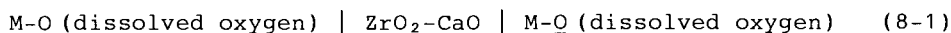
8.1.1 Direct current polarization

(a) Diffusion control. Chapters 6 and 7 discussed the electromotive force of Galvanic cells with the condition of zero current flow across the metal/electrolyte interface. The condition of current flow across the interface will now be considered. When a direct current is applied to a Galvanic cell, current would be transferred between the metal electrode and the electrolyte by the following three steps:

- (1) diffusion of ions in the electrolyte
- (2) a charge transfer reaction at the interface
- (3) diffusion of the related species in the electrode

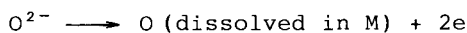
If all of these steps could be very fast, no overpotential would be induced at the interface between the metal electrode and the electrolyte. In reality, this is not the case. The overpotential is easily measured in many cases of the metal electrode in contact with solid or liquid oxides that exhibit ionic conduction.

Further, at high temperature, it is known that the overpotential is induced mainly by slow steps of diffusion. As an example, consider the phenomenon of a finite direct current flow across the following Galvanic cell with the solid electrolyte of calcia stabilized zirconia:



As shown by Eq. (8-1'), when two Faradays of electrons are supplied to the right-hand electrode and taken out from the left-hand, the electrode reaction at the left-hand side would proceed with the following sequence:

- (1) migration of O^{2-} ions in the solid oxide,
- (2) a charge transfer reaction at the interface,



- (3) diffusion of dissolved oxygen in the metal, expressed by M from the interface to the bulk.

When the applied potential is too large, step (3) would be changed to the oxidation of the metal electrode with deposition of a solid oxide, MO at the interface. However, let us assume no deposition and that step (3) is the rate-controlling step. Under this assumption, the concentration distribution of oxygen in the metal electrode can be considered. The distribution of the oxygen can be represented by Fig. 8.1 when only the left-hand side is considered under a direct current flow with a constant electrical potential. In this figure, the diffusion of the oxygen in the metal phase is assumed to be the slowest step. Therefore, the oxygen would be accumulated in the metal close to the interface.

The amount of the accumulation would increase with time, but the interface concentration, expressed by C_i , is fixed at a constant value because of the constant applied potential.

Under this condition the interface overpotential, expressed by ΔE_{over} , can be defined by

$$\Delta E_{\text{over}} = \frac{RT}{2F} \ln \frac{C_i}{C_b} = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}^i}{P_{\text{O}_2}^b} \quad (8-2)$$

where C_i and C_b are oxygen contents at the interface and in the

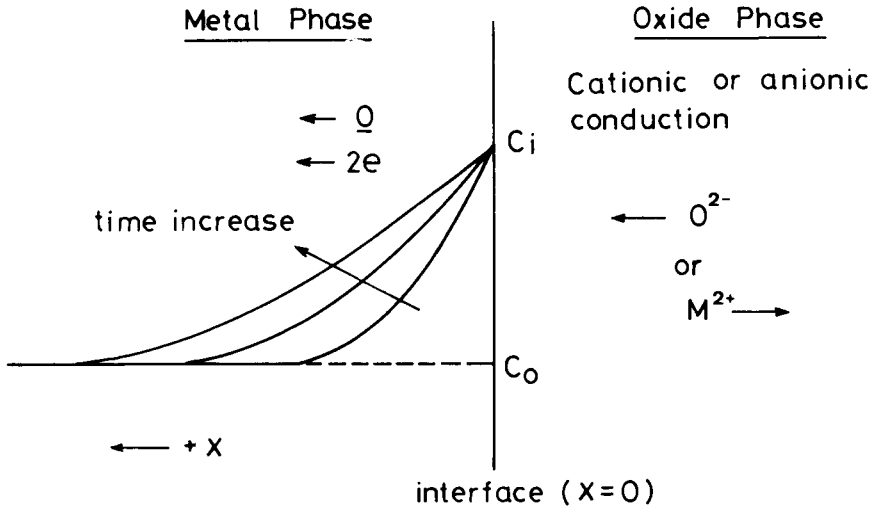


Fig. 8.1. A schematic diagram of oxygen concentration change with time and distance x in the metal phase under a potentiostatic current flow.

bulk, respectively, and $P_{O_2}^i$ and $P_{O_2}^b$ are the corresponding oxygen pressures, respectively.

The oxygen content in the metal phase can be expressed as a function of time, t , and distance, x , from the interface. When this function is expressed by $C(t,x)$, it can be obtained by solving Fick's second law of diffusion with the following boundary conditions:

$$\begin{aligned} C &= C_b & \text{at } x &= \infty \\ C &= C_i & \text{at } x &= 0 \text{ at } t > 0 \end{aligned} \quad (8-3)$$

Fick's second law of diffusion is given by the relationship

$$\left(\frac{\partial C}{\partial t} \right) = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (8-4)$$

where C is concentration, t is time, x is distance, and D is diffusion constant.

Analytical solutions of this differential equation have been given for many different boundary conditions by Crank in 1956 as a book⁽¹⁾.

Accordingly, the solution of Eq. (8-4) for the boundary condition

of Eq. (8-3) is expressed by

$$\frac{C(t,x) - C_i}{C_b - C_i} = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{tD}} e^{-\lambda^2} d\lambda \quad (8-5)$$

where

$$\lambda = \frac{x}{2\sqrt{tD}} .$$

For the present special case, D in the above equations means diffusion constant of oxygen dissolved in the metal phase.

Because the oxygen is not accumulated at the interface, the current density, expressed by i , should be equal to the rate of diffusion of oxygen multiplied by twice the Faraday constant, expressed by $2F$:

$$i = -2FD \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (8-6)$$

where i is given by A/cm^2 . When Eq. (8-5) is differentiated by x and then inserted to Eq. (8-6), one can have

$$i = \frac{2F\sqrt{D} (C_b - C_i)}{\sqrt{\pi t}} . \quad (8-7)$$

Because the interface concentration, C_i , is related to the overpotential by Eq. (8-2), the relation can be inserted to Eq. (8-7).

The current, i , can then be given by the equation

$$i = (2FC_b\sqrt{D}) \cdot \frac{1 - \exp\left[\frac{RT}{2F} \Delta E_{\text{over}}\right]}{\sqrt{\pi t}} . \quad (8-8)$$

This equation tells us that the current density is proportional to the square root of diffusion constant of oxygen, to the exponential overpotential, and to the reciprocal square root of time as long as the constant electrical potential is applied to the Galvanic cell of Eq. (8-1). The experimental proof of Eq. (8-8) will be discussed in the following section of 8.2.

Meanwhile, the direct current can also be supplied to the Galvanic cell under the condition of constant current density at the metal/electrolyte interface. This condition is termed galvanostatic and can be expressed as

$$i = -2FD \left(\frac{\partial C}{\partial x} \right)_{x=0} = \text{constant} \quad . \quad (8-9)$$

Fick's second law of diffusion Eq. (8-4), can also be solved with the boundary condition of Eq. (8-9). The solution gives the following expression for the interface concentration, C_i ;

$$C_i = C_b + \frac{i\sqrt{t}}{F\sqrt{\pi D}} \quad . \quad (8-10)$$

Inserting this equation for C_i into Eq. (8-2), one can obtain the relation between the overpotential and time:

$$\Delta E_{\text{over}} = \frac{RT}{2F} \ln \left[\frac{i\sqrt{t}}{C_b F \sqrt{\pi D}} + 1 \right] \quad (8-11)$$

or

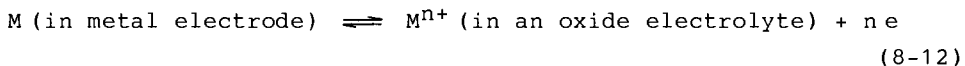
$$\exp \frac{2F}{RT} [\Delta E_{\text{over}}] = \frac{i\sqrt{t}}{C_b F \sqrt{\pi D}} + 1 \quad . \quad (8-11')$$

This equation shows that the exponential overpotential is proportional to the square root time, to the current density, and to the reciprocal square root of the diffusion constant of oxygen.

(b) Charge transfer control. The previous section discussed the overpotential induced by diffusion, and Eqs. (8-8) and (8-11) were given for the relationship between the overpotential, current density, time, and diffusivity. The present section discusses the overpotential induced by a slow charge transfer reaction. In 1967, Vetter⁽²⁾ published an excellent monograph on electrochemical kinetics, including a concise discussion on this case.

The problem is very complicated, but in essence the relationship between the overpotential and the current density is derived from the assumption that the activation energy of the charge transfer reaction would be affected by the overpotential.

For simplification of our discussion, consider the following charge transfer reaction as an example:



where this reaction is termed anodic when the reaction proceeds in the right-hand direction. For the reverse direction, it is called as a cathodic reaction.

Fig. 8.2 illustrates why the activation energy of the reaction,

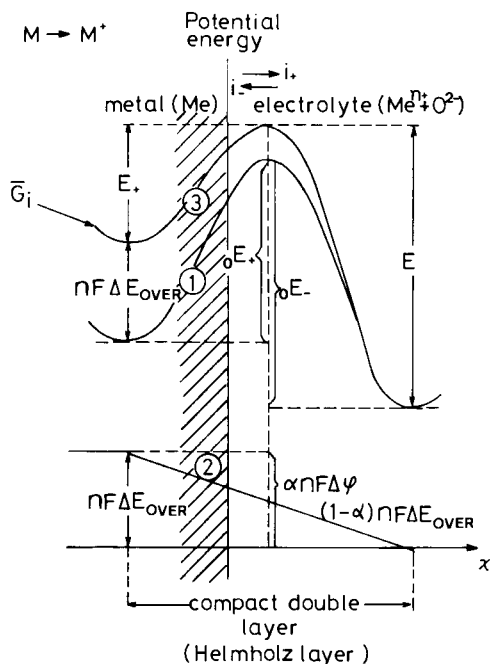


Fig. 8.2. Diagram of the dependence of the anodic (E_+) and cathodic (E_-) activation energies on applied overpotential, ΔE_{Over} across the compact double layer for a metal/oxide interface. Curve ③ $\Delta E_{Over} > 0$; Curve ① $\Delta E_{Over} = 0$ (After Vetter (2) 1967).

Eq. (8-12), would be changed by the overpotential, ΔE_{Over} .

The curve marked by ① shows the initial potential energy of an atom M and M^{2+} in the compact double layer, or Helmholtz double layer of several Angstroms thickness.

This initial potential energy distribution means the distribution under zero net current flows. In spite of zero net current, the same values of the anodic current, i_+ , and the cathodic current, i_- , are flowing across the metal/oxide interface due to thermal vibration.

The two minimum values of the potential energy are not equal, because the potential energy in the metal phase is generally different from that in the oxide phase.

The straight line labeled by ② is the distribution of the electrical potential energy when the current is externally supplied at a constant overpotential of ΔE_{Over} . The electrical potential energy is assumed to be a linear distribution. The intersection

between this line and the vertical line originated at the maximum of the curve ① gives the definition of the transfer coefficient, α , which takes a value between 0 and 1.0;

$$0 < \alpha < 1.0 \quad .$$

The value of α , usually 0.4-0.6, is determined by the kind of electrode reaction and thus, by the shape of the potential energy curve and of double layer thickness.

When current flows at a constant overpotential, the initial curve of the potential energy would be shifted as shown by the curve labeled by ③. Therefore, the activation energies for the anodic and cathodic reactions would be changed as follows:

$${}^{\circ}E_{+} \longrightarrow {}^{\circ}E_{+} - \alpha nF \Delta E_{\text{Over}} \quad (8-13)$$

$${}^{\circ}E_{-} \longrightarrow {}^{\circ}E_{-} + (1 - \alpha) nF \Delta E_{\text{Over}} \quad (8-14)$$

Now, the anodic and cathodic currents can be expressed by, respectively,

$$i_{+} = nF C_M \vec{k} \exp[- ({}^{\circ}E_{+} - \alpha nF \Delta E_{\text{Over}} / RT)] \quad (8-15)$$

$$i_{-} = nF (C_{M^{n+}}) \overleftarrow{k} \exp[- ({}^{\circ}E_{-} + (1 - \alpha) nF \Delta E_{\text{Over}} / RT)] \quad . \quad (8-16)$$

The concentration of M in metal and M^{n+} in oxide are given by C_M and $C_{M^{n+}}$, respectively. The forward and backward rate constants of the reaction, Eq. (8-12), are expressed by $\vec{k}$ and $\overleftarrow{k}$, respectively.

Because the exchange current density, usually expressed by i_0 , is the absolute value of anodic and cathodic current under zero overpotential, it can be expressed by

$$\begin{aligned} i_0 &= | i_{+} | = | i_{-} | \\ &= nF C_M \vec{k} \exp(- {}^{\circ}E_{+} / RT) \end{aligned} \quad (8-17)$$

$$= nF (C_{M^{n+}}) \overleftarrow{k} \exp(- {}^{\circ}E_{-} / RT) \quad . \quad (8-18)$$

Inserting Eq. (8-17) into Eq. (8-15) and Eq. (8-18) into Eq. (8-16), an important relation between the net current density and the overpotential can be derived as follows:

$$\begin{aligned} i &= | i_{+} | - | i_{-} | \\ &= i_0 \left[\exp\left(\frac{\alpha nF}{RT} \Delta E_{\text{Over}} \right) - \exp\left(\frac{-(1-\alpha)nF}{RT} \Delta E_{\text{Over}} \right) \right] \quad . \end{aligned} \quad (8-19)$$

This equation is sometimes called as Butler⁽³⁾-Volmer⁽⁴⁾ equation and shows that the current is a function only of overpotential and temperature and not of time. This feature is very different from the case of the diffusion control, e.g. Eqs. (8-8) and (8-11).

Fig. 8.3 shows the net current density divided by the exchange current. Also the anodic and cathodic currents at 25°C for $\alpha = 0.50$ and $n = 1.0$ according to Eq. (8-19) are shown. Because the net current is the sum of the anodic and cathodic currents, it takes the value between these partial currents as shown by the solid line.

When the anodic polarization is very large, i.e., $\Delta E_{\text{Over}} \gg (RT/\alpha nF)$, the second term of Eq. (8-19) can be neglected, and thus,

$$\Delta E_{\text{Over}} = \frac{RT}{\alpha nF} \ln i - \frac{RT}{\alpha nF} \ln i_0 \quad (8-20)$$

on the other hand, when the cathodic polarization is very large,

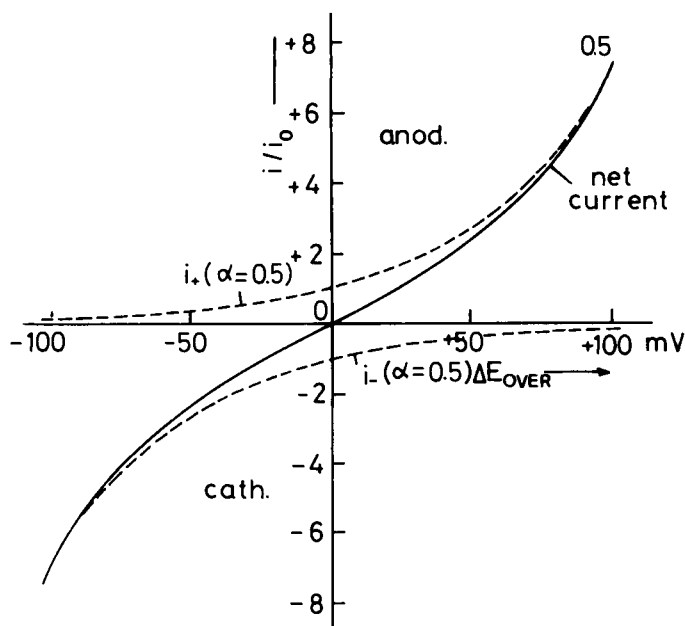


Fig. 8.3. Dependence of change-transfer overvoltage on current density in units of the exchange current density i_0 for current transfer coefficients $\alpha = 0.50$ and the overvoltage-dependence of the partial current densities i_+/i_0 and i_-/i_0 for $\alpha = 0.5$ and $n = 1.0$ (Temp. 25°C) according to Eq. (8-19) (After Vetter (2) 1967).

which means a negative overpotential:

$$\Delta E_{\text{Over}} < 0 \quad \text{and} \quad |\Delta E_{\text{Over}}| \gg \frac{RT}{(1-\alpha)nF} .$$

Then, the first term of Eq. (8-19) can be neglected:

$$\Delta E_{\text{Over}} = \frac{RT}{(1-\alpha)nF} \ln|i| - \frac{RT}{(1-\alpha)nF} \ln i_0 . \quad (8-21)$$

Fig. 8.4 shows how the transfer coefficient, α , and the exchange current density, i_0 , can be estimated when the relationship between the overpotential and net current density is experimentally well measured.

The slope at the large overpotential can give the transfer coefficient, α , because the valence of the cation is usually known. The intersection of the interpolated line with the horizontal axis can give the exchange current density because the value of α is known from the slope. The experimental curve shown in this figure is usually called "Tafel curve"⁽⁵⁾.

The exchange current density of metal/oxide interface at high temperature is too large to be determined by this curve. A special method is necessary for determination of large exchange current densities. This problem will be discussed in Chapter 9.

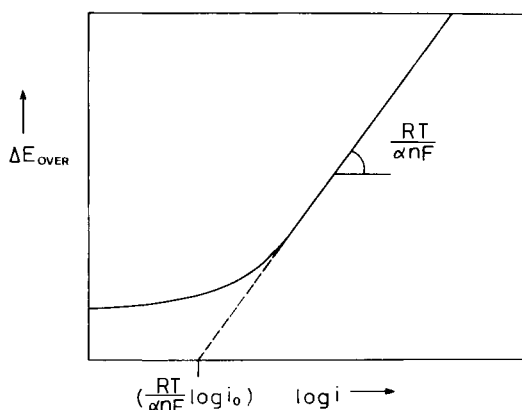


Fig. 8.4. An illustration of how the transfer coefficient, α , and the exchange current density, i , can be obtained from the measured net current with various overpotentials.

8.1.2 Alternating current polarization

(a) Diffusion control. In general, the case of diffusion control is more frequently observed in the metal/oxide system. Therefore, this case is discussed first and the case of charge transfer control is discussed later.

When one cycle of an alternating potential is applied to the Galvanic cell of Eq. (8-1), a concentration gradient of oxygen will be built up in the metal phase because of the slow diffusion of oxygen. The top picture of Fig. 8.5 shows one cycle of the applied potential. Let us consider the concentration distribution at 6 different times, expressed by t_0 , t_1 , t_2 , t_3 , t_4 , and t_5 , which

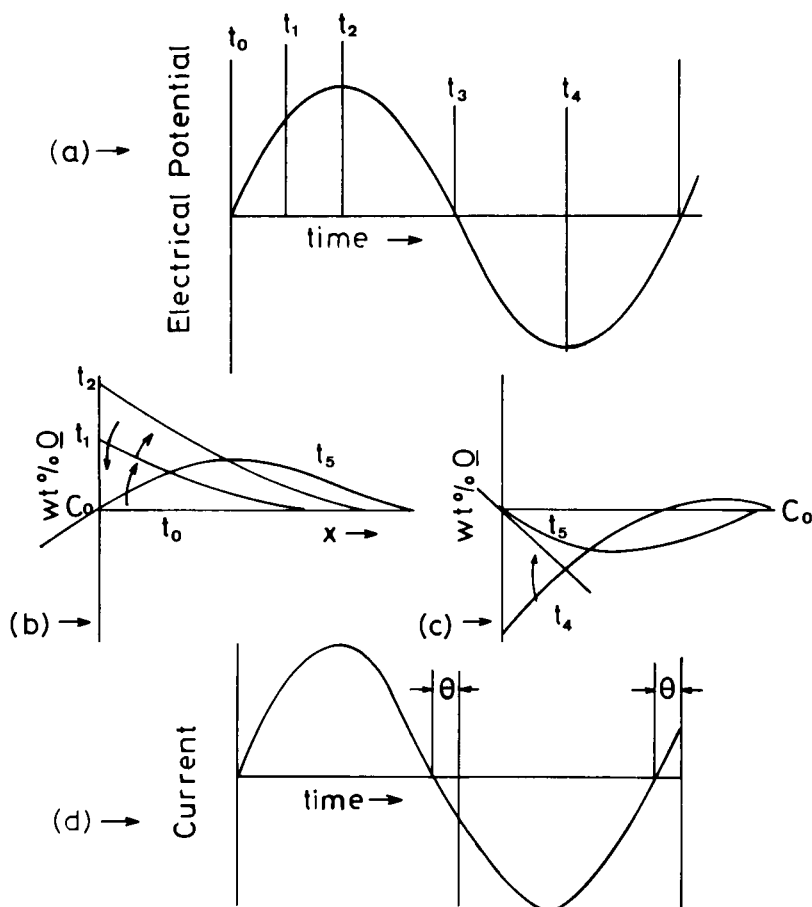


Fig. 8.5. Schematic diagrams of oxygen concentration change ((b) and (c)) when an alternating potential (a) is supplied. (d) is a current deduced from the concentration gradient at $x = 0$.

are shown on the top figure.

When the metal phase of the right-hand side of Eq. (8-1) is considered, the concentration distribution of oxygen can be deduced as shown by two middle figures labeled (b) and (c). These two figures show the relationship between the oxygen dissolved (in wt%) in the metal phase and the distance, x , from the interface.

At $t = t_0$, the concentration should be uniform at the initial concentration expressed by C_0 . At $t = t_1$, the interface concentration will increase and become a maximum at $t = t_2$. After t_2 , it should decrease because the potential is decreasing and should become C_0 at t_3 . However, the oxygen concentration at some distance from the interface would be larger than C_0 because of the slow diffusion. The interface concentration would become minimum at $t = t_4$, and again it should become C_0 at $t = t_5$ because of zero potential.

Because the current is proportional to the concentration gradient at $x = 0$, as expressed by Eq. (8-6), the change of the current with time can be deduced as shown by the bottom figure labeled (d) in Fig. 8.5.

In figures (b) and (c), it should be noted that the current is not zero at t_3 and t_5 even with zero potential.

A comparison of one cycle of potential (a) and of current (d) shows that the maximum of the current appears faster than that of electrical potential with a phase difference of θ . According to the excellent monograph of Vetter⁽²⁾, the above relationship between potential and current can be exactly reproduced by using equivalent circuits.

When the current maximum is faster than the potential maximum, the circuit can be expressed by a resistor and a condenser*. Fig. 8.6 shows two equivalent circuits, which give the same potential-

* Appendix:

- (a) If there is no phase change between a current and a potential, the circuit is composed of only resistances. If the potential maximum appears faster than that of the current, the circuit can be expressed by a resistance and an inductance.
- (b) Capacity reactance $X_C = \frac{1}{\omega C}$ (ohm) or $= \frac{1}{2\pi f C}$ (ohm) where C is the capacitance in Farad, ω is the angular frequency, and f is the frequency.
- (c) Induction reactance $X_L = 2\pi f L$, where L is the inductance in Henry.

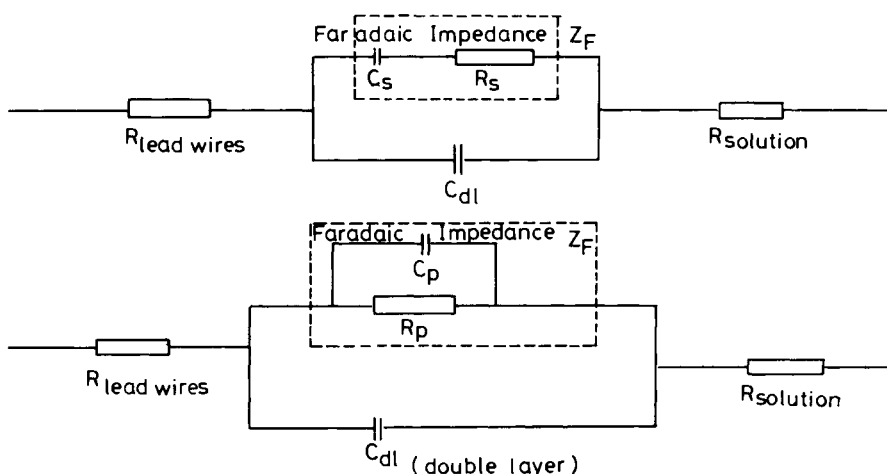


Fig. 8.6. Two equivalent circuits for an AC current flow through a metal and an oxide with ionic conduction.

current relation as discussed in Fig. 8.5. That is, there is no difference in the performance of two circuits.

In Fig. 8.6, the resistances of lead wires and of the electrolyte solution of oxides are expressed as $R_{\text{lead wires}}$ and R_{solution} , respectively. The resistance and the capacitance surrounded by a broken line is usually called Faradaic impedance⁽²⁾. The capacitance of the double layer is connected in parallel to this, because it is usual to have a certain capacitance of the double layer formed at the interface between a metal and an oxide. When diffusion is the rate-controlling step, the Faradaic impedance is referred to as diffusion impedance. The diffusion impedance can be expressed as a function of the diffusion constant of oxygen, its concentration in the metal phase, and the frequency of the current. For derivation of the expression, Fick's second law of diffusion, Eq. (8-4), should be solved for the following condition for semi-infinite mediums:

The initial condition, at $t = 0$ and $x > 0$,

$$C = C_0 \quad (8-22)$$

The boundary condition, $i \sin \omega t = 2FAD \left(\frac{\partial C}{\partial x} \right)_{x=0}$ (8-23)

and at $t > 0$, $x = \infty$

$$C = C_0 \quad (8-24)$$

The solution of Fick's second law of diffusion for the above condition was made in 1899 by Warburg⁽⁶⁾, and in 1903 by Kruger⁽⁷⁾, and was well discussed by Vetter⁽²⁾ (pp. 200-201). According to this solution, the Ohmic and capacitive components of the Faradaic impedance are given by these equations, respectively:

$$R_s = \frac{RT}{(nF)^2 AC_0} \sqrt{\frac{1}{2D\omega}} \quad (8-25)$$

$$C_s = \frac{(nF)^2 AC_0}{RT} \sqrt{\frac{2D}{\omega}} \quad (8-26)$$

where the subscript for R and C is "s", because the components given above are for series connections as shown in the upper picture of Fig. 8.6.

In Eqs. (8-25) and (8-26), n is the valence of O^{2-} , e.g. 2-, F is the Faraday constant, A is the interface area, C_0 is the initial content of oxygen dissolved in the metal, D is the oxygen diffusion constant, and ω is the angular frequency of the alternating current supplied.

According to the theory of alternating current, the impedance, Z, is expressed as a function of Ohmic and capacitive components by the equation

$$Z = \sqrt{R_s^2 + \frac{1}{(\omega C_s)^2}} \quad (8-27)$$

Insertion of Eqs. (8-25) and (8-26) into Eq. (8-27) yields

$$\begin{aligned} Z &= \frac{RT}{(nF)^2 AC_0} \sqrt{\frac{1}{2D\omega} + \frac{1}{2D\omega}} \\ &= \frac{RT}{(nF)^2 AC_0} \sqrt{\frac{1}{D\omega}} \quad (8-28) \end{aligned}$$

This equation tells us that both the Ohmic, R_s , and capacitive ($1/C_s$) components, are equal to each other and proportional to $(1/\sqrt{\omega})$ as long as the Faradaic impedance is induced by diffusion. Thus, the rate controlling step of the reaction, $O^{2-} = \underline{O}(\text{in metal}) + 2e$, can be estimated when the Faradaic impedance can be measured as a function of the frequency of the alternating current supplied.

The resistance and capacitance in a parallel connection, expressed by R_p and C_p , respectively, can be obtained from those in a series connection by using the following relations⁽²⁾:

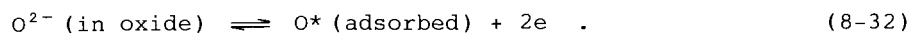
$$R_p = R_s \left(1 + \frac{1}{\omega^2 C_s^2 R_s^2} \right) \quad (8-29)$$

$$C_p = C_s \left(\frac{1}{1 + \omega^2 C_s^2 R_s^2} \right) \quad (8-30)$$

(b) Mixed-control. The equation for the capacitance, Eq. (8-26), remains the same when the current flow is controlled by a mixed rate-controlling step of diffusion and charge transfer reaction, but the equation for the resistance, R_s of Eq. (8-25), becomes as follows⁽²⁾:

$$R_s = \frac{RT}{AnFi_0} + \frac{RT}{(nF)^2 AC_0} \sqrt{\frac{1}{2D\omega}} \quad (8-31)$$

where i_0 is the exchange current density of the charge transfer reaction



The problem for the case of chemical reaction control was solved in 1952 by Gerischer⁽⁸⁾. The Ohmic and capacitive components of the reaction impedance are given by the following equations for the series connection:

$$R_r = \frac{RT}{(nF)^2 C_0 k_r} \left[\frac{1}{1 + (\omega/k_r)^2} \right] \quad (8-33)$$

$$\frac{1}{\omega C_r} = \frac{RT}{(nF)^2 C_i k_r} \left[\frac{(\omega/k_r)}{1 + (\omega/k_r)^2} \right] \quad (8-34)$$

where k_r is the reaction rate constant and the subscript r means the reaction rate-control. At very low frequency where $\omega \ll k_r$, the above two equations can be approximated by

$$R_r = \frac{RT}{(nF)^2 C_0 k_r} \quad (8-35)$$

$$\frac{1}{\omega C_r} = \frac{RT}{(nF)^2 C_i k_r} \left[\frac{\omega}{k_r} \right] \quad (8-36)$$

According to these equations, the resistance becomes a constant value and the capacitive component decreases with a decrease in the frequency.

Fig. 8.7 shows the relationship of the components of the Faradaic impedance and reciprocal square root of the frequency for four

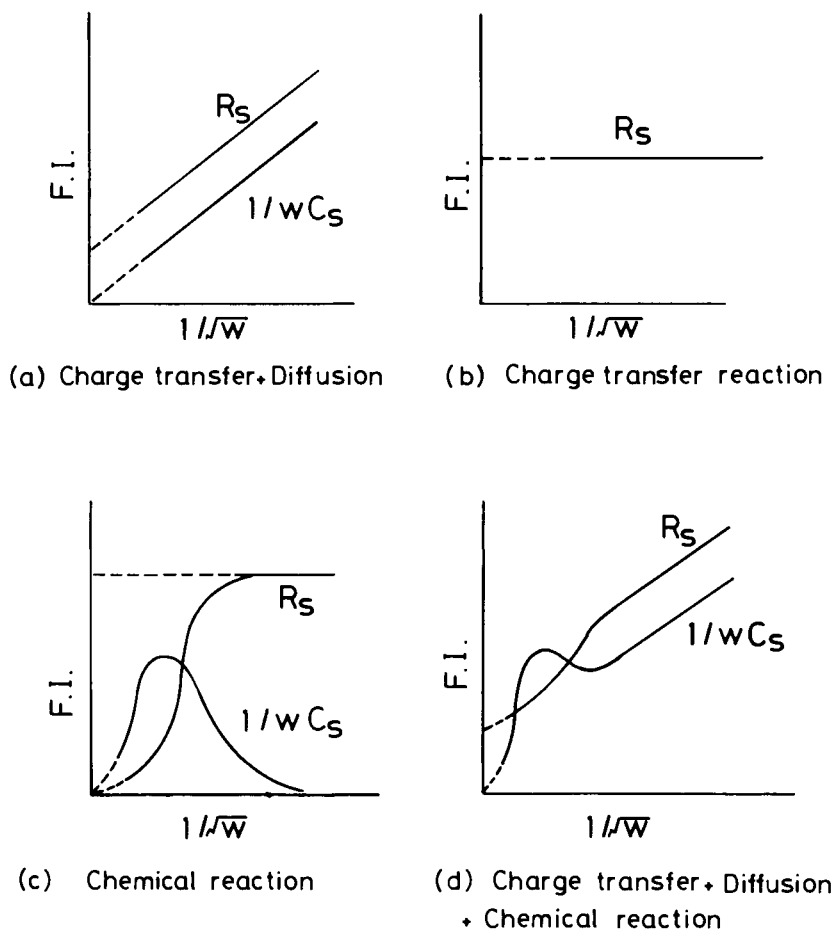


Fig. 8.7. Frequency response of Faradaic impedance.

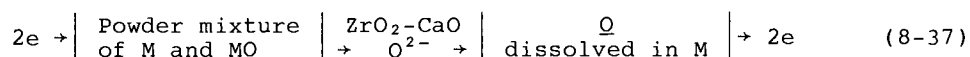
cases of the rate controlling steps.

In figure (b), the capacitive component is zero and the Ohmic component is a constant value when the rate is exclusively controlled by the charge transfer reaction. An experimental study on this frequency response on a metal/oxide interface will be discussed in Chapter 9. Figure (a) shows the relation between Faradaic impedance and reciprocal square root of angular frequency for the case of the mixed control of charge transfer and diffusion. Figure (c) is the frequency response for the case of the rate-controlling step only by a chemical reaction. Finally figure (d) is the frequency response when the rate is mixedly controlled by a charge transfer, diffusion of a species, and a chemical reaction.

8.2 DETERMINATION OF INTERDIFFUSIVITY OF OXYGEN IN METALS

In the previous section, the relationships between overpotential and current density were discussed for various cases of the rate-controlling step in the reaction between a metal and an oxide phase. An application of the theoretical equation will be given in this section for determination of the interdiffusivity of oxygen in metals. The definition of interdiffusivity was given in Chapter 4.

For this illustration, consider the supply of a direct current through the following Galvanic cell:



where the direction of the arrows indicate the direction of motion of electrons and oxygen anions. When a powder mixture of a metal, M, and its oxide, MO, is used, its buffering capacity against the oxygen pressure change is usually very large and thus, an overpotential is induced only at the interface between the solid electrolyte and the metal containing oxygen.

As discussed previously, equations (8-8) and (8-11) can be used to determine the diffusivity of oxygen dissolved in the metal. This method was first exploited in 1966 by Rickert and his coworkers⁽⁹⁾ (10)(11) by using Galvanic cells of linear and cylindrical geometries.

Osterwald and Schwarzlose⁽¹²⁾ (1968) and Pastorek and Rapp⁽¹³⁾ (1969) used this principle for the determination of oxygen diffusivity in metals.

These investigators were the first to exploit the method even with the experimental difficulties at high temperature. The diffusivity of oxygen has been determined in solid silver, solid copper, liquid silver, and liquid copper.

Later in 1976, Kawakami and Goto⁽¹⁴⁾ determined the diffusivity of oxygen in liquid iron at 1550°C. Also, Otsuka and Kozuka determined the oxygen diffusivity in liquid lead⁽¹⁵⁾ in 1975, in liquid copper⁽¹⁶⁾ in 1976, in liquid nickel⁽¹⁷⁾, and in liquid iron⁽¹⁷⁾ in 1977.

In the following discussion, two examples of the experimental procedure and the results will be given: one on liquid iron⁽¹⁴⁾ and the other on solid copper⁽¹³⁾.

Kawakami and Goto⁽¹⁴⁾ constructed the cell assembly shown in Fig. 8.8. The Galvanic cell can be expressed by

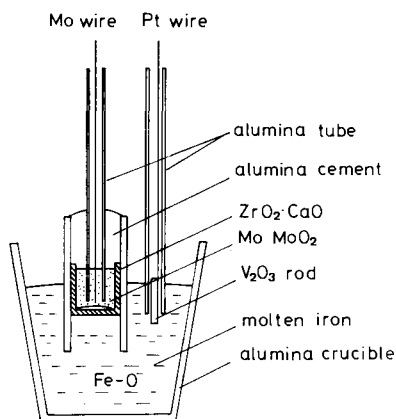
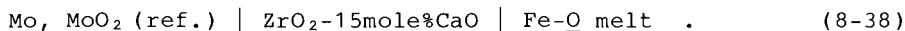


Fig. 8.8. Cell assembly to determine diffusivity of oxygen dissolved in liquid iron at 1550°C by galvanostatic polarization (After Kawakami and Goto (14) 1976).



The equilibrium electromotive force E_0 is given by

$$E_0 = \frac{1}{2F} \left\{ \frac{1}{2} \Delta G_{\text{MoO}_2}^\circ - \Delta G^\circ - RT \ln \left(\frac{1600}{\rho} C_{\text{O}} \right) \right\} \quad (8-39)$$

where $\Delta G_{\text{MoO}_2}^\circ$ is the standard free energy of formation of MoO_2 (- 64,000 cal/mole), ΔG° is the free energy of dissolution of oxygen in molten iron (- 29,300 cal/mole $\underline{\text{O}}$), ρ is the density of molten iron (7.0 gr/cm³), and C_{O} is the concentration of oxygen in iron in mol/cm³. All values are at 1550°C.

After the attainment of the equilibrium, the electromotive force satisfied Eq. (8-39). Then, a constant current in the range of 7.8 to 74.5 mA/cm² was applied. As shown in Fig. 8.8, the crucible of the solid electrolyte was tightly covered by an alumina tube. This structure is very important to satisfy the requirement for unidirectional diffusion of oxygen in molten iron and to prevent the local convection of molten iron. The overpotential was obtained by subtracting the ohmic potential drop of the assembly and thermopotential of Mo and Pt lead wires from the measured total potential.

Fig. 8.9 shows the relationship between the exponential (overpotential + the ohmic potential drop) and the square root of time at three different oxygen contents and current densities. The inter-

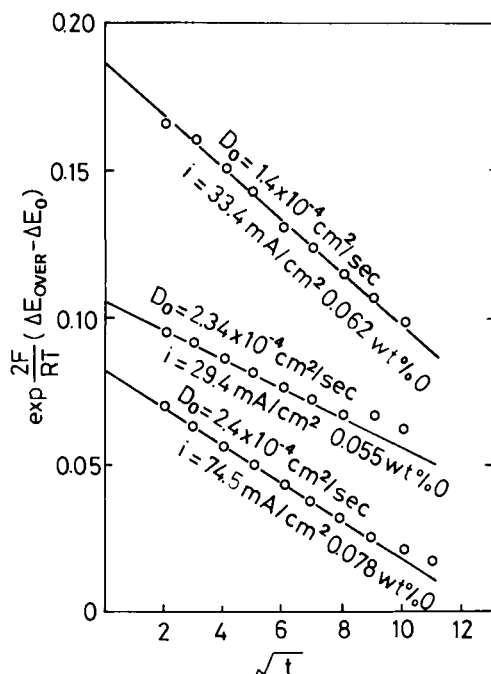


Fig. 8.9. Relation between exponential overpotential and square root time according to Equation (8-11') at 1550°C (After Kawakami and Goto (14) 1976).

section at zero time gives the ohmic potential drop; the diffusivity of oxygen at 1550°C can be obtained from the slope. The slope is not in accordance to that of Eq. (8-11'), but multiplied by exponential of $(2F\Delta E_0)/RT$, where ΔE_0 is the ohmic potential drop of the cell assembly.

Fig. 8.10 shows the relationship between the diffusivity obtained by the method and the initial oxygen content in molten iron at 1550°C.

The diffusivities at less than 500 ppm O appear to be too large because of oxygen permeation through the solid electrolyte. Thus the authors⁽¹⁴⁾ believed the diffusivity of oxygen as $(1.9 \pm 0.7) \times 10^{-4} \text{ cm}^2/\text{sec}$ at 1550°C. This value agreed with the literature values reported by other investigators using different methods.

The above discussion was on oxygen diffusion in a liquid metal. In the following discussion, we will concentrate on an elegant experiment on oxygen diffusion in a solid metal that was reported by Pastorek and Rapp⁽¹³⁾ in 1969.

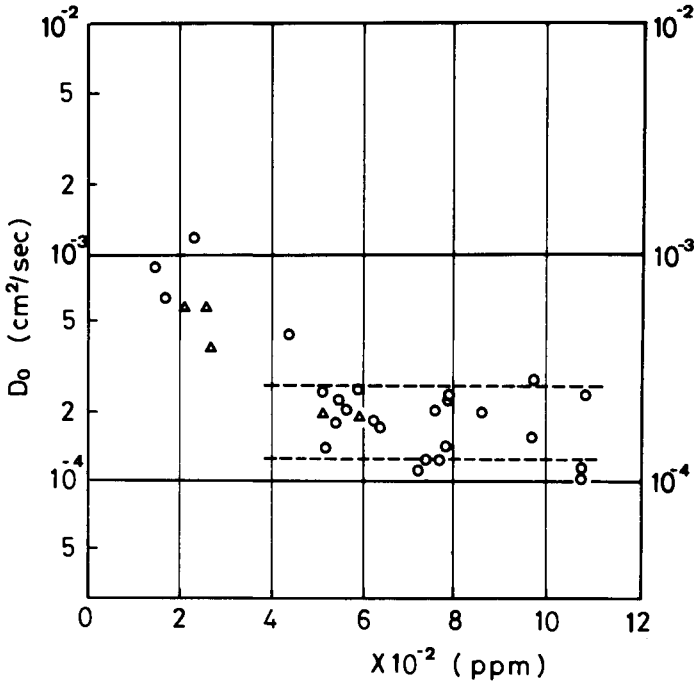
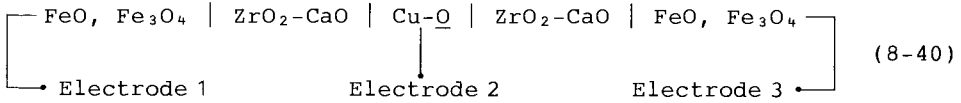


Fig. 8.10. Relation between obtained diffusivity of oxygen and initial content of oxygen dissolved in liquid iron at 1550°C (After Kawakami and Goto (14) 1976).

The experimental assembly was composed of two Galvanic cells in a symmetrical structure as follows:



The cell voltage E can be related to the activity of oxygen, a_{O} , at the electrode/electrolyte interfaces by the equation

$$E - IR_0 = \frac{RT}{2F} \ln \frac{a'_{\text{O}}(\text{Cu})}{a''_{\text{O}}(\text{FeO, Fe}_3\text{O}_4)} \quad (8-41)$$

where R_0 is the ionic resistance of the electrolyte.

Using this symmetrical cell assembly, the direct current was applied under potentiostatic conditions. In such an experiment the potentiometer is set for an electromotive force, E_1 , such that copper is in equilibrium with an oxygen activity somewhat higher

than that for the coexistence of $\text{FeO-Fe}_3\text{O}_4$. At the start of the experimental run, the EMF is increased to E_2 . A value is chosen for which Cu_2O does not form. The new oxygen activity, which is established at both copper/electrolyte interfaces, follows instantaneously with the voltage increase. Since current flows from both $\text{FeO-Fe}_3\text{O}_4$ electrodes (but in opposite directions), a symmetrical concentration is produced in the solid copper. This concentration distribution changes with time and can be calculated. A solution of Eq. (8-4) for the initial conditions

$$N_O = N_O(E_1) \quad \text{for} \quad 0 < x < L, \quad t = 0$$

and the boundary conditions

$$N_O = N_O(E_2) \quad \text{for} \quad x = 0 \text{ and } x = L, \quad t > 0$$

$$N_O = N_O(E_2) \quad \text{for} \quad \text{all } x, \quad t = \infty$$

is given (Crank⁽¹⁾, 1956) by

$$N_O(x, t) = N_O(E_2) - [N_O(E_2) - N_O(E_1)] \times \sum_{n=1,3,5,\dots}^{\infty} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-n^2\pi^2 D_O t}{L^2}\right) \quad (8-42)$$

In this equation $N_O(E_1)$ is the equilibrium atom fraction of oxygen in the copper at an oxygen activity $a_O(E_1)$ when a voltage E_1 is applied to the cell. The thickness of the copper sample is L .

The instantaneous current I for the two cells ($\frac{1}{2}$ for each cell), which is given by

$$I = \frac{16FAD_O}{V_{Cu}} [N_O(E_2) - N_O(E_1)] \times \sum_{n=1,3,5,\dots}^{\infty} \exp\left(\frac{-n^2\pi^2 D_O t}{L^2}\right), \quad (8-43)$$

then follows on substitution of Eq. (8-42) differentiated with respect to x into Eq. (8-6).

Neglecting the ohmic potential drop, and assuming the validity of Henry's law, Eq. (8-41) yields

$$\frac{N_O(E_2)}{N_O(E_1)} = \exp \frac{2F}{RT} [(E_2 - E_1)] \quad (8-44)$$

Equation (8-43) can be written as

$$I = B \sum_{n=1,3,5,\dots}^{\infty} \exp\left(\frac{-n^2 t}{\tau}\right) \quad (8-45)$$

where

$$B \approx [N_O(E_2) - N_O(E_1)] \frac{16 F A D_O}{L V_{Cu}}$$

and

$$\tau = l^2 / \pi^2 D_O \quad .$$

$$I \approx B \exp(-t/\tau) \quad \text{for} \quad t/\tau > 0.5 \quad .$$

A plot of $\log I$ versus t is thus asymptotic to a line with a slope of $-1/2.303\tau$ and an intercept of $\log B$. D_O is obtained from the slope. $N_O(E_1)$ can be calculated from this value for D_O and the intercept value of $\log B$ on substituting these into Eq. (8-44). The saturation solubility of oxygen in copper can also be calculated on applying Sieverts law. The relationship between $\log I$ and time obtained by Pastorek and Rapp⁽¹³⁾ in their determination of D_O for solid copper is shown in Fig. 8.11. The experimental data shows a

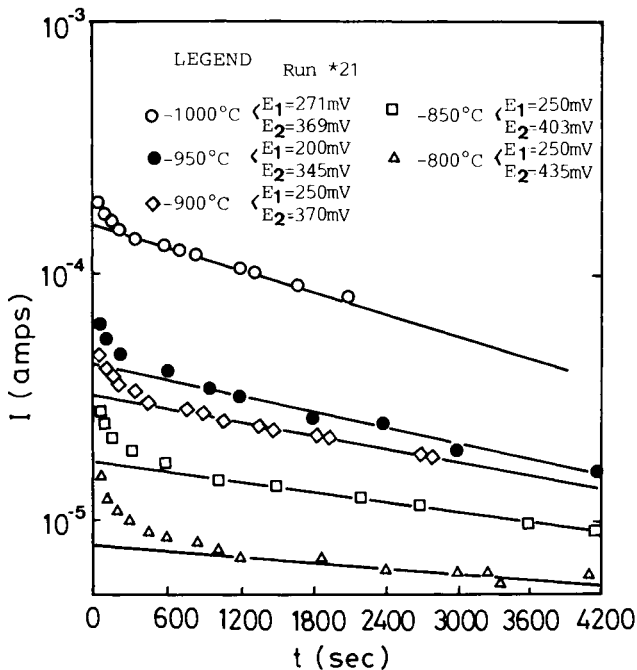


Fig. 8.11. Linear relations between logarithmic current and time at 800 to 1000°C under potentiostatic conditions to determine the diffusivity of oxygen in solid copper (After Pastorek and Rapp (13) 1969).

good linear correlation at longer times (Fig. 8.11) in accordance with Eq. (8-45). Pastorek and Rapp⁽¹³⁾ also obtained good results from galvanostatic polarization experiments. They obtained values for the diffusivity of oxygen in solid copper that are within the reasonable range in comparison to other literature values.

8.3 USE OF SOLID ELECTROLYTES FOR KINETIC STUDIES

In the previous section, the diffusion constant of oxygen in solid or liquid metals was determined from polarization experiments on the oxygen concentration. This implies that the charge transfer reaction, e.g. $O^{2-} = O + 2e$, is very fast and thus, the interface between the metal and the solid electrolyte is in local equilibrium even during current flow. Therefore, the electromotive force can give the local oxygen pressure at the interface, even when a heterogeneous reaction is taking place in the electrode system. In the following discussions, several examples will be given to illustrate the use of the Galvanic cell to clarify the micromechanism of reactions at high temperature.

8.3.1 Rate of gas-solid reactions

Oxygen concentration cells can be used to determine the rate constants of slow surface reactions, such as the oxidation of iron to wüstite by a CO-CO₂ gas mixture.

Experimentally, a thin metal film is attached to the gas-tight polished plate of ZrO₂-CaO, which separates two compartments of different oxygen pressures. As the metal is oxidized, the oxygen pressure at the metal/electrolyte interface is maintained at that of the two phase equilibrium until the metal is completely consumed. An apparent rate constant for the oxidizing reaction can be calculated from the time taken to achieve a constant EMF when a slow surface reaction is the rate-controlling process.

Tare and Schmalzried⁽¹⁸⁾ used this method in 1966 to determine the rate constant for the oxidation of iron foils to wüstite. Fig. 8.12 shows the EMF change with time for the oxidation of a 5- μ m thick iron foil. The iron foil was fixed onto a ZrO₂-CaO electrolyte and then oxidized at 960°C in a CO-CO₂ gas mixture. In this figure, part A is the time necessary for the dissolution of oxygen into the iron foil and the start of nucleation of wüstite. Part B is the time required to oxidize the entire thickness of the iron foil. Part C reflects the change in the composition of wüstite. The EMF is constant with time when the oxide and the gas phase are

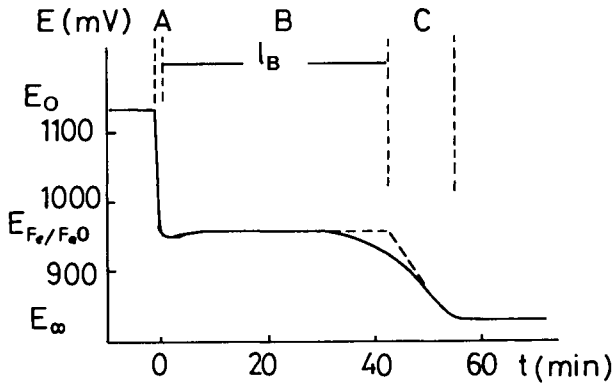


Fig. 8.12. Electromotive force vs. time curve for the oxidation of an iron foil to wüstite. $T = 960^\circ\text{C}$, $\Delta = 5\mu$, $k = 3.7 \times 10^{-8} (\text{mol}/\text{cm}^2 \cdot \text{s} \cdot \text{atm})$ (After Tare and Schmalzried (18) 1966).

in complete equilibrium.

The rate of the surface reaction between wüstite and the oxidizing $\text{CO}-\text{CO}_2$ gas mixture may be formulated for a low oxygen coverage of the active sites on the iron surface by Grabke⁽¹⁹⁾ in 1965 as

$$\frac{dn_O}{dt} = k_1 P_{\text{CO}_2} - k_2 P_{\text{CO}} \Gamma_{\text{O(ad)}} \quad (8-46)$$

where n_O is the number of moles of oxygen that react per cm^2 , $\Gamma_{\text{O(ad)}}$ is the surface concentration of absorbed oxygen atoms, and k_1 and k_2 are the rate constants. Using the equilibrium condition $dn_O/dt = 0$ and integrating over t_B , one obtains k_1 , defined by the above equation, if the relation

$$\int dn_O = \Delta \cdot \rho_{\text{Fe}} / M_{\text{Fe}} \cdot (1-x)$$

is taken into account:

$$k_1 = \frac{\Delta \cdot \rho_{\text{Fe}}}{t_B \cdot M \cdot (1-x)} \left[P_{\text{CO}_2} \left(1 - \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)_{\text{Fe/FeO}} \right) \right]^{-1} \quad (8-47)$$

where Δ is thickness of the foil, ρ is the density, M is atomic weight of iron, and $(1-x)$ is the composition of Fe_{1-x}O in equilibrium with iron. The values of k_1 obtained by Tare and Schmalzried⁽¹⁸⁾ were in the range of 1.4×10^{-8} to $6.5 \times 10^{-8} (\text{mol}/\text{cm}^2 \text{ sec atm})$ at $850^\circ\text{C} \sim 975^\circ\text{C}$. These values are about a factor of two

higher than those obtained by Grabke⁽¹⁹⁾ in 1965. The disagreement in the measured values was apparently caused by non-ideal contact between the iron and $\text{ZrO}_2\text{-CaO}$ and the rough wüstite surface, which grows on the iron foil. Both effects would result in larger values for the constant.

Fig. 8.12 shows a minimum value for the EMF between A and B. This minimum can be considered as supersaturation to form wüstite nuclei on the surface of the iron foil in a $\text{CO}_2\text{-CO}$ mixture. The value of the supersaturation ranged from about 5 to 8%.

Although the principles are very attractive, it is extremely difficult in experiments to establish an absolute dense contact with the electrolyte. Only one report has as yet been published on this method (Tare and Schmalzried, 1966).

8.3.2 Oxygen pressure distribution in a gas phase during a reaction

A concentration gradient is known to exist in the gaseous species of the gas phase close to the reaction surface whenever a heterogeneous reaction between a gas phase and a condensed phase is controlled by a slow rate of mass transport in the gas phase. Fig. 8.13 shows a schematical diagram of an oxygen concentration cell reported by Goto et al. in 1968⁽²⁰⁾. This cell can be used to measure the oxygen pressure distribution in the gas phase close to the reaction surface of liquid iron during its decarburization by the reaction $\text{CO}_2 + \text{C}(\text{Fe-liqu.}) = 2\text{CO}$. Measurements are possible for both the temperature and the electromotive force of the oxygen concentration cell as a function of distance from the liquid iron surface on which the decarburization reaction takes place. The distribution of CO_2 across such a cell calculated from the measured EMF and temperature is shown in Fig. 8.14.

Experimental observation indicates that such a cell is very sensitive to rapid concentration changes in the gas phase. An analysis based on the CO_2 distribution and the observed rates under various conditions has led Goto et al.⁽²¹⁾ (1969) to conclude that the decarburization rate is controlled predominantly by the transport rates of CO_2 and CO in the gas phase when the iron contains more than 0.2% carbon. This conclusion is in agreement with the results of Ito and Sano⁽²²⁾ (1964), Gunji et al.⁽²³⁾ (1964), Baker et al.⁽²⁴⁾ (1964), and Whiteway et al.⁽²⁵⁾ (1968), but not with those of Swisher and Turkdogan⁽²⁶⁾ (1967).

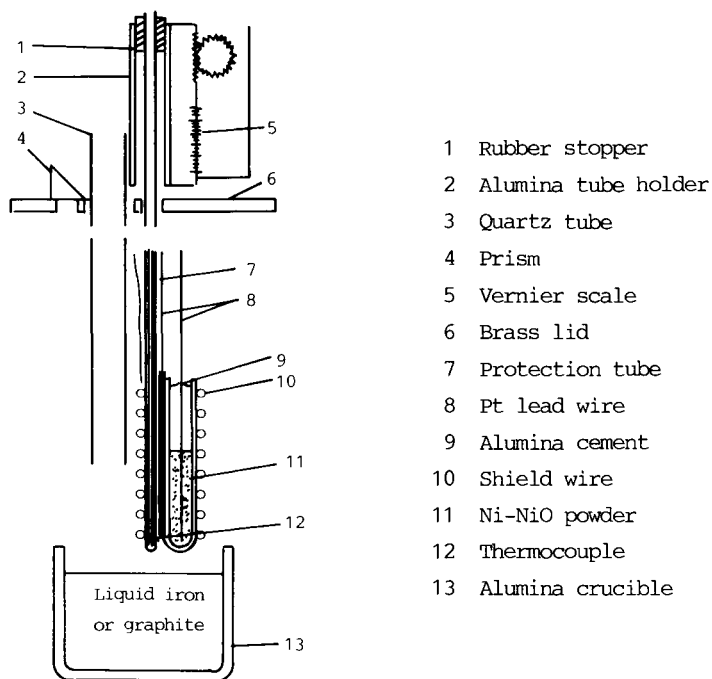


Fig. 8.13. Schematic diagram of an oxygen concentration cell which can be used to measure the oxygen pressure distribution in the vicinity of a reaction surface (After Goto et al. (20) 1968).

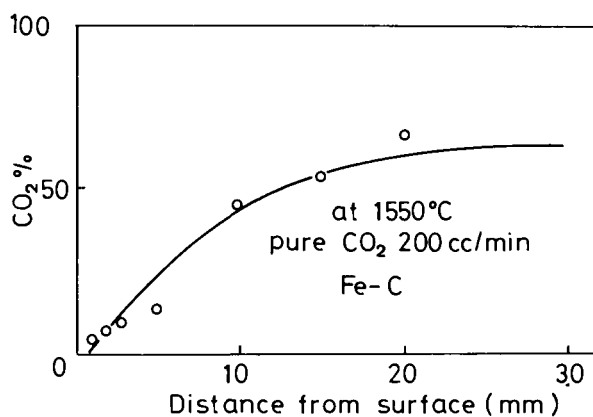


Fig. 8.14. Distribution of CO₂ in the vicinity of the reaction surface of liquid Fe-C alloys during decarburization (After Goto et al. (20) 1968).

8.3.3 The intra-particle oxygen pressure change during a reaction

In kinetic studies of the reduction of sintered oxide particles, only the apparent rate has been usually measured by a thermobalance. However, if the intra-particle gas composition during the reduction is known, this information would increase the accuracy of the analyses. The oxygen pressure in the pores of tamped oxide powder was measured by Kashida et al.⁽²⁷⁾ in 1968 during reduction by reducing gas mixtures. Oxygen concentration cells, such as that shown in Fig. 8.15, have the reducing gas flowing on the outside of the cell assembly. Reduction takes place only from the left side. Figure 8.16 shows the change of the electromotive force and the gas composition in pores during the reduction of WO_3 at 880°C in a H_2 -A gas mixture ($P_{\text{H}_2} = 0.1667 \text{ atm}$).

The lower part of the figure shows the electromotive force between the two measuring electrodes, 1 and 2, located at 15 and 35 mm from the WO_3 surface exposed to the H_2 -A gas mixture. The oxygen pressure at 15 mm was always slightly smaller than that at 35 mm. It is clear that the intra-particle gas composition is constant over a fairly long time. This corresponds to the equilibrium value of WO_3 and $\text{WO}_{2.90}$, $\text{WO}_{2.90}$ and $\text{WO}_{2.72}$, $\text{WO}_{2.72}$ and WO_2 , or WO_2 and W as reported by St. Pierre et al.⁽²⁸⁾ in 1962.

The results for other oxide powders also show that the gas composition in pores does not change smoothly during reduction or oxidation, but rather that it is constant for a certain time at the two phase equilibrium composition values. This is true irrespective of whether or not the reaction takes place topochemically. Similar changes in EMF were observed by Tare and Schmalzried⁽¹⁸⁾ (1966) in the oxidation of iron as shown in Fig. 8.12.

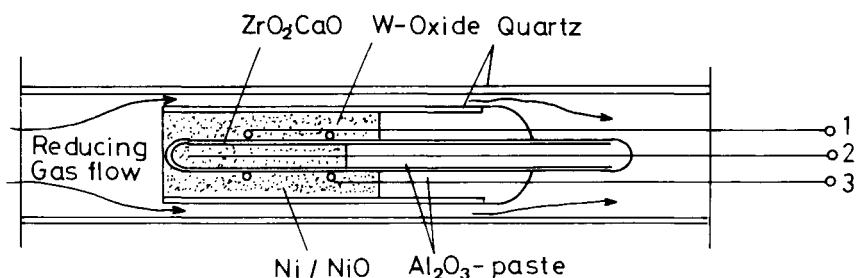


Fig. 8.15. Cell assembly used to measure the intra-particle gas composition during the reduction by hydrogen gas (After Kashida et al. (27) 1968).

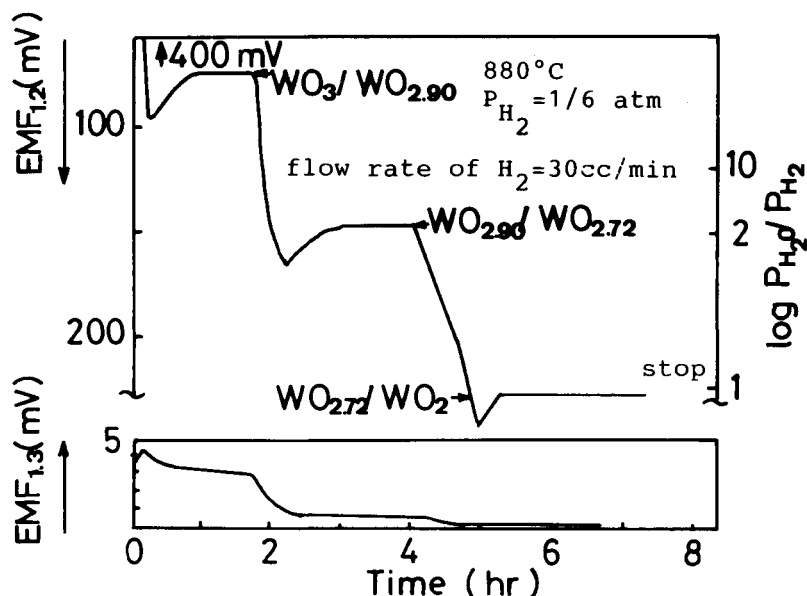


Fig. 8.16. Change of the electromotive force and the gas composition in pores of WO_3 with time at 880°C (After Kashida et al. (27) 1968).

The interpretation of the supersaturation is given in the followings.

Pluschkell and Yoshikoshi⁽²⁹⁾ in 1970 measured the growth rate of the iron phase on single crystals of wüstite by means of a high temperature microscope. The growth rate is controlled by the reaction rate at the ternary phase reaction zone. The rate equation is given as follows:

$$r = \frac{b}{h} k V_{\text{Fe}} \left[\frac{P_{\text{H}_2}}{1 + K_0 \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)} \right] \times \left[1 - \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \right)_{\text{eq.}} \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right) \right] t \quad (8-48)$$

where r is the radius of the reduced iron phase, b is the broadness of the reaction zone, h is the height of the edge of the iron phase, k is an isothermal reaction rate constant, V_{Fe} is the molar volume of iron, K_0 is the oxygen absorption coefficient, P_{H_2} and $P_{\text{H}_2\text{O}}$ are the partial pressures of hydrogen and water vapour, and $(P_{\text{H}_2}/P_{\text{H}_2\text{O}})_{\text{eq.}}$ is the equilibrium gas ratio for the coexistence of iron and wüstite. From this equation, it is clear that during the initial stages of reduction, the growth rate of the iron phase is proportional to the total area of the three phase reaction zone.

Also, the growth rate of the iron phase corresponds to the rate of consumption of the reactant gases. Pluschkell and Yoshikoshi⁽²⁹⁾ have shown quantitatively that the reduction rate is rapidly accelerated by the formation of the iron phase. An "autocatalytic effect" for the metal phase in reduction processes has been reported by Pease and Taylor⁽³⁰⁾ (1921, 1922) in the case of Cu-CuO, and by Benton and Emmett⁽³¹⁾ (1924) for Ni-NiO.

The observed super-saturation, such as that shown in Fig. 8.16, can be interpreted as follows. At the start of the reaction, the area of the reaction zone of the ternary phase coexistence is so small that the reactant gas that is supplied cannot be consumed. When the total area of the reaction zone is increased following the growth of the new phase, all of the transferred reactant gas is consumed. The gas is thus maintained at an equilibrium concentration. When a catalytic action is defined as one for which there is either an increase in the number of reaction sites or a decrease in the activation energy or both as the result of a changing reaction mechanism, the growth of the new phase can be said to be accelerated by an "auto-catalytic action". It seems clear that absolute values of the "super-saturation" are not well reproducible at high temperature solid surfaces.

From the above discussions, one may assume that oxide phases formed at all the steps of the $\text{WO}_3 \rightarrow \text{WO}_{2.90} \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W}$ sequence are also auto-catalytic in direction of reduction.

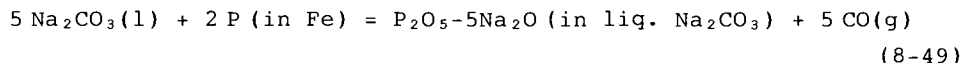
8.3.4 Changes of oxygen pressure and activity of Na_2O during a reaction between liquid slag and a metal at high temperature

One more example of the kinetic study will be given below, in which two Galvanic cells are used to monitor the changes of oxygen pressure and of Na_2O activity.

The Galvanic cell with a solid electrolyte of beta-alumina, e.g. $\text{Na}_2\text{O}-11\text{Al}_2\text{O}_3$, was fully discussed in Chapter 7. The equation of this cell was given by Eq. (7-4) and its equilibrium electromotive force by Eq. (7-5). The activity of soda in $\text{Na}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ ternary liquid solutions at 1300°C has been measured⁽³²⁾ by the Galvanic cell and presented in Fig. 7.8.

In 1983, the author and his coworkers⁽³³⁾ used two kinds of solid electrolytes for a kinetic study of the problem of what are the probable reactions between liquid Na_2CO_3 and liquid iron containing carbon and phosphorus at 1300°C . One of the probable reactions is

considered to proceed as follows:



This reaction equation has not been well clarified to proceed as written. Thus, Eq. (8-49) is expressed only to show that sodium carbonate would be decomposed into Na_2O and CO_2 , and the phosphorus in liquid iron would be oxidized by this carbon dioxide and transferred to the liquid $\text{Na}_2\text{CO}_3\text{-Na}_2\text{O-P}_2\text{O}_5$ system.

The cell assembly with two solid-electrolyte sensors dipped into the slag phase is shown in Fig. 8.17. The electromotive forces expressed by E_1 , E_2 , and E_3 will give the activity of Na_2O in the slag, oxygen pressure at the metal/slag interface, and vapor pressure of sodium in the gas phase, respectively. The electromotive force expressed by E_1 is that of the Galvanic cell of

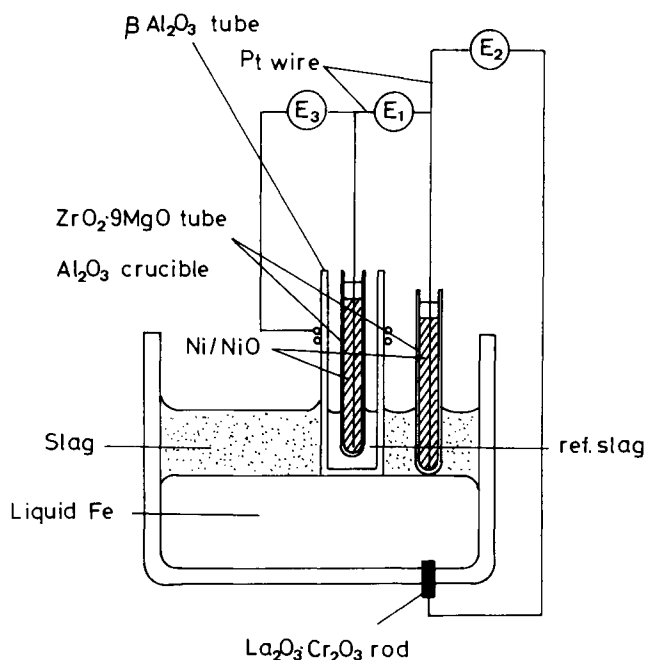
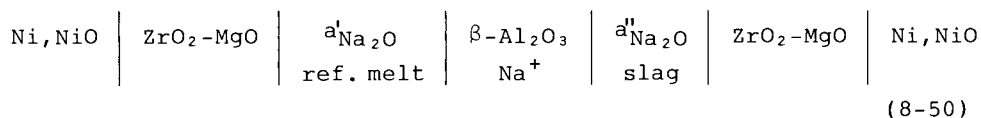


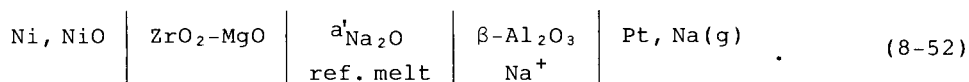
Fig. 8.17. Schematic diagram of the Galvanic cells with the electrolyte tubes of $\beta\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2\text{-MgO}$ to measure the activity of sodium oxide in slag, the oxygen pressure at slag-metal interface and the sodium vapor pressure in gas phase (After Kawashima et al. (34) 1984).



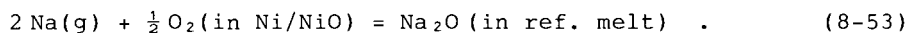
The virtual cell reaction induced by supplying 2 faradays will be only the transport of 1 mole of Na_2O between the outside and the inside of the beta-alumina tube. Thus, E_1 can be expressed by the equation

$$E_1 = \frac{RT}{2F} \ln \frac{a'_{\text{Na}_2\text{O}}}{a''_{\text{Na}_2\text{O}}} \quad (8-51)$$

The electromotive force expressed by E_3 is that of the Galvanic cell of



The virtual cell reaction by supplying 2 faradays will be



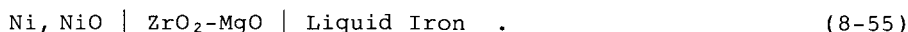
Therefore, the electromotive force E_3 can be expressed by the equation

$$E_3 = \Delta G^\circ_{\text{Na}_2\text{O}} - \frac{RT}{2F} \ln \left[\frac{a'_{\text{Na}_2\text{O}}}{P_{\text{Na}}^2 \cdot P_{\text{O}_2}^{\frac{1}{2}}} \right] \quad (8-54)$$

where $\Delta G^\circ_{\text{Na}_2\text{O}}$ is the standard free energy of formation of liquid Na_2O (known), $a'_{\text{Na}_2\text{O}}$ is the activity of soda in the reference slag (measured in advance: see Chapter 7), and P_{O_2} is the equilibrium oxygen pressure in a mixture of powders of nickel and its oxide (known).

Therefore, the vapor pressure of sodium in the gas phase, P_{Na} in the above equation, can be obtained from the measurements of the temperature and the electromotive force, E_3 .

The EMF expressed E_2 is that of the Galvanic cell of



Thus the electromotive force can be expressed by the equation

$$E_2 = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}(\text{Ni/NiO})}{P_{\text{O}_2}(\text{at Fe/oxide})} \quad (8-56)$$

Fig. 8.18 shows the changes of the oxygen pressure (top), the activity of Na_2O (middle), and the wt% of phosphorus dissolved in the pig iron (pig iron is the name of crude iron containing carbon, silicon, phosphorus, and sulfur). When about 20 gm of Na_2CO_3 was added to about 192 gm of pig iron at 1302°C , the oxygen pressure decreased greatly due to the evolution of sodium vapor from the decomposition of sodium carbonate. The vapor pressure of sodium was between 0.5 and 1.0 atm during the reaction according to E_3 of the above Galvanic cell of Eq. (8-52). The decrease in the activity of Na_2O is probably due to the formation of phosphate, and the extremely small oxygen pressure obtained during the dephosphoriza-

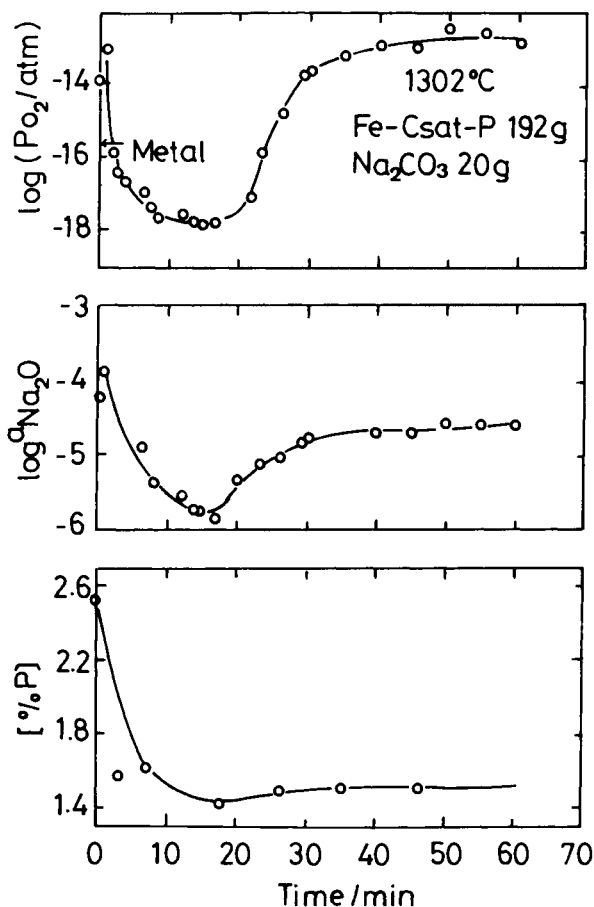


Fig. 8.18. The changes of oxygen pressure at iron/fused oxide interface and activity of Na_2O during dephosphorization (After Nagata and Goto (33) 1983).

tion provides favorable conditions for the simultaneous desulfurization of the pig iron. In contrast, this is not possible when lime powder containing Fe_2O_3 is added to pig iron⁽³³⁾.

Fig. 8.19 is a comparison of the results shown in Fig. 8.18 with other results for different initial contents of phosphorus. This

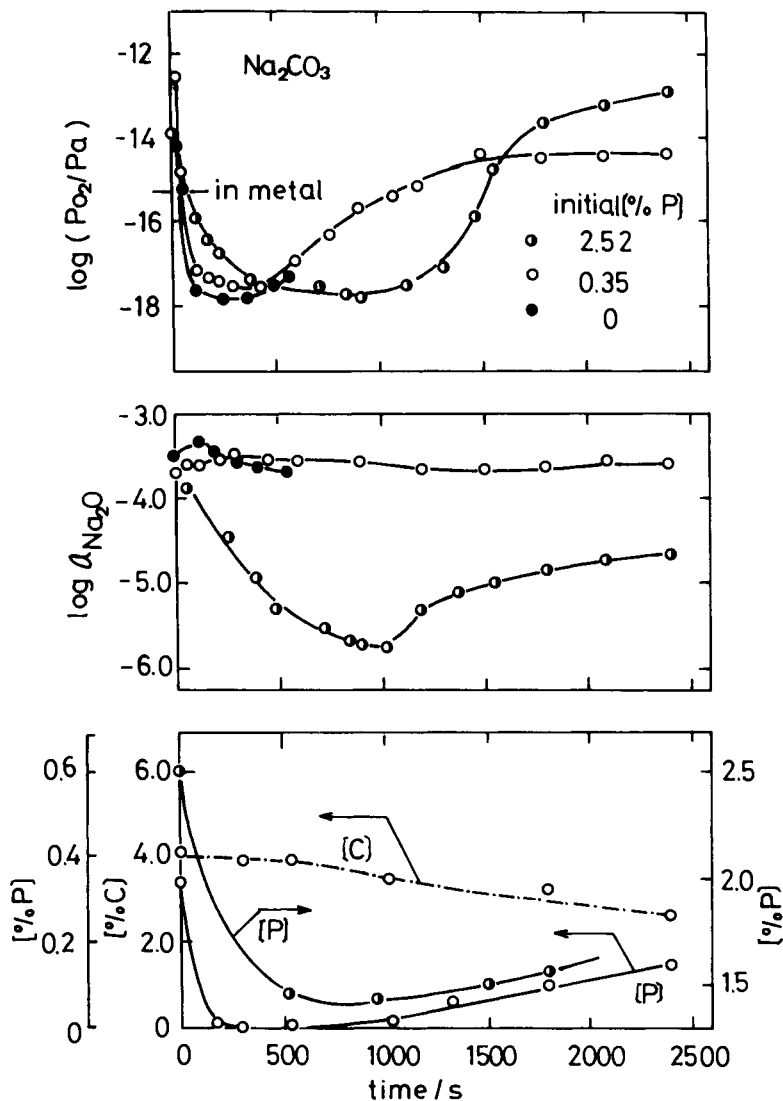
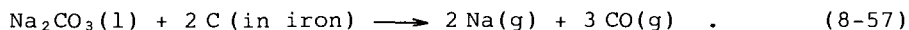


Fig. 8.19. Change in P_{O_2} , $a_{\text{Na}_2\text{O}}$, [%P] and [%C] during dephosphorization of the carbon-saturated iron with various initial phosphorous contents, 0%, 0.35% and 2.52%, by Na_2CO_3 flux (After Kawashima et al. (34) 1984).

figure indicates that the oxygen pressure plotted black circles decreases down to 10^{-18} atm even with zero content of phosphorus, and the activity of Na_2O is nearly constant in the slag when liquid iron contains a small quantity of phosphorus.

The experimental observation of the oxygen pressure and vapor pressure for zero content of phosphorus suggests another probable reaction in addition to Eq. (8-49) as follows:



When the liquid iron contains phosphorus, this reaction would proceed in parallel to the dephosphorization reaction of Eq. (8-49). The decrease of the carbon content during the dephosphorization reaction has been observed as shown in the bottom picture of Fig.8.19.

This study was made because of its industrial importance. In a Japanese steel company, the harmful impurity of phosphorus in iron has been removed in large industrial scale operations since 1982 by the addition of Na_2CO_3 powder to the pig iron at 1300 to 1400°C. In spite of this industrial application, the reaction mechanism is not well clarified at this time. The information obtained only from Galvanic cells is not enough to elucidate the reaction mechanism, but would be helpful in gaining a deeper insight of the phenomenon at high temperature.

The main subject of the present chapter is on the change of the electromotive force of Galvanic cells at high temperature with time. Namely the electromotive force is always discussed in relation to time.

In the first section the overpotential is given as functions of time and applied current to the Galvanic cells with oxide electrolytes for various cases of the rate-controlling steps of the electrode reactions.

In the second section it is shown that this overpotential is usually induced by slow steps of diffusion at high temperature. Because of this reason the diffusivity of oxygen dissolved in solid or liquid metals can be measured from the polarization experiment. Several examples are given for the determination of the diffusivity of oxygen by this method.

In the last section the application of the Galvanic cells to kinetic studies at high temperature is presented with the several examples.

REFERENCES TO CHAPTER 8

- (1) J. Crank, "The Mathematics of Diffusion", Oxford Press, London, (1956).
- (2) K.J. Vetter, "Electrochemical Kinetics" — Theoretical Aspects, Academic Press, New York, (1967).
- (3) J.A.V. Butter, Trans. Faraday Soc., 19 (1924), p. 729 and p. 734.
- (4) T. Erdey-Gruz and M. Volmer, Z. Physik. Chem., 150A (1930), p. 203.
- (5) J. Tafel, Z. Physik. Chem., 50 (1905), p. 641.
- (6) E. Warburg, Wied. Ann., 67 (1899), p. 493.
- (7) F. Kruger, Z. Physik. Chem., 1 (1903), p. 45.
- (8) H. Gerischer, Z. Physik. Chem., 201 (1952), p. 55.
- (9) H. Rickert and R. Steiner, Z. Physik. Chem., 49 (1966), pp. 127-137.
- (10) H. Rickert, H. Wagner and R. Steiner, Chemie-Ingr-Tech., 38 (1966), pp. 618-622.
- (11) H. Rickert and A.A.El Miligy, Z. Metallk., 59 (1968), pp. 635-641.
- (12) J. Osterwald and G. Schwarzlose, Z. Physik. Chem., 62 (1968), pp. 119-126.
- (13) R.L. Pastorek and R.A. Rapp, Trans. Metall. Soc. AIME, 245 (1969), pp. 1711-1720.
- (14) M. Kawakami and K.S. Goto, Trans. Iron and Steel Inst. of Japan, 16 (1976), pp. 204-207.
- (15) S. Otsuka and Z. Kozuka, Met. Trans., 6B (1975), p. 399.
- (16) S. Otsuka and Z. Kozuka, Met. Trans., 7B (1976), p. 147.
- (17) S. Otsuka and Z. Kozuka, Trans. Japan Inst. of Metals, 18 (1977), pp. 690-696.
- (18) V.B. Tare and H. Schmalzried, Trans. Metall. Soc. AIME, 236 (1966), pp. 444-446.
- (19) H.J. Grabke, Ber. Bunsenges. Phys. Chem., 69 (1965), pp. 48-57.
- (20) K.S. Goto, M. Kawakami and M. Someno, Trans. Iron and Steel Inst. of Japan, 8 (1968), pp. 346-347.
- (21) K.S. Goto, M. Kawakami and M. Someno, Trans. Metall. Soc. AIME, 245 (1969), pp. 293-301.
- (22) K. Ito and K. Sano, Tetsu-to-Hagane, 50 (1964), pp. 873-877 and 51 (1965), pp. 1252-1259.
- (23) K. Gunji, Y. Katase and H. Aoki, Tetsu-to-Hagane, 50 (1964), pp. 1828-1830 and 53 (1967), pp. 764-766.
- (24) L.A. Baker, N.A. Warner and A.E. Jenkins, Trans. Metall. Soc. AIME, 230 (1964), pp. 1228-1235.
- (25) S.G. Whiteway, R.J.W. Peters, W.D. Jamieson and C.R. Masson, Canadian Metall. Q., 7 (1968), pp. 211-215.
- (26) J.H. Swisher and E.T. Turkdogan, Trans. Metall. Soc. AIME, 239 (1967), pp. 602-610.
- (27) K. Kashida, K.S. Goto and M. Someno, Trans. Metall. Soc. AIME, 242 (1968), pp. 82-87.
- (28) G.R.St. Pierre, W.T. Ebiyara, M. Pool and R. Speiser, Trans. Metall. Soc. AIME, 224 (1962), pp. 259-264.
- (29) W. Pluschkell and H. Yoshikoshi, Arch. Eisenhüttenw., 41 (1970), pp. 715-721.
- (30) R.N. Pease and H.S. Taylor, J. Am. Chem. Soc., 43 (1921), pp. 2179-2188 and 44 (1922), pp. 1637-1647.
- (31) A.F. Benton and P.H. Emmett, J. Am. Chem. Soc., 46 (1924), pp. 2728-2737.
- (32) K.S. Goto, K. Nagata and S. Yamaguchi, Iron and Steelmaker, November, (1983), pp. 43-50.
- (33) K. Nagata and K.S. Goto, J. of Japan Inst. of Metals, 47 (1983), pp. 726-727, "Measurement of Local Oxygen Potentials in Liquid

Pig Iron, Slag, Gas, and at the Slag-Metal Interface during Dephosphorization by Na_2CO_3 Flux".

- (34) T. Kawashima, S. Yamaguchi, K. Nagata and K.S. Goto, J. of Japan Inst. of Metals, 48 (1984), pp. 779-786, "A Study of Dephosphorization of Pig Iron with Soda-based Fluxes by Using Chemical Sensors".

Chapter 9

ELECTROCHEMICAL KINETICS AT THE INTERFACE BETWEEN METALS AND LIQUID OXIDES WITH IONIC CONDUCTION

9.1 IONIC THEORY OF LIQUID OXIDES

In the previous chapter, the electrochemical kinetics for the interface between a metal and a solid oxide with ionic conduction was discussed. The application of the galvanic cell to kinetic studies at high temperature was also presented. In the present chapter, the kinetics at the interface between a metal and a liquid oxide will be covered from the more general view point of electrochemistry.

When metal compounds are dissolved in water at room temperature, they are usually decomposed to ions. The science of aqueous solutions of ions has a long history with good maturity. This branch of science is called "electrochemistry".

Meanwhile, electrochemistry has also been developed on solid and liquid ionic compounds at high temperature. Solid-state electrochemistry at high temperature has been rapidly advanced since the 1960's. However, the electrochemistry of molten salts and of fused oxides has advanced rather slowly but steadily for a long time.

Regardless of the ionic compounds to be studied, theories and scientific laws in electrochemistry should be universally applied to any electrochemical phenomena both at high and low temperatures.

The purpose of the present chapter is to demonstrate the universality of electrochemical theories, when they are applied to metal/fused oxide systems.

Some oxide melts play very important roles in metal refining by absorbing harmful impurities from the metals. These oxides are called "SLAGS". Therefore, the electrochemistry of fused oxides has been developed not only as an academic curiosity but also for its industrial importance.

In the following discussion, fused oxides are sometimes called slags when studied for their metallurgical importance.

In 1906 Aikon obtained a patent for the continuous electrolysis of liquid $\text{FeO-SiO}_2^{(1)}$. Since then several investigators have tried to demonstrate the ionic nature of liquid slags. In 1938 Herasymenko

(2) proposed a new concept: "Electrolytic dissociation in liquid slags is complete and the presence of electroneutral molecules is excluded. The common elements found in the manufacture of steel possess a different tendency to form complexes with oxygen anions". The ionic species considered are Ca^{2+} , Mg^{2+} , O^{2-} , S^{2-} , Fe^{2+} , AlO_3^- , SiO_4^{4-} , PO_4^{3-} , and other complex anions.

Prior to the publication of Herasymenko's paper, reaction equilibria between slag and metal had often been expressed using the assumption that the slag is composed of both free oxides and interoxide compounds and that these oxides obey the law of mass action. Herasymenko's primary intention was to abandon entirely these unnecessary assumptions.

Figures 9.1, 9.2, and 9.3, which are taken from the publications of Herasymenko and Speight⁽³⁾⁽⁴⁾ are presented as examples of the new way of expressing reaction equilibrium. Figure 9.1 shows that the equilibrium distribution of oxygen between slag and metal depends very much upon the ionic fraction of the free oxygen anion⁽³⁾⁽⁴⁾. This calculation used Winkler and Chipman's laboratory data for basic slags⁽⁵⁾. Figure 9.2 shows how both the ionic fraction of free oxygen anions and the equilibrium ratio decrease with an increase of the ionic fractions of SiO_4^{4-} and PO_4^{3-} ⁽³⁾. Figure 9.3 is a nomogram for estimating the equilibrium distribu-

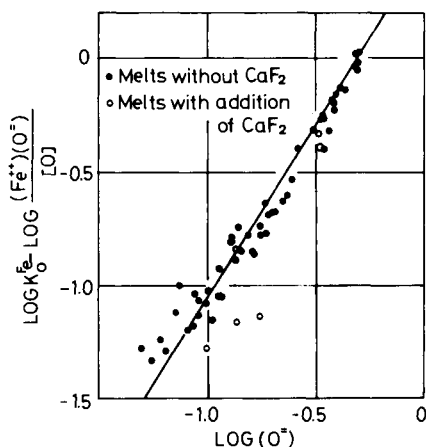


Fig. 9.1. The dependence of apparent equilibrium constant, K_O^{Fe} on the ion fraction of free oxygen anions. (After Herasymenko and Speight (3), 1950).

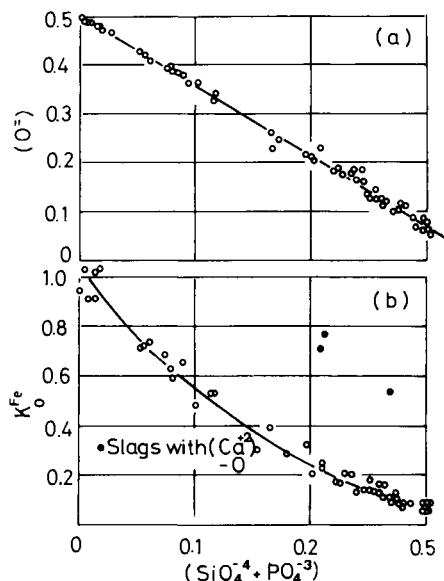


Fig. 9.2. The relation among the ionic fraction of free oxygen, the apparent equilibrium constant, K_O^{Fe} , and ionic fraction of anion complexes in basic slag. (After Herasymenko and Speight (3), 1950).

tion of sulfur between slag and metal from the wt% FeO in the slag and the acidity of the slag⁽⁴⁾. The ratio $(S^{2-})/[S]$ is almost independent of temperature and carbon content⁽⁴⁾. The acidity is given in terms of the weight equivalents of SiO_2 ; each mole of SiO_2 consumes two oxygen ions and each mole of P_2O_5 and Al_2O_3 consumes three oxygen ions in the formation of SiO_4^{4-} , PO_4^{3-} and AlO_3^{3-} , respectively. This new concept of Herasymenko's has stimulated many physical and chemical studies of metallurgical slags.

Among the developments are:

- a) New definitions of basicity and acidity of slags.
- b) Measurements of the thermodynamic activity of component oxides of slags and the consideration of these activities in terms of probable ionic structures.
- c) New thermodynamic models of the ionic structures of slags. (For example, the models of Toop and Samis⁽⁶⁾, Masson⁽⁷⁾, and Yokokawa and Niwa⁽⁸⁾, see a review by Gaskell⁽⁹⁾).
- d) Measurements of the electrical conductivity, diffusivity, viscosity and consideration of these properties in relation to

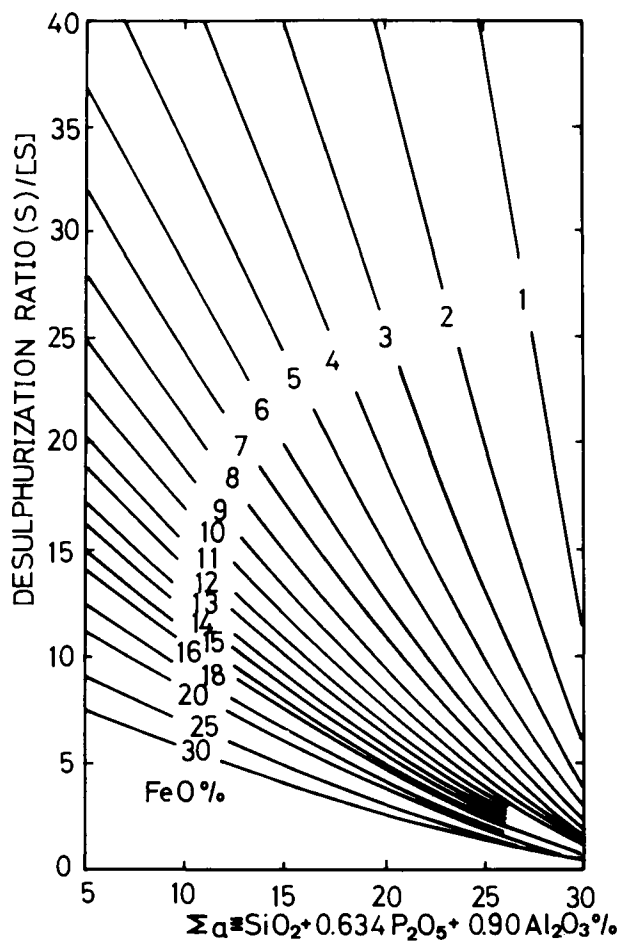


Fig. 9.3. A nomogram for estimation of desulfurization ratio from the composition of the slag. (After Herasymenko and Speight (4), 1950).

the probable ionic structure.

- e) Electrolysis and consideration of the charge carriers in slags,
- f) Electrochemical kinetic studies on slag/metal interfaces.

Some of these new developments were reviewed at the First International Symposium on Metallurgical Slags held in 1980⁽⁹⁻¹⁴⁾.

However, the electrolysis, electrode kinetics, and rate of charge transfer reaction are not often reviewed. This chapter will address these problems.

9.2 ELECTROLYSIS OF LIQUID OXIDES AND NATURE OF CHARGE CARRIERS

If metallurgical slags are liquids of small electronic conductivity containing ionic species, they can be decomposed by electrolysis. Experimental study of the electrolysis of slags to determine the charge carriers was conducted between 1943 and 1968 by the following investigators: Derge and coworkers (1943-1956) (15-19), Bockris and coworkers (1948-1960) (20-23), Ohtani and Gokcen (1959) (24), Ito and Yanagase (1960) (25), Dickson and Dismukes (1962) (26), Adachi and Ogino (1962-1969) (27-29), Engell and Vygen (1968) (30) and Esin and Kirianov (1955) (31).

In 1943, Martin and Derge⁽¹⁵⁾ measured the electrical conductivity of liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ melts in the temperature range 1500°C to 1600°C . Their publication also contained a review of 14 papers published between 1907 and 1941 which had a direct bearing on this subject. One can imagine how Herasymenko could develop his new clear concept of an ionic theory of slags after these 14 experimental studies.

As a result of their electrical conductivity studies, Martin and Derge suggested that slags are highly ionized and in their three electrolysis experiments they found that calcium migrated with the positively charged groups and silicon migrated with the negatively charged groups. Subsequent to these studies, several investigators have tried to determine quantitatively the transference numbers of ionic species in liquid slags. Figure 9.4 shows the electrolysis cell used by Bockris, Kitchener, and Davies⁽²¹⁾. The transference numbers of Li^+ and K^+ in the silicate melts were determined. This figure has been already shown in Chapter 2 as Fig. 2.7 but again this is shown here to compare with other types of the electrolytic cells. Within experimental error, the charge carrier was found to be exclusively K^+ ions in $\text{K}_2\text{O-SiO}_2$ binary melts and Li^+ ions in $\text{Li}_2\text{O-SiO}_2$ binary melts at 1100°C to 1350°C .

Figure 9.5 shows the electrolytic cell used by Adachi and Ogino⁽²⁷⁾ to determine the current efficiency during the electrolytic decomposition of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-MgO-Al}_2\text{O}_3$, and other silicate systems at 1450°C . A carbon anode is immersed in the surface of the slag and two separate copper droplets are placed at the bottom; one is used as the cathode and the other is used to determine the extent of transfer of Si or Al in the absence of any current flow. When electrons were supplied to the bottom copper droplet, its content of silicon or aluminum clearly increased. Thus, from

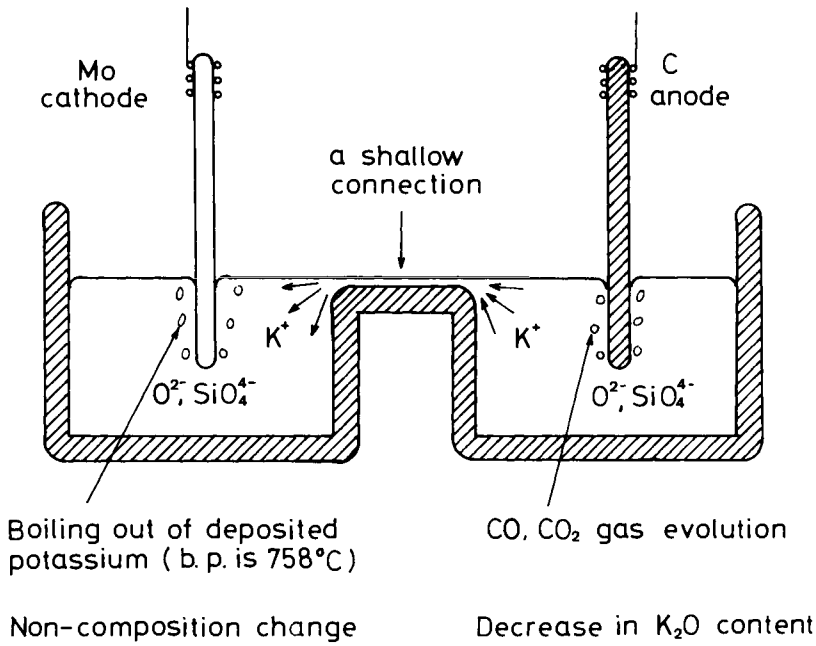


Fig. 9.4. The electrolytic cell to determine transference number of ionic species in silicate melts. (After Bockris et al., (21), 1948).

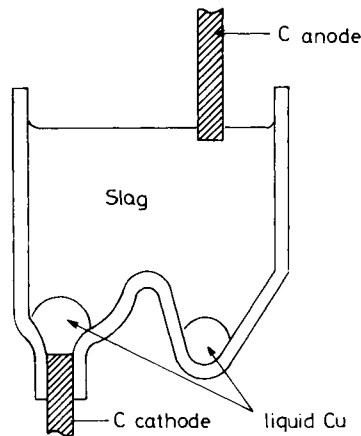


Fig. 9.5. The electrolysis cell to determine the true current efficiency in fused silicates and aluminates at 1450°C. (After Adachi and Ogino, (27), 1964).

chemical analysis after the current flow, the current efficiency was calculated according to Faraday's law. It was found that the current efficiency increased with increasing contents of silica and alumina in the slag. Although reoxidation prevented the efficiency from being 100%, Adachi and Ogino believed that the charge carrier is exclusively Ca^{2+} or Mg^{2+} and the virtual reaction is the decomposition of SiO_2 and Al_2O_3 .

Figure 9.6 shows the cell assembly used by Esin and Getrin⁽³¹⁾ in 1959 to determine the transference number of Ca^{2+} in $\text{CaO-Al}_2\text{O}_3$ melts at 1450°C using radioactive Ca^{45} . The transference number of Ca^{2+} in 50% CaO -50% Al_2O_3 at 1450°C was 1.00 ± 0.04 . A radioactive tracer technique has also been used by Simnad, Yang and Derge⁽¹⁸⁾ to measure the mobility of Fe in FeO-SiO_2 melts in 1956.

In 1956, Ohtani and Gokcen⁽²⁴⁾ conducted a unique experiment to remove sulfur from pig iron by the flow of direct current through the slag. This experiment used the cell assembly shown in Fig. 9.7. The graphite crucible containing carbon-saturated iron was inductively heated. Sulfur had been added to the iron and sulfur-free CaO-SiO_2 or $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slags were used.

Figure 9.8 shows the change in the sulfur content under various experimental conditions at 1500°C . Curve S-I was drawn from the results of two experimental runs numbered H-1 and H-2. The slag composition was 60% SiO_2 -40% CaO and the supplied current was zero for H-1 and 0.1 apm for H-2. The initial sulfur content of 0.75%

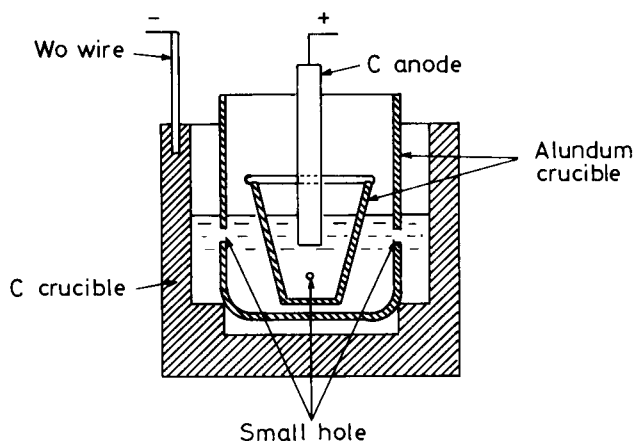


Fig. 9.6. The electrolysis cell to determine transference number of Ca^{2+} in fused aluminates at 1450°C . (After Esin and Getrin, (31), 1959).

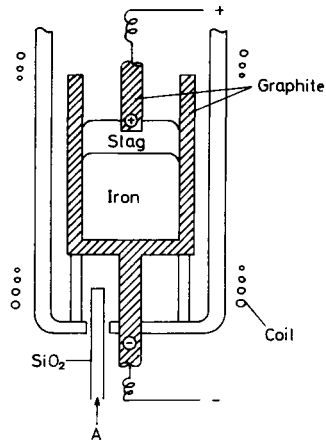


Fig. 9.7. The cell assembly to measure the effect of the direct current upon the desulfurization of liquid iron by silicate slag at 1500°C. (After Ohtani and Gokcen, (24), 1956).

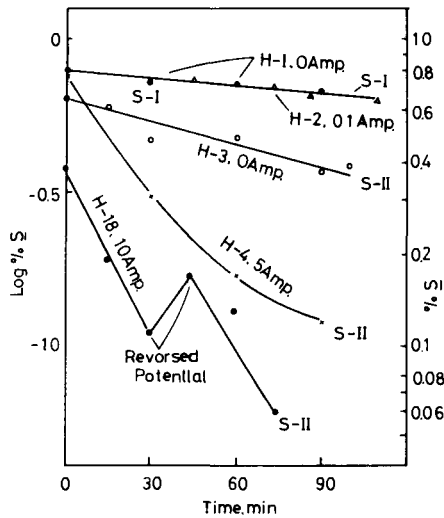


Fig. 9.8. Relation between logarithmic weight percent sulfur in iron and time for various currents supplied at 1500°C. (After Ohtani and Gokcen (24), 1959).

decreased very slowly to 0.64% during 120 minutes. The other three curves marked as S-II were obtained with 46%SiO₂-53%CaO but with different currents of 0, 5, and 10 amp.

It is clear that desulfurization is accelerated by the flow of current. In particular, it is interesting that sulfur is transferred in the reverse direction when the direction of the current supply is reversed. The current efficiency for sulfur transfer increased almost 50% with an increase of the initial sulfur content up to 1.0 wt%. These phenomena demonstrate that reactions between slag and metal are electrochemical in nature and that their rates can be controlled by the external current supply.

In 1953, Derge and Simnad⁽¹⁷⁾ measured the transference number of electrons or positive holes in FeO-SiO_2 binary melts contained in solid iron crucibles at 1400°C . The transference number of electrons was about 0.9 at 10% SiO_2 , and decreased to about 0.1 at silica saturation.

This problem was studied further by Dickson and Dismukes by electrolysis of FeO-CaO-SiO_2 melts in solid iron crucibles⁽²⁶⁾. Figure 9.9 shows the anode current efficiency obtained from measurement of the decrease in weight of an iron rod anode in a Hittorf experiment using separated compartments. The curve designated Ref. 3 in this figure is from the results of Simnad and Derge⁽¹⁷⁾. This figure clearly shows that melts with less than 50% FeO are essentially ionic conductors and that the electronic conduction

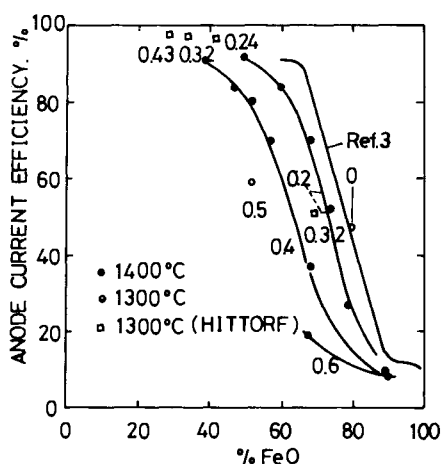


Fig. 9.9. The relation between anodic current efficiency and wt% FeO in FeO-CaO-SiO_2 ternary melts for various wt% $\text{CaO/wt}\%\text{SiO}_2$ ratio at 1300 to 1400°C . (After Dickson and Dismukes (26), 1962).

increases with increasing FeO content and CaO content.

In 1968, Engell and Vygen⁽³⁰⁾ measured the ionic and electronic partial conductivities of CaO-SiO₂-FeO-Fe₂O₃ melts at 1600°C, with a molar ratio of CaO/SiO₂=0.79 and with iron oxide contents ranging from 0 to 44mol%. Figures 9.10 and 9.11 show the variation of the electrical conductivity at 1600°C with the mole ratio of Fe³⁺ to the sum of Fe²⁺ and Fe³⁺ for melts containing 7 different iron oxide contents. In these experiments, the ratio of ferrous to ferric cation was controlled by a gas mixture of constant oxygen pressure which varied in the range of 6 × 10⁻⁶ to 1.0 atm. Engell and Vygen⁽³⁰⁾ expressed the results shown in Figures 9.10 and 9.11 by the equation.

$$\sigma_{\text{total}} = \sigma_0 - ax + bx (1-x)$$

(9-1)

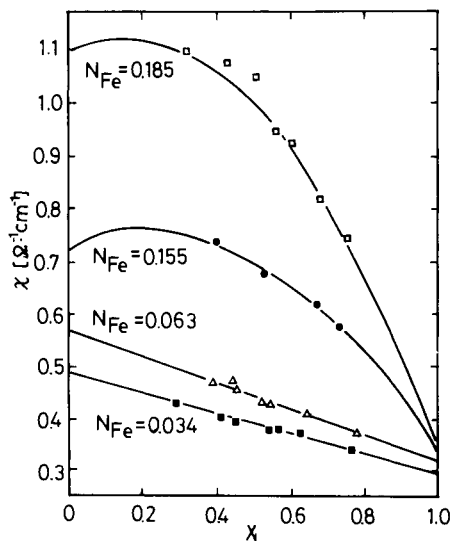


Fig. 9.10. Relation between electric conductivity and ion fraction of Fe³⁺/(Fe²⁺+ Fe³⁺) expressed by x in CaO-FeO-Fe₂O₃-SiO₂ melts with CaO/SiO₂=1.0 for various mole fractions of Fe at 1600 °C. (After Engell and Vygen (30), 1968).

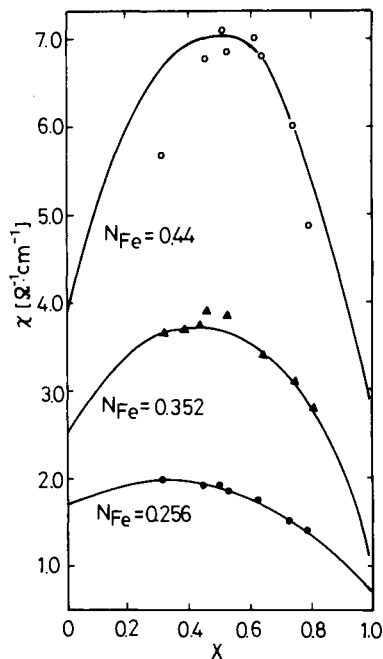


Fig. 9.11. Relation between electric conductivity and ion fraction of Fe³⁺/(Fe²⁺+ Fe³⁺) expressed by x in CaO-FeO-Fe₂O₃-SiO₂ melts with CaO/SiO₂=1.0 for various mole fractions of iron at 1600°C. (After Engell and Vygen, (30), 1968).

where σ_{total} is the conductivity shown as x in the two figures, σ_0 is the constant at $x=0$, and a and b are the constants for the best fit of Eq. (9-1) to the results. x is the mole ratio of Fe^{3+} to the sum of Fe^{3+} and Fe^{2+} . They proposed that the first term and the second term are the ionic conductivity due to Ca^{2+} and Fe^{2+} and the third term is the electronic conductivity. Using these assumptions, they estimated the transference numbers of ions and electrons separately for slags containing different mole fractions of iron oxide. With the mole fraction of iron oxide less than 0.063, the conduction is wholly ionic. However, when the iron oxide mole fraction becomes 0.44 with $x=0.5$, the transference number of electrons attains a maximum value of about 0.5. This paper by Engell and Vygen is valuable as it gives the partial conductivities of both cations and electrons as functions of the slag composition under different oxygen pressures at 1600°C.

The relation between the electric conductivity and tracer diffusivity in oxides had been discussed in Chapter 3.

If the tracer diffusivity of an ionic species is known, then the partial conductivity of the species in a slag can be estimated from the Nernst-Einstein equation

$$\sigma_{\text{ion}} = \frac{n_i (Z_i e)^2}{kTf} D_{\text{ion}}^{\text{tr}} \quad (9-2)$$

where $D_{\text{ion}}^{\text{tr}}$ is the tracer diffusivity, n_i and Z_i are the concentration and valence of the ionic species, e is the unit charge, k is Boltzmann's constant, T is the absolute temperature, and f is the correlation factor for successive jumps of ions. Fig. 3.7 in chapter 3 shows the measured tracer diffusivities of Na^+ and Ca^{2+} as functions of the diffusivities estimated from the electrical conductivities as reported by Goto, Sasabe and Kawakami⁽³²⁾. The reason for the observed deviation is not well understood but the Nernst-Einstein equation seems to be helpful in the estimation of the partial ionic conductivity from measurements of tracer diffusivity.

Table 9.1 shows a compilation of the transference numbers of ionic species and electrons in metallurgical slags obtained from the above literature survey and with the help of a review paper by Adachi and Ogino⁽²⁸⁾. The Russian publications are indirectly

TABLE 9.1

Transference number of ionic species and electrons in fused oxides and in metallurgical slags.

Temperature in Celcius	Liquid Oxides Systems	Charge Carrier	Transference Numbers	Refs.
1100°C-	K ₂ O-SiO ₂	K ⁺	1.0 ± 0.04	(21)
1350°C	Li ₂ O-SiO ₂	Li ⁺	1.0 ± 0.04	(21)
1550°C-	CaO-SiO ₂	Ca ²⁺ (?)	1.0	(21)
1650°C		Ca ²⁺ (⁴⁵)	1.0	(31)
1400°C	FeO-SiO ₂	Fe ²⁺ and e	Function of Compo.	(17) (33)
1400°C	FeO-CaO- SiO ₂	Ca ²⁺ , Fe ²⁺ and e	Function of Compo.	(26)
1600°C	FeO-Fe ₂ O ₃ - CaO-SiO ₂	Ca ²⁺ , Fe ²⁺ and e	Function of Compo.	(30)
1450°C	50%CaO- 50%SiO ₂	Ca ²⁺ (⁴⁵)	1.0 ± 0.04	(34)
1550°C	23%CaO-18% Al ₂ O ₃ -59%SiO ₂	Ca ²⁺ Al ³⁺ Si ⁴⁺	0.66 ? ?	(35)
1550°C	37%CaO-18% Al ₂ O ₃ -45%SiO ₂	Ca ²⁺ Al ³⁺ Si ⁴⁺	Ca ²⁺ = 0.89 ? ?	(35)
Temp.range for liquid	Na ₂ O-CaO- 4SiO ₂	Na ⁺ Ca ²⁺	0.70 0.35	(36)
	K ₂ O-BaO- 4SiO ₂	K ⁺ Ba ²⁺	0.84 0.14	

In this table, e means the excess electrons or positive holes and the transference number is defined by $t_i/(t_{ion} + t_e)$.

cited from Adachi and Ogino's paper. From this table the following general conclusion can be drawn.

- 1) Alkali and Alkali earth cations are the main charge carriers in metallurgical slags which do not contain a large quantity of iron oxide.
- 2) When the slags contain a large quantity of iron oxide, they exhibit a significant electronic conduction.
- 3) The transference numbers of the cations of acidic oxides are not necessarily negligibly small.

The non-negligible transference numbers of Si^{4+} , Al^{3+} , and P^{5+} suggest that the migration of these cations takes place by the jumping of single cations through the coulombic forces of O^{2-} anions. This micromechanism of the migration of Si^{4+} , Al^{3+} and P^{5+} may be acceptable if one considers the large sizes of the anion complexes proposed in the thermodynamic models of Toop and Samis⁽⁶⁾, Masson⁽⁷⁾, and Yokokawa and Niwa⁽⁸⁾.

9.3 ELECTRODE KINETIC THEORY ON LIQUID OXIDES/METAL INTERFACE

During the period of 1962 to 1971, Esin and his coworkers published 14 papers⁽³⁷⁻⁵⁰⁾ on the electrochemical polarization at the interface between liquid slags and metals or solid graphite. Figure 9.12 shows the cell assembly⁽⁴²⁾ used to study the effect of

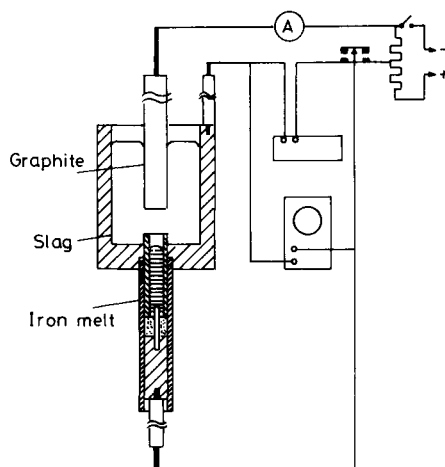


Fig. 9.12. A schematic picture of the cell assembly to study the effect of composition on the anodic polarization of iron melts containing carbon and nickel. (After Esin and his coworkers (42), 1967).

composition on the anodic polarization of an iron melt containing carbon and nickel. Figures 9.13 and 9.14 show the relationship between the current and the overpotential during the anodic polarization of liquid carbon-saturated iron⁽⁴⁰⁾.

As already discussed in Chapter 8, the slope of the lines in

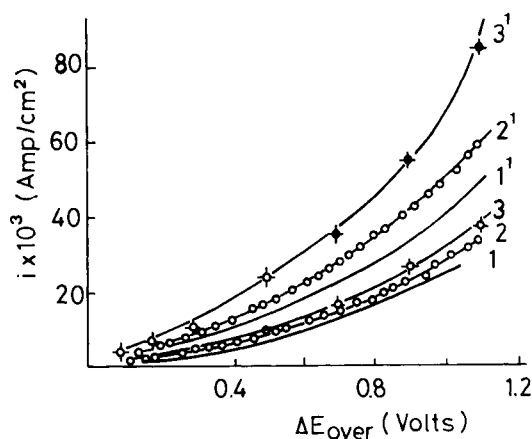


Fig. 9.13. Relation between current density and applied overpotential measured by using the cell assembly of Fig. 9.12. (After Esin and his coworkers, (40), 1967).

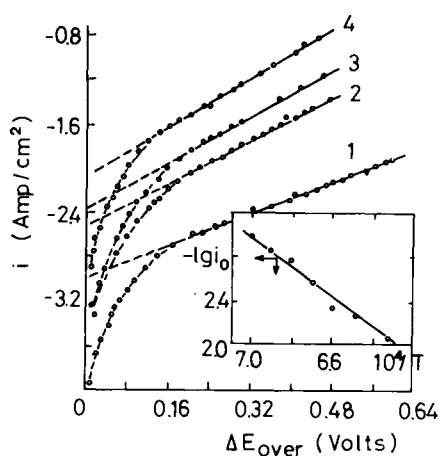


Fig. 9.14. Relation between logarithmic current density and overpotential and the small diagram showing relation between logarithmic exchange current density and reciprocal absolute temperature. (After Esin and his coworkers, (40), 1967).

Fig. 9.14 can give the transfer coefficient and the intersections with the vertical axis can give the exchange current density according to Eq. (8-21). However, this would not be true if the rate is controlled by the diffusion step. The approach taken by Esin and his coworkers is unique in that they tried to apply the theories of electrode kinetics developed for aqueous solutions to high temperature systems. However, because of poorly defined experimental conditions, the reproducibility of the results is poor. Their experimental conditions are too complicated: the true interfacial area cannot be obtained due to the evolution of CO gas and sometimes, two or three electrode reactions are taking place simultaneously. The cell assembly seems to be too complicated for high temperature experiments. Consequently, the present author and his coworkers have simplified the experimental conditions and have tried to clarify the phenomena occurring at the interface between slags and metal electrodes⁽⁵¹⁻⁶¹⁾.

9.3.1 Polarization at the interface between solid platinum and fused oxides at high oxygen pressure

Figure 9.15 shows the experimental apparatus⁽⁵⁵⁾ used for measurement of the impedance at the interface between solid platinum

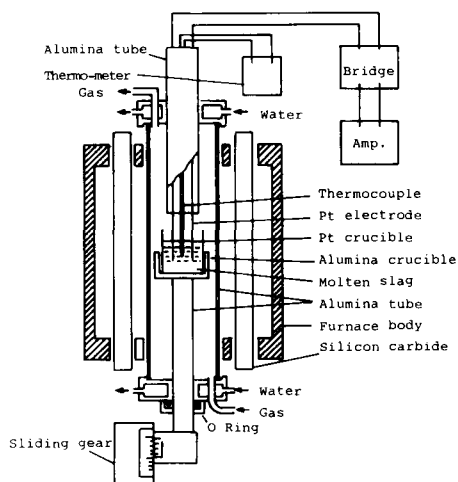


Fig. 9.15. A schematic diagram of the cell assembly used for polarization experiments at interface between solid platinum and liquid oxides under high oxygen pressure. (After Kagohashi and Goto, (55), 1973).

and liquid oxides under high oxygen pressure. Three platinum electrodes are used as a working electrode, a reference electrode, and a counter electrode. The reference electrode also serves as the thermocouple. Figure 9.16 shows the equivalent circuit for the AC polarization when the current is supplied to two platinum electrodes having the same contact area with the fused oxide. In this figure, R_s and C_s are the ohmic and capacitive components of the Faradaic impedance. When electrons are supplied to the platinum electrode, an electrochemical reaction takes place at the interface between the solid platinum and the liquid oxide. Under well defined experimental conditions, only a single electrochemical reaction will take place even at high temperature. The rate controlling step of this "charge transfer" reaction would be exclusively in a transport process rather than at the reaction rate itself. When we review papers on the kinetics of oxidation of metals and alloys at high temperature, we are convinced that the rate controlling step is in a transport process in the oxide phase as long as the metals are covered by a thick oxide layer. This implies that the exchange of electrons between the metal atoms and the ionic particles is very rapid in comparison to the diffusion rate of the ionic species or the ionic and electronic defects. The present author believes that this is also true for the charge transfer reaction between the metal and the liquid slag.

Figure 9.17 shows the relationship between the direct current and the reciprocal square root of time, when three constant potentials are applied to the solid platinum immersed in fused Na_2O -60mole% SiO_2 at 900°C ⁽⁵⁴⁾. In this figure, the overpotentials of 10, 20, and 30 millivolts are the constant potentials maintained between

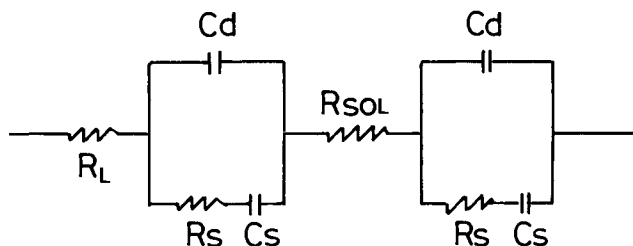


Fig. 9.16. An equivalent circuit of lead wire/solid platinum/liquid oxide solution/solid platinum with two Faradaic impedances in series connections.

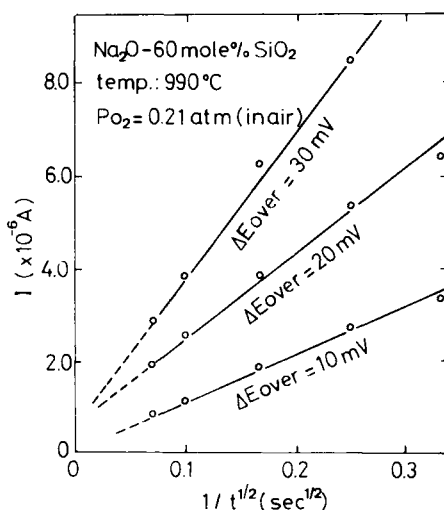


Fig. 9.17. Relation between direct current and reciprocal square root of time, when three constant overpotentials are applied to platinum immersed in liquid sodium silicate at 900°C. (After Kawakami and Goto, (54), 1973).

the reference and working electrodes and the current on the y-axis is the current between the working and counter electrodes. Similar experimental results have been obtained from studies of fused PbO-SiO_2 and PbO-GeO_2 at 900°C to 1400°C. The current decreases linearly with the square root of reciprocal time and increases with an increase in temperature and with an increase in oxygen pressure. As all the results satisfy the theoretical solutions of Fick's second law of diffusion as Eq. (8-8) in Chapter 8, the experimental results clearly show that the rate controlling step is in the transport process and not in the charge transfer reaction itself. Figure 9.18 shows the Faradaic impedance as a function of the square root of reciprocal frequency when alternating current is supplied to platinum electrodes immersed in fused PbO-GeO_2 melts (55). Figure 9.19 shows the effect of oxygen pressure upon the Faradaic impedance. These two figures indicate that the ohmic component is equal to the capacitive component and the Faradaic impedance increases with decreasing frequency and with decreasing oxygen pressure and decreasing temperature. These experimental observations support the contention that the rate controlling step

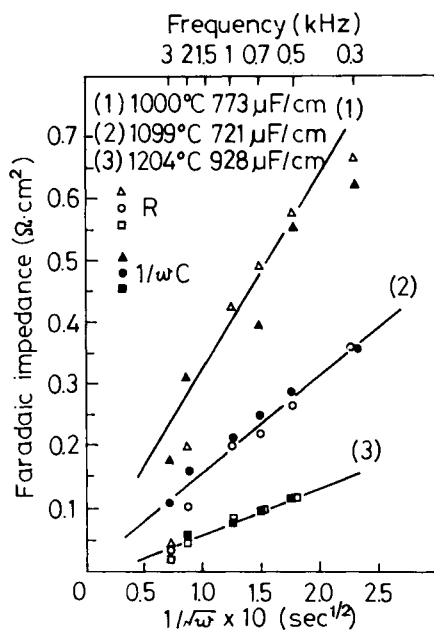


Fig. 9.18. Relation between Faradaic impedance and reciprocal square root of frequency for three temperatures. (After Kagohashi and Goto, (55), 1973).

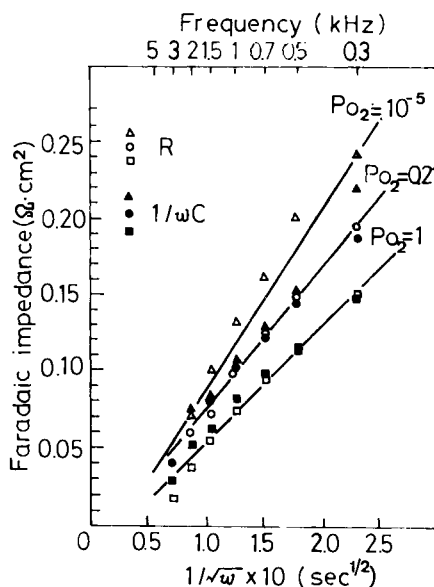


Fig. 9.19. Relation between ohmic and capacitive components of Faradaic impedance and reciprocal square root of frequency for three oxygen pressures. (After Kagohashi and Goto, (55), 1973).

is exclusively in the transport process which is in good agreement with the rate controlling step deduced from the direct current polarization as shown in Figure 9.17. In an attempt to obtain more direct experimental proof of diffusion control the present author and his coworker have developed the rotating disk electrode dipped in fused oxides⁽⁵⁷⁾. Figure 9.20 shows the platinum disk electrode, which can be horizontally rotated in fused oxides during the flow of direct current between the disk and the counter electrode. Figure 9.21 shows the relationship between the current and the square root of rotating speed for three disk diameters in PbO-SiO_2 melts at 1000°C in air. Using the theories of hydrodynamics, Levich⁽⁶²⁾ derived an expression relating the current to the rotating speed and disk diameter as

$$I = 1.95 nF (D)^{2/3} (\nu)^{-1/6} (r)^2 C^b (\omega)^{1/2} \quad (9-3)$$

where I is the current, n is the valency, F is Faraday's constant, D is the diffusivity, ν is the kinematic viscosity of the melt, r is the radius of the disk, C^b is the bulk concentration of the

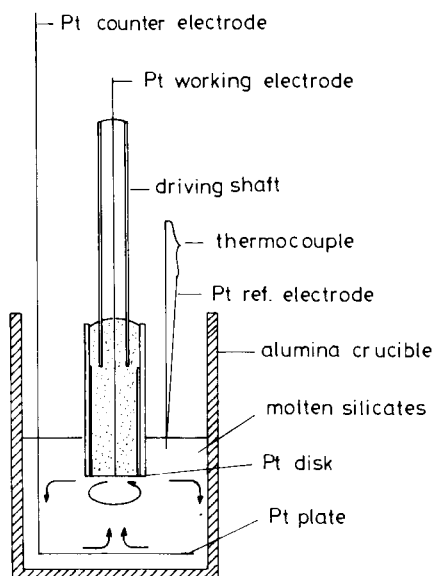


Fig. 9.20. Structure of rotating electrode made of platinum disk dipped in fused oxides. (After Kawakami and Goto, (57), 1974).

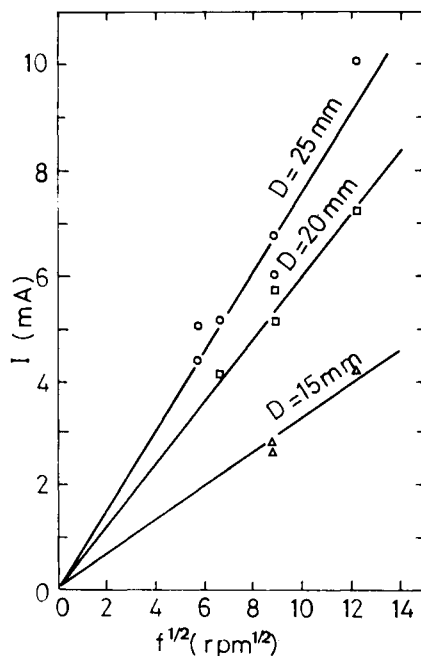


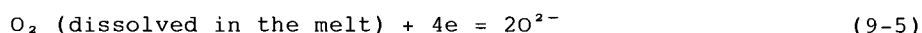
Fig. 9.21. Relation between current and square root of number of rotation per minute for three disk diameters in PbO-SiO₂ melts at 1000°C. (After Kawakami and Goto, (57), 1974).

diffusing species, and ω is the angular velocity of rotation. Levich's equation can be used providing the flow between the disk and the melt is laminar. The results shown in Fig. 9.21 in which there is a linear relationship between the current and the square root of rotating speed satisfy this equation. From these results it is seen that the rate of the electrochemical reaction is controlled by the diffusion of some species in the melt and that local equilibrium always prevails at the interface between the platinum and the oxide melt. The equations expressing the current and overpotential as functions of time and diffusivity of the diffusing species can be obtained from electrode kinetics⁽⁶³⁾, as discussed in Chapter 8.

The overpotential of the working electrode to the reference electrode is given as follows⁽⁶⁴⁾;

$$\Delta E_{\text{over}} = \frac{1}{4F} (\mu_{\text{O}_2}^{\text{w}} - \mu_{\text{O}_2}^{\text{R}}) - \frac{1}{zF} \int_R^{\text{w}} t_{\text{M}}^{\text{z}} + d\mu_{\text{MO}} \quad (9-4)$$

where ΔE_{over} is the overpotential, μ_{O_2} is the chemical potential of oxygen, superscripts W and R denote the working and reference electrodes, respectively, F is Faraday's constant, z is the valency of the cation M^{z+} , μ_{MO} is the chemical potential of the component oxides in the melt and $t_{M^{z+}}$ is the transference number. When oxygen pressure is high, the content of dissolved oxygen in the melt is also large and thus the virtual electrode reaction would be



Under these conditions the second term of Eq. (9-4) can be neglected. The following equation for potentiostatic experiments can be obtained from the solution of Fick's second law of diffusion for semi-infinite media⁽⁵⁴⁾

$$I = 4FA \sqrt{\frac{D}{\pi}} C_{\text{O}_2}^b \left[\exp \left(\frac{4F}{RT} \Delta E_{\text{over}} \right) - 1 \right] \frac{1}{\sqrt{t}} \quad (9-6)$$

where I is the current, A is the interfacial area, D is the O_2 -diffusivity, $C_{\text{O}_2}^b$ is the bulk concentration of dissolved oxygen, ΔE_{over} is the overpotential and t is time. This equation is quite well satisfied by the experimental results shown in Figure 9.17. When the Faradaic impedance is caused by slow diffusion in the melt, the solution of Fick's second law of diffusion can give its ohmic and capacitive components as follows⁽⁶⁵⁾

$$R_s = \frac{1}{\omega C_s} = \frac{RT}{z^2 F^2 A C_{\text{O}_2}} \sqrt{\frac{D_{\text{O}_2}}{\omega}} \quad (9-7)$$

where R_s and C_s are resistivity and capacitance of the series connection, ω is angular frequency of the alternating current, C_{O_2} is the oxygen content dissolved in the melt, and D_{O_2} is its diffusivity. In Figures 9.18 and 9.19, R_s is always equal to $1/(C_s)$ and the impedance is always proportional to $1/\omega^{1/2}$. When the oxygen pressure is decreased, the content of dissolved oxygen decreases and thus, the impedance increases. When the temperature is increased, the diffusivity of the oxygen in the melt increases, and thus, the impedance decreases. The results shown in Figures 9.18 and 9.19 satisfy these relationships. Thus, the present author and his co-workers have proposed that the virtual electrode reaction would be the electron transfer between diatomically dissolved oxygen and the

oxygen anion with a charge of minus two⁽⁵²⁻⁵⁷⁾, as expressed by Eq. (9-5).

9.3.2. The interface between solid silicon and silicate melts at low oxygen pressures

In high temperature systems the virtual electrode reaction is not always clear and thus many investigators have not accepted the interpretation of the polarization experiments. Thus the present author and his coworkers have selected pure solid silicon as the metal electrode which is immersed in a stable silicate melt under mixtures of argon and hydrogen. Under such conditions, the virtual electrode reaction could only be the reduction of SiO_2 or the oxidation of metallic silicon depending upon the polarity of the current flow. Using this combination of electrode and silicate melt, some polarization experiments have been conducted in the temperature range from 1100°C to 1400°C ⁽⁵⁸⁻⁶¹⁾. The cell assembly is shown in Figure 9.22. The solid silicon rod used as the working electrode is immersed at the center of the melt to a fixed depth such as to produce a known interfacial area. Another silicon rod

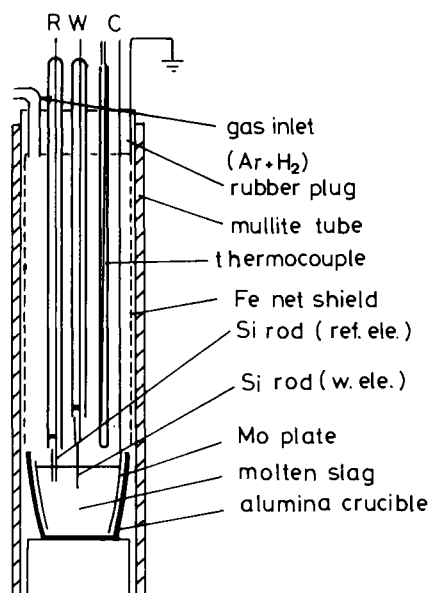


Fig. 9.22. A sectional view of the electrolysis cell composing of a solid silicon rod dipped at center of fused silicates. (After Kawakami, Nagata and Goto, (61), 1978).

is immersed as the reference electrode. The counter electrode is a molybdenum plate so shaped as to have a uniform current density on its working electrode. The gas atmosphere was a mixture of hydrogen and argon. Figure 9.23 shows the change of overpotential in both directions by galvanostatic polarization at 1367°C on solid Si/liquid 40%CaO-40%SiO₂-20%Al₂O₃⁽⁶⁰⁾. Figures 9.24 and 9.25 show the relationship between the overpotential and the square root of time for various current densities and both directions of flow of direct current. The duration of the current supply is 1 milli-second in Fig. 9.24 and 100 milliseconds in Fig. 9.25.

The results in Figures 9.24 and 9.25 indicate that the rate is predominantly controlled by the diffusion of SiO₂ in the silicate melt. Both terms on the right hand side of Eq. (9-4) have been used to obtain the following relation for the overpotential ΔE_{over} in mV⁽⁶⁰⁾;

$$\Delta E_{\text{over}} = \frac{4.606TR}{z^2 F^2 J k \sqrt{\pi D}} i \sqrt{t} \quad (9-8)$$

The value of k was evaluated as 1.8×10^{-3} in the range of experi-

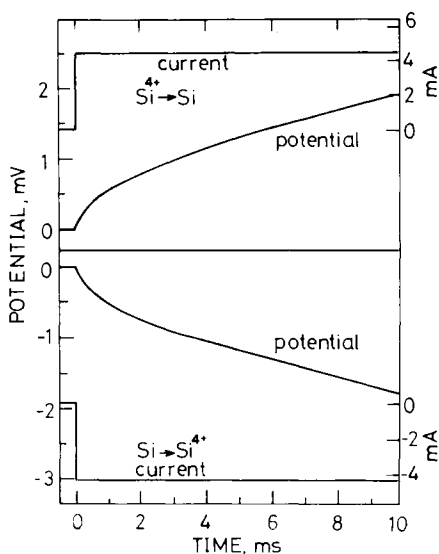


Fig. 9.23. Relation between overpotential and time, when constant currents are supplied to solid Si/fused silicate with both directions of reduction and oxidation of silicon at 1367°C. (After Nagata and Goto. (60), 1977).

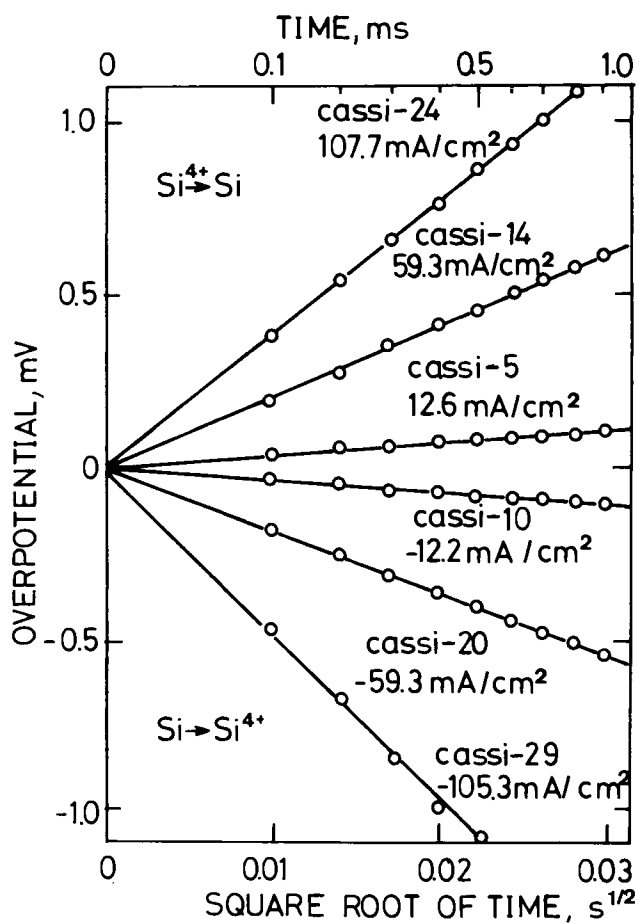


Fig. 9.24. Relation between overpotential and square root of time for various constant current densities with redox reaction of silicon when the currents are supplied for one milisecond. (After Nagata and Goto, (60), 1977).

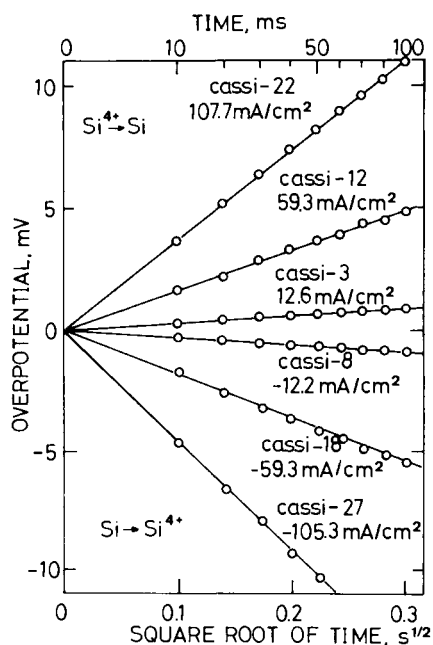


Fig. 9.25. Relation between overpotential and square root of time for redox reaction of silicon, when constant currents are supplied for 100 milliseconds. (After Nagata and Goto. (60), 1977).

mental temperature and composition from activity data⁽⁶⁰⁾. Figure 9.26 shows the relation between the logarithm of the interdiffusivity and the reciprocal of the absolute temperature. Both the open circles and the filled circles are the results from the polarization experiments conducted by the present author and his coworkers^(58,59). The line expressed as "calculated" is the weighted mean value value of the tracer diffusivities of Ca and Si in the slag with the same composition. Diffusion data by Majdic and Wagner and by Oishi have been obtained using the diffusion-couple method. The good agreement between these data and those obtained from the polarization experiments is illustrated in Figure 9.26. This good agreement indicates that the virtual electrode reaction is only the reduction of SiO_2 or the oxidation of silicon and its rate is exclusively controlled by the interdiffusion of SiO_2 and CaO in the melt.

Figure 9.27 shows the relationship between the overpotential and the square root of time for 30wt% Li_2O -70wt% SiO_2 at 1195°C

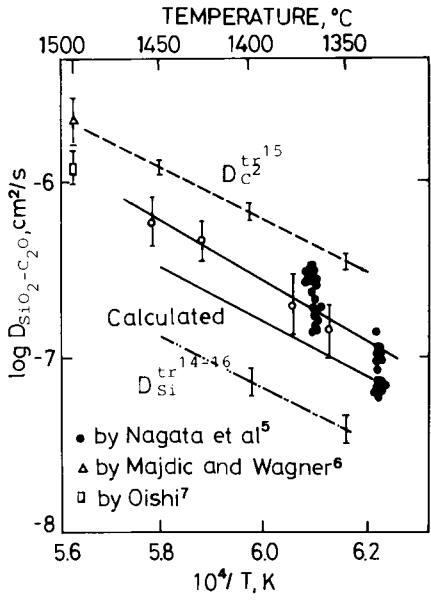


Fig. 9.26. Comparison between the quasi-binary interdiffusivity of CaO and SiO_2 and tracer diffusivities of Ca^{2+} and Si^{4+} . Both open plots and black plots are obtained by polarization experiment. (After Nagata and Goto, (60), 1977. References for 5.6.7 in the figure are given in ref. (60)).

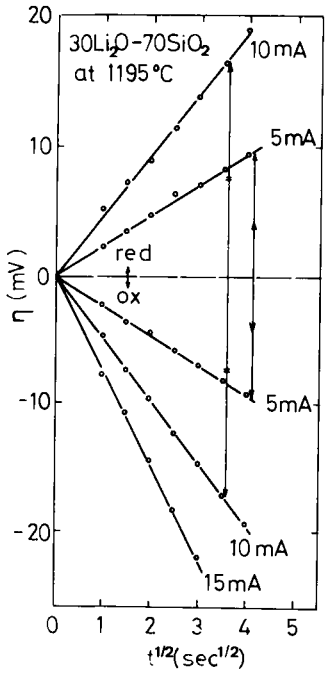


Fig. 9.27. Relation between overpotential and square root of time, when constant currents are supplied to solid Si /liquid $\text{Li}_2\text{O}-\text{SiO}_2$ at 1195°C . (Kawakami, Nagata, and Goto, (61), 1978).

using various direct current densities⁽⁶¹⁾. The gas atmosphere used was again a hydrogen/argon mixture. From the slope of the lines in Figure 9.27, the interdiffusivities of Li_2O and SiO_2 can be calculated. These are shown in Figure 9.28. The results in this figure agree with the data obtained by the diffusion-couple method and provide direct proof of the nature of the rate controlling step in the transfer of silicon between the metal and the slag. The present author believes that these electrochemical experiments are a very reliable method to determine the rate-controlling step provided that the experimental conditions are well defined.

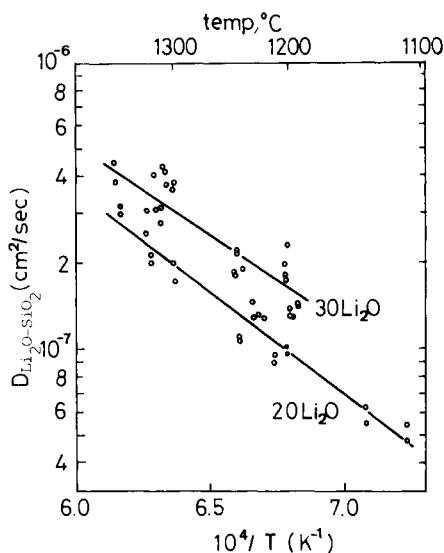


Fig. 9.28. Relation between logarithmic interdiffusivity and reciprocal absolute temperature for 20% Li_2O and 30% Li_2O binary silicate melts. (After Kawakami, Nagata, and Goto, (61), 1978).

9.3.4. Determination of exchange current densities by double pulse method

In the above, it was demonstrated that the diffusion step is usually the rate-controlling step of reactions at metal/fused oxide interface. This means that the charge transfer reaction is very rapid and thus the exchange current density, i_0 defined by Eq. (9-9), can not be easily measured.

$$i_F = i_0 \left\{ \frac{C_R}{C_R} \exp \left[\frac{\alpha n F \Delta E}{RT} \right] - \frac{C_0}{C_0} \exp \left[- \frac{(1-\alpha) n F \Delta E}{RT} \right] \right\} \quad (9-9)$$

where i_F is current through the electrode, i_0 is exchange current density, α is charge transfer coefficient and ΔE_{over} is overpotential. C and $\bar{C}$ are concentration of reductant or oxidant at the interface and in the bulk, respectively.

Here, the reaction is expressed by;



For very fast charge-transfer reactions, the method given in Fig. 8.4 in the previous chapter can be used to determine the exchange current density, simply because the total reaction would be controlled by diffusion.

In 1957, Gerischer and Krause⁽⁶⁶⁾ proposed the double pulse method for determination of the large exchange current density. Fig. 9.29 shows the explanation of this double pulse method. Initially, a short pulse of high current density i_1 is applied to charge the double layer. Then the current density is lowered to the

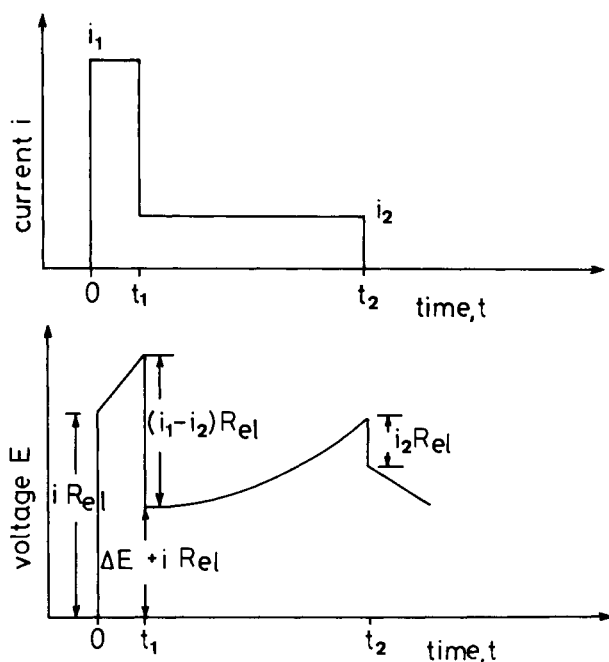


Fig. 9.29. A schematic diagram to explain the principle of the double pulse method. (After Prange, Heusler and Schwerdtfeger, (72), 1984).

value i_2 of the second pulse. The value of i_2 is chosen so that the overpotential stays constant, namely $dy/dt = 0$ at $t = t_1$. Hence, no further charging of the double layer occurs and the current i_2 is equal to the Faradaic current density. After some time overpotential increases again due to the development of the concentration overpotential. Under this condition, the exchange current density i_0 can be obtained by

$$i_2 = \frac{i_0 n F y}{RT} \quad (9-11)$$

This equation is obtained from Eq. (9-10) for the case of $nFy \leq RT$ and $C/\bar{C} \doteq 1.0$.

However, when the charge transfer reaction is extremely rapid, the concentration overpotential may be negligibly small even at t_1 . For such a case, Matsuda, Oka and Delahay⁽⁶⁷⁾ proposed an elegant mathematical analysis in 1959.

When t_1 is sufficiently small, the overpotential, y for i_2 is proportional to square root of time as given by

$$\frac{y(t_1)}{i_2} = \frac{RT}{2Fi_0} + \frac{RT\sqrt{t_1}}{\sqrt{\pi DF^2 C}} \quad (9-12)$$

where t_1 is time and D is the diffusivity of the ion migrating in the solution.

Fig. 9.30 and Fig. 9.31 show the linear relation between y for i_2 and t_1 at electrode systems of Ni/Ni^{2+} and Ag/Ag^+ at 450°C , respectively. The measurements were made by Nishikawa and Haruyama⁽⁷³⁾ in 1983. The system is composed of solid Ni or Ag and liquid LiCl of eutectic composition containing NiCl or AgCl , respectively.

Fig. 9.32 is the similar relation reported by Prange, Heusler and Schwerdtfeger⁽⁷²⁾ in 1984. They measured the exchange current density of $\text{Fe} = \text{Fe}^{2+} + 2e$ in fused CaF_2 - FeO at 1450°C . Their work is very impressive, because they could obtain the exchange current density even at temperature as high as 1450°C . In Table 9.2, the exchange current densities on metal/liquid salt systems at high temperature are compiled.

In Table 9.2, the fused system containing oxides is a CaF_2 - FeO solution studied by Prange, Heusler, and Schwerdtfeger⁽⁷²⁾.

In 1973, Emi, Sakuraya and Sanbongi⁽⁷⁴⁾ tried to measure the

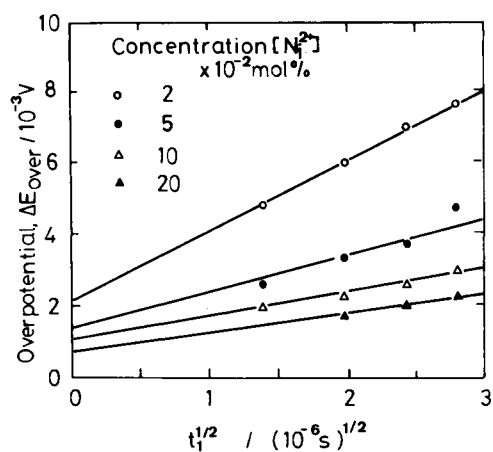


Fig. 9.30. Relation between overpotential and square root of time of the first pulse for Ni/Ni²⁺ in molten KCl-LiCl at 450°C. (After Nishikata and Haruyama, (73), 1983).

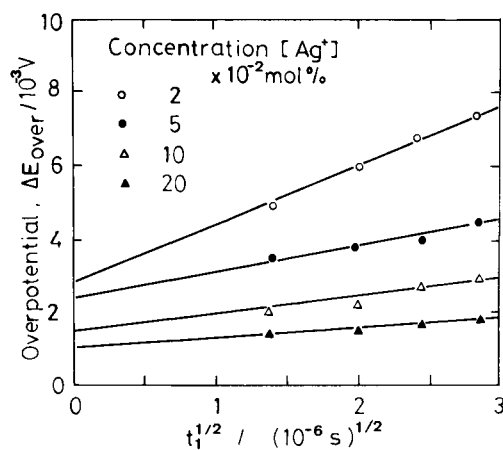


Fig. 9.31. Relation between overpotential and square root of time of the first pulse on solid silver/Ag⁺ in molten KCl-LiCl at 450°C. (After Nishikata and Haruyama, (73), 1983).

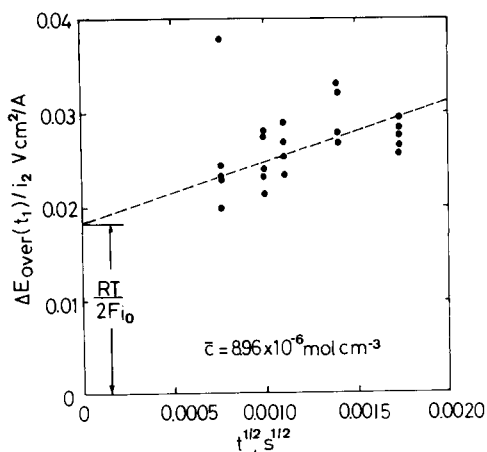


Fig. 9.32. Relation between overpotential divided at the end of first pulse by current density of second pulse, and square root of time of the first pulse on solid Fe/liquid FeO-CaF₂ at 1450°C. (After Prange, Heusler, and Schwerdtfeger, (72), 1984).

TABLE 9.2

Exchange current densities of metal/liquid salt electrodes reported in literature.

Electrode	Fused Salts	T°C	$\bar{C}$	i_0 A/cm ²	C_D	Refs.
Ag/Ag ⁺	NaNO ₃ - KNO ₃	250	9.8 10 (mole/cm ³)	1.5 *	121 (F/cm ²)	(68)
Ag/Ag ⁺	KAlCl	285	8.1 10	3.7 0.85	100	(69)
Ni/Ni ²⁺	LiCl- KCl	450	5.0 10	2.0 0.75	*	(70)
Pb/Pb ²⁺	LiCl- KCl	450	8.71 10	1.64 0.78	30- 120	(71)
Fe/Fe ²⁺	CaF ₂ - FeO	1450	8.95 10	4.0 0.6	304	(72)
Ni/Ni ²⁺	LiCl- KCl	450	0.02mole%	9.32 0.52	300	(73)
Pt/Pt ²⁺	LiCl- KCl	450	0.02mole%	1.88 0.08	164	(73)
Ag/Ag ⁺	LiCl- KCl	450	0.02mole%	16.0 0.42	204	(73)

* not given in the paper.

exchange current density of the electrode dipped in fused $\text{Na}_2\text{O-SiO}_2$ system at 1200°C - 1400°C . Both the Tafel plot method (e.g. Fig. 8.4) and the double pulse method were used. The obtained exchange current densities ranged between 40 to 120 mA/cm^2 . These results are not included in Table 9.2, because the double pulse method used by them did not seem to be successful and the virtual electrode reaction proposed, not clear.

Concluding Remarks

Metallurgical slags are fused mixtures of basic and acidic oxides, which contain free cations and free oxygen anions produced by the basic oxides and large polymeric anions produced by the acidic oxides. This concept was proposed by Herasymenko in 1938 and has stimulated and will continue to stimulate the intellectual curiosity of many investigators studying fused oxides at high temperatures. In the present chapter, direct evidence as to the ionic theory obtained from experimental measurement of the electrolytic decomposition of metallurgical slags has been reviewed. The transference numbers of cations and electrons have also been reviewed and compiled in Table 9.1. Because of the availability of these quantitative data, one can apply the theories of electrode kinetics of aqueous solutions to the slag/metal reactions even at high temperature. Several studies of the polarization at slag/metal interfaces have been reported by the present author and his coworkers. The rate of the charge transfer reactions is clearly controlled by the slow step of diffusion in the slag and thus the interdiffusivities of ionic species in the slag have been quantitatively determined from the polarization experiments. The exchange current densities of metal/salt systems have been compiled in Table 9.2, which had been determined by double pulse method. However, the exchange current density on metal/fused oxide systems have not yet been studied except by Prange, Heusler, and Schwerdtfeger⁽⁷²⁾, and by Emi, Sakuraya, and Sambongi⁽⁷⁴⁾.

Also, the complex impedance plot or Cole-Cole plot have not been studied extensively on metal/fused oxide systems. However, in 1979, Numata and Haruyama⁽⁷⁵⁾ obtained the Cole-Cole plot on Ni/Ni^{2+} (in LiCl-KCl), and in 1984, Hino and Ban-ya⁽⁷⁶⁾ obtained the Cole-Cole plot on $\text{Pt/fused Na}_2\text{O-SiO}_2$ systems.

Therefore, the future problems to be worked out on metal/fused oxide systems are the accurate measurements of the exchange current

density and double layer capacitance both by double pulse method and by Cole-Cole plot.

REFERENCES TO CHAPTER 9

- 1 R.H. Aikon, U.S.A. Patent 816141 (March 27, 1906).
- 2 P. Herasymenko, "Electrochemical Theory of Slag-Metal Equilibria" Part I and II Trans. Faraday Soc., 34(1938), pp. 1245-1257.
- 3 P. Herasymenko and G.E. Speight, "Ionic Theory of Slag-Metal Equilibria, Part I-Derivation of Fundamental Relationships", J. of Iron and Steel Inst. 166(1950), 169-183.
- 4 P. Herasymenko and G.E. Speight, "Part II-Applications to the Basic Open-Hearth Process", J.I.S.I. 166(1950), 289-303.
- 5 T.B. Winkler and J. Chipman, Trans. AIME 167(1946), pp. 111-133, Metals Technology (1946), Vol. 13, Technical Publication No. 1987, April, 1946.
- 6 G.W. Toop and C.S. Samis, Trans. TSM-AIME 224 (1962), 878 pp.
- 7 C.R. Masson, Proceedings of Royal Society, A287 (1965), 201 pp.
- 8 T. Yokogawa and K.Niwa, Trans. of Japan Inst. of Metals, 10 (1969), 3 pp.
- 9 D.R. Gaskell, "Thermodynamic Models of Liquid Silicates", Canadian Metall.Q., 20 (1981), pp. 3-19. Special Issue for International Symposium on Metallurgical Slags.
- 10 T. Yokokawa, "Redox Equilibria in Slags", *ibid.*, pp. 21-26.
- 11 C.R. Masson, "Application of Temkin's law to Polyionic Melts", *ibid.*, pp. 27-29.
- 12 J.H.E. Jeffes, "The Relationship of Structure and Thermodynamic Properties of Polyanionic Compounds" *ibid.*, pp. 37-50.
- 13 K.S. Goto, K. Nagata, and Y. Ukyo, "Transport Properties of Multicomponent Liquid Slags Under Isothermal and Nonisothermal Conditions", Canadian Metall. Q., 20 (1981), pp. 117-127.
- 14 A. Yazawa, Y. Takeda, and Y. Waseda, "Thermodynamic Properties and Structure of Ferrite Slags and their Process Implication", *ibid.*, pp. 129-134.
- 15 A.E. Martin and G. Derge, Trans. AIME 154 (1943), pp. 104-114.
- 16 M.T. Simnad, W.E. Dennis and G. Derge, Rev. Sci. Instr. 23 (1952), pp. 248-249.
- 17 M.T. Simnad and G. Derge, J. of Chem. Phys. 21 (1953).
- 18 M.T. Simnad, L.Yang and G. Derge, Trans. AIME 202 (1956), pp. 690-934.
- 19 E.A. Dancy and G.J. Derge, Trans. Metall. Soc. of AIME 236 (1966), pp. 1642-1648.
- 20 J. O'M. Bockris, J.A. Kitchener, S. Ignatowicz and J.W. Tomlinson, Faraday Soc. Discussions 4 (1948), 265 pp. and Trans Faraday Soc., 48 (1952), 75 pp.
- 21 J. O'M. Bockris, J.A. Kitchener and A.E. Davies, Trans. Faraday Soc., 48 (1952), pp. 536-548.
- 22 J. O'M. Bockris and G.W. Mellors, J. of Phys. Chem., 60 (1956), pp. 1321-1328.
- 23 D.L. Hill, G.J. Hills, L. Young and J. O'M. Bockris, J. of Electroanalytical Chem., 1 (1959/60), pp. 79-83.
- 24 M. Ohtani and N.A. Gokcen, Proceedings of Metall. Soc. Conferences Vol. 8 (1959), Physical Chemistry of Process Metallurgy, Part 2, pp. 1213-1227, edited by G.R.St. Pierre.
- 25 H. Ito and T. Yanagase, Trans. Japan Inst. of Metals, 1 (1960), pp. 115-120.

- 26 W.R. Dickson and E.B. Dismukes, *Trans. Met. Soc. AIME*.(1962).
- 27 A. Adachi and K. Ogino, *Denki Kagaku* 32 (1964), pp. 145-149.
- 28 A. Adachi and K. Ogino, "Yöyü-en" Vol. 5 (1962), pp. 1149-1171.
- 29 A. Adachi, K. Ogino, and S. Hara, *Trans. I.S.I.J.* 9 (1969), pp. 153-161.
- 30 H.J. Engell and P. Vygen, *Ber. Bunsengesell. Phys. Chemie* 72 (1968), pp. 5-12.
- 31 O.A. Esin and G.A. Getrin, *Doklad. Akad. Nauk. SSSR*, 128(1959), *Tekh. Nauk.* (1955) No. 12, 28 pp.
- 32 K.S. Goto, M. Sasabe and M. Kawakami, "Relation between Diffusivity and Electrical Conductivity on Oxide Slags at 900 to 1600°C", *Trans. I.S.I.J.* 17 (1977), pp. 212-214.
- 33 T. Bäck, *Acta. Chem. Scand.*, 8 (1954), 166 pp.
- 34 O.A. Esin, G.A. Getrin, *Doklad. Akad. Nauk. SSSR*, 128 (1959), No. 3, 569 pp.
- 35 V.I. Markin, L.A. Schwartzman, and S.F. Khokhlov, "Metallurgy and Metallography", (1958), 23 pp., published by USSR Academy Press.
- 36 V.I. Markin and V.V. Pokidyshev, "Physical Chemistry of Steel-making", (1961), 246 pp., published by USSR Academy Press.
- 37 O.A. Esin, et al., "Diffusion Constant Current", *Dokladi Akademii Nauk SSSR* 145 (1962), pp. 360-362; 388-390.
- 38 O.A. Esin, et al. "Chemical Polarization at High Temperature", *Dokladi Akademii Nauk SSSR*, 152 (1963), pp. 1173-1175.
- 39 O.A. Esin, et al., "Kinetic Study of Desulfurization of Pig Iron by Slag by Means of Polarization Method of Alternative Current", *Izvestia Akademii Nauk SSSR Metalli* (1965), No. 1, pp. 33-38.
- 40 O.A. Esin, et al., *Electrokhimya* Vol. 3 (1967), No. 6, pp. 775-779.
- 41 O.A. Esin, et al., *Izvestia Vysshee Uchebnoe Zavedenie Tshernaja Metallurgia* (1967), No. 3, pp. 10-14.
- 42 O.A. Esin, et al., *Electrokhimya* Vol. 3 (1967), No.3, pp. 288-293.
- 43 O.A. Esin, et al., *Electrokhimya* Vol. 3 (1967), pp. 1012-1015.
- 44 O.A. Esin, et al., *Izvestia Vysshee Uchebnoe Zavedenie Tshernaja Metallurgia* (1967), No.7, pp. 5-10.
- 45 O.A. Esin, et al., *Izvestia Vysshee Uchebnoe Zavedenie Tshernaja Metallurgia* (1968), No.3, pp. 12-16.
- 46 O.A. Esin, et al., *Electrokhimya* Vol.5 (1969), No.2, pp. 159-165.
- 47 O.A. Esin, et al., *Electrokhimya* Vol. 5 (1969), No.6, pp. 685-691.
- 48 O.A. Esin, et al., *Izvestia Bischix Uchebnix Zavedenie Chernar Metallurgia* (1969), No.8, pp. 19-23.
- 49 O.A. Esin, et al., *Izvestia Vysshee Uchebnoe Zavedenie Tshernaja Metallurgia* (1971), No.12, pp. 13-17.
- 50 O.A. Esin, et al., *Izvestia Vysshee Uchebnoe Zavedenie Tshernaja Metallurgia* (1971), No.12, pp. 12-21.
- 51 H. Itaya and K.S. Goto, *Tetsu-to-Hagane* 59 (1973), pp. 405-413.
- 52 M. Kawakami and K.S. Goto, *Tetsu-to-Hagane* 59 (1973), pp. 196-204.
- 53 M. Kawakami and K.S. Goto, *Bulletin of Japan Institute of Metals* 12 (1973), pp. 523-531.
- 54 M. Kawakami and K.S. Goto, *Metall. Trans. AIME* 4 (1973), pp. 1097-1101.
- 55 W. Kagohashi and K.S. Goto, *Trans. ISIJ* 13 (1973), pp. 377-384.
- 56 W. Kagohashi and K.S. Goto, *Tetsu-to-Hagane* 59 (1973), pp. 63-71.
- 57 M. Kawakami and K.S. Goto, *Metall. Trans. AIME* 5 (1974), pp.

- 2244-2246.
- 58 K. Nagata, M. Kawakami and K.S. Goto, Proceedings of International Symposium on Metal-Slag-Gas Reactions and Processes (1975), pp. 183-198, Toronto, Canada.
 - 59 M. Kawakami, K. Nagata, M.M. Sasabe and K.S. Goto, Tetsu-to-Hagane 62 (1976), pp. 1159-1168.
 - 60 K. Nagata and K.S. Goto, Ironmaking and Steelmaking (1977), No. 1, pp. 23-28.
 - 61 M. Kawakami, K. Nagata and K.S. Goto, J. Electrochem. Soc. 125 (1978), pp. 395-400.
 - 62 V.G. Levich, "Physiochemical Hydrodynamics", (1962), pp. 60-72, Prentice-Hall, New Jersey.
 - 63 K.J. Vetter, "Electrochemical Kinetics" (1967), Academic Press, London.
 - 64 C. Wagner, "Advances in Electrochemistry and Electrochemical Engineering", ed. by P. Delahay and C.W. Tobias, Vol. 4 (1966), pp. 1-46, Interscience Publishers.
 - 65 E. Warburg, Wied Ann., 67 (1899), pp. 493.
 - 66 H. Gerischer and M. Krause, Z. Phys. Chemie, Neue Folge, Vol.10 (1957), pp. 264-269 and Vol.14 (1958), pp. 184-196.
 - 67 H. Matsuda, S. Oka, and P. Delahay, J. Amer.Chem. Soc., Vol.81 (1959), pp. 5077-89.
 - 68 D. Inman, J.O.M. Bockris, and E. Blomgren, J. Electroanal. Chem., Vol.2 (1961), pp. 506-514.
 - 69 K. Schulze and H. Hoff, Z. Naturforsch., Vol.26a (1971), pp. 1472-1477.
 - 70 H.A. Latinen, R.P. Tischer and D.K. Roe, J. Electrochem. Soc., Vol. 107 (1960), pp. 546-555.
 - 71 A.D. Graves and D. Inman, J. Electroanal. Chem., Vol.25 (1970), pp. 357-372.
 - 72 R. Prange, K. Heusler, and K. Schwerdtfeger, Metall. Trans. B, Vol.15B (1984), pp. 281-288.
 - 73 A. Nishikata and S. Haruyama, J. Japan Inst. Metals, Vol.47 (1983), pp. 198-204.
 - 74 T. Emi, T. Sakuraya and K. Sanbongi, Proceedings of Fourth Japan-USSR Joint Symposium on Physical Chemistry of Metall. Processes (1973), Tokyo.
 - 75 H. Numata and S. Haruyama, J. Japan Inst. Metals, Vol.43 (1979), pp. 866-871.
 - 76 M. Hino and S. Ban-ya, Proceedings of 2nd Intern. Symp. on Metallurgical Slags and Fluxes, edited by H.A. Fine and D.R. Gaskell, published by Metall Soc. of AIME (1984), U.S.A., pp. 669-684.

Chapter 10

INDUSTRIAL APPLICATION OF OXYGEN SENSORS WITH SOLID ELECTROLYTES
OF OXYGEN ANION CONDUCTION

10.1 INTRODUCTION

In this chapter and the following chapters, a term "SENSOR" is often used and thus the definition of sensor must be given at the beginning.

Fig. 10.1 shows the function of a "sensor", by which a small change of temperature, pressure, concentration of components, or other property can be converted in situ to an electronic signal. The electronic signal can be amplified by an appropriate circuit to operate the automatic control system of an industrial device. The sensor can be defined as " a small electronic device that converts, in situ, any microchanges of properties into an electronic signal ". Integrated circuits and automatic control systems were highly developed in 1980's. But in contrast to these remarkable developments, it was sometimes very difficult to develop the reliable sensor.

Many kinds of sensors are now widely used for security of every day life at home, for automatic control of electronic equipments, and for process controls in many industries. They will be discussed in Chapters 12 and 13.

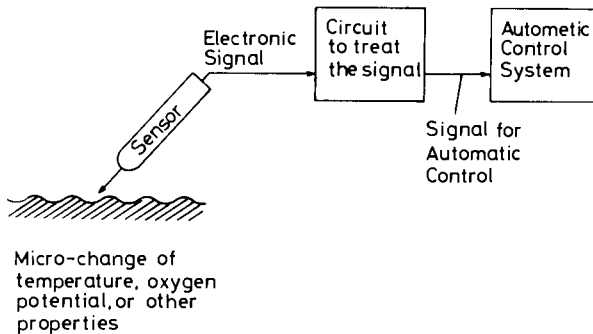


Fig. 10.1. A picture to show the function of "Sensor" for automatic control of industrial process, machines and equipments.

However, in the present chapter only the oxygen sensor and its uses in industry are covered. It is a good example of application of solid state electrochemistry to industrial problems.

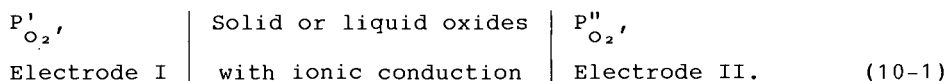
The principle of the oxygen sensor is based on the theoretical relation between the electromotive force and oxygen pressures at two electrodes of the oxygen concentration cells.

When the oxygen concentration cell is designed and constructed with the intension of satisfying the function of the sensor defined above, it is called as the oxygen sensor.

A brief history of the oxygen concentration cell and the development of the oxygen sensor is given below.

The oxygen concentration cell can be defined as a type of galvanic cell whose electromotive force is generated by the difference in the chemical potential of oxygen or, in other words, in the oxygen concentration at the two electrodes under isothermal and isobaric conditions.

As the electrolytes used are the solid or liquid oxides with predominant ionic conductivity at elevated temperatures, this category of galvanic cells can be expressed by the following general cell formula;



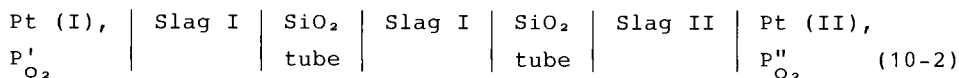
In 1908, Haber⁽¹⁾ measured the electromotive force of this type of cell, using Thüringer hard glass as the electrolyte. Eight years later, Treadwell⁽²⁾ tried to use fused borates, silicates, or solid porcelain as the electrolyte and to control the oxygen pressure at the electrodes by using the two phase mixtures of Fe and FeO, or Cu₂O and CuO. A similar study was independently reported by Baur, et al.⁽³⁾

After the extensive study by Treadwell,⁽²⁾ the oxygen concentration cells have been investigated in many countries. Among them, Esin⁽⁴⁾ in Russia has constructed various types of the oxygen concentration cells.

In 1957, Sanbongi, Ohtani and Omori⁽⁵⁾ reported a review including all reports after Treadwell, and hence the details will not be reported here, except for the industrial applications.

The first industrial application of the oxygen concentration cells was reported by Onaka⁽⁶⁾ in 1944. To control the refining

operation of steels, he tried to determine the oxidizing power of the slag of an acid open hearth furnace from the electromotive force of the cell



where the electrolyte was composed of solid silica containing iron oxide absorbed from slag I.

Onaka showed that the electromotive force is exclusively generated by the difference in the oxygen potential of the two slags or in the ratio of Fe^{2+} to Fe^{3+} . Then he tried to determine the oxygen concentration in molten steels from the electromotive force of the following cell;⁽⁷⁾

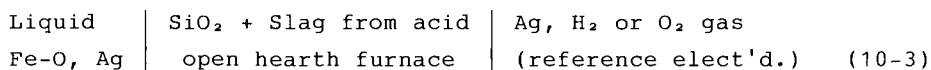


Figure 10.2 shows the structure of this cell and Fig. 10.3 the relation between the electromotive force and the oxygen content in steels determined by the conventional vacuum fusion method.

A similar experiment was made in 1958 by Sanbongi and Ohtani supported by Fuji Iron and Steel Corp., using solid magnesia as the

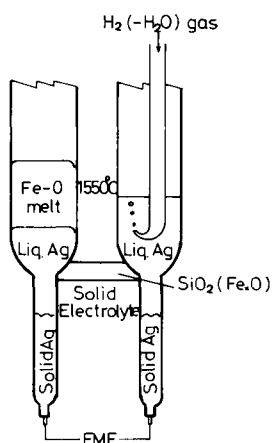


Fig. 10.2. Schematic diagram of galvanic cell to determine oxygen pressure in liquid iron used by Onaka⁽⁷⁾. The electrolyte is made of silica containing iron oxide. (After Onaka, 1949 (7)).

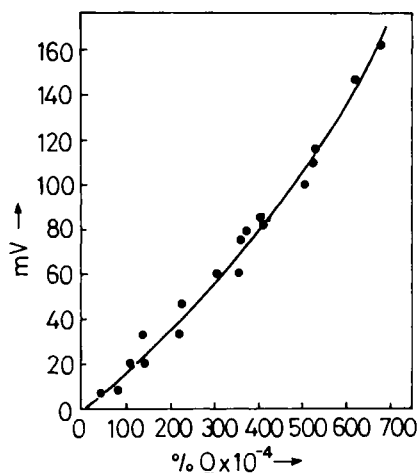


Fig. 10.3. Relation between the EMF of the cell of Fig.10.2 and the oxygen content determined by the conventional vacuum fusion method. (After Onaka, 1949 (7)).

electrolyte. (8)

These oxygen concentration cells can not be called oxygen sensors, because the samples are taken intermittently and they are used as the electrode materials.

In Japan, however, these two investigations played an important role in the development of the oxygen sensor with the solid electrolyte, which can be directly immersed in molten steel during its refining in large furnaces.

The investigations on the oxygen concentration cell by Haber⁽¹⁾, Treadwell⁽²⁾, Bauer⁽³⁾, Onaka⁽⁷⁾ and by Ohtani and Sanbongi⁽⁸⁾ are all quite unique but had limited industrial use for the following reasons:

- (1) The electric conduction mechanism in the electrolytes was not clearly known. Virtual cell reactions were not clearly known accordingly.
- (2) Since solid oxides with large ionic conductivity were unknown at that time, the internal resistance of the cells was too large to have a reproducible electromotive force.
- (3) When liquid oxides are used instead of solid ones, the internal resistance of the cell can be reduced but, in many cases, the liquid electrolytes react with the electrode materials. Therefore, the stability of the electromotive force was not

acceptable.

These difficulties could be overcome to some extent by the art of the construction of the galvanic cells and the careful measurements of the electromotive forces. However, the difficulties limited the applications of the oxygen concentration cells to specific experiments.

To solve these theoretical problems, C. Wagner⁽⁹⁾⁽¹⁰⁾ reported two theoretical works in 1933 and in 1966, which strictly related the conduction mechanism of the oxide electrolytes to the electromotive force at elevated temperatures.

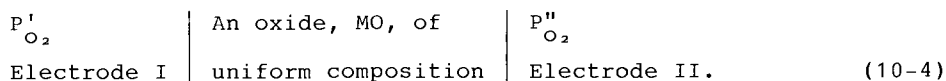
Furthermore, Kiukkola and Wagner⁽¹¹⁾ discovered that zirconia or thoria base solid solutions can be used as the electrolyte to have very stable and reproducible electromotive forces, simply because of their very large oxygen ion conductivity above 500°C. Thanks to this celebrated publication, high temperature electrochemistry was extensively developed all over the world in the 1960's.

Two review papers were published on this development in 1970 by Rapp and Shores⁽¹²⁾ and in 1972 by Goto and Pluschkell⁽¹³⁾ documenting 242 and 295 publications, respectively. However, these review papers did not deal with the industrial application of the oxygen sensors and thus the present chapter is made to summarize the uses of the oxygen sensors in industry.

The use in steelmaking industry will be discussed in Chapter 11. The details of the relation between the conduction mechanism in the oxide electrolytes and the electromotive force have been given in Chapter 6 but the theoretical electromotive forces are briefly summarized for the two cases as follows:

1. For the Case of the Oxide Electrolytes of Uniform Composition

The cell can be described as follows:



The charge carriers in the oxide, MO, would be M^{2+} , O^{2-} , electrons or positive holes. Using the assumption of the local equilibrium in the electrolyte, Wagner⁽⁹⁾ obtained the Gibbs free energy change of the thin slice of the electrolyte, when the infinitesimal

current was supplied to the cell under isobaric conditions. Then, this infinitesimal Gibbs free energy change was integrated from the leftmost to the rightmost side of the electrolyte to obtain the total free energy change of the virtual cell reaction. Using the relation, $\Delta G = -nFE$, one gets the following expression for the electromotive force:

$$\begin{aligned}
 E &= \frac{RT}{4F} \int_{P'_{O_2}}^{P''_{O_2}} (t_{M^{2+}} + t_{O^{2-}}) d \ln P_{O_2} \\
 &= - \frac{RT}{2F} \int_{a'_M}^{a''_M} (t_{M^{2+}} + t_{O^{2-}}) d \ln a_M \\
 &= - \frac{RT}{2F} \int_{a'_M}^{a''_M} (1 - t_e) d \ln a_M \quad (10-5)
 \end{aligned}$$

where, E : the electromotive force

F : the Faraday constant

P'_{O_2} and P''_{O_2} : the oxygen pressures at the two electrodes

a'_M and a''_M : the chemical activities of the metal at the two electrodes

t_i : means the transference number of the charge carriers.

For zirconia base solid electrolytes, the transference number of oxygen is known to be unity at a higher oxygen pressure, and thus all other transference numbers become zero. Therefore, Eq. (10-5) gives simply

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P'_{O_2}} \quad (10-6)$$

At an oxygen pressure lower than that for chromium-chromium oxide equilibrium, the transference number of electrons can not be neglected and is given as a function of oxygen pressure. In this case, Eq. (10-5) can be integrated to yield Eq. (6-16) in Chapter 6. The detailed discussion was given in Chapter 6.

2. For the Case of the Binary Oxide Electrolytes of Non-uniform Composition

Using $AO-BO_2$ as the binary oxides, the cell can be described by

$$\begin{array}{c|c|c} \text{Electrode I} & \text{AO-BO}_2 \text{ of non-uniform} & \text{Electrode II,} \\ \mu'_{\text{O}_2} & \text{composition} & \mu''_{\text{O}_2} \end{array} \quad (10-7)$$

where μ_{O_2} denotes the chemical potential of oxygen, and the possible charge carriers would be ionic species, A^{2+} , B^{4+} and O^{2-} , and positive holes or electrons.

If the local equilibrium condition applies throughout the electrolyte, the Gibbs free energy change due to the migration of the carriers induced by the externally supplied current can be calculated, and the electromotive force can be expressed by the following equation: (10)

$$\begin{aligned} E = & -\frac{1}{F} \left[-\frac{1}{4} (\mu''_{\text{O}_2} - \mu'_{\text{O}_2}) + \frac{1}{2} \int t_{\text{A}^{2+}} d\mu_{\text{AO}} + \frac{1}{4} \int t_{\text{B}^{4+}} d\mu_{\text{BO}_2} \right. \\ & \left. + \frac{1}{4} \int (t_e \text{ (or } t_p) d\mu_{\text{O}_2} \right] \end{aligned} \quad (10-8)$$

where, t_i means the transference number of charge carrier i , and μ_i means the chemical potential of O_2 , AO or BO_2 .

The local equilibrium being assumed, the Gibbs-Duhem relation will be satisfied throughout the electrolyte; then

$$d\mu_{\text{AO}} = -\frac{N_{\text{BO}_2}}{N_{\text{AO}}} d\mu_{\text{BO}_2}, \quad (10-9)$$

where N_{AO} and N_{BO_2} are the mole fraction of oxides, AO and BO_2 . Inserting Eq. (10-9) and $\mu_{\text{O}_2}^\circ + RT \ln P_{\text{O}_2}$ for μ_{O_2} in Eq. (10-8), one has

$$E = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}''}{P_{\text{O}_2}'} - \int \left[\frac{1}{2F} t_{\text{A}^{2+}} - \frac{1}{4F} \frac{N_{\text{AO}}}{N_{\text{BO}_2}} t_{\text{B}^{4+}} \right] d\mu_{\text{AO}} - \frac{RT}{4F} \int t_e d \ln P_{\text{O}_2} \quad (10-10)$$

The first term in the right hand side of this equation is the same as E in Eq.(10-6), and the second term is the electromotive force induced by the difference between the diffusivities of the cation species. The third term, arising from the internal current, caused by the migration of electrons or positive holes in the electrolyte, means the decrease of the measurable electromotive force.

In the case of Zirconia or thoria base solid solution, the transference numbers of the cation species are zero. Thus the

second term becomes zero regardless of non-uniforming of the electrolytes composition. This is one of the reasons why these electrolytes give very stable and reproducible electromotive force.

In contrast, beta-alumina phases⁽¹⁴⁾⁽¹⁵⁾ ($A_2O-nM_2O_3$, where, A is Na, Rb, Ag, K, Li, or Tl and M is Al, Ga or Fe^{3+}) have a very large cationic conductivity even at lower temperatures. However, its use is very limited, because the second term can not be neglected due to easy vaporization of alkali metal oxides.⁽¹⁶⁾

10.2 OXYGEN ANALYSIS IN WASTE GASES OF BOILERS AND VARIOUS INDUSTRIAL FURNACES

The most important material to construct the oxygen sensor is the zirconia stabilized with CaO, MgO, or Y_2O_3 . The impurity level and the magnitude of sintering would be related to the performance of the oxygen sensor. Therefore, at the beginning of this section, the preparation of the solid electrolyte is given with some information about the impurity contents.

In laboratory zirconia-lime solid solutions can be made from the aqueous solution of zirconium nitrate, $(ZrO)(NO_3)_2$ and calcium carbonate, $CaCO_3$. Slowly drying the solution, the compounds deposit in very fine powders. The decomposition of the nitrate and carbonate at 700°C to 800°C gives the mixture of zirconia and lime. After pressing the powders in a desired shape, sintering at 1500°C gives the solid solution of zirconia and lime with the fluorite type crystal structure with white color. However, commercial zirconia-base solid electrolytes sometimes have a yellowish color due to the impurities.

Table 10.1 is the flow sheet of the industrial production of the solid electrolyte reported⁽¹⁷⁾ from a Japanese company. Table 10.2 shows the impurity contents in the commercial electrolytes and their physical properties.⁽¹⁷⁾

The users' claims are mostly the spalling of the electrolytes, the precision in size and shape of the electrolytes, and the effects of the impurities upon the electromotive force and the life time of the oxygen sensors for industrial uses. As Table 10.2 shows, the major impurities are SiO_2 , TiO_2 , Al_2O_3 and Fe_2O_3 . However, the impurities would hardly affect the electromotive force in a short time because of the absence of the cationic conduction as explained above. In a long time, silica and ferric oxide would react with the electrode materials, decreasing the life time of the oxygen sensor.

TABLE 10.1
A flow sheet of manufacturing of ZrO₂-base solid solutions for the solid electrolyte

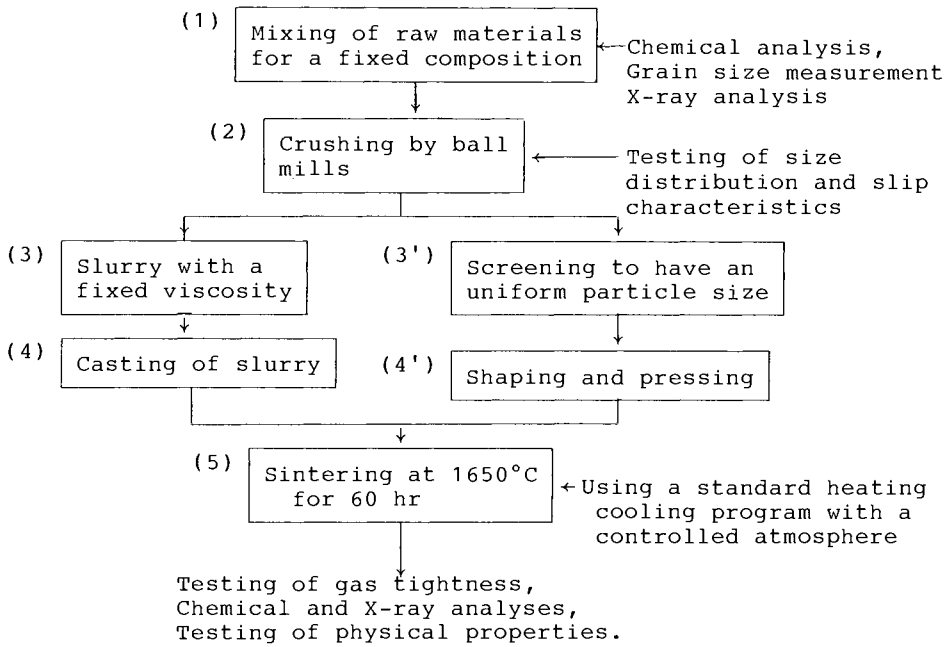


TABLE 10.2
Chemical composition and physical properties of a commercial stabilized zirconia for electrolyte use

Stabilizers	CaO			MgO	Y ₂ O ₃
	9mol%	11mol%	15mol%	15mol%	15mol%
Chemical composition(%)					
SiO ₂	1.63	1.58	1.66	0.6	0.49
TiO ₂	0.28	0.24	0.27	0.24	0.26
Al ₂ O ₃	0.69	0.71	0.67	0.29	0.27
Fe ₂ O ₃	0.16	0.17	0.18	-	-
CaO	4.7	5.8	7.7	0.36	0.04
MgO	0.89	0.92	0.99	5.2	-
Y ₂ O ₃	-	-	-	-	13.2
Na ₂ O	0.03	0.02	0.04	0.03	0.03
K ₂ O	tr.	tr.	tr.	tr.	tr.
ZrO ₂	91.62	90.55	88.5	93.27	85.67
Physical properties					
Max. water absorption(%)	0.29	0.1	0	0.05	0.02
Apparent porosity(%)	1.56	0.06	0.01	0.24	0.07
Apparent density	5.5	5.36	5.13	5.60	5.41
Degree of stabilization(%)	74	93	100	100	100

The electromotive force observed at extremely low oxygen pressures would be influenced by the ferric oxide impurity in the electrolyte, because ferric oxide decomposes to yield oxygen at such pressures and, if existing at grain boundaries, the ferric oxide provide the path for oxygen transfer.

Figure 10.4 shows the specific resistivity of commercial electrolytes.⁽¹⁷⁾ The electrolyte stabilized by Y_2O_3 has a large conductivity even at lower temperatures.

Because chemical and physical properties are different for various electrolytes, careful selection is necessary to have a long life and stable electromotive force of the oxygen sensors for various industrial uses.

The first try to use the oxygen sensor with the solid electrolytes for gas analysis has been reported independently by Weissbart and Ruka⁽¹⁸⁾ in 1961 and by Goto and St. Pierre⁽¹⁹⁾ in 1962. The cell⁽¹⁹⁾ can be expressed by

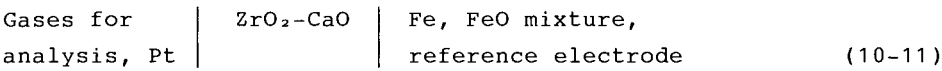


Figure 10.5 shows the structure of this cell.⁽¹⁹⁾

In steel industry, this sensor was used by Matsushita, et al⁽²⁰⁾

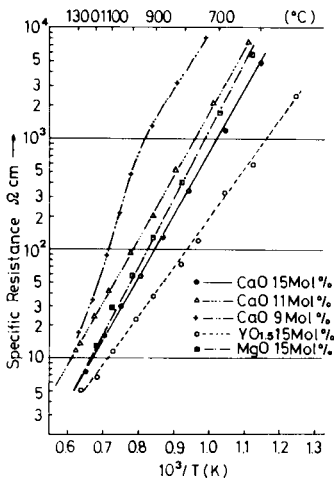


Fig. 10.4. Reciprocal temperature and the specific resistivity of commercial zirconia base solid electrolyte. (Courtesy of Nippon Kagaku Togyo Co. Ltd.)

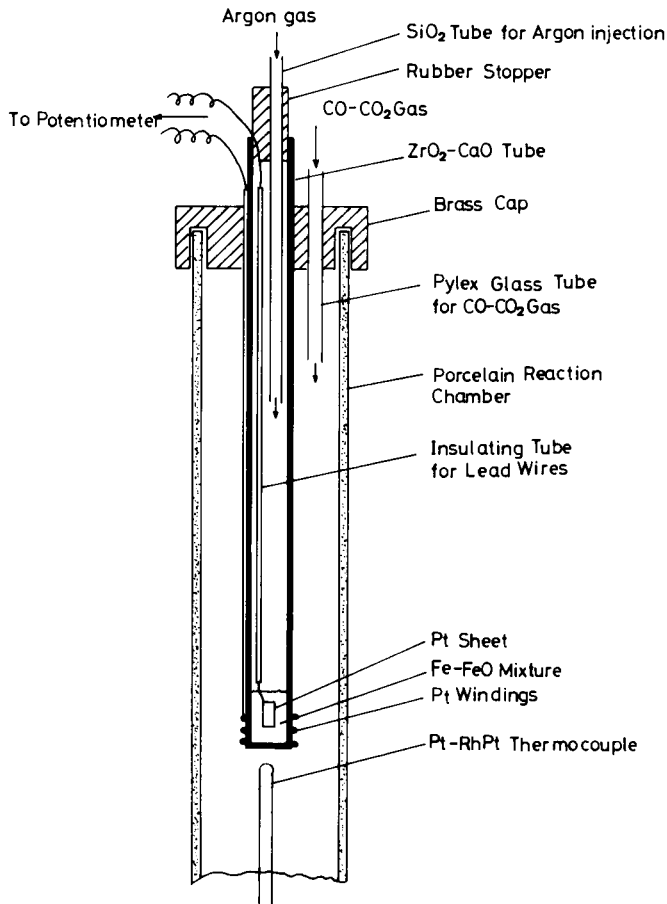


Fig. 10.5. A prototype of the oxygen concentration cell to analyze the gas composition. (After Goto and St. Pierre, 1962 (19)).

to determine continuously the oxygen content in the waste gas of the open hearth furnace. As shown in Fig. 10.6, the waste gas was continuously sampled by the steam ejector and sent to the oxygen concentration cell. Figure 10.7 shows the change of the electromotive force with respect to time, when the standard electrode is made of a mixture of nickel and its oxide powders. During the use of No.1 burner, the electromotive force gave the oxygen pressure in the waste gas but during the use of No.2 burner, it gave the oxygen pressure in air used for the combustion of the fuel oil. From this measurement, an optimal amount of the secondary air for

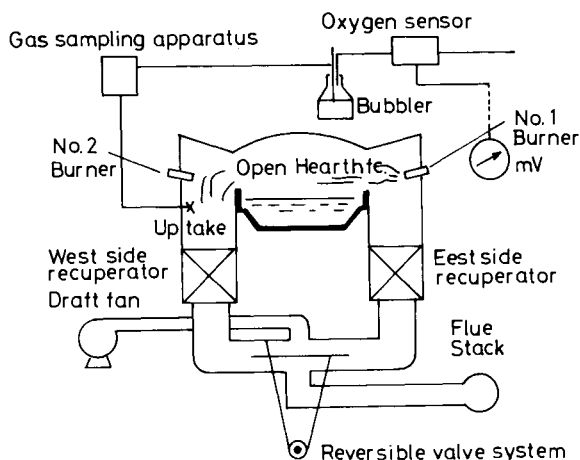


Fig. 10.6. Schematic diagram of the open hearth furnace and the galvanic cell to make the continuous analysis of its waste gas. (After Matsushita et al., 1966 (20)).

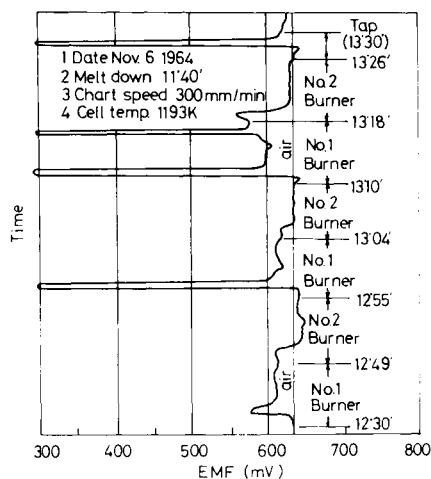


Fig. 10.7. The sheet with the recorded EMF as the function of time obtained by the experimental set-up of Fig. 10.6. (After Matsushita et al., 1966 (20)).

the combustion was determined. However, the life time of the cell was only 3 to 4 days for its continuous use, probably due to iron oxide powders generated by oxygen lancing.

After this study, Fischer and Janke⁽²¹⁾ made an extensive study

TABLE 10.3.

The comparison of five commercial oxygen sensors.

Specification	A	B	C	D	E
Cell design	OBE	COE	OBE	COE	COE
Electrolyte	ZrO ₂ ·CaO	ZrO ₂ ·CaO	ZrO ₂ ·CaO	ZrO ₂ ·CaO	—
Cell temperature	850°C	815.6°C	850°C	850°C	815.6°C
Sample gas flow rate	200–300ml/min	0.97–42.5l/m	500ml/min	250ml/min	0.24–42.5l/min
Flow sensitivity	Less than 0.1% per 50ml/min	Less than 0.01% per 470ml/min	—	—	—
O ₂ input ranges	1–100ppm 0.1–10%	0–1%, 0–5% 0–10%, 0–25%	1–100ppm 0.1–20%, 1–20% 98–100%	0.8–150ppm 80–150000ppm 0.8–150%	0–0.5%, 0–1% 0.5%, 0–10% 0–20%, 0–100%
Speed of response	1 sec for 63% 3 sec for 90% (250ml/min)	1 sec for 63% (9.44ml/min)	1 sec for 63% 3 sec for 90% (500ml/min)	1 sec for 63% (250ml/min)	3 sec for 63%
Temperature of sample gas	0–50°C	150°C	—	–45–120°C	—
Power requirements	AC100V, 300W	AC115V, 300W	AC100V, 130W	—	AC118V, 120W

* OBE means "open on both ends" and COE means "closed one end".

on the behaviors of the oxygen sensors as the oxygen analyzer for high temperature gases.

Towards the end of the 1960's, many companies manufacturing industrial instruments started to make commercial oxygen sensors using the solid electrolytes. Table 10.3⁽²²⁾ includes five commercial oxygen sensors. For the sake of easy handling and long life time, air and platinum are used as the reference electrode in all sensors in Table 10.3. The deterioration by harmful elements of the platinum electrode during the gas analysis is always the problem of these sensors, so that platinum is fixed to the electrolyte with various special techniques developed by each manufacturing company. The oxygen sensors in Table 10.3 can be used for the following purposes:

- 1) Continuous oxygen analysis of waste gases of boilers and various industrial furnaces
- 2) Oxygen analysis in various heat treatment furnaces in ferrous and nonferrous industry

- 3) Oxygen analysis in heating and decomposition furnaces in petroleum industry
- 4) Oxygen pressure determination of sintering bed in iron making industry⁽²³⁾
- 5) Permeability determination of moisture through the coating and mold materials for electronic parts.⁽²⁴⁾

Manufacturing of the oxygen sensor was very much accelerated in Japan by a new law to prevent the pollution of air, effective since June, 1971. In this law, equations are proposed to estimate NO_x content from the oxygen pressure in the industrial waste gases.

The lower limit of oxygen analysis was reported⁽¹³⁾ to be close to the equilibrium oxygen pressure of Cr and Cr_2O_3 or about 10^{-28} atm at 800°C . However, in reality it is not so, particularly when the gas has no buffering capacity with respect to the leaked-in oxygen gas.

The flow rate dependency of the electromotive force for inert gas-oxygen mixtures has been reported by Etsell and Flengas,⁽²⁵⁾ Iwase, Fujimura and Mori,⁽²⁶⁾ and Sunayama, et al.⁽²⁷⁾ Figures 10.8 and 10.9 show⁽²⁷⁾ the relation between the determined oxygen pressure in argon and the linear velocity of the gas flow in the

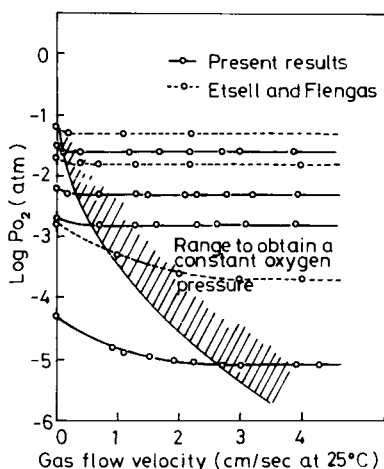


Fig. 10.8. The linear velocity of argon gas and logarithm of oxygen pressure obtained from the EMF of the galvanic cell. (After Sunayama et al., 1975 (27)).

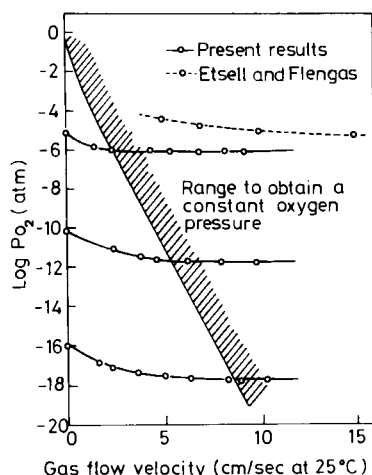


Fig. 10.9. The linear velocity of argon gas at the vicinity of the gas electrode converted to 25°C and the obtained oxygen pressure. (After Sunayama et al., 1975 (27)).

vicinity of the gas electrode made of a platinum wire. When the oxygen content was lowered, the larger flow rate was needed to have a constant and reproducible oxygen content in argon. The larger flow rate seems to be needed to exclude the effect of oxygen leaked in from various parts of the gas train and through the solid electrolyte.

Fig. 10.10 shows how to control the burner of the boiler with the help of the oxygen sensor and the pressure sensor. The ratio of the feeding rate of oil and air is automatically controlled by the signal of the oxygen sensor at the outlet of the combustion system. The steam pressure is continuously measured by the pressure sensor and its electronic signal can be used to control the feeding rate of the fuel.

Fig. 10.11 is the picture of a heat-treatment furnace. Metal parts are contained in the vessel made of heat resistant steels and heated in nitrogen atmosphere. Because the nitrogen usually contains oxygen as its impurity, the metal parts are oxidized. To avoid the oxidation, the oxygen pressure in the vessel is continuously measured by the oxygen sensor. When the atmosphere contains too much oxygen, propane gas is automatically supplied to change the atmosphere to a reducing gas.

In this way, the metal parts can be heated without the deterioration by the oxidation. This system shown in Fig. 10.11 has been developed by Oriental Engineering Company, Japan in 1979 and since

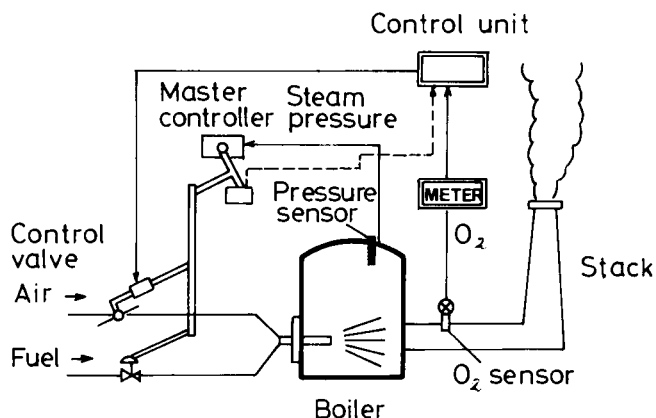


Fig. 10.10. A schematic picture to show how to use the oxygen sensor for automatic control of combustion in a boiler. (Courtesy of Nihon Gaishi Co. Ltd.)

then widely used in industry of heat treatment of alloys and steels.

The oxygen sensor shown above is very sensitive at lower oxygen pressures but not so sensitive at high oxygen pressure around 1 atm, because the electromotive force is determined by logarithm of oxygen pressure as given by Eq. (10-6). To increase the sensitivity at high oxygen pressure, the oxygen sensor with diffusion-limited currents is developed. Fig. 10.12 is showing the principle of the sensor, reported by Nakazawa et al. in 1984⁽²⁸⁾. (See also Fig. 7.25).

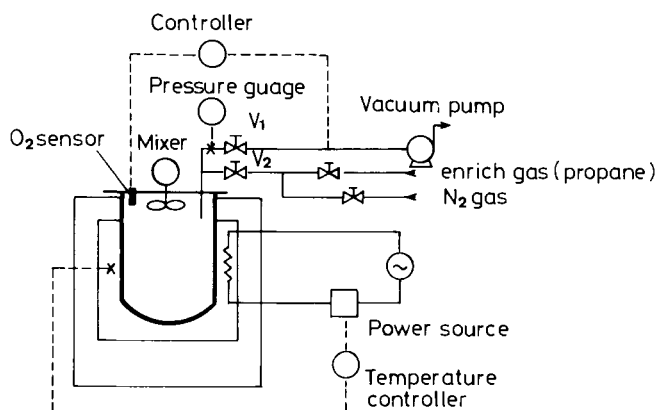


Fig. 10.11. A sectional diagram of the furnace with a closed vessel in which the oxygen pressure is automatically controlled with the oxygen sensor. Metal products are heat treated. (Courtesy of Toyo Engineering Co. Ltd.)

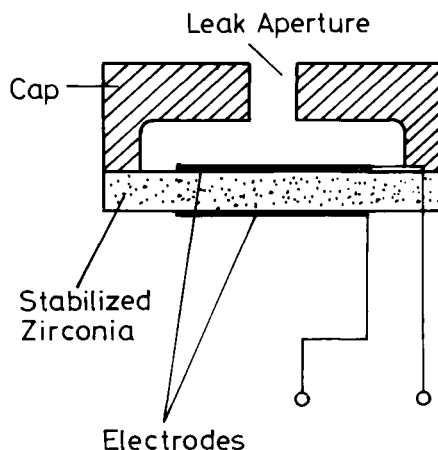


Fig. 10.12. Construction of limiting current type oxygen sensor operated at 350°C. (After Nakazawa et al, 1984 (28)).

When the direct current is supplied through the solid electrolyte with such a direction to pump out oxygen in the upper small compartment, the oxygen must be diffused in through the small hole from the outside gas. When the current is increased by increasing the applied potential, the rate of diffusion of oxygen through the hole will be increased. However, once the steady state is established for the concentration distribution of oxygen at the small hole, the current can be no more increased.

Fig. 10.13 shows the relation between the current and the applied potential for various oxygen concentration in the outside gas. The constant currents limited by the diffusion are approximately proportional to the ambient oxygen concentration. This proportionality can be used to determine the oxygen content.

Fig. 10.14 shows the structure of the oxygen sensor and the sizes of the parts commercialized by Fujikura Ltd., Japan in 1984. It is noted that the sensor is very small with the long nominal life time of 3 years. The sensor seems very elegant but the way of its use must be careful because of extra-currents from the decomposition of water vapor, CO_2 , or the electrolyte itself.

Fig. 10.15 shows the relation between the current and applied potential for two cases: one for dry air and the other for air with moisture. The constant current for dry air is simple but for air

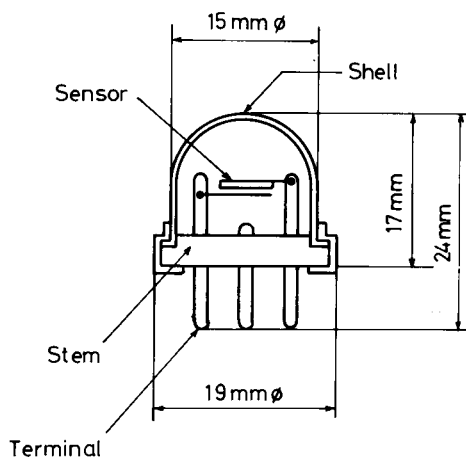
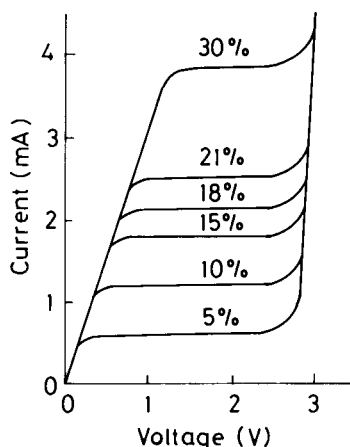


Fig. 10.13. Diffusion-limited currents at 350°C at various oxygen concentrations. (After Nakazawa et al, (28)). 1984 (28)).

Fig. 10.14. Structure of the sensor and sizes of parts of the oxygen sensor. (After Nakazawa et al, 1984

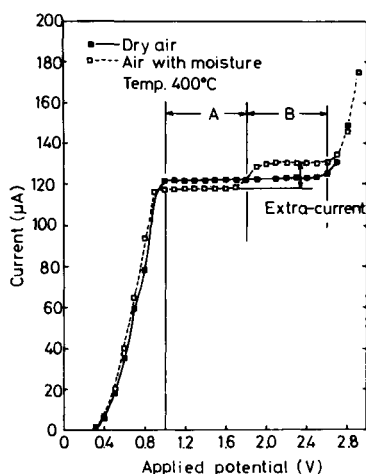


Fig. 10.15. A diagram to show extra-current by decomposition of H_2O contained in air. (After Yamaguchi et al, 1984 (29)).

with moisture, the diffusion-limited current has one more step as shown in "B" range of the diagram. This step is due to decomposition of the moisture. When the applied potential is further increased, the solid electrolyte would be partially reduced yielding the large electronic conduction. This type of the oxygen sensor can be used for oxygen analysis of the closed atmosphere, in which man must work safely, of gases in various industrial furnace, and of gases for biochemical experiments. The use of sensors for car engine is also developed as given in the next section.

10.3 TOTAL OXYGEN DEMAND IN WASTE WATER AND COMBUSTION CONTROL OF GASOLINE ENGINES

Two special applications of the above oxygen sensors are the determination of total oxygen demand of polluted water and NO_x control of vehicle engines.

The total oxygen demand, TOD, is used as an index of magnitude of pollution of water. The procedure for its determination is to sample a fixed quantity of polluted water, heat it to a high temperature with a catalyst and with excess of oxygen gas. Then, the quantity of oxygen consumed to combust organic compounds contained in the sampled water can be measured by an oxygen sensor with the solid electrolyte. Furthermore, the quantity of carbon

dioxide produced is determined by an infrared absorption gas analyzer to have total carbon, TC. Thus, the combination of an automatic water sampler, the oxygen sensor, and the infrared absorption gas analyzer makes it possible to check continuously TOD and TC in the industrial waste water. This combined set is commercially available in Japan. The sample water of 10 g is intermittently taken, and TOD and TC can be determined in the range of 10 to 10000 ppm and 5 to 500 ppm, respectively.

Another special application of the oxygen sensor is its use for vehicle engines to control the NO_x content in the exhaust gas by measuring the oxygen content in the exhaust gas and feeding it back to the carburetor to control the ratio of air to fuel to minimize the NO_x content. This unique study was reported in 1973 independently by Fleming, et al.⁽³⁰⁾ and by Düker and Neidhard.⁽³¹⁾

Later in 1975, Düker, et al.⁽³²⁾ reported a detailed study on the relation of the life time to the quantities of stabilizers of CaO , Y_2O_3 , and MgO , and to the structure of the oxygen sensor. The life time was reportedly corresponding to that for the vehicle running distance of 24000 km. Figure 10.16 shows the relation between the contents of CO , NO_x , and hydrocarbon in the exhaust gas and the weight ratio of air to fuel supplied to a reciprocating engine. In the figure, the curve of an isothermal electromotive force of

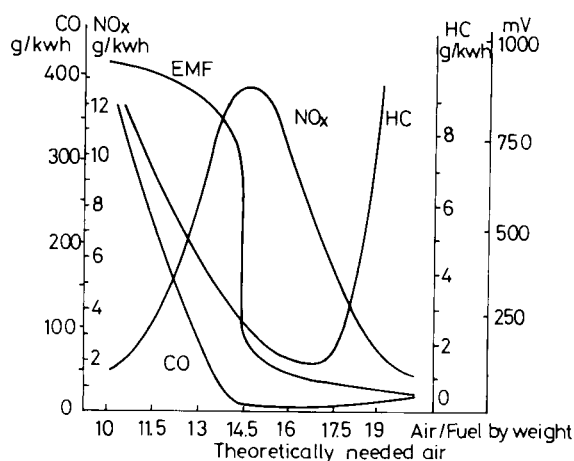


Fig. 10.16. Contents of CO , NO_x and hydrocarbons in waste gas of a gasoline engine as a function of ratio air to fuel. The EMF curve is the values obtained by the oxygen sensor shown in Fig.10.18. (After Düker, et al., 1975 (32)).

the oxygen sensor (shown in Fig.10.18) is also given to show its stepwise change at the quantity of air needed theoretically for a complete combustion. Figure 10.17 shows the principle how to automatically control the ratio of air to fuel to minimize the NO_x content with the aid of the catalyst. The best mode of operation of the engine is its combustion at 14.5 of Air/Fuel weight ratio, because the quantities of NO_x , CO and hydrocarbon expressed by HC in Fig.10.16 are most optimal to convert later them to H_2O , CO_2 and N_2 by the active platinum catalyst. Figure 10.18 shows the construction of the oxygen sensor used. The inner platinum electrode is fixed to the solid electrolyte with the coating technique

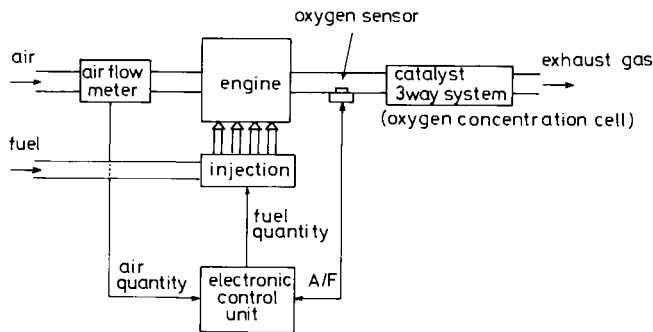


Fig. 10.17. Principle to control the ratio of air to fuel based on the EMF of oxygen sensor to minimize the contents of harmful gases in the waste gas. (After Düker et al, 1975 (32)).

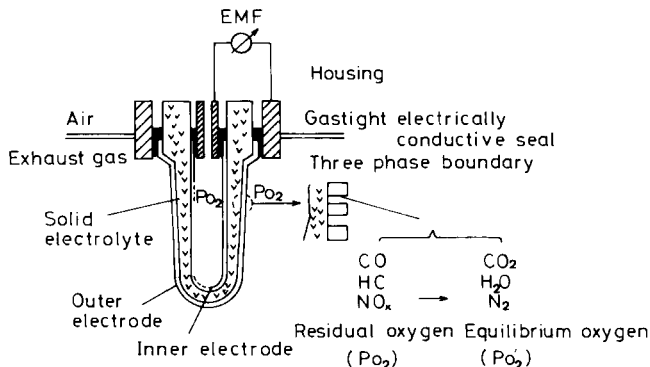


Fig. 10.18. Schematic diagram of the oxygen sensor to make the continuous analysis of the waste gas of the engine. (After Düker et al, (32)).

of thick film. The outer one is made with the evaporation method by plasma flame. This spinel layer would protect the platinum electrode from compounds of P, S and Pb contained in the exhaust gas. The oxygen sensor gives the electric signal at 300°C to 900°C with a response time of 5×10^{-3} sec and its internal resistance is $10^5 \Omega$ at 400°C.

Düker, et al⁽³¹⁾ reported that the electrical conductivity was large even at lower temperatures with zirconia stabilized by 8 mol% Y_2O_3 , and that the mechanical strength of the electrolyte increases by the addition of 3 % SiO_2 but at the sacrifice of the conductivity.

More than 1,800,000 pieces of this type of oxygen sensor had been used during 1982 by Toyota Motor Corp., Japan and more than 800,000 pieces by Nissan Motor Corp.

The above type of oxygen sensor is very sensitive, as long as the engine is operated with the air/fuel ratio of 14.5 by weight, as shown as Fig.10.16.

Another mode of operation of car engine is the combustion with the air/fuel ratio of about 16 to save the gasoline per mile. For such mode, the lean gas mixture is supplied to the engine and the exhaust gas naturally contains excess oxygen. In this case, the oxygen sensor of diffusion-limited current type is more sensitive.

Fig.10.19 is the structure of the oxygen sensor with two holes

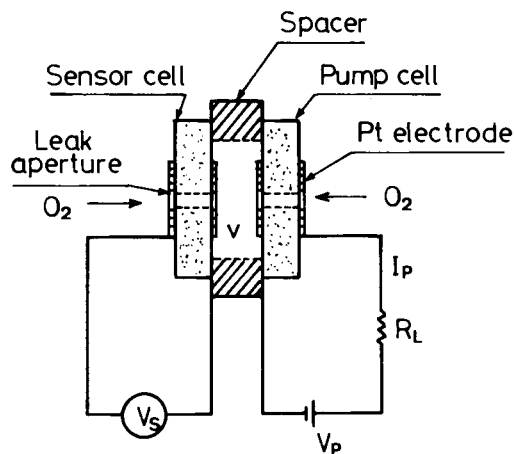


Fig. 10.19. Structure of oxygen sensor of diffusion-limited current type with two holes. The current is supplied to only the right cell. (After Hetrick, Fate and Vassel, 1981 (33)).

and two electrolyte layers, reported by Hetrick et al in 1981⁽³³⁾. The current is supplied only to the right cell assembly and the left galvanic cell is giving the oxygen pressure in the small compartment. When the oxygen pressure in the compartment becomes to a certain value, the current density of the right cell assembly gives the ambient oxygen content at the outside according to the calibration curve of the current versus the oxygen content.

Fig.10.20 is the sectional view of the layered oxygen sensor made on sapphire substrate, which was reported by Valasco et al in 1982⁽³⁴⁾. The principle of the measurement is same with that of the sensor shown in Fig.10.19.

Fig.10.21 is the structure of the sensor, developed and actually used for cars by Toyota Motor Corp, reported by Saji et al in 1984⁽³⁵⁾. The porous ceramic layer is used on the outside electrode and the steady-state concentration gradient is established in this porous layer with the diffusion-limited current.

Fig.10.22 is a picture to show the combustion control system of car engine with lean gas mixture. Also, this picture shows how various other types of sensors are used for smooth and economic operation of the car engine⁽³⁶⁾. The oxygen sensor of diffusion-limited current type had been developed primarily to operate the engine with the lean gas mixture. By this developments, 20 % saving of gasoline is reported by Toyota Motor Corp.⁽³⁷⁾

This is an example demonstrating how the sensor is important for the economic operation of the devices.

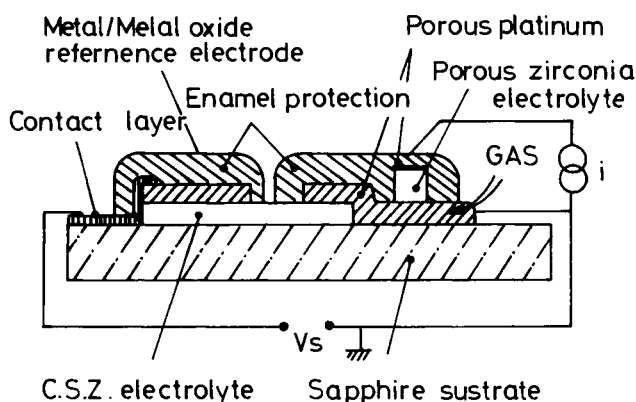


Fig. 10.20. Sectional view of the oxygen sensor of diffusion-limited current type with layered structure. The current is supplied only to the right galvanic cell. (After Valasco, Schnell and Croset, 1982 (34)).

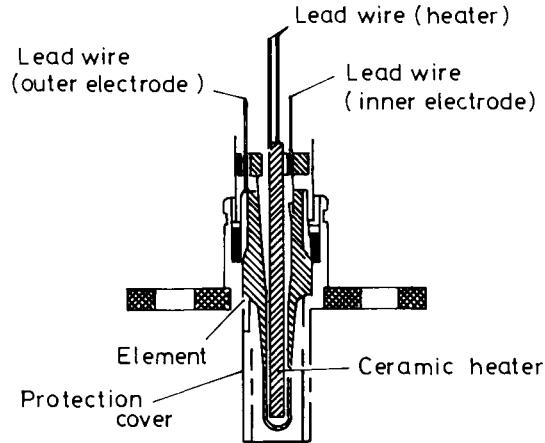


Fig. 10.21. Sectional view of the oxygen sensor of diffusion-limited current type with porous ceramic layer for use in car engines. (After Saji, et al, 1984 (35)).

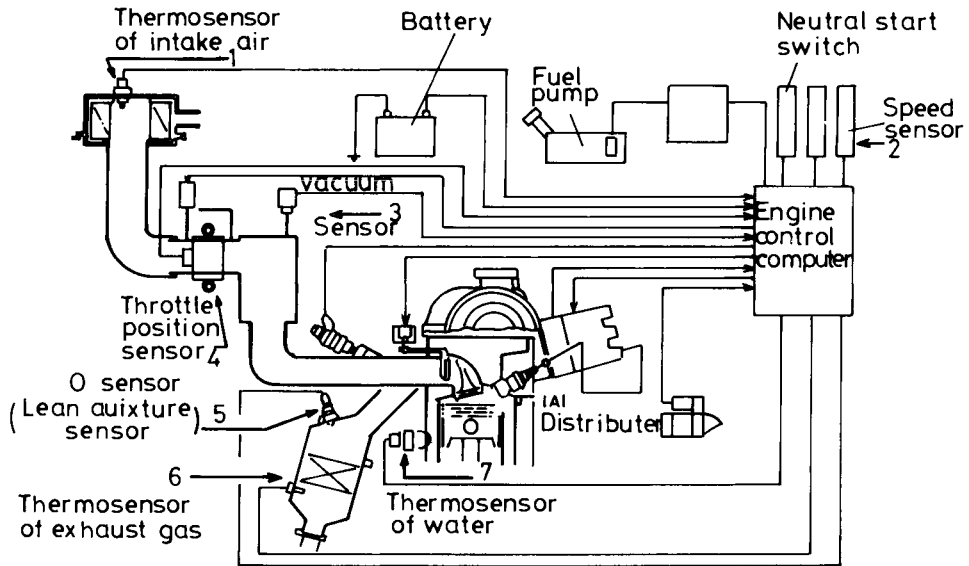


Fig. 10.22. Combustion control system of car engines with lean gas mixture and various sensors used for the engine. (After Kobayashi et al, 1984 (36)).

10.4 DETERMINATION OF OXYGEN CONTENT IN LIQUID METALS AT PLANTS OF NONFERROUS METALLURGY

In 1965, Pluschkell and Engell⁽³⁸⁾ first reported on the oxygen content determination in molten copper by the electromotive force method using zirconia-lime solid electrolyte. Recently, Janke and Fischer⁽³⁹⁾⁽⁴⁰⁾ studied on many copper alloys with this method. Kametani and Yamauchi⁽⁴¹⁾⁽⁴²⁾ have measured the oxygen potential change during vacuum treatment of molten copper and molten matte. In parallel with these basic studies, Dompas and Lockyer have studied for 7 years the application of the oxygen sensor to copper refining industry and reported their results in 1972.⁽⁴³⁾ They have continuously dipped the oxygen concentration cell in molten copper in the launders of wirebar casting, of an anode reverberatory furnace, and of continuous casting of tough pitch billets. In Fig.10.23, the cell is dipped in copper at the connection of the launder and the continuous casting machine. From the obtained electromotive force, the quantities of the air to the burner to heat the launder and of the adding deoxidizer are controlled to maintain a constant oxygen content in copper for continuous casting. Figure 10.24 shows the measured electromotive force and the oxygen content determined by the conventional method. Until 1972, this new monitoring method has been used as the standard operation of the wirebar production of 300,000 t. The life time of the oxygen sensor and the details of the structure are given in Refs.44) and 45).

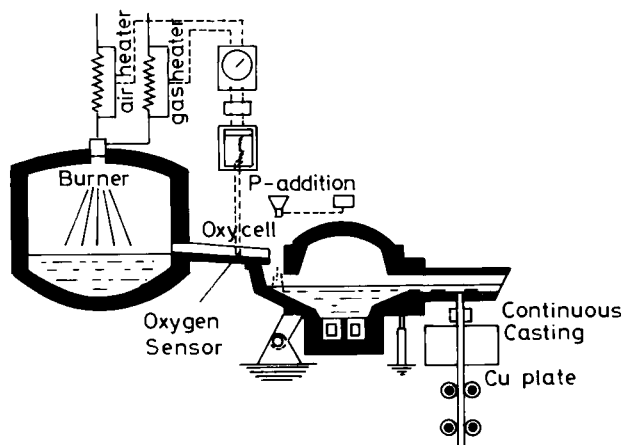


Fig. 10.23. Back-feed control system for continuous casting of tough pitch copper billet using the oxygen concentration cell at the exit of the launder. (After Dompas and Lockyer, 1972 (43)).

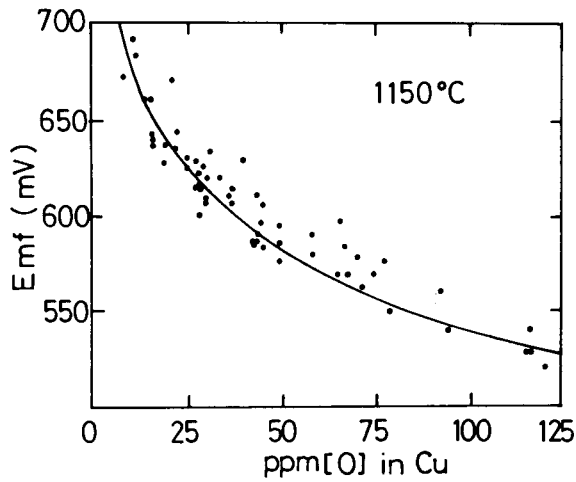


Fig. 10.24. The EMF obtained by the method of Fig.10.23 and the oxygen content in copper determined by vacuum fusion analysis. (After Dompas and Lockyer, 1972 (43)).

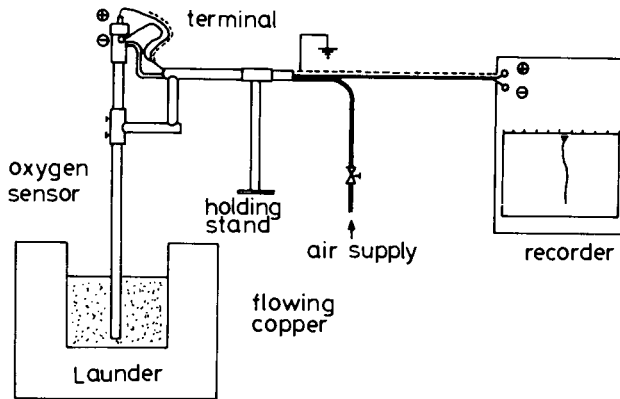


Fig. 10.25. A schematic picture to show how to measure the oxygen content continuously in the flowing molten copper in the launder. (Courtesy of Hitachi Seisen Co. Ltd., 1977).

Fig. 10.25 shows the use of the oxygen sensor to measure the oxygen content in the molten copper flowing in the launder to the continuous casting machine. Fig.10.26 is the example of the measurement. By this way, the oxygen sensor is widely used to control exactly the oxygen content in copper wires. The introduction of the sensor has been resulted in reduction of cost of wire bar production,

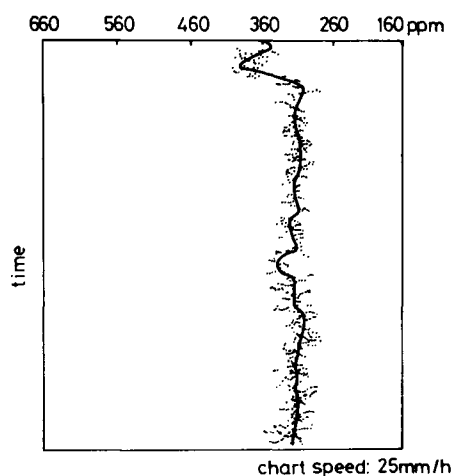


Fig. 10.26. An example of the continuous oxygen analysis by the oxygen sensor in the flowing molten copper. (Courtesy of Hitachi Seisen Co. Ltd., 1977).

because the conventional analysis of quenched samples became unnecessary and the ratio of the fault product of copper wires became distinctly smaller.

Stimulated by this success, Kozuka and his coworkers have tried to apply the oxygen sensor to other processes of copper smelting and of other nonferrous metallurgy.

Figs.10.27, 28, 29 and 30 are the part of Kozuka's work⁽⁴⁶⁾⁽⁴⁷⁾.

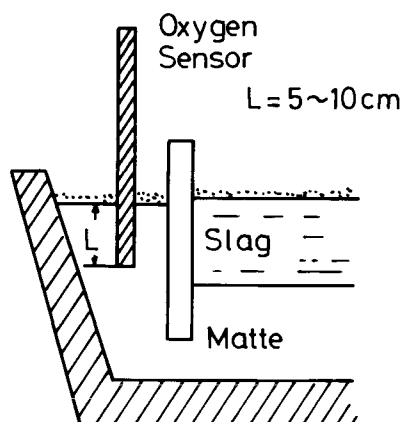
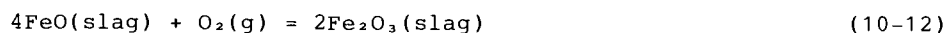


Fig. 10.27. A sectional view of forehearth of copper-smelting blast furnace. The oxygen sensor is dipped in liquid matte for 2 hours. (After Kozuka, 1979 (46)(47)).

Fig.10.27 is the sectional view of the forehearth of the blast furnace of copper smelting. The oxygen sensor is dipped in liquid matte of $\text{Cu}_2\text{S}-\text{FeS}$ at $1100-1200^\circ\text{C}$.

Fig.10.28 shows change of temperature of liquid matte (top picture) and of its oxygen pressure (middle).

Kozuka⁽⁴⁶⁾⁽⁴⁷⁾ has noted that the oxygen pressure would be determined by the activity ratio of FeO and Fe_2O_3 in the slag. Namely, the oxygen pressure measured in the matte is equal to the equilibrium oxygen pressure of the reaction in the slag of



The standard Gibbs free energy change of the reaction can be expressed by

$$\Delta G^\circ = -RT \ln \frac{a_{\text{Fe}_2\text{O}_3}^2}{P_{\text{O}_2} a_{\text{FeO}}^4} \quad (10-13)$$

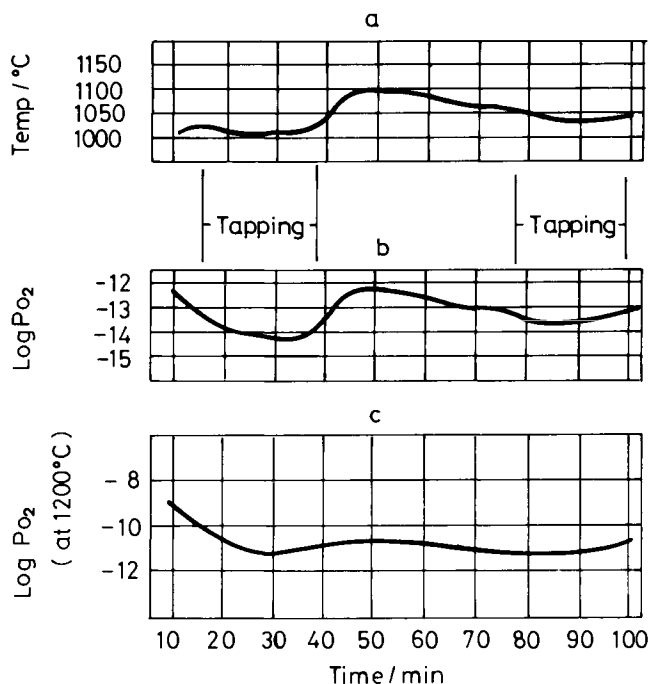


Fig. 10.28. Changes of temperature (top) and oxygen pressure (middle) of the liquid matte. The bottom picture shows the oxygen pressure, when the matte is assumed at 1200°C . (After Kozuka, 1979 (46)(47)).

where $a_{\text{Fe}_2\text{O}_3}$ and a_{FeO} are the activities of Fe_2O_3 and FeO in the slag, respectively.

Because the values of ΔG° are known, and the oxygen pressure can be obtained from the electromotive force, the activity ratio can be estimated. The ratio was nearly constant at 1000 to 1200°C. Therefore, the oxygen pressure shown in the top figure for changing temperature can be converted to that at a single temperature of 1200°C, as given by the bottom figure. This procedure to draw the bottom picture is reasonable as long as the matte is in a thermodynamic equilibrium with the slag.

Fig.10.29 is the sectional view of the self-fluxing furnace for smelting of copper. The long oxygen sensor is dipped in the liquid matte in the settler (46)(47). In the figure, the distance between the lower end of the sensor and the furnace bottom is expressed by "L", which is again used in the following figure, Fig.10.30. In this figure, the changes of the electromotive forces of the oxygen sensor and of the thermocouple are shown during 12 minutes of dipping in the matte. The temperature is between 1160°C and 1230°C and the oxygen pressure is between 8×10^{-10} atm and 7×10^{-9} atm.

In general, pyrometallurgy is an industrial process to refine a metal from its ores by selective oxidation and reduction. Therefore, the exact control of both temperature and oxygen pressure is very important. The oxygen sensor is widely used for this reason.

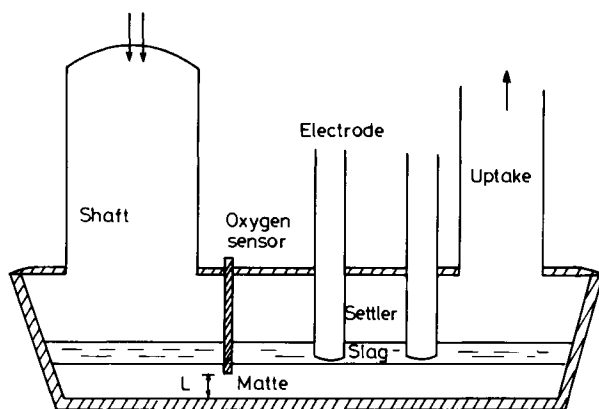


Fig. 10.29. A sectional view of the self-fluxing furnace for smelting of copper. The oxygen sensor is dipped in liquid matte in the settler. (After Kozuka, 1979 (46)(47)).

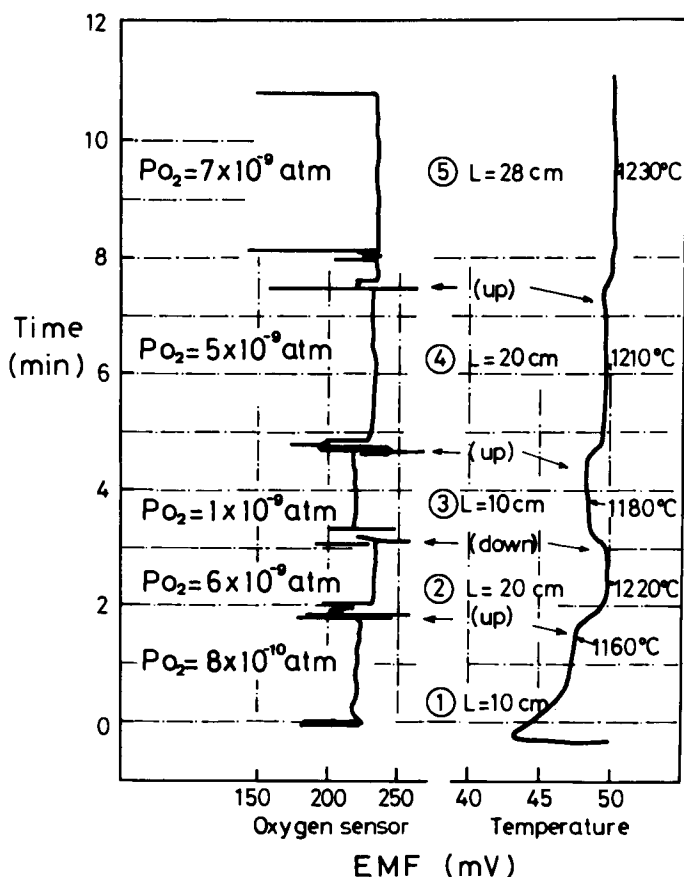
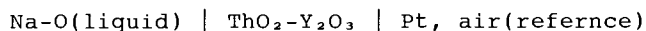


Fig. 10.30. The electromotive forces of the oxygen sensor and thermo-couple in millivolts, both dipped in liquid matte. "L" means the distance between the furnace bottom and the top of the oxygen sensor. (After Kozuka, 1979 (46)(47)).

At the end of this section, one more example of the oxygen sensor will be given for its use for atomic reactors. For the safe operation of the atomic reactors, it is very important to check continuously the oxygen content in liquid sodium used as the coolant. Three papers in 1965 and 1968 have been already documented in Ref.13). Two papers in 1975 by Berkey and Read,⁽⁴⁸⁾ and by Roy⁽⁴⁹⁾ reported the wide use of the following sensor in the world for the fast bleeder reactors;



(10-14)

$$E(\text{volts}) = K_1 - K_2 \log(\text{ppm } \underline{O}) \quad (10-15)$$

According to Roy,⁽⁴⁹⁾ K_1 and K_2 are constant at a given temperature and are 1.828 and 0.075, respectively, at 483°C. Yttria is used as the stabilizer to have a good conductivity at its service temperature of 350°C to 500°C. Because of the partial positive hole conduction at the oxygen pressure of higher than 10^{-6} atm, the electromotive force measured must be calculated according to Eq. (10-5). When the thoria-yttria solid electrolyte was highly purified and then isostatically pressed, followed by complete homogenizing by sintering, its corrosion resistance against liquid sodium increased very much and the life time became 5,000 hrs under the continuous service.⁽⁴⁹⁾ The lower limit of the oxygen analysis was reported 0.1 ppm $\underline{O}$ in liquid sodium.⁽⁴⁹⁾

Concluding Remarks

Since a very celebrated paper by Kiukkola and Wagner in 1957, several hundreds of papers have been published throughout the world, all using zirconia-or thoria-base solid electrolytes. The reasons of this wide use of the special solid oxides are simply because of their excellent oxygen ion conductivity and their thermodynamic stability with high melting points. The former reason gives the very small internal resistance of the galvanic cells, which is very necessary to have a stable and reproducible electromotive force. The latter reason is as well important to exclude any solid state reactions between the electrolyte and the electrode materials even at high temperatures. This means that the wide variation of combinations of electrode materials is possible to make very different types of galvanic cells with miscellaneous objectives.

However, the industrial applications have many difficulties which are quite different from the case of the applications to basic studies:

First, the electrolytes must be made by mass-production with constant and good qualities in chemical, physical and mechanical properties.

Secondly, the oxygen sensors are sometimes used continuously in the gas or liquid metals containing many harmful elements. Thus, to have a long life, special ways should be developed for each case to prevent the deterioration of the electrode and electrolyte.

Thirdly, in the industrial applications, untrained employees use

the sensor in rough ways. Thus, the oxygen sensors must be mechanically and thermally very strong.

The above difficulties have been eventually solved with the help of the art of peoples with different origins and technical traditions, because the principle of the oxygen sensor is simple and universal.

REFERENCES TO CHAPTER 10

- 1 F. Haber, *Z. Anorg. Chem.*, 57 (1908), 154.
- 2 W.D. Treadwell, *Z. Elektrochem.*, 22 (1916), 411.
- 3 E. Baur, A. Peterson and G. Fülleman, *Z. Elektrochem.*, 22 (1916), 409.
- 4 O.A. Esin, *Izv. Akad. Nauk SSSR, Metally. O.T.N.* (1948), 561.
- 5 K. Sanbongi, M. Ohtani and Y. Omori, Report of No.19th Committee of Japan Society for the Promotion of Science, No.19-4674, (1957), July.
- 6 T. Onaka, *Tetsu-to-Hagane*, 30 (1944), 62.
- 7 T. Onaka, Report of No.19th Committee of Japan Society for the Promotion of Science, No.19-2023, (1949), September and (1950), January.
- 8 M. Ohtani and K. Sanbongi, *Tetsu-to-Hagane*, 49 (1963), 22.
- 9 C. Wagner, *Z. Phys. Chem.*, B21 (1933), 25.
- 10 C. Wagner, "Advances in Electrochemistry and Electrochemical Engineering", IV, Interscience Publishers, (1966), 1.
- 11 K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, 104 (1957), 379.
- 12 R.A. Rapp and D.A. Shores, "Physicochemical Measurements in metals Research" II, Interscience Publishers, (1970), 123.
- 13 K.S. Goto and W. Pluschkell, "Physics of Electrolytes", II, Academic Press, (1972), 539.
- 14 W.R. Roth, General Electric Inc., Technical Information Series, Report No.74 CRDO 54, (1975), March.
- 15 A. Imai and M. Harata, *J. Appl. Phys.*, 11 (1972), 184.
- 16 K.S. Goto, Symposium on Solid Electrolytes, The Japan Institute of Metals, Tokyo, (1974), January 28.
- 17 M. Takeuchi, Private Communication, Manager of Nippon Kagaku Togyo Co., Ltd., (1975), May.
- 18 J. Weissbart and R. Ruka, *Scientific Instruments*, 593 (1961), 32.
- 19 K.S. Goto, Ph. D. Thesis, (1962), Ohio State University, his Adviser was Professor St. Pierre.
- 20 Y. Matsushita, K.S. Goto, A. Cho, K. Igarashi, M. Tate and H. Sasao, *Tetsu-to-Hagane*, 52 (1966), 393.
- 21 W.A. Fischer and D. Janke, *Arch. Eisenhüttenw.*, 39 (1968), 89.
- 22 Y. Endo, Private Communication, Mitaka Instrument Co., Ltd., (1975), May 10.
- 23 H. Yoshikoshi, Private Communication, Nippon Kokan K.K., (1975), June 20.
- 24 R. Kano, Private Communication, Electrotechnical Laboratory, The Ministry of International Trade and Industry, (1975), June 20.
- 25 T.H. Etsell and S.N. Flengas, *Met. Trans.*, 3 (1972), 27.
- 26 M. Iwase, S. Fujimura and T. Mori, *J. Japan Inst. Metals*, 39 (1975), 952.
- 27 H. Sunayama, K. Tsuda, K. Hori and K.S. Goto, *Tetsu-to-Hagane*, 61 (1975), S52.
- 28 M. Nakazawa, A. Asada, and H. Osanai, "Denshi Tokyo" No.23 (1984), pp. 155-156, a Journal published by Tokyo Section of Institute of Electrical and Electronics Engineers, Inc.
- 29 T. Yamaguchi, K. Mochida, H. Osanai, T. Nakamoto, K. Ishibashi, M. Nakazawa, Y. Isono, and A. Asada, "Fujikura Densen Giho" 68 (1984), 37-43.
- 30 W.J. Fleming, D.S. Howarth and D.S. Eddy, 2nd Automotive Engrs. Automobile Eng. Meeting, Paper 730575, (1973), May 14-18.
- 31 H. Düker and H. Neidhard, 2nd Automotive Emission Conf. Ann Arbor (1973).
- 32 H. Düker, K-H. Friese and W-D. Häcker, Automotive Engrs. Automobile Eng. Meeting, Paper 750223, (1975), February 24-28.
- 33 R.E. Hetrick, W.A. Fate and W.C. Vassell, SAE paper 810433(1981).

- 34 G. Valasco, J. Ph. Schnell, and M. Croset, *Sensors and Actuators*, 2 (1982), 371.
- 35 K. Saji, H. Takahashi, H. Kondo, T. Takeuchi, and I. Igarashi, *Proc. 4th Sensor Symposium*, (1984), 147.
- 36 N. Kobayashi, T. Akatsuka, J. Nakano, and K. Motosugi, *Jidosha Gijutsu* 38 (1984), 1130-33.
- 37 I. Igarashi and T. Takeuchi, "Lean A/F ratio sensor", *Kagaku Sensor News* 1 (1985), No.2, pp. 40-44.
- 38 W. Pluschkell and H-J. Engell, *Z. Metallk.*, 56 (1965), 450.
- 39 D. Janke and W.A. Fischer, *Arch. Eisenhüttenw.*, 44 (1973), 15.
- 40 W.A. Fischer and D. Janke, *Metallwissenschaft und Technik*, 26 (1972), 1123.
- 41 H. Kametani and C. Yamauchi, *Trans. Japan Institute of Metals*, 13 (1972), 13.
- 42 C. Yamauchi and H. Kametani, *Trans. Japan Institute of Metals*, 13 (1973), 261.
- 43 J.M. Dompas and P.C. Lockyer, *Met. Trans.*, 3B (1972), 2597.
- 44 J.M. Dompas and J.van Melle, *J. Inst. Metals*, London, 98 (1970), 304.
- 45 J.M. Dompas and L. Hens, *BNFMRA Conference*, Liege, Paper No.4, (1971), October.
- 46 Z. Kozuka, *Proceedings of Intern. Conf. on Advances in Chemical Metallurgy*, January 6-9 (1979), Bombay, and *Proceedings of Australia/Japan Extractive Metallurgy Symposium*, July 16-18, (1980).
- 47 Z. Kozuka, *Nihon Kogyokai-shi*, Paper No.(99-1143), (1983), pp. 337-345, "Applications of Solid Electrolyte Sensors on the Non-ferrous Metallurgy".
- 48 E. Berkey and W.H. Read, *Proc. of Int. Symp. on Metal-Gas-Slag Reactions and Processes*, Toronto, (1975), 921.
- 49 P. Roy, *Proc. of Int. Symp. on Metal-Gas-Slag Reactions and Processes*, Toronto, (1975), 919.

Chapter 11

SOLID-OXIDE OXYGEN SENSORS FOR THE STEELMAKING INDUSTRY

11.1 STRUCTURE OF COMMERCIAL OXYGEN SENSORS

In the steelmaking industry, the oxygen content in various steel products is precisely controlled by an oxygen sensor. One sensor design that has been used extensively is based on solid oxides. The principle of the measurement of oxygen content in molten steel was fully discussed in section 6.3. Equations (6-33), (6-34), and (6-35) are theoretical relations to explain the principle of the measurement. Figure 6.13 is a schematic diagram that shows the method of the measurement in laboratory scale, while Fig. 6.14 shows the relation, obtained in the laboratory, between the electromotive force and the oxygen content in molten steel at 1600°C.

This chapter discusses the actual use of the oxygen sensor in steelmaking processes. First, the structure of commercial oxygen sensors and their performance are briefly presented. Then, several examples of the improvement in steelmaking processes following the introduction of oxygen sensors are given. Finally, the use of the sensors in liquid slags is discussed, accompanied by the experimental results of the present author and his coworkers at steelmaking shops.

The development of reliable commercial oxygen sensors follows the invention⁽¹⁾ of chemically stable solid electrolytes by Kiukkola and Wagner in 1957. However, in 1949, Onaka⁽²⁾ had already tried to measure the oxygen content in molten steel by the electromotive force method, which was referred to in Chapter 10. In 1963, a similar work was reported by Ohtani and Sanbongi,⁽³⁾ who used a solid electrolyte of magnesia. In 1966, Matsushita and Goto⁽⁴⁾ proved experimentally the relation between electromotive force and the oxygen content in steel, using the new solid electrolyte invented by Kiukkola and Wagner⁽¹⁾.

After these laboratory experiments, metallurgists of two Japanese steel works conducted extensive large-scale experiments to create commercial oxygen sensors of the consumable type. The two steel works are Kawasaki Works of Nippon Kokan KK and Hirohata Works of Nippon Steel Corporation. Their sensors were designed to

be dipped in molten steels during the refining processes. The details of their development at Kawasaki were reported by Ihida and Kawai⁽⁵⁾ in 1972; the work at Hirohata was reported by Kumai et al.⁽⁶⁾ in 1973, by Hiromoto et al.⁽⁷⁾ in 1974, and by Hiromoto et al. in 1977⁽⁸⁾. Around 1975, several worldwide instrument companies began to supply the oxygen sensors of the consumable type.

According to the author's investigation, more than 31,000 consumable oxygen sensors were used during 1977 by steel companies in Japan. The consumption increased to more than 185,000 sensors in 1980, and to more than 323,000 by 1982. The rate of increase was about 60,000 pieces per year between 1977 and 1982 in Japan.

Fig. 11.1 is a schematic cross section of the oxygen sensor for molten steels. This type of sensor is vertically dipped in molten steel for 10 to 20 seconds only once and cannot be used repeatedly.

The steel cap is used to avoid contamination by the slag, and the cap is easily dissolved away when the sensor is dipped into molten steel. A small tube with a closed end is made of ZrO_2 , which is stabilized by MgO or CaO . The reference electrode is made of a metal wire embedded in a mixture of Cr and Cr_2O_3 . The electrode for molten steel is made of a thick Mo rod, which is slow to

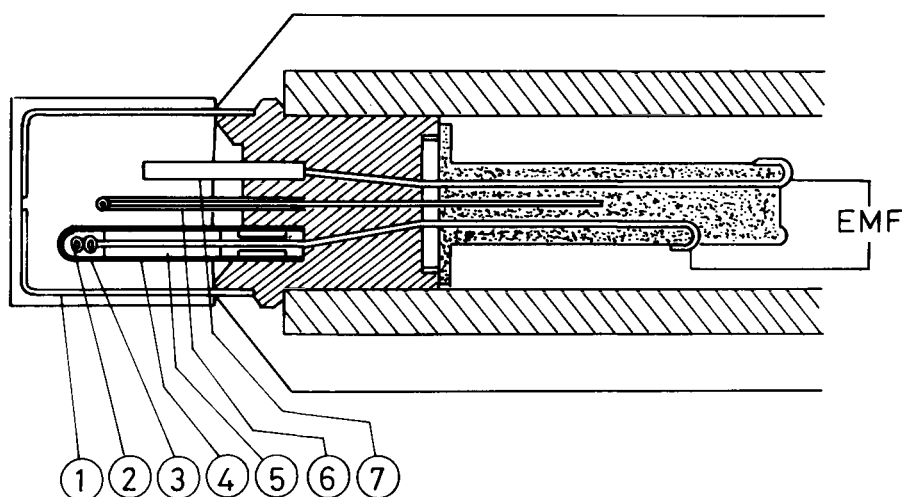


Fig. 11.1. Cross section of commercial consumable oxygen sensor to be dipped vertically into molten steel. Numbered parts are (1) thin steel cap, (2) reference electrode of Cr/Cr_2O_3 mixture, (3) metal electrode, (4) solid electrolyte of ZrO_2-MgO , (5) inert refractory packing, (6) thermocouple with thin protection tube of SiO_2 , and (7) thick Mo rod electrode for molten steel.

dissolve in molten steel. The temperature is measured by a small thermocouple made of Pt and Pt-Rh wires.

Fig. 11.2 shows another type of oxygen sensor, called "needle sensor." The principal structure was invented by Janke and Schwerdtfeger⁽⁹⁾ in 1978, and the commercial sensor was developed by Yamari-Electronite Co. Ltd. in 1984.

The needle sensor shown in Fig. 11.2 is made by the plasma spray technique. A thin layer of a mixture of Cr and Cr_2O_3 is sprayed onto the surface of a Mo needle, and then a layer of ZrO_2 -MgO is applied by the same technique.

The advantage of the needle sensor is its rapid response time because of faster heat conduction through the thin layers. The production cost is much less than that of the conventional type shown in Fig. 11.1.

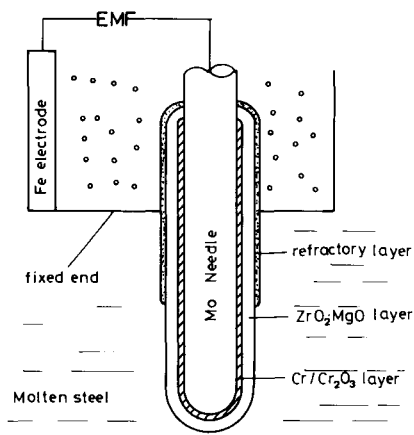


Fig. 11.2. Cross section of commercial "Needle Sensor." Thin layers of reference electrode of $\text{Cr}/\text{Cr}_2\text{O}_3$ and of solid electrolyte of ZrO_2 -MgO are made by plasma spray method (courtesy of Yamari Electronite Co. Ltd.)

Fig. 11.3 shows the response curves of the two types of oxygen sensors. Both oxygen sensors were simultaneously dipped into molten steel at 1600°C . It can be seen that the electromotive force of the needle sensor is stabilized faster than that of the conventional type.

The electromotive force of the sensor usually shows a peak at the initial stage of dipping, which is caused by the temperature difference between the inside and the outside of the solid electro-

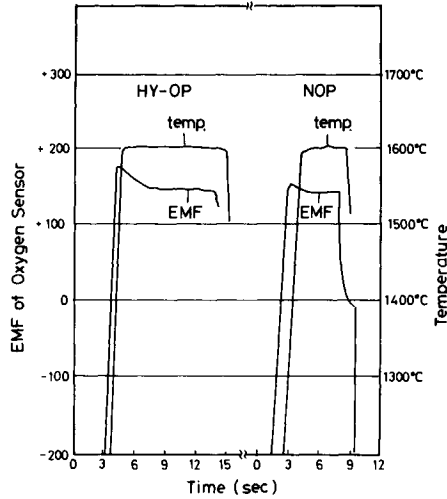


Fig. 11.3. Response curves of oxygen sensors shown in Figs. 11.1 and 11.2. The response (right curves) seems more rapid for needle type because of its rapid heat conduction and smaller heat capacity. (Courtesy of Yamari Electronite Company Limited).

lyte. In 1977, Suzuki and Ejima⁽¹⁰⁾ reported Fig. 11.4 on the electromotive forces of thermocouples that were dipped in molten steel. The hot junction of one thermocouple was inserted into the reference side and another thermocouple was inserted into the molten-steel side. The tests were done three times. From the results of Fig. 11.4, Suzuki and Ejima⁽¹⁰⁾ calculated the electromotive force of the oxygen sensor when its temperature was not isothermal. The calculated electromotive force showed the initial peaks as usually observed.

Fig. 11.5 shows the relation between the oxygen contents estimated from the carbon content and from the EMF of the oxygen sensor reported by Kawawa, Imai, and Tokunaga⁽¹¹⁾ in 1976. The agreement between the two oxygen contents shows that this commercial sensor can be used for the quick oxygen analysis of molten steels. However, the commercial sensors do not always give an electromotive force that is equal to the theoretical value. Thus, their performance should be studied before they are used for process control of steel refinings. The disagreement between values was discussed earlier in more detail by the present author⁽¹²⁾.

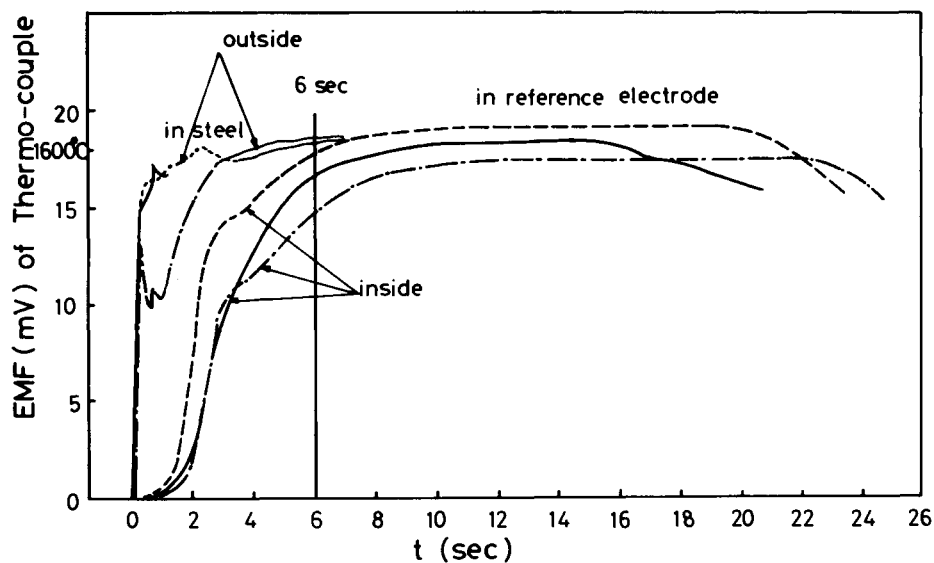


Fig. 11.4. Electromotive forces of thermocouples dipped in molten steel and placed in the mixture of $\text{Cr}/\text{Cr}_2\text{O}_3$ (reference mixture) covered by the electrolyte tube. (After Suzuki and Ejima, 1977(10)).

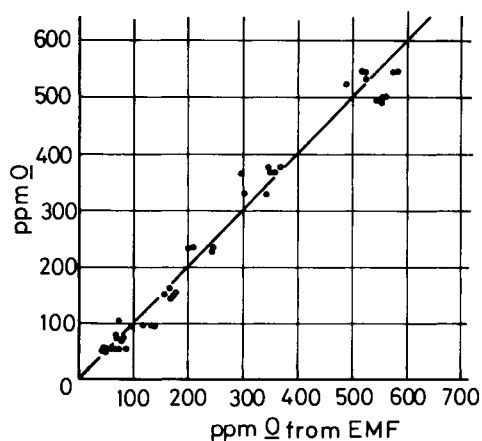


Fig. 11.5. Comparison between the oxygen contents estimated from the carbon content and from the electromotive forces of the oxygen sensors at 1600°C . (After Kawawa, Imai, and Tokunaga, 1976(11)).

11.2 CHANGE OF OXYGEN CONTENT IN STEEL DURING ITS REFINING

Before the oxygen sensor can be regularly used to automatically control the processes of steelmaking, the change in oxygen content of steel during the processes must be clarified. For this purpose, the oxygen sensor is dipped into molten steel manually, as shown by Fig. 11.6. In this refining process, molten steel is sucked up to the upper container (marked by RH) from the ladle through one of two legs and continuously returned to the ladle through the other leg.

Since the upper container is a vacuum, harmful gaseous elements are removed from the molten steel there.

When the oxygen sensor must be dipped into molten steel in the converter, the converter is tilted down and the sensor can be dipped in manually.

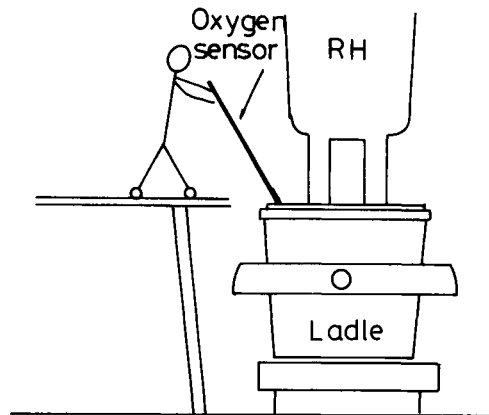


Fig. 11.6. Method of dipping of oxygen sensor into molten steel during RH treatment.

In 1977, Hiromoto et al.⁽⁸⁾ measured the dissolved oxygen with oxygen sensors after refining in the converter, which can contain 100 tons of steel. Fig. 11.7 shows their results on the relation between the oxygen content and carbon content in molten steels for three temperature ranges. The lowest curve is the equilibrium relation. This figure also suggests that the oxygen is supersaturated, and the relation must thus be expressed by the experimental equation. After systematic measurements of oxygen content as a function of temperature and of the carbon and manganese contents,

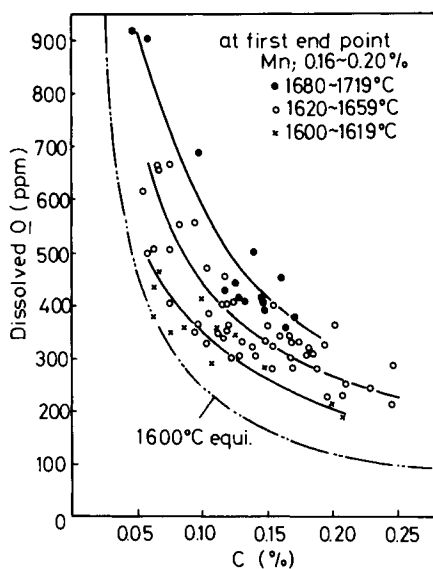


Fig. 11.7. Relation between the carbon content and the dissolved oxygen content from EMF in the converter just before tapping, (by Hiromoto et al. 1977, (8)).

they established an equation to estimate the oxygen content expressed in ppm:

$$[\text{ppm } \underline{O}] = \frac{10.99}{[\%C]} - 880 [\%Mn] + 1.63 T (^{\circ}\text{C}) - 2236 \quad (11-1)$$

where $[\%C]$ and $[\%Mn]$ are weight percentages of carbon and manganese, and T is temperature.

The equation can be used to estimate the oxygen content from only the carbon content and temperature, because the manganese content is usually constant. This means that the expensive oxygen sensor is not necessary for every heat of refining, once the relation is established for a certain refining condition.

While the molten steel is tapped from the converter, the steel is deoxidized in the lower ladle by the addition of Al, Fe-Si, and Fe-Mn. After this process, the molten steel is treated by argon injection from the bottom of the ladle. In 1977, Kawawa, Imai, and Tokunaga⁽¹³⁾ used sensors to measure the change in oxygen content during argon bubbling of deoxidized steels for continuous casting.

Figure 11.8 shows how oxygen decreases with argon bubbling

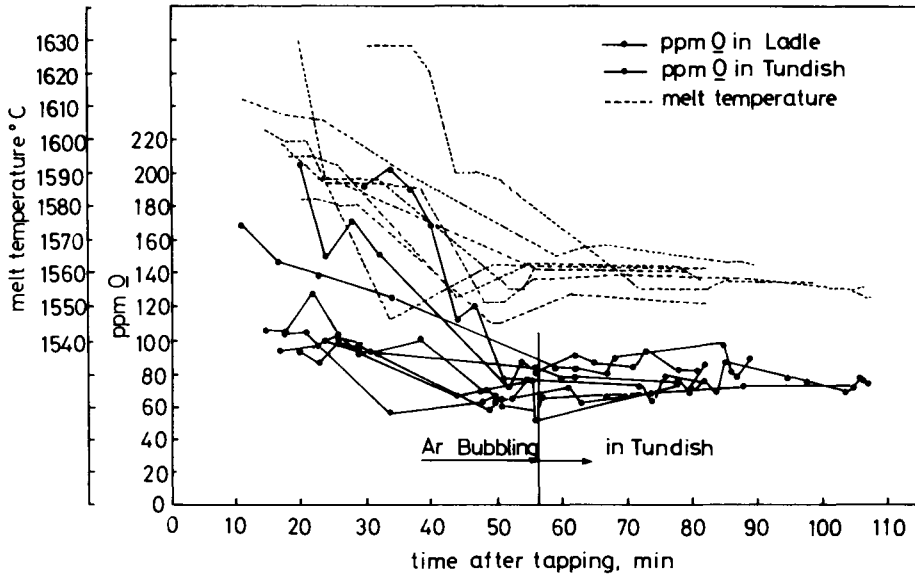


Fig. 11.8. Change of temperature and oxygen content during argon bubbling of semi-killed steel and in tundish for continuous casting. (After Kawawa, Imai, and Tokunaga, 1977(13)).

(black circles). The open circles show the oxygen content in steels contained in the tundish of the continuous casting machine. From this figure, it is clear that the oxygen content is effectively decreased by argon bubbling.

Furthermore, they⁽¹³⁾ reported that the steel is not uniform in its temperature and composition except during the argon bubbling, as also reported by Pluschkell⁽¹⁴⁾.

As mentioned earlier (Fig. 11.6), the steel is sometimes subjected to a vacuum treatment. The change of oxygen content during this treatment was studied by Suzuki et al.⁽¹⁵⁾ in 1975. Figure 11.9 gives the results of their measurement⁽¹⁵⁾ by oxygen sensors. In this figure, open circles represent the content of oxygen dissolved as monoatoms determined by the oxygen sensor. The black circles represent total oxygen, including both the dissolved oxygen and the oxygen of the oxide inclusions suspended in the molten steel. The total oxygen content can be measured by the conventional vacuum fusion analysis.

This figure shows that the total oxygen content and the dissolved oxygen content decrease in parallel with the vacuum treatment.

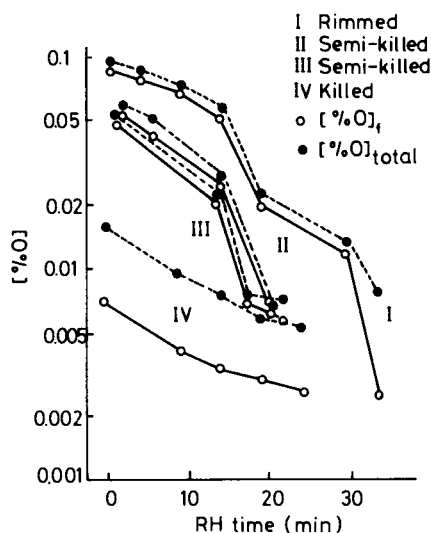


Fig. 11.9. Decrease of free and total oxygen contents during RH treatment. (After Suzuki et al., 1975 (15)).

Another very important problem in steel refining is the relation between the oxygen content just before casting and the aluminum content in the solidified ingots. In 1977, I-ida et al.⁽¹⁶⁾ studied this problem, and Fig. 11.10 reveals their results. The electromotive force expressed on the horizontal axis is proportional to the logarithm of the oxygen content. By this relation, the aluminum content can be precisely controlled by the oxygen sensor.

The above are the examples to show how the oxygen sensor has been used to clarify the change of the oxygen content in steels during refining processes. After these basic studies, the oxygen sensors have been regularly used "On-line" during steelmaking processes with the distinct economic merits. For this purpose, the sensor must be less expensive, with good reproducibility in the shape of the EMF curves. Also, an effective system must be developed to convert the EMF signals to the actions to be taken for a certain process of steelmaking. These problems will be discussed in the following section.

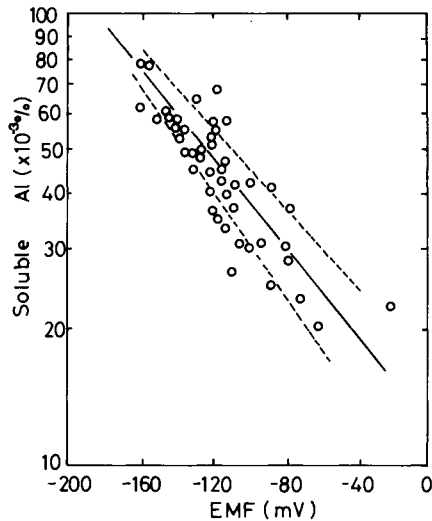


Fig. 11.10. Relation between the EMF before casting and the content of soluble aluminum in the solidified ingots. (After I-ida et al., 1977 (16)).

11.3 ON-LINE USE OF OXYGEN SENSORS

"On-line" use can be defined as the cyclic and regular use of the oxygen sensors with distinct economic merits to steelmaking operations.

The first successful use of on-line sensors with good economic merit in Japan was made in 1974 by Metallurgists⁽⁷⁾ at the Hirohata Works of Nippon Steel Corporation.

Fig. 11.11 is a schematic diagram of a computing system to control the aluminum content in the final products of steelmaking. The system was combined with the shooting machine of aluminum shots and with the secondary microcontrol system of aluminum.

Fig. 11.12 is a cross-sectional view of the steelmaking converter, with the main lance for oxygen supply and with the sub lance for the automatic dipping of the oxygen sensor. This method of dipping was developed in 1977 by Ariga and Ogawa⁽¹⁷⁾. The sensor is automatically lowered down to dip into molten steel.

Fig. 11.13 shows how the magnitude of scattering of aluminum content decreased by the introduction of the system shown in Fig. 11.11, which was reported by Hiromoto et al.⁽⁸⁾ in 1977. The upper

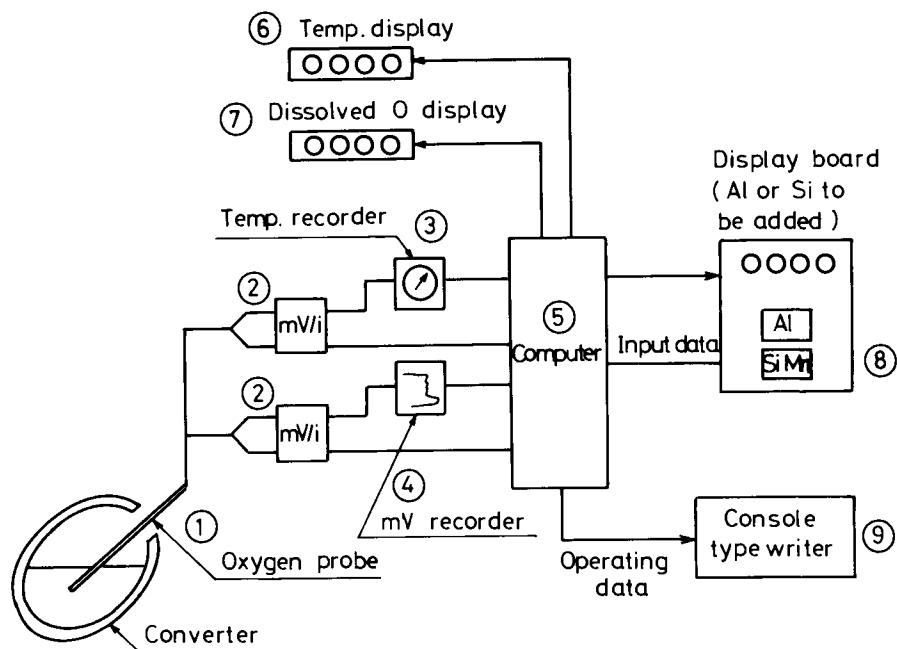


Fig. 11.11. Computing system to control the content of soluble aluminum in Al-Si killed steel and the magnitude of the deoxidation of Si-semi-killed steel. (After Hiromoto et al., 1977 (8)).

part of the figure shows the scattering of the aluminum content expressed by wt%/1000 before the on-line use of oxygen sensors, and the lower part shows conditions after the on-line use. By comparing the two parts, it can be clearly seen that the use of the oxygen sensors is very effective in improving the quality of steel products with an optimal content of aluminum.

Another clear example of the economic merit is the decrease of scrap off of steels during rolling. In case of steels semi-killed by silicon, the surface flaws often appear at the end parts of steel slabs, deoxidation during rolling; if so, the head part of the "H" shape slabs must be cut off. Thus, Hiromoto et al.⁽⁸⁾ in 1977 dipped oxygen sensors into the steel contained in the mold and, according to the value of the electromotive force, shots of aluminum were added to the ingot during solidification.

Fig. 11.14 shows how much of the slab head must be cut off as a function of the dissolved oxygen content before and after the on-line use of the oxygen sensors, combined with the addition of

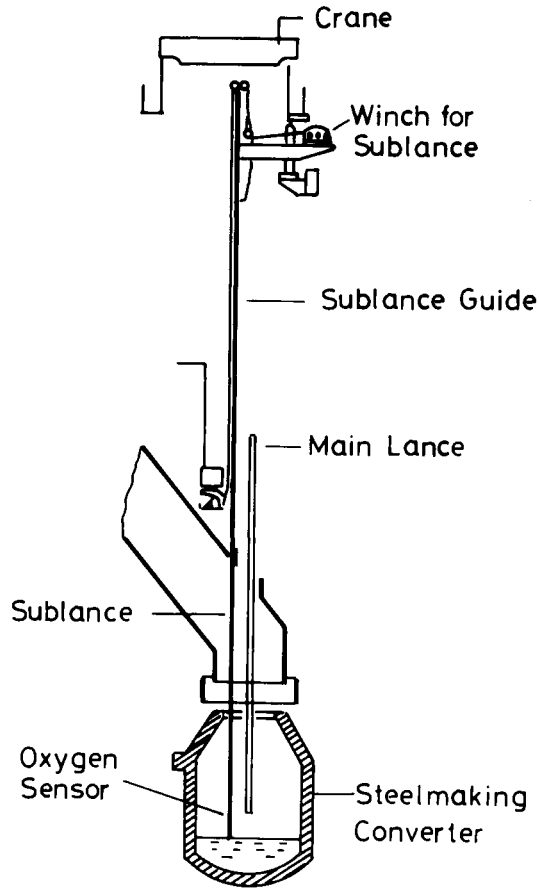


Fig. 11.12. View of sublance system to dip oxygen sensors automatically to steel in converter. (After Ariga and Ogawa, 1977 (17)).

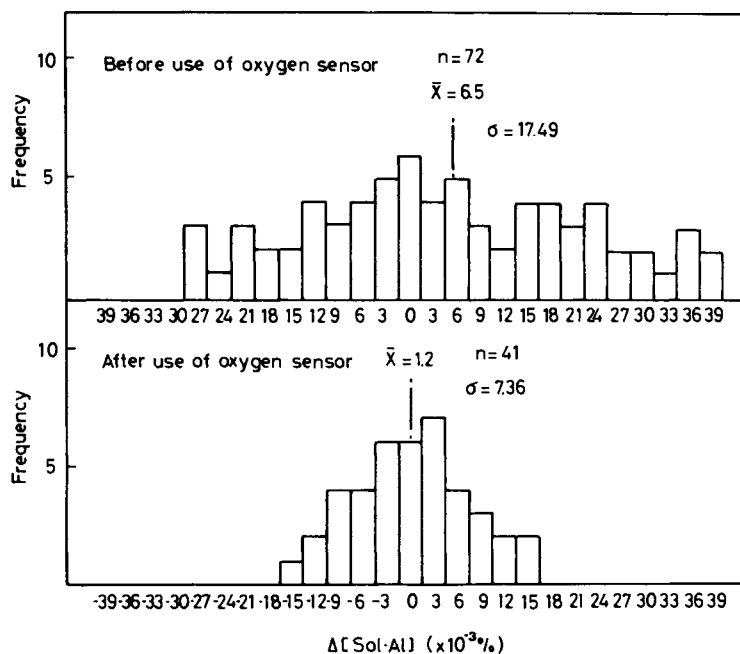


Fig. 11.13. Improvement in deviation from target value of the content of soluble aluminum in Al-killed steels before and after the use of oxygen sensors. (After Hiromoto et al., 1977 (8)).

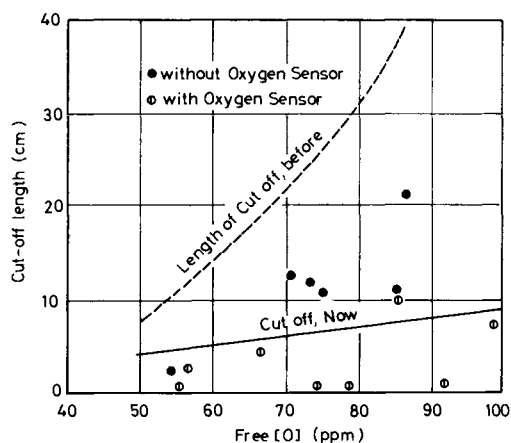


Fig. 11.14. Relation between the free oxygen content and the length of cut-off due to surface flaws before and after the use of oxygen sensor. (After Hiromoto et al., 1977 (8)).

aluminum shots. The decrease of the cut-off length means an increased yield of steel, and, thus, it is directly related to the production cost.

The more automatic use of the sensors is their on-line use with the sub lance of the steelmaking converter as shown by Fig. 11.12. As described above, the sensors are automatically attached to the end of the sub lance and then slide down in parallel to the main lance in the upright state of the converter. Because the converter is not tilted down, this way of using the sensor yielded in a longer life of the refractory of the furnace.

The oxygen content in steels can be precisely measured just before tapping. Thus, the quantity of deoxidizer can be computed for optimal deoxidation during tapping. Fig. 11.15, which was reported by Ariga and Ogawa⁽¹⁷⁾ in 1977, shows how the process has been improved in three aspects: (a) the percentage of rejection of ingots due to flaws, (b) the percentage of successful operations of capping, and (c) the standard deviation of scattering of oxygen content in ppm. Here, (a), (b), and (c) correspond to the upper,

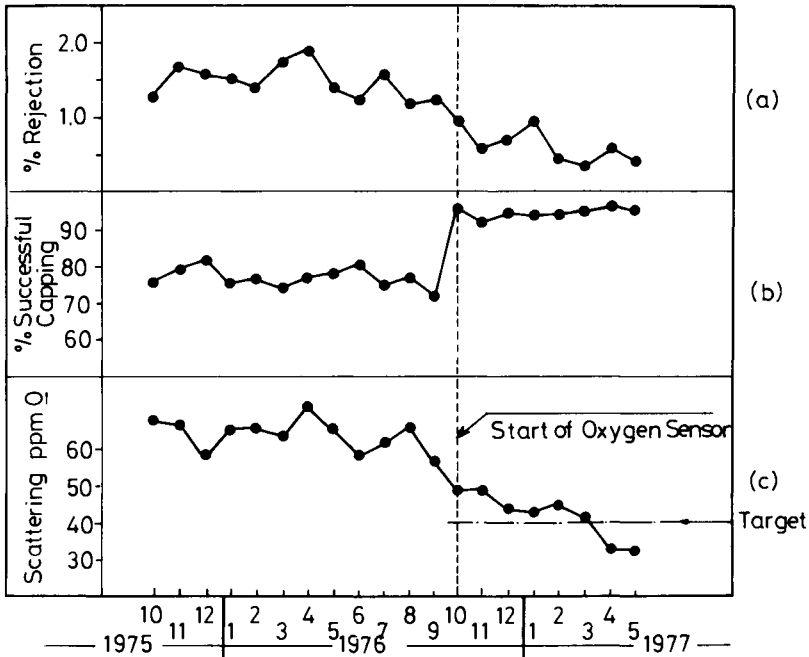


Fig. 11.15. Improvement in capping operation and scattering of oxygen contents by use of oxygen sensors. (After Ariga and Ogawa, 1977 (17)).

middle, and lower diagrams, respectively. The horizontal axis gives the months of 1975, 1976, and 1977. The figure shows that the production of steels was improved in three aspects after the use of the oxygen sensors began in October of 1976.

The above are rather simple examples of the use of oxygen sensors for process control in steelmaking, but sensors are sometimes used in more different ways, as discussed in reference (12).

11.4 OXYGEN SENSORS FOR LIQUID SLAGS

Ironmaking and steelmaking from the oxide ores are based in principle on the combination of selective reduction and selective oxidation at elevated temperature.

When one considers the thermodynamics of selective reduction and oxidation, it seems quite clear that temperature and oxygen pressure are the most important factors for the control of reactions in such furnaces as blast furnaces and steelmaking converters. Historically, many engineers have tried to measure the temperature distribution in these furnaces. However, the oxygen pressure distribution is not well known, though many believe it to be important.

By using the assumption of the local equilibrium, the oxygen pressures in the gas phase as well as in the liquid iron can be estimated to some extent from the local composition and temperature. However, the estimation is not easy for the slags in the liquid oxide phase, because the redox reaction related to the oxygen pressure is usually not clearly known.

In the following, the results of a series of measurements of local oxygen pressure in liquid slags, made by the author and his coworkers, are presented. For these measurements, oxygen sensors with solid electrolytes of $\text{ZrO}_2\text{-CaO}$ and $\text{ZrO}_2\text{-MgO}$ were extensively used.

In 1968, the author and his coworkers⁽¹⁸⁾ measured the change of oxygen pressure in liquid PbO-SiO_2 , when the oxygen pressure in the gas phase is rapidly changed. Later, the diffusion constant of oxygen was determined in PbO-SiO_2 , $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, and other oxide melts⁽¹⁹⁾.

Using this method, the oxygen pressure has been measured in synthetic slags of the $\text{FeO-Fe}_2\text{O}_3\text{-CaO-SiO}_2$ system and in actual steelmaking slags of an LD converter with a capacity of 100 tons of steel⁽²⁰⁾.

Similarly, the oxygen pressure in the Q-BOP slags (a Q-BOP converter is a special type of steelmaking converter with bottom-blowing of pure oxygen gas) has been measured at the initial, intermediate, and final stages of blowing⁽²¹⁾.

The use of oxygen sensors in slags has further expanded their application to ironmaking technology. Oxygen pressure has been measured in pig iron and in slag as they flow out from the tap holes of blast furnaces⁽²²⁾.

Also, as mentioned in Chapter 8, the oxygen pressure in the slag was measured during the dephosphorization of pig iron⁽²³⁾. The change in the activity of Na_2O was measured using beta-alumina as the solid electrolyte⁽²⁴⁾. These works were introduced in Chapter 8, and they are not discussed here.

11.4.1 Oxygen pressure in liquid oxide phase

In 1968, the author and his coworkers⁽¹⁸⁾ inserted the following two oxygen sensors into the gas phase and into the liquid PbO-SiO_2 phase at 930°C in the same reaction chamber:

Reference, Ni, NiO, Pt | $\text{ZrO}_2\text{-CaO}$ | Pt, gas phase (11-2)

Reference, Ni, NiO, Pt | $\text{ZrO}_2\text{-CaO}$ | Pt, PbO-SiO_2 melt (11-3)

where the equilibrium electromotive force, E , can be given by

$$E = \frac{RT}{4F} \ln \frac{P_{\text{O}_2} \text{ (in gas or oxide melt)}}{P_{\text{O}_2} \text{ (in reference electrode)}} \quad (11-4)$$

where R is the gas constant, T is absolute temperature, F is Faraday constant, and P_{O_2} is the oxygen pressure.

When the gas in the reaction chamber was rapidly changed from air to argon or from argon to air, the electromotive force of the sensor in the gas phase responded rapidly; within a few seconds, it stabilized at certain values corresponding to the oxygen pressure of air or argon. On the other hand, the electromotive force of a sensor dipped in the oxide melt changed rather slowly, but after 60 minutes it stabilized at the same value of the sensor in the gas phase. This experimental observation suggested that the oxygen would be dissolved into the oxide melt and it would be diffusing in or out, depending upon the oxygen pressure in the gas phase.

In 1974, Sasabe and Goto⁽¹⁹⁾ improved the structure of the cell

assembly so that the diffusion constant of oxygen could be measured. The oxygen pressure was measured exactly at the bottom of the slags column. Under this condition, the diffusion problem can be treated as a case of planar nonsteady-state diffusion, neglecting the presence of the small oxygen sensor dipped into the melt. The diffusion constant was obtained at 1300 to 1450°C in 40 % CaO-45 wt% SiO₂-15 wt% Al₂O₃, 40 CaO-40 SiO₂-20 Al₂O₃, and 25 CaO-65 SiO₂-10 Al₂O₃ melt. The measured diffusion constant was of the magnitude of 10^{-4} cm²/sec.

In 1965, Mulfinger and Scholze⁽²⁵⁾ measured the diffusion constant of helium dissolved in 16 mol% Na₂O-10 mol% CaO-74 mol% SiO₂ melt. The diffusivity of He was also of the magnitude of 10^{-4} cm²/sec.

As long as the oxide melt does not contain any transition metals as impurities, it can be assumed that oxygen is physically dissolved as diatomic molecules. This way of dissolution is the same as the case of oxygen dissolved in water at room temperature. Because the helium is dissolved physically in the oxide melt, the same order of the diffusion constant for oxygen and helium would support the assumption of diatomic molecules of oxygen in the oxide melt.

Sasabe and Goto⁽¹⁹⁾ measured the permeability of oxygen through a fixed thickness of the oxide melts using oxygen sensors, and, thus, they could estimate the physical solubility of the oxygen in CaO-SiO₂-Al₂O₃ ternary melts.

11.4.2 Oxygen pressure in actual steelmaking slag

After the above laboratory study, Kawakami, Goto, and Matsuoka⁽²⁰⁾ measured the local oxygen pressure in slag contained in an actual LD converter at a steelmaking plant.

Fig. 11.16 is a schematic diagram of the oxygen sensor used in the plant tests. The solid electrolyte was a more-corrosion-resistant ZrO₂-9 mol% MgO tube of 6 mm OD. A platinum wire was tightly wound on the outside surface of the electrolyte tube to detect the oxygen pressure in the slag. The oxygen sensor was fixed at the end of the sensor holder and manually dipped about 10 cm deep into the slag in the converter, which was tilted down to direction of the working floor.

The tests were carried out in a 100-ton LD converter at the Hirohata Works of the Nippon Steel Corporation. The measurements were made at the end of a normal blowing operation. Both tempera-

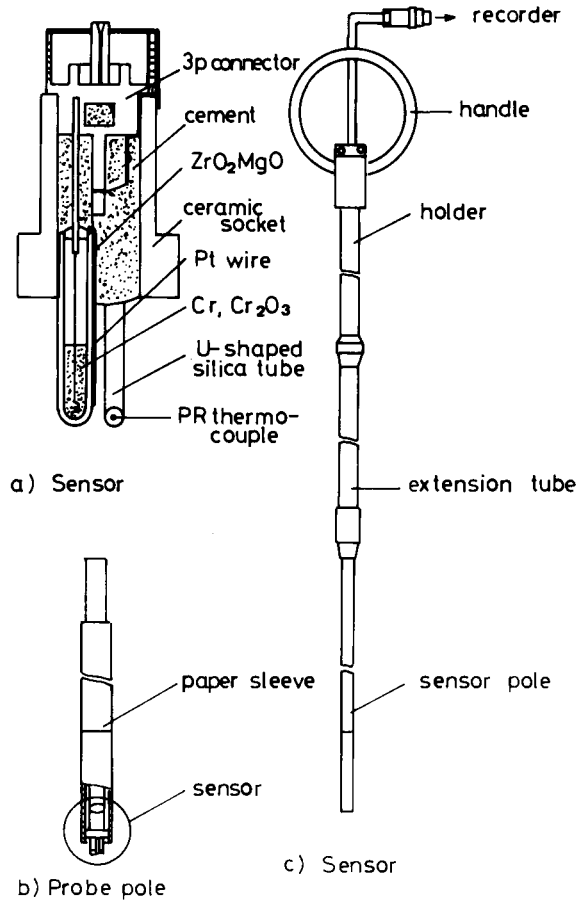


Fig. 11.16. Schematic diagram of the oxygen sensor for the slag phase in the LD converter. (a) sensor tip, (b) sensor pole, (c) sensor holder. (After Kawakami, Goto, and Matsuoka, 1980 (20)).

ture and oxygen pressure in the slag were simultaneously measured. The oxygen pressure in molten steel has also been measured by commercial oxygen sensors. Finally, spoon samples of the slag were taken for chemical analysis.

Fig. 11.17 shows three sets of response curves: one for steel, two for slag. When the sensor is dipped into the slag, the temperature of the sensor slowly increases. Assuming an uniform temperature in the sensor, one can estimate the oxygen pressure according to Eq. (11-4). The oxygen pressure so obtained is shown at the top of Fig. 11.17.

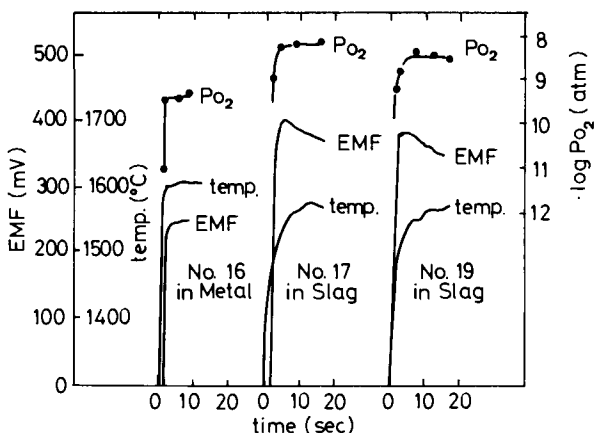


Fig. 11.17. Response curves of temperature and EMF both in the metal and the slag phases of a 100,000 kg LD converter. (After Kawakami, Goto, and Matsuoka, 1980 (20)).

From all experimental results (not only from Fig. 11.17), it has been found that the oxygen pressure in the slag at the blow-end is about 10^{-8} atm, and that in steels is about 10^{-9} atm. This finding means that the slag is more supersaturated than the steel with respect to oxygen.

Fig. 11.18 shows the relation between ratio of wt % Fe^{3+} to the total wt % Fe and the logarithm of oxygen pressure obtained by the EMF measurement at 1450°C. The black circles show the results on an $FeO-Fe_2O_3-CaO-SiO_2$ system in laboratory experiments. The open circles show the results in the laboratory, but on slags containing 10 wt % MgO . The ratio between wt % CaO and SiO_2 is always maintained at 1.0 to have a constant basicity. The six open squares were obtained in the plant tests at the blow-end. The six triangles on the horizontal axis were obtained in the slag converging the carbon-saturated iron melt at 1450°C. This experiment was carried out in an ill-defined condition, because iron oxide in the slag was reduced by carbon in molten iron. However, these six results suggested that the oxygen sensor can be also used in the slag flowing out with pig iron from the blast furnace. This suggestion was later proved by the plant tests⁽²²⁾ as described below.

In Fig. 11.18, the solid line is the best-fit line of the experimental results, and the broken line is estimated from the equilibrium data by Timucin and Morris⁽²⁶⁾, where the slag composi-

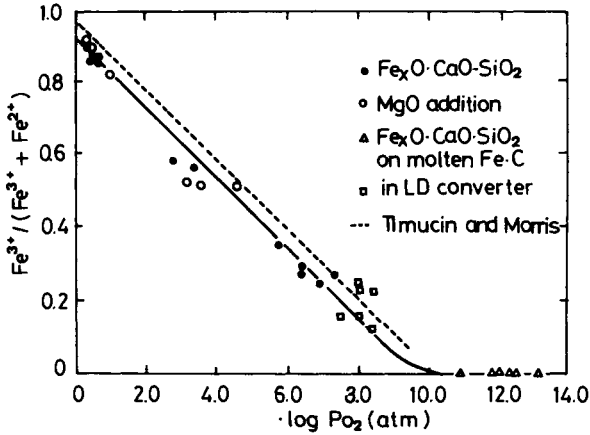
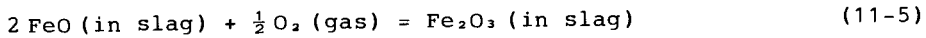


Fig. 11.18. Relation between oxygen pressure and the ratio of wt % Fe^{3+} to the sum of wt % Fe^{3+} and wt % Fe^{2+} in the slag phase. Temperature on closed and open circles and triangles were all 1723 K. Broken line after Timucin and Morris is drawn based on their data of 30 wt % SiO_2 -30 wt % CaO -40 wt % $(\text{Fe}_2\text{O}_3-\text{FeO})$ at 1723 K. Open square data were obtained roughly at 1823 K. (After Kawakami, Goto, and Matsuoka, 1980 (20)).

tion was such that silica and lime contents were both 30 wt % and the total iron oxide content was 40 %.

Because the results obtained by the oxygen sensors (shown by the solid line) reasonably agreed with the broken line, the oxygen pressure at the blow-end can be considered to be fixed by the following reaction equilibrium:



Therefore, under this situation, the oxygen pressure is determined by the activities of FeO and Fe_2O_3 at a constant temperature as follows:

$$K = \frac{a_{\text{Fe}_2\text{O}_3}}{a_{\text{FeO}}^2 P_{\text{O}_2}} \quad (11-6)$$

where K is the equilibrium constant of Eq. (11-5) and a_{FeO} and $a_{\text{Fe}_2\text{O}_3}$ are activities of FeO and Fe_2O_3 . The oxygen pressure expressed by P_{O_2} means that in the slag, which is measured by the oxygen sensors.

From the measurement, it was known that the oxygen pressure in the slag of the blow-end is an equilibrium oxygen pressure between FeO and Fe_2O_3 . However, the value of the oxygen pressure in the slag (10^{-8} atm) is one order of magnitude higher than that of steel.

In 1982, using specially designed oxygen sensors, Nagata, Nakanishi, Sudo, and Goto⁽²¹⁾ measured the oxygen pressures in liquid iron, slag, and gas in a Q-BOP converter of 230 tons capacity at Chiba Works of Kawasaki Steel Corporation.

Fig. 11.19 shows the results of the measurements. The solid line shows the oxygen pressure in the steel and the broken line shows that in the slag. The chain line shows the oxygen pressure in the gas phase. The horizontal axis represents the quantity of oxygen gas blown in from the furnace bottom expressed by normal cubic meters per ton of hot metal.

The temperature of the metal bath increases from 1400°C to 1600°C at the blow-end.

The converter was tilted down at three different times after

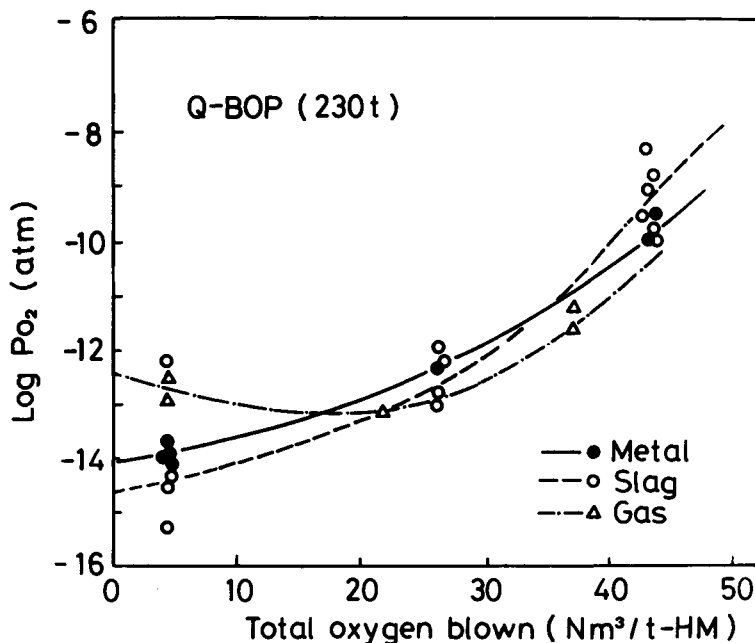


Fig. 11.19. Changes of oxygen pressures in gas, in slag, and in metal during the blowing of the 230 ton Q-BOP converter of Kawasaki Steel Corporation. (After Nagata et al., 1982 (21)).

blowing the oxygen gas: 4.0, 26, and 43 Nm³ per ton of hot metal. The oxygen sensors were manually dipped into both the slag and the metal to the optimal depths.

The oxygen pressure in the gas phase was measured by a sensor attached to the end of sublances. The sublance with the sensor was vertically slid down into the furnace with its upright state.

In Fig. 11.19, the reproducibility of the measurement seems very good for molten steel but not good for the slag. However, in general, the oxygen pressure in the steel was initially at 10^{-14} atm and about 4×10^{-13} atm at the intermediate state, and finally at 1×10^{-10} atm.

The oxygen pressure in the slag was smaller than that of steel for most of the blowing period. However, it becomes nearly 10^{-9} atm, which is larger than that in steel in the final stage.

The oxygen pressure in the gas phase was initially higher but later smaller than that in the steel.

The results of the measurement in the slag were plotted on the diagram of the relation between [%Fe³⁺/total Fe] and log P_{O₂} in the same manner as Fig. 11.18. The results were compared to the equilibrium relations for various basicities by Timucin and Morris (26). From the comparison, it was found that the oxygen pressure was fixed only at the final state by the reaction equilibrium of FeO and Fe₂O₃.

The oxygen pressure at the initial and intermediate slags are much smaller than the equilibrium oxygen pressures.

In these periods of the blowing, the slags are not homogeneous, but rather are a mixture of solid charged particles, gas bubbles, and a small quantity of liquid slag. Thus, the authors⁽²¹⁾ believed that the dipped oxygen sensor detected the oxygen pressure of gas bubbles instead of slag, because the gaseous oxygen pressure should be very small due to the high carbon content in the iron bath.

From both measurements on LD and Q-BOP converters, one can compare the local oxygen pressures in slag and steel for the two reactors.

Fig. 11.20 shows the relation between the logarithm of oxygen pressure and the carbon content in steel bath at 1600°C. A horizontal line at 10^{-8} atm shows the oxygen pressure in the slag of the LD converter. The four black triangles are those of the slag in the Q-BOP converter. Open and black circles are oxygen pressures

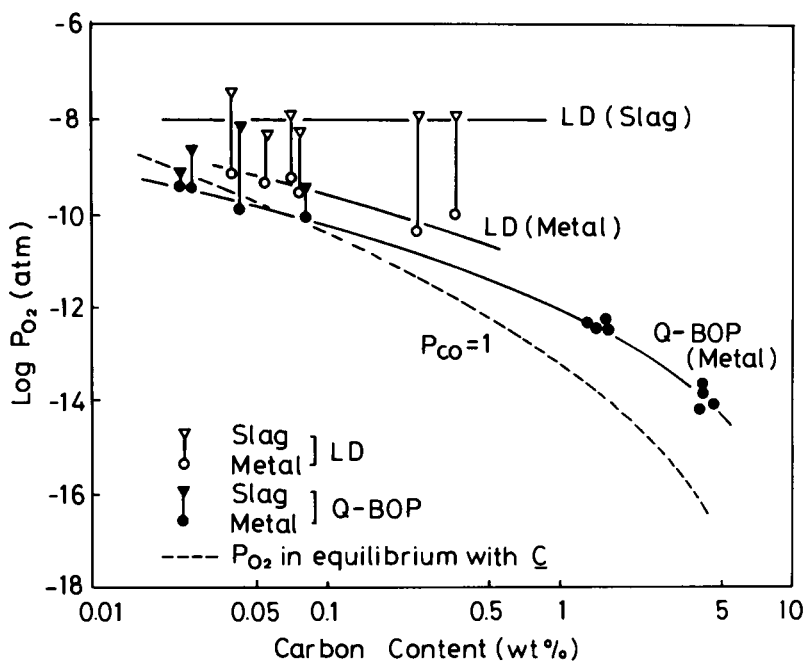


Fig. 11.20. Oxygen pressures in slags and steels at the blow-end of converter and at the initial, intermediate, and blow-end of Q-BOP converter as a function of carbon content. (After Nagata et al., 1982 (21)).

of the steel bath in LD and Q-BOP converter, respectively.

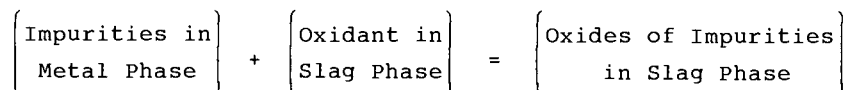
The broken curve is the equilibrium oxygen pressure with respect to dissolved carbon and one atm carbon monoxide. It is clear that oxygen is very much supersaturated in both the slag and the metal in the case of the LD converter. However, in the Q-BOP converter, the oxygen is in equilibrium, at least at the final stage of the blowing. These observations are in accordance with the differences in the mode of oxygen supply in both reactors.

In the LD converter, oxygen gas is supplied from the top side of the bath. Thus, it is quite natural that the oxygen pressure in the LD slag is very much higher than in the metal. Further, it is generally believed that the magnitude of stirring is relatively small in LD converters but very strong in Q-BOP converters.

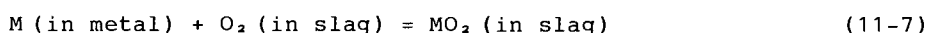
In the Q-BOP converter, oxygen gas is injected from its bottom. Thus, the oxygen pressure would be very high only in the vicinity of the injection nozzles. Therefore, the degree of the supersatura-

tion of the oxygen should be relatively small.

When the oxygen pressure in the slag is measured at the blow-end of steelmaking processes, the magnitude of nonequilibrium between slag and metal phase can be estimated. This magnitude is usually defined by the change in Gibbs free energy of the refining reaction, which can be generally expressed by



Namely,



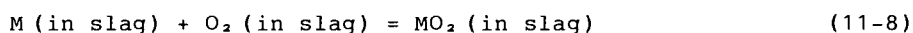
where M means an impurity metal to be removed off. The change in Gibbs free energy of this reaction can be given by

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{MO_2}}{a_M \cdot P_{O_2} (\text{in slag})} \quad (11-7')$$

where ΔG° is the standard free energy change and a_M and a_{MO_2} are the activities of the impurity metal and its oxide, respectively.

In Eq. (11-7'), the oxygen pressure, P_{O_2} , represents that in the slag, which has been measured as shown in Fig. 11.20.

If the local equilibrium prevails in the slag, the following reaction should be also in equilibrium.



For this reaction, the equilibrium constant, K is given by

$$K = \frac{a_{MO_2}}{a_M (\text{slag}) \cdot P_{O_2}} \quad (11-9)$$

Therefore,

$$a_{MO_2} = K \cdot P_{O_2} \cdot a_M (\text{slag}) \quad (11-10)$$

According to the first and second laws of thermodynamics, the following expression is valid under constant temperature and pressure.

$$\Delta G^\circ = -RT \ln K \quad (11-11)$$

Inserting Eqs. (11-10) and (11-11) to the right hand side of Eq. (11-7'), one can have

$$\Delta G = RT \ln \frac{a_M^s}{a_M^m} \quad (11-12)$$

where a_M^s means the activity of M in slag and a_M^m in the metal.

Also according to thermodynamics, the chemical potential, μ is defined by

$$\mu = \mu^\circ + RT \ln a \quad (11-13)$$

where μ° is the chemical potential of a component in its standard state.

Inserting Eq. (11-13) to the right-hand side of Eq. (11-12), ΔG can be expressed equally well by

$$\Delta G = \mu_M^{(\text{in slag})} - \mu_M^{(\text{in metal})} \quad (11-14)$$

where $\mu_M^{(\text{in slag})}$ means the chemical potential of the impurity, M in slag and $\mu_M^{(\text{in metal})}$ in metal.

From the above discussion, it is clear that the magnitude of nonequilibrium defined by Eq. (11-7') is equally well determined by the difference in the activity of the impurity in both phases and also in its chemical potential in both phases.

In actual calculation of the magnitude of nonequilibrium, Eq. (11-7') can be used, because ΔG° is usually known for various reactions, and a_M and a_{MO_2} can be estimated from the composition of steel and of slag, respectively.

In 1985, Goto, Yamaguchi and Nagata⁽²⁷⁾ made the estimation of the magnitude of nonequilibrium for five different types of steelmaking converters used in Japanese steel companies.

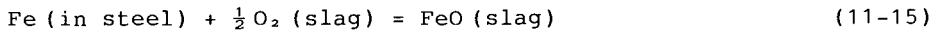
The details of the calculation are given in Ref. (27), but, in essence, the data of chemical analysis of slags and steels have been collected from major steel companies in Japan.

Because thermodynamic studies are available on molten steels and slags, the activities of the impurities for Eq. (11-7') can be estimated from the chemical composition. The temperature of a steel

bath, usually at 1600°C, was inserted in Eq. (11-7'). The oxygen pressure in the slag was assigned to be 10^{-8} or 10^{-9} atm, depending on mode of blowing, and it was inserted to Eq. (11-7').

Fig. 11.21 is an example of the results of calculation from an LD-AB converter, into which a gas mixture of argon, oxygen, and nitrogen is injected from the bottom.

The vertical axis gives the magnitude of nonequilibrium defined by Eq. (11-7') for two impurities of Mn, and P and for the following reactions:



The horizontal axis is the content of oxygen in the steel expressed by parts per million, which is usually proportional to refining time. (In other words, the horizontal axis corresponds

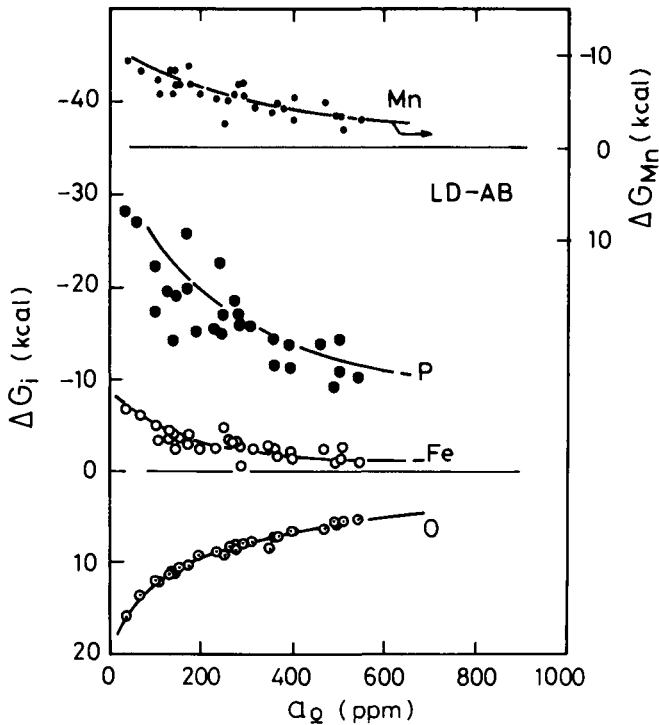


Fig. 11.21. Magnitude of non-equilibrium between slag and steel in an LD-AB converter as a function of oxygen activity at blow-end at 1600°C. (After Goto, Yamaguchi and Nagata, 1985 (27)).

to the refining time).

This figure shows that the magnitudes of nonequilibrium for four reactions between slag and steel generally decrease with refining time. Because the Gibbs free energy changes are negative, Mn, P, and Fe should be further oxidized and transferred to the slag phase. The free energy change for reaction of Eq. (11-6) is positive; thus, the reverse reaction of Eq. (11-16) should be proceeded with increasing of oxygen content in the steel.

11.4.3 Oxygen pressure in slag flowing out from blast furnaces

In blast furnace slag, iron oxide is contained in the range of 0.1 to 1.0 wt %, depending on the stability of the furnaces operation. Thus, oxygen pressure measurement in the slag might be helpful to estimate the operational condition in the blast furnace.

The oxygen sensor used for the slag had the same structure as the one used for the LD and Q-BOP converter slags. However, Pt-13 percent Rh. Pt thermocouples were fixed at both the outside and inside of a magnesia-stabilized tube. The oxygen sensor was dipped about 10 cm into the slag and into the pig iron, above and below the slag skimmer, respectively.

The measurements were made from October of 1979 until November of 1981 at No. 2, 3, and 5 Blast Furnaces of the Chiba Works of Kawasaki Steel Corporation. The measurement of pig iron started at 15 minutes after the start of tapping. At 15-minute intervals, both the temperature and oxygen pressure of the pig iron were measured. The pig iron usually flows for about three or four hours.

The flow of the slag starts after one or two hours of pig iron flow. After the stabilization of the slag flow, the oxygen sensor was dipped into the slag every 8 or 10 minutes. Every time the sensor was dipped in, samples of both pig iron and slag were taken for chemical analysis.

Fig. 11.22 shows that the temperatures of the outside and inside of the electrolyte tube become equal after 30 seconds and, thus, the electromotive force of the oxygen sensor stabilizes after 30 seconds.

Because the oxygen pressure was very low (10^{-14} atm), the measured EMF was corrected for the partial electronic conduction of the electrolyte according to

$$P_{O_2} = \left[\left(P_e^{\frac{1}{4}} + P_{O_2}^{\frac{1}{4}}, \text{ ref.} \right) \exp \left(\frac{EF}{RT} \right) - P_e^{\frac{1}{4}} \right]^4 \quad (11-17)$$

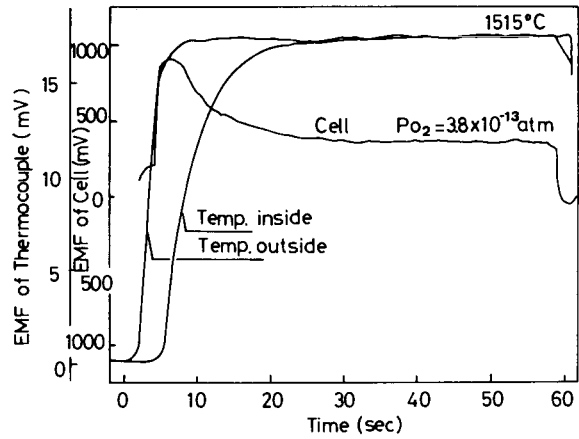


Fig. 11.22. Profiles of the electromotive forces of the oxygen sensor for slag. (After Nagata et al., 1982 (22)).

where P_e is the oxygen pressure where the ionic partial conductivity becomes equal to the electronic partial conductivity of the solid electrolyte.

Figure 11.23 shows an example of the changes of oxygen pressures and temperatures in pig iron and slag. In this example, the slag flow started about two hours after the start of tapping. The

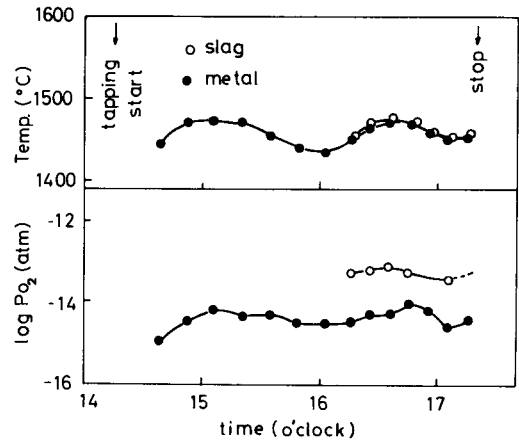


Fig. 11.23. Change of P_{O_2} and temperature in pig iron and slag during tapping. (After Nagata et al., 1982 (22)).

temperatures are usually the same for pig iron and slag, but the oxygen pressures are not. The oxygen pressure in the slag was about an order of magnitude higher than the oxygen pressure in the pig iron.

Figure 11.24 shows the summary of all the measurements in 1979, 1980, and 1981. In this figure, open circles at the top part are the oxygen pressures measured in the slag, and the black circles at the middle are the oxygen pressures in the pig iron. Small horizontal lines at the lower part represent the equilibrium oxygen pressure of the reaction of



From the results of the measurements over a long period of time, as shown in Fig. 11.24, it has been clarified that the oxygen pressure in the slag is about 10^{-13} atm and in the pig iron is about 10^{-14} atm. Further, both phases of the slag and iron are supersaturated with respect to oxygen pressure determined by the reaction equilibrium of Eq. (11-18).

Figure 11.25 shows the relation between the wt % FeO analyzed and calculated from the EMF, assuming the activity coefficient to be 0.0212. The linear relation given in this figure suggests that the oxygen pressure in the slag is determined by the local

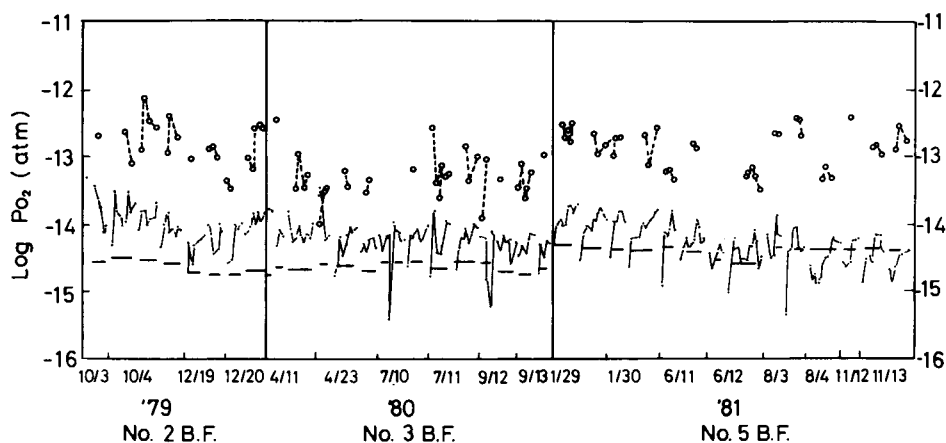


Fig. 11.24. Oxygen pressures in slag and pig iron flowing out from the blast furnaces of Kawasaki Steel Corporation. (Small horizontal lines mean the equilibrium pressures. $\circ \cdots \circ$ means P_{O_2} in slag. $\bullet$ means P_{O_2} in pig iron.) (After Nagata et al., 1982 (22)).

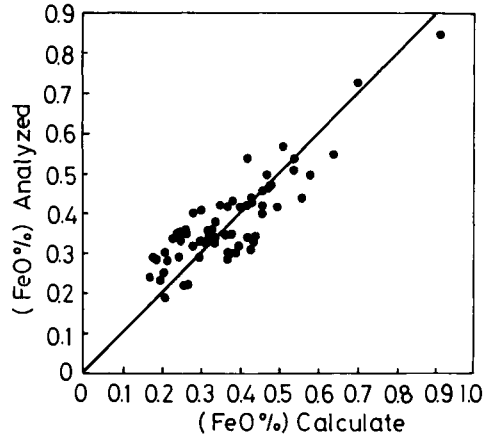
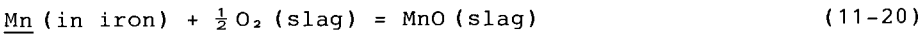
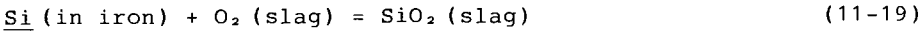


Fig. 11.25. Comparison of the measured and calculated (% FeO) in slag. (After Nagata et al., 1982 (22)).

equilibrium of FeO dissolved in the slag and iron droplets suspended in the slag.

Because the oxygen pressure has been measured in the slag, the Gibbs free energy change of Eq. (11-7') can be again calculated.

The following two reactions are studied:



The procedure of the calculation is very similar to the case of Fig. 11.21.

Fig. 11.26 shows the changes in Gibbs free energy of the reactions of Eq. (11-19) and Eq. (11-20) at its top and middle part, respectively. At the lower part, the change in Gibbs free energy is given for the desulfurization by



From this figure, it can be concluded that silicon should be further oxidized off from pig iron, and manganese is nearly at equilibrium. Because the Gibbs free energy change is positive, the sulfur would be transferred to the iron phase from the slag.

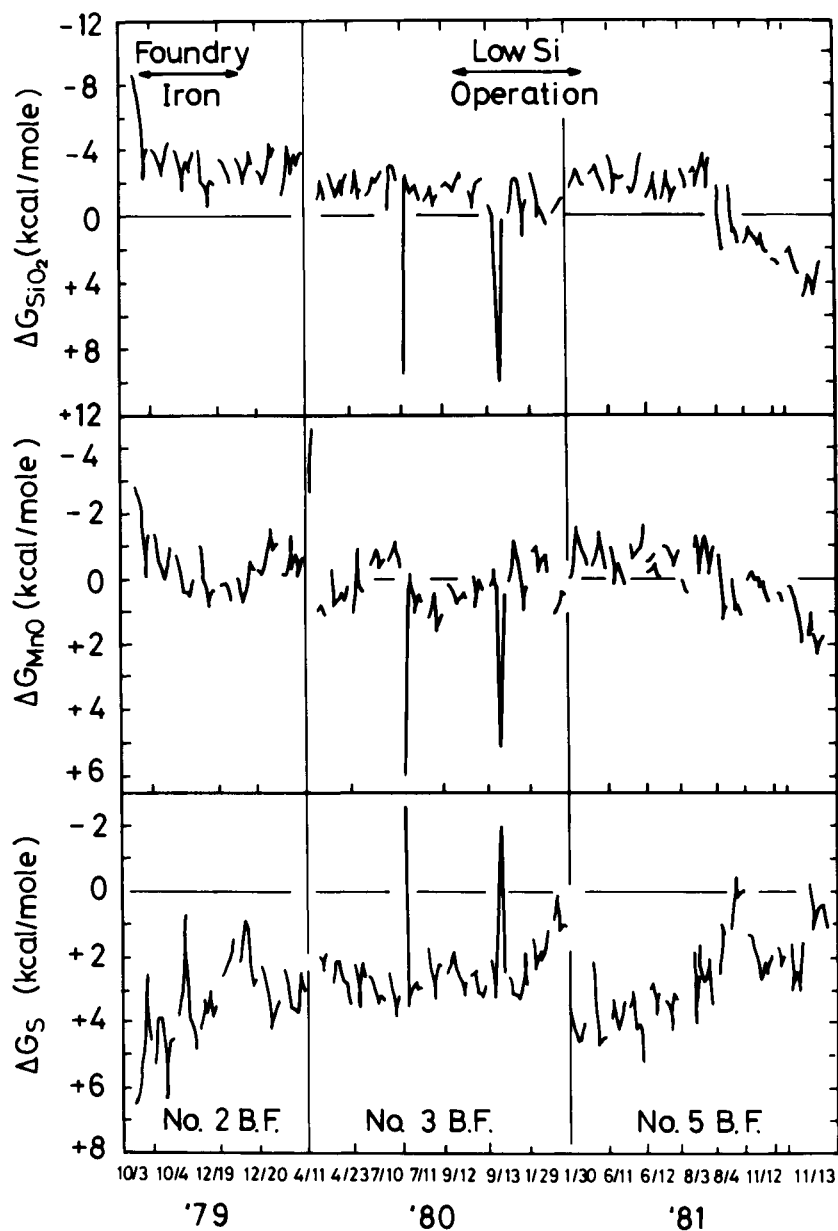


Fig. 11.26. Changes in Gibbs free energy of the transfer reactions of Si, Mn, and S between slag and pig iron calculated from P_{O_2} . (After Nagata et al., 1982 (22)).

The eventual object of the series of the experiments by the author and his coworkers is to draw a diagram of isopressure lines of oxygen on the sectional picture of various furnaces as a function of refining time. For this eventual purpose, the oxygen pressures in the slags are by no means enough. However, the local oxygen pressure of the slags has been helpful in developing a deeper understanding of the reaction mechanisms of slag/metal reactions, with the magnitude of the nonequilibrium of the reactions.

REFERENCES TO CHAPTER 11

- (1) K. Kiuukkola and C. Wagner, J. Electrochem. Soc. 104 (1957) p. 379.
- (2) T. Onaka, Report of No. 19th Committee of Japan Society for Promotion of Science, No. 19 - 2023 (1949) September and (1950) January.
- (3) M. Ohtani and K. Sanbongi, Tetsu-to-Hagane 49 (1963) p.22.
- (4) Y. Matsushita and K.S. Goto, Trans. Iron and Steel Inst. Japan 6 (1966) p.132.
- (5) M. Ihida and Y. Kawai, Trans. ISIJ 12 (1972) p. 269.
- (6) H. Kumai, Y. Arima, T. Saeki, T. Hiraoka, and K. Ishikura, Tetsu-to-Hagane 59 (1973) s 438.
- (7) T. Hiromoto, T. Saeki, S. Nisugi, Y. Arima, T. Hiraoka, K. Tama, and G. Igaki, Report of 19th Committee of JSPS (1974) February.
- (8) T. Hiromoto, T. Saeki, Y. Igaki, T. Nisugi, and K. Ishikura, Tetsu-to-Hagane 63 (1977) p. 2326.
- (9) D. Janke and K. Schwerdtfeger, Stahl und Eisen, 98 (1978) p. 825.
- (10) K. Suzuki and A. Ejima, Report No. 18 of 2nd National Meeting on Oxygen Probes for Steelmaking, July 11, 1977, Tokyo.
- (11) T. Kawawa, R. Imai and T. Tokunaga, Report No. 9 of 1st National Meeting on Oxygen Probes for Steelmaking, December 6, 1976, Tokyo.
- (12) K.S. Goto, Steelmaking Proceedings, Vol. 61 (1978) pp. 492 - 507, published by Iron and Steel Soc. of AIME.
- (13) T. Kawawa, R. Imai, and T. Tokunaga, Report No. 16 of 2nd National Meeting on Oxygen Probes for Steelmaking, July 11, 1977, Tokyo.
- (14) W. Pluschkell, Stahl und Eisen, 96 (1976) Nr. 14, p. 657.
- (15) K. Suzuki, M. Kato, A. Ejima and H. Nakamura, Kawasaki Steel Technical Report 7 (1975), 137 and K. Suzuki, A. Ejima, M. Kato, and K. Sanbongi, Trans. of Iron and Steel Institute of Japan 17 (1977), p. 477.
- (16) Y. I-ida, K. Enomoto, A. Nanba, K. Kuroda, and H. Hino, Tetsu-to-Hagane, 63 (1977), s 538.
- (17) S. Ariga and H. Ogawa, Report No. 17 of 2nd National Meeting of Oxygen Probes for Steelmaking, July 11, 1977, Tokyo.
- (18) K.S. Goto, M. Sasabe, and M. Someno, Trans. Metallurgical Soc. AIME, 242 (1968), pp. 1757 - 1759.
- (19) M. Sasabe and K.S. Goto, "Permeability, Diffusivity, Solubility of Oxygen Gas In Liquid Slag." Metallurgical Trans., 5 (1974), pp. 2225 - 2233.
- (20) M. Kawakami, K.S. Goto, and M. Matsuoka, Metallurgical Trans. B. 11 B (1980), pp. 463 - 469.
- (21) K. Nagata, K. Nakanishi, F. Sudo, and K.S. Goto, Tetsu-to-Hagane, 68 (1982), pp. 227 - 283.
- (22) K. Nagata, N. Tsuchiya, M. Sumito, and K.S. Goto, "Oxygen Potentials in Liquid Pig Iron and Slag and Analysis of Reactions in Blast Furnace by Means of Affinities of the Reactions," Tetsu-to-Hagane, 68 (1982), pp. 2271 - 2278.
- (23) K. Nagata and K.S. Goto, Tetsu-to-Hagane, 67 (1981), s 189 and 68 (1982), s 17 (both are oral presentations).
- (24) K.S. Goto, "A Review of the Electrolytic Properties of Metallurgical Slags", contained in Proceedings of Second International Symposium on Metallurgical Slags and Fluxes, edited by Fine and Gaskell (1984) pp. 839 - 862, Published by Metallurgical Soc. of AIME.

- (25) H.O. Mulfinger and H. Scholze, *Glastech. Ber.*, 35 (1962), pp. 466 - 478 and pp. 495 - 500.
- (26) M. Timucin and A.E. Morris, *Metallurgical Trans., AIME*, 1 (1970), p. 3193.
- (27) K.S. Goto, S. Yamaguchi and K. Nagata, *Tetsu-to-Hagane*, 71 (1985) pp. 958 - 964.

Chapter 12

VARIOUS CHEMICAL SENSORS WITH SOLID OXIDES

12.1 CLASSIFICATION OF SENSORS

Sensors were defined at the beginning of Chapter 10 and shown schematically in Fig.10.1. A sensor can be considered to be a small device composing electronic systems. Its function is to convert a property change in materials to electronic signals.

This electronic device has been used in a variety of industries; for factory automation, for electronic equipment, and for smooth motion of robots. The sensor is also widely used in cars, video tape recorders, televisions, electronic ovens, air conditioners, fire alarms, etc. Nowadays, it is rather difficult to find electric equipments in which sensors are not used.

Therefore, it is very difficult to make a strictly scientific classification of these hundreds of sensors. However, the present author has addressed himself to this problem to put sensors in perspective. First of all, the sensors can be classified to two categories; physical sensors and chemical sensors. Table 12.1 and Table 12.2 show the sub-classifications of physical and chemical sensors, respectively.

A chemical sensor is defined as the sensor in which chemical reactions are involved to transduce the electronic signals. Here the chemical reaction means the electrochemical reaction, chemical adsorption, and all kinds of chemical reactions. In contrast to this, a physical sensor can be defined as a transducer in which no chemical reaction is involved. Thus, all phenomena taking place in the sensor are strictly physical in nature.

In Table 12.2, the sensors for gaseous species, for humidity, and for ionic species in aqueous solutions are presented with elemental materials for the sensors. Little space is devoted to biochemical sensors because they are out of the scope of the present book.

The oxygen sensor with the solid electrolyte has been fully discussed in Chapters 6, 8, 10, and 11, because it is presently the most successful sensor in the chemical sensors. The sensor with solid electrolytes for other gaseous species has been discussed in Chapter 7.

The success of a sensor is determined by its reliable performance

TABLE 12.1
Classification of physical sensors.

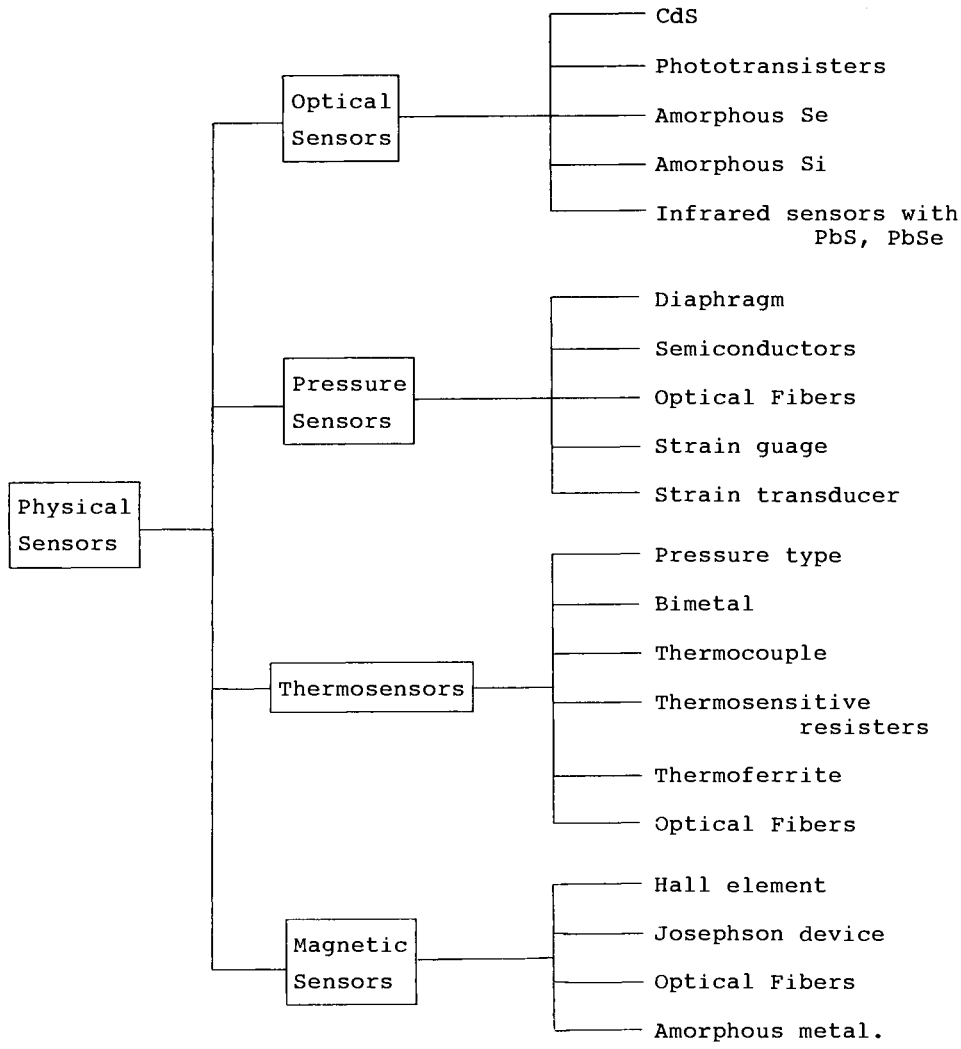
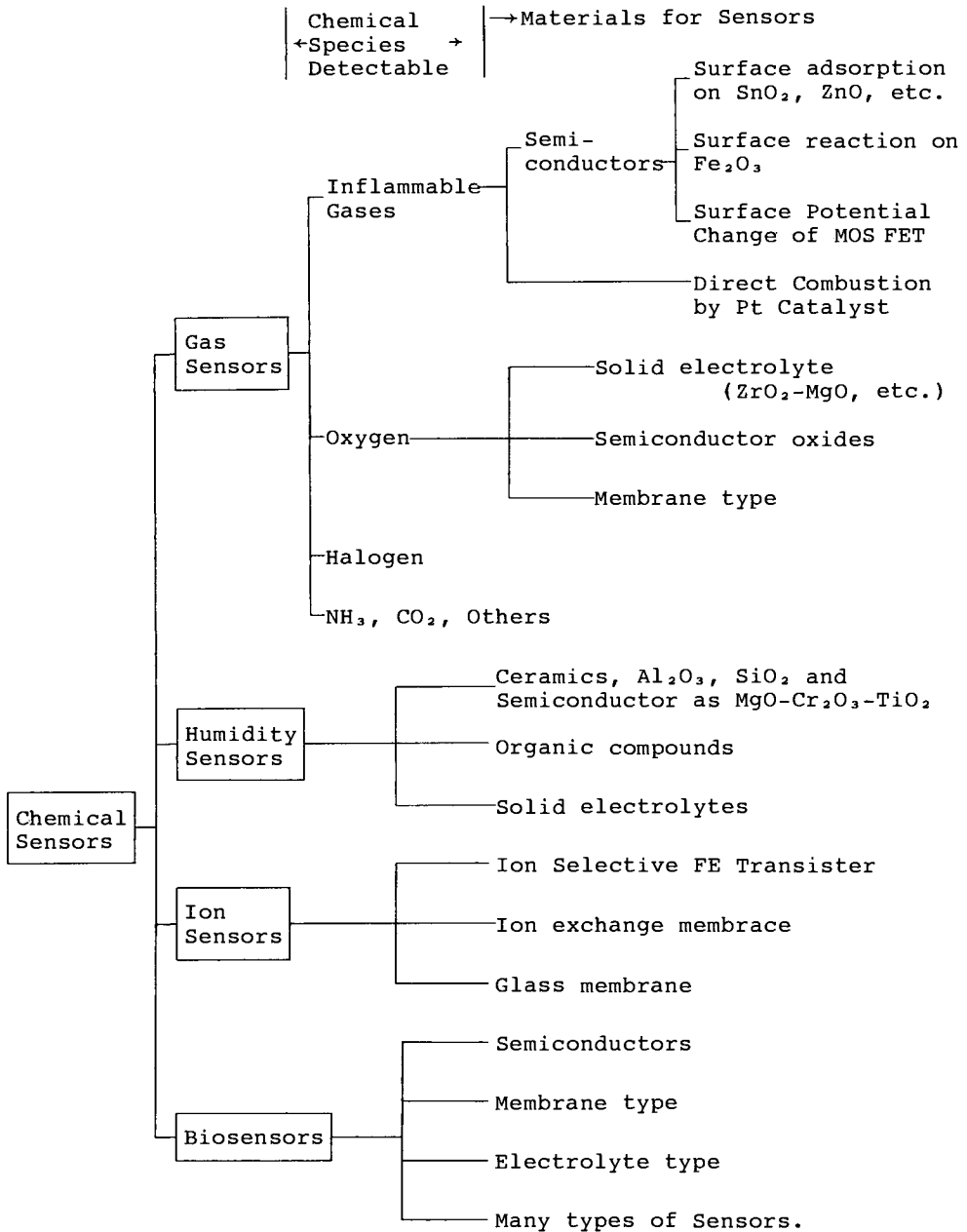


TABLE 12.2

Classification of chemical sensors.



in a variety of industry. Thus, in this chapter, only three kinds of chemical sensors are discussed, because these sensors are good examples of application of solid state electrochemistry to electronic devices.

First, the gas sensors with semiconducting oxides are discussed, because the sensors are related to the nonstoichiometry of oxides presented in Chapter 2.

Second, the humidity sensor with oxides either of ionic conduction or semiconduction is discussed. Transducing occurs by change in electric resistance of oxides induced by chemical adsorption of water molecules.

Finally, the gas sensor with a metal-oxide-semiconductor transistor is discussed. The electronic performance of this transistor is changed by chemical adsorption of gases on the gate electrode metal. This change is used as the principle of sensing of gases.

The principle of all three kinds of sensors is based upon the change of the electronic property of the oxides induced by chemical adsorption of gaseous species.

12.2 GAS SENSORS WITH SEMICONDUCTOR OXIDES

In 1962, Seiyama, Kato, Fujiishi and Nagatani⁽¹⁾ reported a new gas sensor for gaseous species. As discussed in Chapter 2, the oxides of transition metals show semiconduction, and the electrical conductivity is fixed by oxygen pressure. However, the sensor devised by Seiyama et al. is based on the idea that the surface and the grain boundary resistance of oxides is controlled by adsorption of gaseous species, not only by the reaction with oxygen. Further, it is surprising that the chemical adsorption is very selective for different gaseous species, depending upon the surface condition and temperature of the oxides.

Figure 12.1 is the experimental arrangement reproduced from their paper⁽¹⁾. The thin film of zinc oxide was used as the sensor element. The current, depending upon the resistance of the film, was converted to voltage by a variable resistance, R_S , which is recorded on the chart without amplification. The input voltage of the recorder is adjustable by use of the variable resistance, R_S .

The film of zinc oxide (20 to 1000 Å thick) was prepared by vacuum evaporation of zinc onto the glass, followed by air oxidation

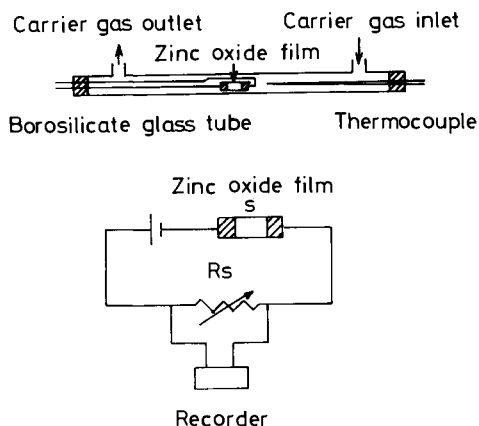


Fig. 12.1. Experimental arrangement. (After Seiyama et al., 1962(1)).

at 450°C for 10 hours. Both ends of the film were platinized to connect to the lead wires.

This sensor element was set in a borosilicate glass tube, as shown by the upper picture of Fig.12.1. The sensor is operated about at 400°C. When a small amount of CO₂, benzene, ethyl alcohol, etc. was added to nitrogen carrier gas, the conductivity of the film increased.

Zinc oxide is an n-type semiconductor, and these gases can thus be considered as electron donors. On the other hand, the adsorption of oxygen decreased the conductivity, which can be expected from the relation between the conductivity and the oxygen pressure of n-type oxides.

The lower diagram of Fig.12.2 shows the change of the output of the sensor with time in comparison with the output of the conventional gas chromatography with the thermal conductivity cell. A small amount of commercial propane was added to the carrier gas of nitrogen. The peaks apparently correspond to different gaseous species, because the rate of adsorption and desorption is different for different gases.

When the calibration curve is obtained in advance, the content of the gases can be obtained from the area of the peaks. This sensor can detect toluene, benzene, ethyl ether, ethyl alcohol,

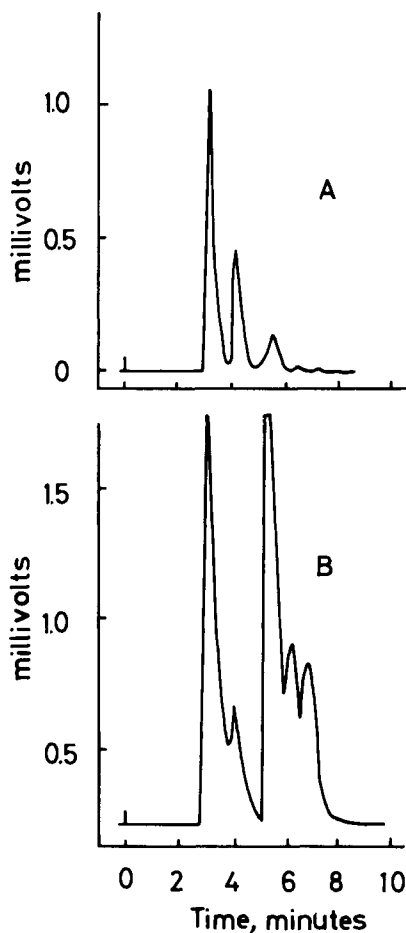


Fig. 12.2. Results of commercial propane gas using thermal conductivity cell (A) and zinc oxide film (B). (After Seiyama et al., 1962⁽¹⁾)

propane, and carbon dioxide down to a content of 1 to 50 ppm.

This short report by Seiyama et al.⁽¹⁾ in 1962 gave rise to a variety of gas sensors, that were based upon the change in electronic properties of oxides--not only of semiconduction, but even of ionic conduction.

To control the rate of adsorption of the gases, noble metals such as platinum and palladium were added to the oxides in 1967 by Loh⁽²⁾ and by Shaver⁽³⁾. From these two works, the response time and the sensitivity were very much improved, promising wide

commercial uses for the sensor.

In 1983, Professor Seiyama organized an international meeting on chemical sensors, and its proceedings were published by Elsevier Publishing Company⁽⁴⁾. In this proceedings, 50 reports were included for the session on the semiconductor gas sensor.

Several good examples are given below to show the new developments of this gas sensor since its invention by Seiyama in 1962.

Various types of gas sensors have been studied, but they can be classified to three types: thin film, thick film, and sintered piece. Most commercial sensors are of the sintered piece type.

Oyabu and his coworkers⁽⁵⁾ constructed various types of the gas sensors using SnO_2 with n-type semiconduction. Figure 12.3 shows the cross section of their thin-film gas sensor. This sensor can selectively detect carbon monoxide and ethanol gases. The sensor element shown by Fig. 12.3 was fabricated by vapor deposition and by techniques used in the semiconductor industry. The sensor element is composed of sensitive SnO_2 film, a polished ferrite substrate, and RuO_2 thick film as a heater. The palladium-doped thin film of SnO_2 , 0.3 to 0.35 microns thick, was grown with 10^{-5} Torr onto an SiO coating of the ferrite substrate. The source was a mixture of the powders of SnO_2 and of Pd (0.2 wt% of the mixture).

Gold electrodes were printed, and a silicate dielectric coating was made on the RuO_2 film. The film of SnO_2 was oxidized at 550°C for 30 to 60 min to increase the sensitivity. This sensor is designed to detect ethanol or carbon monoxide.

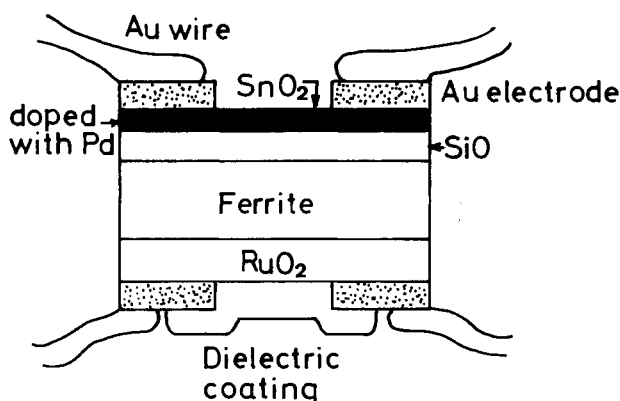


Fig. 12.3. Cross section of the thin film sensor. (After Oyabu et al., 1983 (5)).

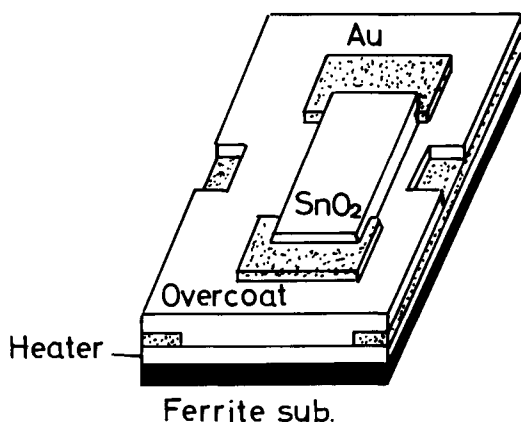


Fig. 12.4. Schematic diagram of thick film sensor.(After Oyabu et al., 1983 (5)).

Fig. 12.4 shows the structure of the gas sensor with a thick film of SnO_2 . The sensor chip consists of the screen-printed layers, which are (from the top) the gas-sensing layer, aurum electrodes, overcoat, aurum electrodes for the heater, and the heater on the ferrite substrate.

The performance of the sensor of Fig. 12.3 is shown in the following two figures. Fig. 12.5 shows the relation between the resistance ratio and content of isobutane, CO , H_2 , and ethanol in air measured at 350°C . In this figure, R_{50} is the resistance of the SnO_2 film at 50 ppm content of the gases concerned.

Figure 12.5 indicates that this sensor can detect only ethanol, when it is heated at 350°C . However, when the same sensor is operated at 250°C , it can detect carbon monoxide, as shown in Fig. 12.6. When the air contains both ethanol and carbon monoxide, it is difficult to detect them separately.

Figure 12.7 shows the relation between the resistance ratio and content of gases up to 3000 ppm in air at 250°C , and it indicates that this sensor is sensitive for hydrogen gas.

These types of thin- or thick-film semiconductor oxides are now commercially available in Japan and in other countries. Oyabu et al.⁽⁵⁾ have developed, by using the above sensors, a gas sensing system to avoid the explosion of inflammable gas in apartment houses. This system can detect leaking gas selectively, and it can display the species of leaking gases with the content in air with

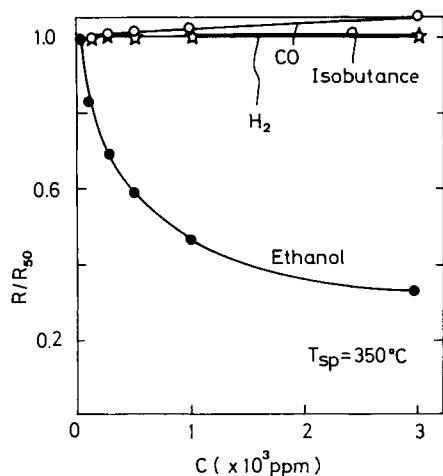


Fig. 12.5. Sensitivity characteristics for carbon monoxide, isobutane, hydrogen and ethanol gases. Specimen temperature is held at 350°C. (After Oyabu et al., 1983 (5)).

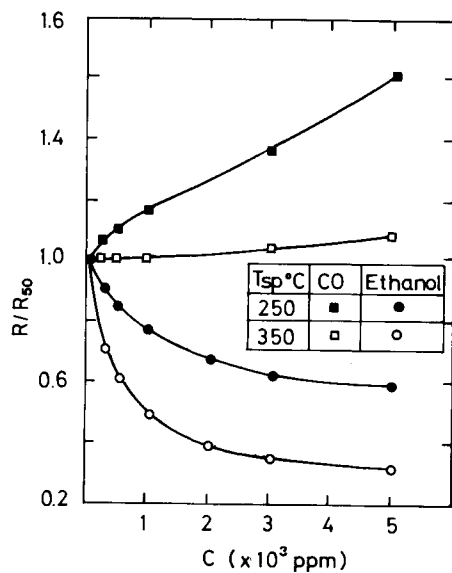


Fig. 12.6. Sensitivity characteristics for carbon monoxide and ethanol gases at specimen temperature of 250°C and 350°C. (After Oyabu et al., 1983 (5)).

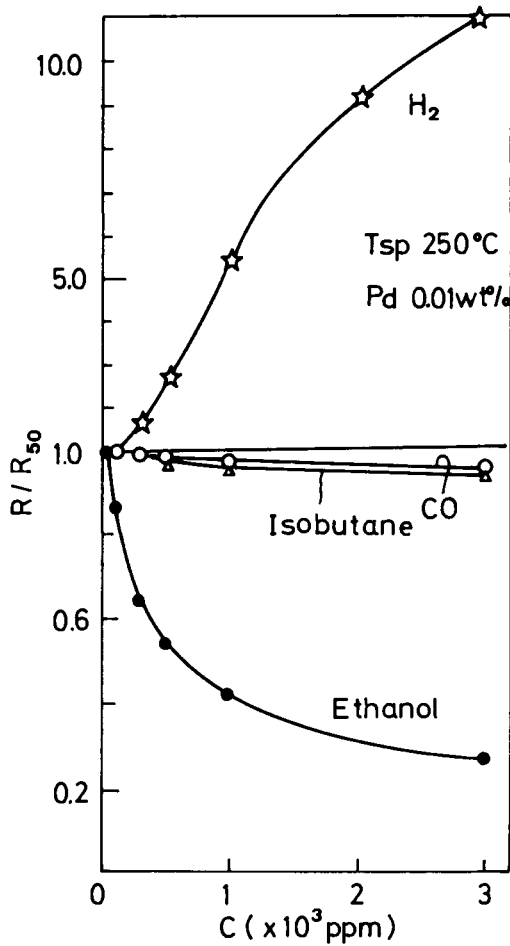


Fig. 12.7. Sensitivity of thick film sensor as a function of gas concentration at the specimen temperature of $250^\circ C$. Pd-black was doped. (After Oyabu et al., 1983 (5)).

the aid of a microcomputer. They have proposed that the system be linked to many houses, but with a single controlling room in which the location of leaking is displayed and the valves of the gas supply are closed automatically.

Another strong demand for sensors has been made from automobile industry. This demand was already emphasized by Wolber and Wise⁽⁶⁾ in 1979.

As discussed in Chapter 10, the oxygen sensor with the solid electrolyte has been widely used for passengers car with gasoline engines. However, this type of the oxygen sensor is rather costly and sensitive only at the stoichiometric ratio of air and fuel.

For more-complete combustion of gasoline, a slight excess air is desirable. Such a "lean-mixture sensor" has been developed by Saji and his coworkers⁽⁷⁾ at Toyota Motor Corporation. They used a porous piece of TiO_2 ceramic containing fine platinum particles, with two platinum lead wires embedded in it. The power of TiO_2 and platinum black were uniformly mixed, then pressed into a disk, and sintered in air.

Fig. 12.8 shows the change of resistance of the disk of TiO_2 at 360°C versus oxygen content in nitrogen for various contents of hydrogen. The gas mixture was supplied to the reaction chamber at 2 L/min.

Because TiO_2 is known as an n-type semiconductor, the increase of oxygen causes an increase in the resistance in accordance to the

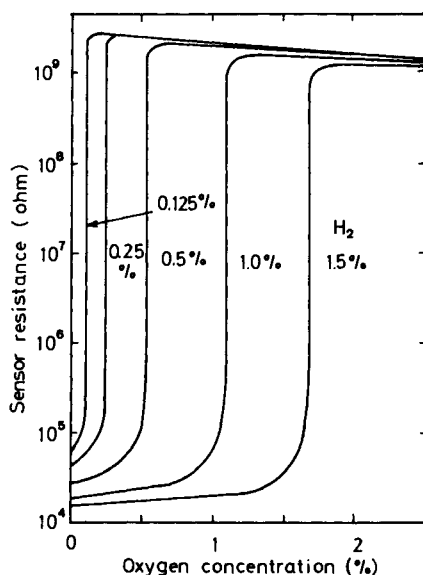


Fig. 12.8. Resistance characteristics of TiO_2 oxygen sensor in H_2 - O_2 - N_2 gas system as a function of oxygen concentration with various hydrogen concentrations as a parameter. (After Saji et al., 1983 (7)).

step-wise increases in Fig. 12.8. However, it is noted that the excess of oxygen is needed for the step-wise increase. For an example, when 1.0 % H_2 is contained, only 0.5 % of O_2 is theoretically needed for $2H_2(g) + O_2(g) = 2H_2O(g)$. However, Fig. 12.8 shows that about 1.0 % of O_2 is needed for the step-wise increase of the resistance. This finding means that this sensor can be used to control the gasoline engines operated by the lean gas mixture. The lean gas mixture is very effective in decreasing the consumption of gasoline per kilometer per unit weight of the car.

To find other oxides suitable in oxygen sensors for cars, Yamamura, Ninomiya, and Sekido⁽⁸⁾ made a systematic study on the perovskite oxides of $La_{1-x}Sr_xCo_{1-y}M_yO_{3-y}$, where M means Ni, Mn, or Fe.

A sintered disk of $La_{0.35}Sr_{0.65}Co_{0.7}Fe_{0.3}O_{3-\delta}$ was exposed to various gas atmospheres at 500°C to 800°C. Fig. 12.9 shows the step-wise change of the resistance when the minor gas in nitrogen is converted from CO to oxygen.

Table 12.3 shows the composition of the complex oxides used as the sensor chip.

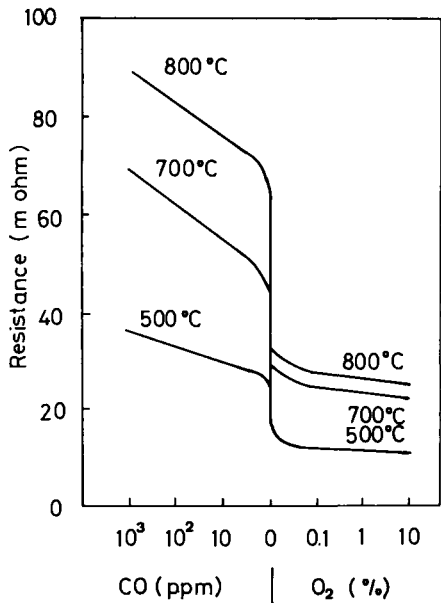


Fig. 12.9. Change of resistance of sensor having $La_{0.35}Sr_{0.65}Co_{0.7}Fe_{0.3}O_{3-\delta}$. (After Yamamura et al., 1983 (8)).

TABLE 12.3.

Mobilities of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (After Yamamura et al., 1983(8)).

Symbols of Samples	Composition	$\mu (\times 10^{22} \text{ cm/s.V})$ in air	$\mu (\times 10^{22} \text{ cm/s.V})$ in CO 10 ppm/N ₂
A	$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$	1.8	1.7
B	$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$	3.2	3.1
C	$\text{La}_{0.35}\text{Sr}_{0.65}\text{CoO}_{3-\delta}$	2.0	2.4
E	$\text{La}_{0.35}\text{Sr}_{0.65}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$	1.2	1.2
G	$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$	0.25	0.26

All the oxides in this table are known as mixed conductors by excess electrons and by oxygen anions via oxygen vacancies. This study by Yamamura et al. is interesting because they have interpreted the conductivity change by only changes of the concentration of charge carriers. As Table 12.3 shows, the mobility of the carriers is independent of the gas atmosphere at 900°C. This means that the conductivity of the oxides is changed by the reaction between gases and the oxide crystals, but not by the adsorption of gases on the surface.

This result is only possible when the diffusion is very fast in the oxides. This fast diffusion can be achieved by the mechanism of mixed conduction, where the rate of migration of electrons is almost equal to that of oxygen.

In the previous chapters, it has been well discussed that the electric conductivity of oxides is controlled by the concentration of crystal defects and electronic defects and their mobility. Therefore, it is easily understandable that the electrical conductivity of the surface of oxides is also very much affected by the adsorption of gases. However, when considering this phenomena more deeply, one will be confused with many problems which are not yet clarified. The problems are: What are the states of adsorbed molecules? How many molecules, ions, or atoms are adsorbed per unit area of the oxides? What are the theoretical relations among the electrical conductivity, the state of the adsorbates, and their concentration per unit area?

In case of gas sensors with solid electrolytes, a simple theoretical equation has been established for the relation between the electromotive force of the sensor and the concentration of gases. Therefore, the reliability of the sensor can be easily evaluated by comparison between the theory and the output of the sensor.

The phenomenon of absorption of gases on the surface of oxides seems very complicated. However, Seiyama and his coworkers⁽⁹⁾⁽¹⁰⁾ have tried to clarify the phenomenon of the gas adsorption. In 1976, they⁽⁹⁾ invented desorption chromatograms with a temperature program. This technique was used to determine the quantity of the desorbed gas, when the oxide sample with an adsorbed gas is heated with a fixed heating rate under a stream of nitrogen or helium. Namely, the characteristic temperature of desorption of a gaseous species is different for the different states of bonding between the adsorbed atoms and the atoms composing the oxide. This was well studied by Yamazoe et al.⁽¹¹⁾ in 1983. Figure 12.10 shows the relation between the output potential of the gas chromatograph and temperature of the powder sample of SnO_2 , when the samples with

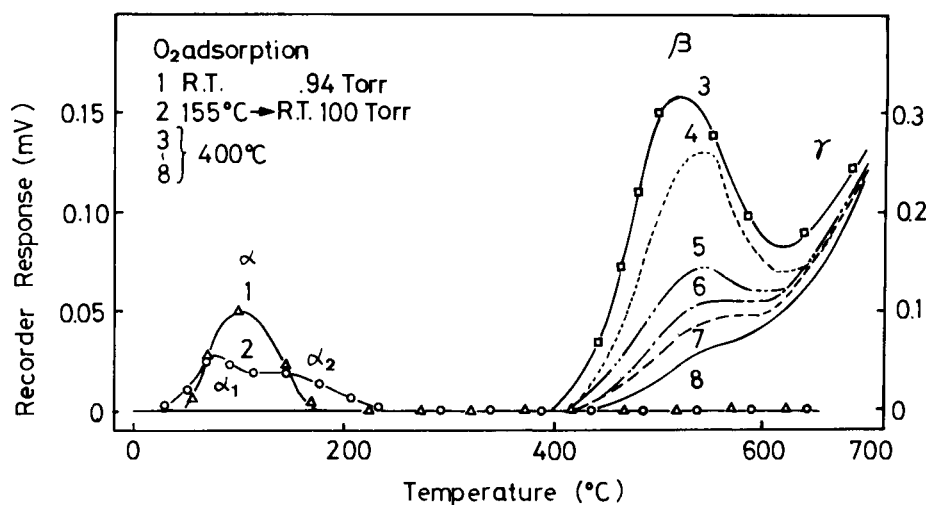


Fig. 12.10. TPD chromatograms of oxygen after oxygen adsorption on SnO_2 under various conditions. The adsorption temperatures and pressures are indicated in the figure. The adsorption pressure of curves 3 to 8 are 99, 48, 16, 6, 3, and 2 Torr, respectively. The heating rate for curves 3 to 8 was $10^\circ\text{C}/\text{min}$. (After Yamazoe et al., 1983 (11)).

adsorbed oxygen are heated up under a helium stream. The vertical axis represents the quantity of oxygen gas desorbed from the surface of SnO_2 powders. The large desorption expressed by α, β , and γ means that the oxygen is adsorbed on the surface of SnO_2 with at least three different states of the bonding.

In the case of curves 1 and 2 in this figure, the oxygen is adsorbed at lower temperatures; for curves 3 to 8 at 400°C , oxygen is adsorbed at different pressures of oxygen gas.

Yamazoe et al.⁽¹¹⁾ also measured the spectrum of electron spin resonance on powder sample of SnO_2 with adsorbed oxygen. From the spectrum, the peaks (expressed by α_1 , α_2 , β , and γ) are assumed to be caused by desorption of O_2 , O_2^- , O^- or O^{2-} , and lattice oxygen, respectively.

Yamazoe et al.⁽¹¹⁾ conducted a similar study of the adsorption of H_2O gas and H_2 gas on the surface of SnO_2 powder. Table 12.4 is the summary of their results. In the table, the most probable

TABLE 12.4.

Adsorption of O_2 , H_2O , and H_2 on SnO_2 . (After Yamazoe et al., 1983(11)).

Gas	Type(T_M) ^a	Species	$\Delta\sigma$ ^b	Adsorbed amounts (θ) ^c ($\times 10^{-8}$ mol/m ²)(%)	Adsorption conditions
O_2	$\alpha_1(80^\circ\text{C})$	O_2	0	0.32(0.021)	$155^\circ\text{C} \rightarrow \text{RT}$, 100 Torr
	$\alpha_2(150^\circ\text{C})$	O_2^-	-	0.35(0.022)	$155^\circ\text{C} \rightarrow \text{RT}$, 100 Torr
	$\beta(520^\circ\text{C})$	O^- or O^{2-}	-	12.4 (0.79)	400°C , 99 Torr
	$\gamma(>600^\circ\text{C})$	Lattice Oxygen	-	6.3 (0.40) ($<700^\circ\text{C}$)	400°C , 2 Torr
H_2O	$\alpha(110^\circ\text{C})$	H_2O	~ 0	70.1 (4.5) 79.9 (5.1)	$600^\circ\text{C} \rightarrow \text{RT}$, 13 Torr RT, 13 Torr
	$\beta(400^\circ\text{C})$	$-\text{OH}$	+	231 (15) 117 (7.5)	$600^\circ\text{C} \rightarrow \text{RT}$, 13 Torr RT, 13 Torr
	$\alpha(100^\circ\text{C})$	$\begin{cases} -\text{OH} \\ -\text{SnH} \end{cases}$	-	14.7 (0.94) 1.9 (0.12)	RT, 90 Torr $200^\circ\text{C} \rightarrow \text{RT}$, 101 Torr
	$\beta(220^\circ\text{C})$	?	?	1.2 (0.07)	$200^\circ\text{C} \rightarrow \text{RT}$, 101 Torr
	Irreversible	$-\text{OH}$ (H_2O)	+	$\begin{cases} 25.4 (1.64) \\ \text{(as } \alpha\text{-H}_2\text{O)} \\ 334 (21.5) \\ \text{(as } \beta\text{-H}_2\text{O)} \end{cases}$	$200^\circ\text{C} \rightarrow \text{RT}$, 62 Torr

^a T_M means the temperature of desorption maximum.

^b Changes of electric conductivity with the adsorption.

^c θ means surface coverage (see text).

species of the adsorbates are given, along with the temperature of their desorption peaks. The surface coverage, expressed by θ in the table, is defined as the number of adsorbed molecules of O_2 , H_2O , or H_2 per surface tin atom; the value was estimated assuming that all the surface of SnO_2 was covered with $\{110\}$ planes. As usual, the surface area was measured by BET method.

From Table 12.4, it can be understood that the adsorption phenomena taking place on the surface of SnO_2 are not simple. Therefore, it seems very difficult to relate the change in the electrical conductivity to the concentration of the adsorbing gas with simple models.

This difficulty also explains why commercial gas sensors, which are fabricated under different conditions, are very different in their performance.

12.3 HUMIDITY SENSORS WITH RESISTIVITY CHANGE OF OXIDES

In 1968, Anderson and Parks⁽¹²⁾ published a report on electrical conductivity of silica with adsorbed water. In this report, they indicated how the resistivity of silica gel changes with changes in humidity, as shown in Fig. 12.11. The resistivity of a sample

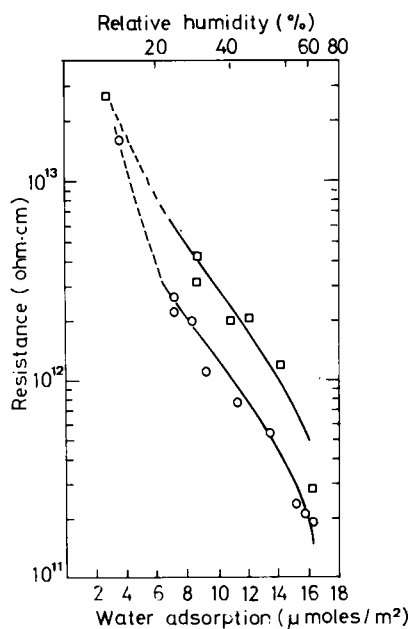


Fig. 12.11. Resistivity of silica gel as a function of water content at 25°C: circles, first run; squares, second run. (After Anderson and Parks, 1968 (12)).

of silica gel with size of $1 \times 3 \times 10 \text{ mm}^3$ was measured at 25°C . The water adsorption on the horizontal axis expressed by micro-moles per m^2 was estimated from the total amount of water adsorbed divided by the total surface area measured by BET method.

Anderson and Parks⁽¹²⁾ have also studied both the infrared spectrum of the samples and the isotopic effect of the resistance, using D_2O . From their experimental results, they concluded that the conduction mechanism is ionic and that protons are probably the dominant charge carriers.

Table 12.5 summarizes their conclusions. It indicates that the state of adsorption of water is in three states, depending on the magnitude of surface coverage. In this table, $\text{H}_3\text{O}^+(\text{aq})$ means a liquidlike water. When water is present as more than one monolayer, the infrared spectrum suggests that clustering of water molecules takes place, forming patches of a liquidlike network of hydrogen-bonded water molecules. Because of the comprehensive nature of the work of Anderson and Parks⁽¹²⁾ in clarifying the mechanism of resistance change, their paper is widely believed to be one of the triggers in the development of humidity sensors.

TABLE 12.5.

States of absorption of H_2O on silica gel. (After Anderson and Parks, 1968 (12)).

Fractional H_2O surface coverage	Favored state of protons	Transport mechanism
$\theta = 0$	H^+	H^+ hopping on SiOH surface
$0 < \theta < 1$	H_3O^+	H_3O^+ diffusion on SiOH surface and H^+ transfer between adjacent H_2O molecules in clusters
$\theta > 1$	$\text{H}_3\text{O}^+(\text{aq})$	H^+ transfer between adjacent H_2O molecules within a continuous film of water

Earlier, however, in 1963, Stover⁽¹³⁾ reported on a humidity sensor based on the resistance change of an alumina element.

In 1966, Kanoh and Kawasaki⁽¹⁴⁾ reported on a humidity sensor using magnetite colloid. Also in 1966, Kawasaki, Minowa and Inamatsu⁽¹⁵⁾ reported on a humidity sensor using metal oxides. These are the papers reported in 1960's. More papers on humidity sensors were

reported in the 70s and 80s.

For an example, Nitta, Terada and Hayakawa⁽¹⁶⁾ reported in 1980 on the humidity sensitivity of porous ceramics of the MgCr_2O_4 - TiO_2 system. The intention of their work was to find a reliable sensor element that has a good reversibility with a short response time, even by repeated heating to clean off the adhesion of dust, dirt, oil, and other poisonous materials. For this purpose, the ceramic element should have lower resistance and good porosity, but should be sintered at higher temperature.

From this viewpoint, Nitta, Terada, and Hayakawa⁽¹⁶⁾ selected the system of MgCr_2O_4 - TiO_2 , with various contents of TiO_2 . Table 12.6 shows the chemical composition and the crystal phase for 13 samples. The samples were sintered at 1350°C for 6 hours. When the

TABLE 12.6.

Phase analysis of products obtained on sintering in the system $\text{MgO-Cr}_2\text{O}_3\text{-TiO}_2$.^{*} (After Nitta et al., 1980 (16)).

Specimen No.	Standing comp.(mol%)			Phase analysis of product
	MgO	Cr_2O_3	TiO_2	
MCT-1	50	50	0	Spinel
MCT-2	47.4	47.4	5.2	Spinel
MCT-3	44.4	44.4	11.2	Spinel
MCT-4	41.2	41.2	17.6	Spinel
MCT-5	39.4	39.4	21.2	Spinel, MgTi_2O_3 -type
MCT-6	37.5	37.5	25.0	Spinel, MgTi_2O_3 -type
MCT-7	35.5	35.5	29.0	Spinel, MgTi_2O_3 -type
MCT-8	33.3	33.3	33.3	Spinel, MgTi_2O_3 -type
MCT-9	31.0	31.0	38.0	Spinel, MgTi_2O_3 -type
MCT-10	28.6	28.6	42.8	Spinel, MgTi_2O_3 -type
MCT-11	23.1	23.1	53.8	Spinel, MgTi_2O_3 -type
MCT-12	16.7	16.7	66.6	Spinel, MgTi_2O_3 -type, $\text{Cr}_2\text{Ti}_2\text{O}_7$ -type, rutile
MCT-13	9.1	9.1	81.8	Spinel, MgTi_2O_3 -type, $\text{Cr}_2\text{Ti}_2\text{O}_7$ -type, rutile

* Each composition was sintered at 1350°C for 6 h.

sample contained less than 20 mol% TiO_2 , it was composed of a single phase of MgCr_2O_4 -type spinel. The porosity was 33 to 38 %, with specific surface area of 0.1 to $1.6 \text{ m}^2/\text{gram}$.

Figure 12.12 shows the relation, at 20°C , between the resistivity of two plate-shaped samples and the relative humidity. The sample number is the same as those in Table 12.6. The response time was within several seconds. To determine the reproducibility of the relations given in Fig. 12.12, the samples were subjected to high humidity of more than 95 % for a long time. However, the resistivity always returned to the original value when the sample was reheated above 350°C . The reproducibility was proved even after 1000 cycles of heating to take off absorbing water.

Further, it was also proved that the cleaning by heating above 450°C could recover any deterioration caused by extremely severe contamination by oil vapor and by other organic vapors.

These properties of the ceramic element are very promising for the development of gas sensors with a long period of stable

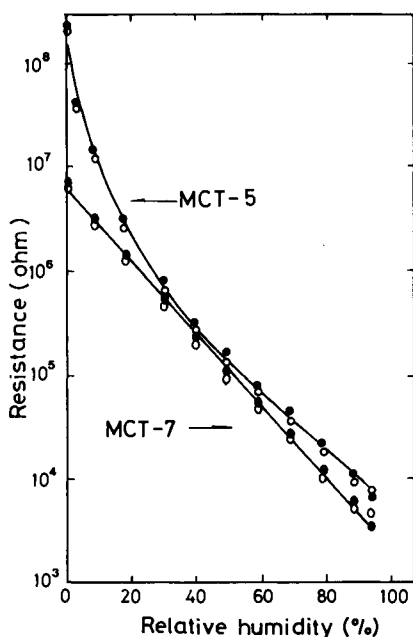


Fig. 12.12. Humidity-resistance characteristics at 1.0 V (ac) and 20°C . (After Nitta, Terada, and Hayakawa, 1980 (16)).

operation.

After 1980, many papers were published on humidity sensors with oxide elements. Some of the interesting sensors are introduced below.

Because a sensor is a kind of electronic device, it is desirable that it can be easily accommodated into the electronic circuit for the automatic controlling system. Figure 12.13 shows the structure of the sensor with the capacitance change with humidity, reported by Nabeta, Suzuki, and Inuzuka⁽¹⁷⁾ in 1983. The fabrication of this sensor is based on reactive ion plating. The lower electrodes of Pd, Au, etc., ($1000 \text{ \AA}$ thick) are deposited by iron plating on a cleaned substrate of borosilicate glass or sapphire. The upper electrode, which is $120 \text{ \AA}$ thick, is formed by vacuum evaporation, with good pores for permeation of water vapor.

After the deposition of the lower electrodes, an alumina film is grown by reactive ion plating. In the vacuum chamber, metal of aluminum is evaporated by an electron gun. Aluminum vapor is then ionized and transferred onto the substrate with the ionized oxygen through a leak valve.

The details of the deposition of alumina film are not given here, but its condition very strongly affects the performance of the sensor element.

Figure 12.14 shows the capacitance change versus relative

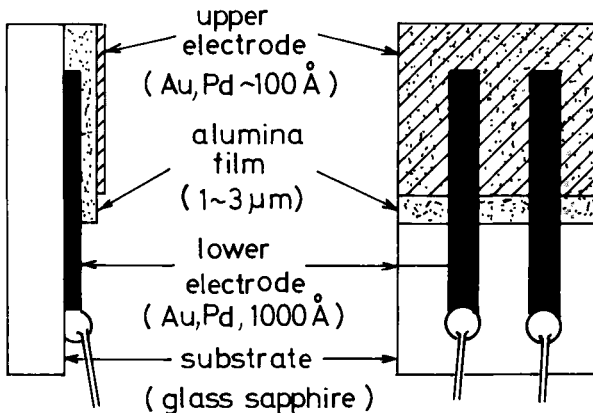


Fig. 12.13. Structure of humidity sensor. (After Nabeta et al., 1984 (17)).

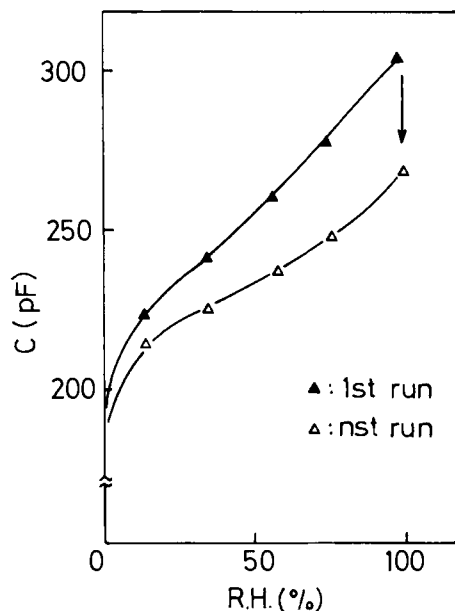


Fig. 12.14. The Capacitance change due to humidity cycles. (After Nabeta et al., 1983 (17)).

humidity. As seen in this figure, the capacitance of the sensor decreases gradually during several humidity cycles. However, after this decrease, the sensor is still operatable with a good reproducibility for many cycles.

When the sensor is treated in boiling water, it seems passivated, because the reproducibility is increased even more.

Figure 12.15 shows the structure of a commercial humidity sensor reported by Nitta, Fukushima, and Matsuo in 1983.⁽¹⁸⁾ The sensor ceramic shown in the figure is composed of monoclinic zirconia and cubic magnesia phase. The porosity was about 8%, and this porosity is good enough for the rapid chemisorption and desorption of humidity.

A heating coil is attached around the above ceramic element. The function of this heater is to maintain a constant operating temperature and also to clean the sensor element by heating to the higher temperature.

Figure 12.16 shows the relation between the resistance of the sensor and the content of water vapor. As the content of water

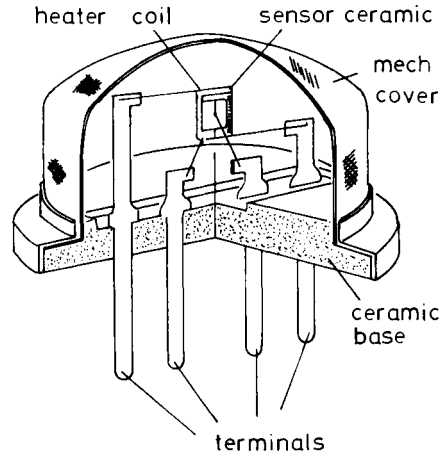


Fig. 12.15. Construction of water vapor gas sensor. (After Nitta et al., 1983 (18)).

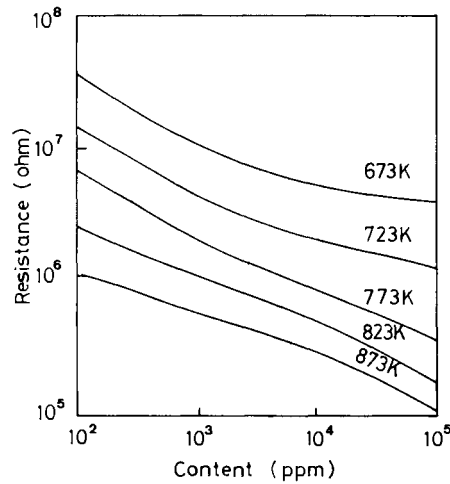


Fig. 12.16. Relationship between water vapor content and resistance. (After Nitta et al., 1983 (18)).

vapor is increased from 10^2 to 10^5 ppmw, the resistance decreases very much. According to this work, the sensor element is considered as an n-type semiconductor; if so, the absorbed water molecules act as the donor.

Thus, the tetragonal phase of ZrO_2 is usually considered as an

n-type semiconductor.

Because the ceramic elements for humidity sensors are sometimes unreliable for longtime service, many oxide systems have been exploited.

In 1983, Arai, Ezaki, Shimizu, Shippo and Seiyama⁽¹⁹⁾ reported on a variety of perovskite-type oxides with semiconductivity. Table 12.7 summarizes the oxide systems and includes their sintering temperatures and durations. From the thermo-electromotive force given in the table, the authors have determined the type of semiconduction. In Table 12.7, the conductivity of the elements is changed by changing the atmosphere from air to 20 Torr P_{O_2} or 20 Torr P_{H_2} . Thus, when these oxides are used, the humidity must be measured at a fixed oxygen pressure.

Figure 12.17 shows the effect of sintering conditions on the conductivity versus humidity characteristics of $Sr_{0.9}La_{0.1}SnO_3$. The caption gives the slope of the line (α), relative density, and surface area. This figure is a good example of how strongly the condition of the fabrication affects the performance of the sensor element. The perovskite-type oxides seemed very important because it may be possible to modify preferably the water adsorptive property with an optimal electronic property by selecting appropriate combinations of the cationic constituents.

TABLE 12.7.

Determination of Semiconductor type. (After Arai et al., 1983⁽¹⁹⁾).

Specimen	Thermo-EMF ($\mu V/deg$)	Temp. ($^{\circ}C$)	Resistance (Ω)	Conductivity change due to absorption*		Semi-conductor type
				O_2 ($S.cm^{-1}$)	H_2 ($S.cm^{-1}$)	
$Sr_{0.9}La_{0.1}SnO_3$ (1500 $^{\circ}C$, 6hr)	-349	400	4×10^6	-1.11×10^{-5}	$+1.39 \times 10^{-2}$	n
$Ca_{0.9}La_{0.1}SnO_3$ (1500 $^{\circ}C$, 6hr)	-229	550	5×10^6	-1.31×10^{-6}	$+1.04 \times 10^{-4}$	n
$Sr_{0.9}La_{0.1}TiO_3$ (1350 $^{\circ}C$, 3hr)	-307	675	2.8×10^6	-3.93×10^{-5}	$+3.05 \times 10^{-5}$	n
$Ca_{0.9}La_{0.1}TiO_3$ (1350 $^{\circ}C$, 3hr)	-370	697	1.6×10^6	-1.22×10^{-5}	$+8.50 \times 10^{-3}$	n
$SrTiO_3$ (1200 $^{\circ}C$, 3hr)	300	597	-	-	-	p
	-1200	256	-	-	-	n

* Measurement temperature 400 $^{\circ}C$, P_{O_2} 20 Torr, P_{H_2} 20 Torr.

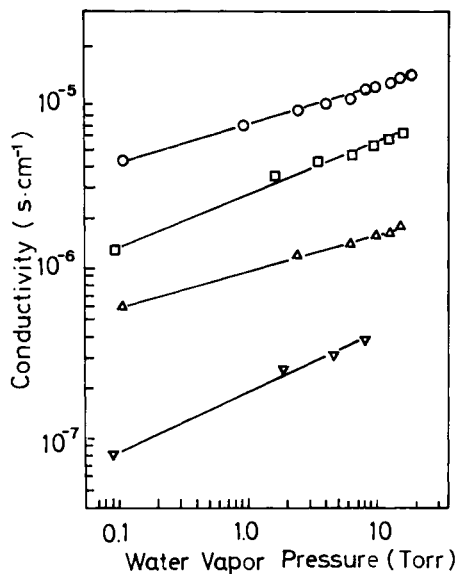


Fig. 12.17. Effect of sintering on conductivity-humidity characteristics of $\text{Sr}_{0.9}\text{La}_{0.1}\text{SnO}_3$. (After Arai et al., 1983 (19)).

One final sensor deserves mention. In 1983, Uchikawa, Miyao, Horii, and Shimamoto⁽²⁰⁾ fabricated a composite film, 30 to 35 microns thick. This film is made of methylphenyl silicone prepolymer, SiO_2 , TiO_2 , and $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$.

On a substrate of alumina, the composite film was very sensitive to humidity, as shown by Fig. 12.18. The relation between the resistance and the relative humidity of laboratory air is dependent upon the temperature of heat treatment of the composite film.

The film heated at 400°C , shown by (a) of Fig. 12.18, seems most stable, because the relation of the resistance versus humidity is nearly constant for six months.

The sensor proposed by Uchikawa et al.⁽²⁰⁾ is based on the inhibiting action of OH bonded to the surface, which is produced by the thermal decomposition of the silicon polymer at 500°C . Heating at the higher temperature would cause the formation of fine particles of silica, and the resistance would thus increase with time as is usually the case with ceramic humidity sensors.

Uchikawa et al.⁽²⁰⁾ determined the surface concentration of OH quantitatively by using the reaction of the surface OH groups with

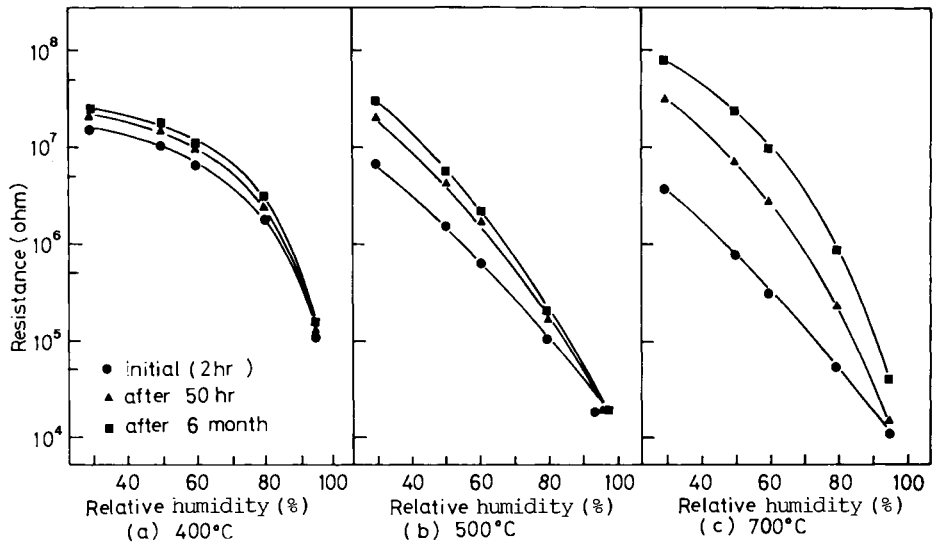


Fig. 12.18. Humidity-resistance characteristics and changes with time in laboratory air of the composite film with heat treatment temperatures of (a)400°C, (b)500°C, and (c)700°C. (After Uchikawa et al., 1983 (20)).

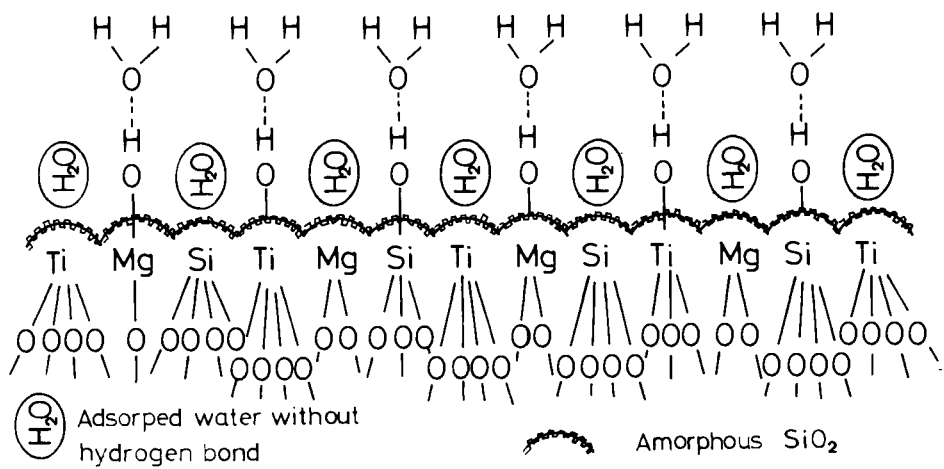


Fig. 12.19. Surface model for water adsorption of the composite film heat-treated at 500°C. (After Uchikawa et al., 1983 (20)).

the organometallic reagent on the catalyst. As a result, they proposed the surface model shown in Fig. 12.19 for the composite film,

which was heat-treated at 500°C.

According to their model, the sites with OH bondings are not active for adsorption of water molecules. Only the sites with circles H₂O molecules in the figure can be active for the adsorption. Thus, the number of active sites is far smaller than that on the film heat-treated at 700°C and on the films of usual ceramic elements.

The conduction mechanism is proposed as the protonic one.

Although the surface model proposed does not clearly explain the observed property, the composite film of inorganic and organic compounds seems to offer another possibility for designing more-reliable humidity sensors with longer life times.

12.4 GAS SENSORS WITH METAL-OXIDE-SEMICONDUCTOR TRANSISTORS

The term "MOS" comes from the initial letters of Metal, Oxide, and Semiconductor. The MOS transistor is used more widely for computers because of its higher speed of switching action when compared with conventional transistors.

Fig. 12.20 shows the sectional view of an MOS transistor.

The simple explanation of fabrication of this transistor is as follows:

- (1) the n-channel is formed by doping phosphorus on the p-type silicon wafer,
- (2) the dielectric silica layer of about 1000 Å is formed by the

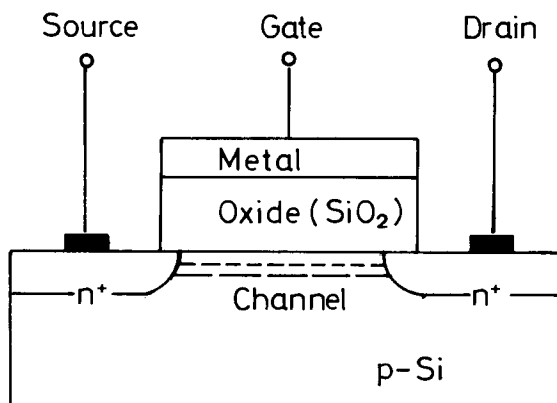


Fig. 12.20. Schematic cross-section of Metal-Oxide-Semiconductor-Field-Effect-Transistor (MOS-FET).

oxidation,

(3) the metal gate layer is made of aluminum or other metals.

Intuitively, it can be expected that the electron current from the source, in this figure, to the drain through a thin n-type channel will be controlled by the electrical potential applied to the gate electrode. This expectation is qualitatively correct, but the phenomenon must be explained more carefully. When a positive potential is applied on the gate metal electrode, only the negatively charged doping atoms are attracted to the direction of the surface of the silicon side. It will reach a point at which the electron concentration starts to increase at the silicon surface. Namely, the current can flow between the source and the drain. In other words, the channel starts to open at this special gate voltage, which is called "threshold voltage".

Figure 12.21 shows the relation between the conductance from source to drain and the gate voltage (left side of figure) and the relation between the drain current and the drain voltage (right side). This figure is reproduced from an excellent monograph on gas sensors that use MOS transistors. It was published by Lundström and Svensson⁽²¹⁾ in 1985.

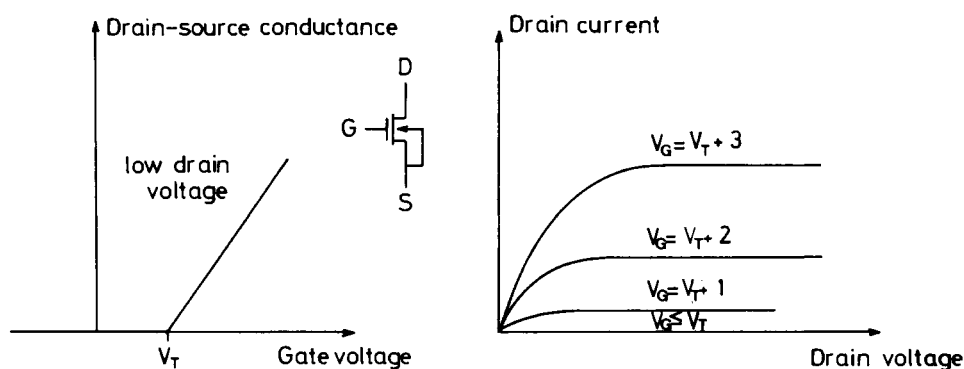


Fig. 12.21. Characteristics curves for an MOS transistor. The symbol of the n-channel MOS transistor is also shown. The arrow indicates the p-type substrate, which is normally connected to the source. (After Lundström and Svensson, 1985 (21)).

As shown in the figure, the conductance of the channel between the source and the drain is zero until the threshold voltage is reached. From that point on, the conductance increases linearly.

The right figure shows that the drain current remains zero as long as the drain voltage is less than the threshold voltage.

When the drain voltage is small, the drain current (I_D) can be given by

$$I_D = \frac{\mu C_g W}{L} \left[(V_G - V_T) V_D - \frac{V_D^2}{2} \right] \quad (12-1)$$

where μ is mobility of electrons, C_g is the capacitance between the gate and silicon, W is width of the gate, L is the length of the n-channel, V_G is the gate voltage, V_T is the threshold voltage, and V_D is the drain voltage. When V_D is much larger than $(V_G - V_T)$, the drain current stages constant stays constant and is given by

$$I_D = \frac{\mu C_g W}{L} \left[\frac{(V_G - V_T)^2}{2} \right] \quad (12-2)$$

Because some gaseous species can be chemically absorbed to the interface between the gate metal and silica layer, the effective charge at the interface will be changed. Therefore, the threshold voltage changes according to the amount of the adsorbed gas.

This novel idea was first proved in 1975 by Lundström and his coworkers.⁽²²⁾⁽²³⁾ Figure 12.22 is reproduced from one of their papers.⁽²³⁾ The relation between $(1/\Delta V)$ and $(1/\sqrt{P_{H_2}})$ is given in

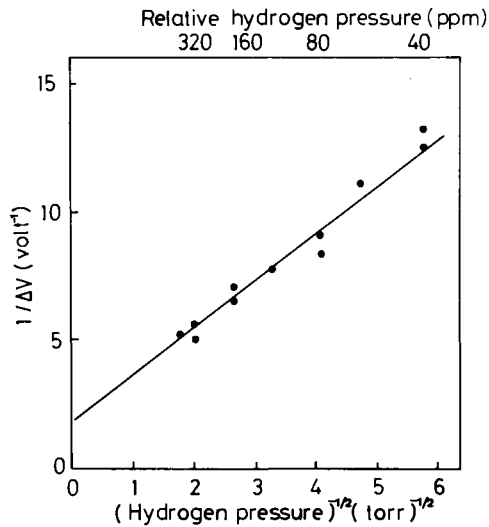


Fig. 12.22. $1/\Delta V$ vs $(\text{hydrogen pressure})^{-\frac{1}{2}}$ for hydrogen-in-air mixture (20 % O_2 in N_2) at $150^\circ C$. (After Lundström et al., 1975(23)).

this figure at 150°C, where ΔV means the change of the threshold voltage induced by the adsorption of hydrogen gas by the palladium gate. They have used palladium as the gate metal because palladium can absorb hydrogen very rapidly even at room temperature.

Figure 12.23 shows results on an MOS device that can detect ammonia in air at 150°C.

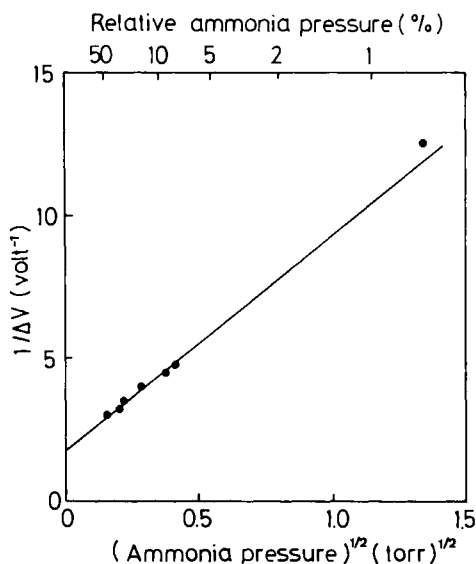


Fig. 12.23. $1/\Delta V$ vs. $(\text{ammonia pressure})^{-\frac{1}{2}}$ for ammonia in air at 150°C. (After Lundström, Shivaraman, and Svensson, 1975 (23)).

The experimental results in the two figures can be expressed by the equation

$$\Delta V = \frac{\Delta V_{\max} C \sqrt{P_i}}{1 + C \sqrt{P_i}} \quad (12-3)$$

where ΔV is change of threshold voltage, $\Delta V_{\max}$ is the maximum observable voltage shift, C is an experimental constant, and P_i means partial pressure of hydrogen or ammonia contained in air.

This experimental equation agrees with the theoretical relation derived from the Langmuir isotherm⁽²³⁾. Therefore, it would be expected that the MOS sensor can be conveniently used as long as only a single gaseous species can be adsorbed on the palladium surface.

In Figs. 12.22 and Fig. 12.23, either hydrogen or ammonia is

contained in the air with the small quantity. Thus, the concentration of adsorbed oxygen on the palladium surface is practically constant, and so this factor is included in the constant, expressed by C in Eq. (12-3).

Lundström, Shivaraman, and Svensson⁽²³⁾ have made the estimation of the shift of the threshold voltage with the help of the known value of the dipole moment of hydrogen adsorbed on nickel surface. The estimated shift was in a reasonable agreement with the observed shift.

Figure 12.24 is reproduced from the superb monograph by Lundström and Svensson.⁽²¹⁾ This figure clearly explains the chemical dissolution and adsorption and their effect upon the performance of the MOS transistor and capacitor.

As shown by the top figure, absorbed hydrogen diffuses to the interface between palladium and silica. Then, the diffused-in hydrogen is adsorbed at the interface, acting as dipoles at the metal/insulator interface. Thus, the dipole layer gives rise to an extra voltage in series with externally applied voltage. Then, the threshold voltage is decreased by a value equal to this extra voltage.

The magnitude of the extra voltage can be estimated from the dipole moment of the adsorbed atom and its surface coverage.

Part (b) of Fig. 12.24 shows the shift of the curve of the drain current versus the gate voltage due to hydrogen adsorption. Part (c) shows the shift of the curve of the capacitance versus the voltage by hydrogen adsorption for the MOS capacitor.

Table 12.8 gives the detection limits of H_2 , H_2S , or NH_3 estimated by Lundström and Svensson⁽²¹⁾. They estimated the detection limits from the dipole moment and the concentration of the adsorbed gas on palladium at $150^\circ C$. Lundström and his coworkers also studied the fabrication procedure in developing commercial MOS gas sensors with the reliable performance⁽²¹⁾.

In 1986, sensors with MOS transistors and capacitors are available in several countries of the world.

The possible applications of the Pd-MOS devices are summarized as follows⁽²¹⁾:

- 1) A simple leak detector
- 2) A smoke detector or fire alarm
- 3) A monitor for biochemical reactions
- 4) A detector of hydrogen in process industry, for corrosion

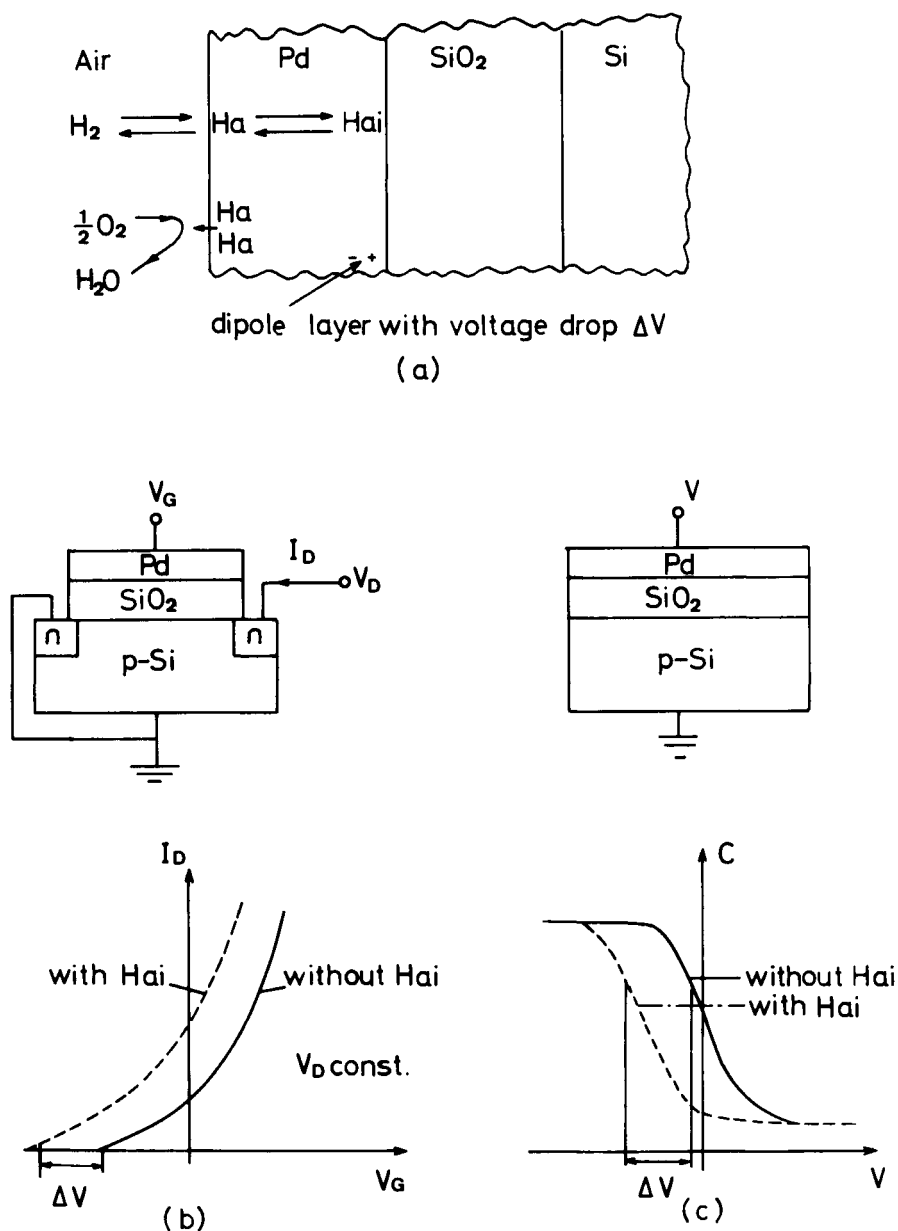


Fig.12.24. Schematic picture demonstrating chemical reactions on the palladium surface, hydrogen transport, and surface and interface adsorption of atomic hydrogen (a). The effect of the hydrogen dipole layer at the interface on a Pd-MOS transistor (b), and capacitor (c), respectively, are also indicated. (After Ingemar Lundström and Christer Svensson, 1985 (21)).

TABLE 12.8.
Estimated detection limits of palladium devices (Sensor temperature 150°C).

Gas	Estimated detection limit for minimum detectable voltage shift	
	$\Delta V_{\min}$	
	10 mV	1 mV
H ₂ in air	0.5 ppm	0.005 ppm
in inert atmosphere	0.03 ppb	0.0003 ppb
H ₂ S in air	5 ppm	0.05 ppm
NH ₃ in air	10 ppm	0.1 ppm

(After Lundström and Svenson, 1985 (21)).

monitoring and for surveillance of battery charging.

The MOS gas sensors discussed above are very interesting devices, because the chemical reactions are directly used to actuate the micro-electronic devices, which are fabricated by advanced technology.

Another interesting device is the gas sensor using Schottky barrier diodes, which has been first reported by Steele and MacIver in 1976⁽²⁴⁾.

Fig. 12.25 shows the usual current/voltage characteristics of the diode and includes schematics of three types of the diodes⁽²¹⁾.

The principle of the gas detection by this type of sensor is based on the change of the Schottky barrier height by the gas adsorption at the interface between the metal and semiconductor, compound, or oxide, as shown in Fig. 12.25.

Figure 12.26, reported by Ruths et al. in 1981⁽²⁵⁾, shows how the current/voltage characteristics differ in air and in 154 ppm H₂ in N₂ in case of the Pd | SiO_x | Si diode.

Also, Fig. 12.27, reported by Yamamoto et al. in 1980, shows the current/voltage characteristics for various hydrogen contents in air in the case of a diode with a Pd-TiO₂ barrier⁽²⁶⁾.

In 1976, Steele and MacIver used CdS as the substrate semiconductor under Pd to detect 500 to 5000 ppm H₂ in air. Since then, however, other substrate semiconductors have been used, including

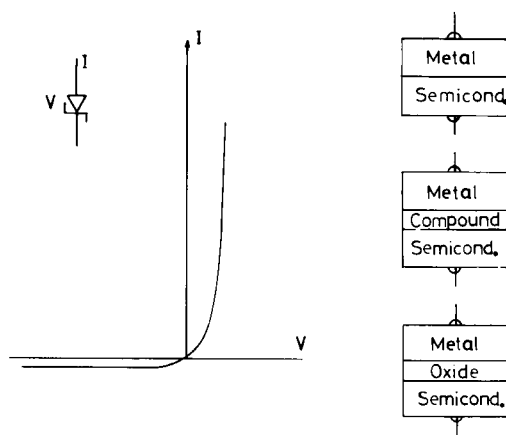


Fig. 12.25. Current-voltage characteristics of a Schottky barrier diode and three types of such diodes. The three types could be, for example, palladium-silicon, palladium-palladium silicide-silicon, and palladium-silicon dioxide-silicon structures. (After Ingemar Lundström and Christer Svensson, 1985 (21)).

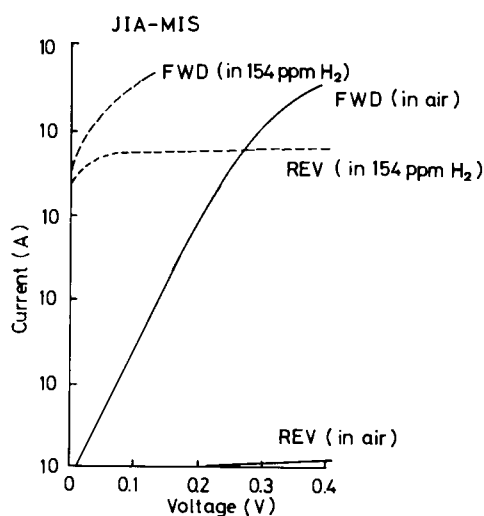


Fig. 12.26. Room temperature forward and reverse I-V characteristics of an MIS diode in air and in 154-ppm H₂ in N₂. (After Ruths et al., 1981 (25)).

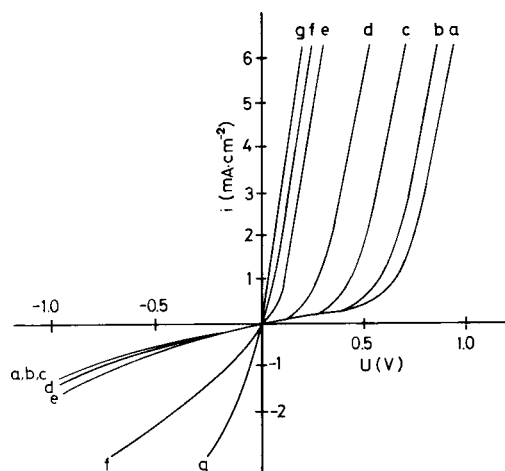


Fig. 12.27. Current-voltage characteristic of a Pd-TiO₂ Schottky diode in air with different hydrogen concentrations. The partial pressures are (a)0, (b)14 ppm, (c)140 ppm, (d) 1400 ppm, (e) 7150 ppm, (f)1%, and (g)1.5%. The temperature was 25°C. (From Yamamoto et al., 1980 (26)).

ZnO⁽²⁶⁾⁽²⁷⁾, TiO₂⁽²⁶⁾, and Si⁽²⁸⁾⁽²⁹⁾.

In all the above gas sensors with an MOS structure or a Schottky barrier diode structure, the gases to be detected are absorbed by the metal electrode but not by the dielectric layers. In the previous section, the humidity sensors with Al₂O₃ or SiO₂ sensor chip were introduced. Consequently, it is a natural extension to use the sensor chips as the dielectric oxide layer of the MOS transistor or the diodes to construct a new type of gas sensor.

A humidity sensor with an MOS structure was reported in 1981 by Jachowicz and Senturia⁽³⁰⁾ and in 1983 by Jachowicz⁽³¹⁾.

Figure 12.28 shows a cross section of the sensor. This humidity sensor is based on changes of sheet resistance of the dielectric upper layer with the number of water molecules adsorbed from ambient gas. This principle is shown in the upper small pictures of Fig. 12.28. The sensor has two electrodes, A and B, in the first level of metalization and a third electrode in the second level. The third electrode eliminates the unsensitive region of the sensor by short connection of A and B interelectrode sheet resistance. For the upper dielectric layer, silica is deposited by CVD with a thickness of 300 Å.

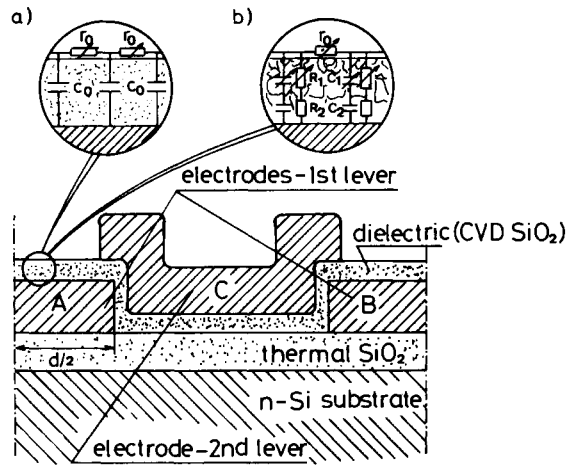


Fig. 12.28. Schematic cross-section of the sensor; a)-model without water molecule penetration inside dielectric, b)-model with water molecules present inside dielectric. (After Jachowicz, 1983 (31)).

The sensor has only two regions sensitive for humidity, namely, the dielectric surfaces directly over electrode A and B.

The impedance between electrode C and A change with the adsorption of moisture. A variety of electronic signals can be taken from this device, depending on the circuit design that is connected.

Another example of an MOS humidity sensor is shown in Fig. 12.29;

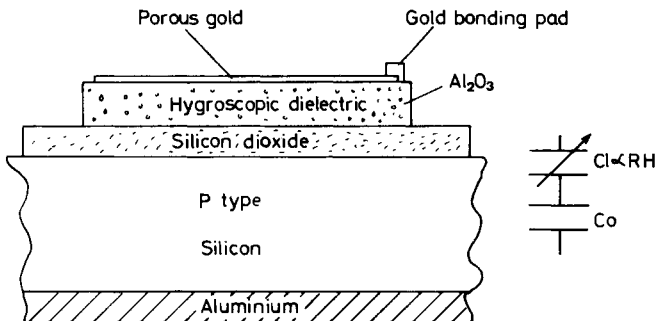


Fig. 12.29. Sectional view of humidity sensitive capacitor. (After G.J. Rogers et al., 1983 (32)).

it was reported by Rogers et al. in 1983⁽³²⁾. The device comprises a humidity-sensitive MOS capacitor that is made of porous alumina or hygroscopic dielectric. Water adsorbed by the hygroscopic dielectric causes a change in capacitance according to the humidity of the surroundings.

Thin aluminum oxide films were formed by anodizing 1-micron-thick aluminum evaporated on thermally grown silicon dioxide. The condition of anodizing in aqueous solution affects the sensitivity of the sensor. The capacitance changes several times by the adsorption of moisture.

In the previous part of the present chapter, gas sensors with semiconductor oxides were introduced. The principle of the gas detections was based on the resistivity change of the semiconducting oxides induced by chemical adsorption of gaseous molecules. Then, when such semiconducting oxides are used as the gate electrode of an MOS transistor, the devices can be used to selectively detect various gases. Several examples of this type of sensor were introduced in the proceedings of International Meeting of Chemical Sensors⁽⁴⁾ in 1983; thus this type is not discussed again here. Instead, one more principle of gas sensing will now be introduced: a humidity sensor using a piezoelectric oxides. The principle of sensing is as follows: First, moisture is absorbed into an organic film formed on the surface of a piezoelectric oxide. Second, the total weight of the film and the oxide crystal is thus increased by the moisture absorption. Because the total mass is increased, the frequency of vibration of the oscillating crystal must be decreased. Consequently, the humidity can be estimated from the shift of the frequency.

This idea was originally reported by King in 1964⁽³³⁾. Based on this idea, a humidity sensor with a computer was commercially developed in 1964 by the E.I. De Pont De Nemours & Co.

Several technical papers have been published on sensors with piezoelectric oxides. An example of such a paper⁽³⁴⁾ is one on a humidity sensor with a coating made by plasma polymerization. The piezoelectric quartz crystal was coated by polymerized styrene and sulfonic acid groups.

An experimental relation between the frequency difference, ΔF , and water concentration in ppm, [ppm H₂O], is as follows:

$$\log \Delta F = 0.397 \log [\text{ppm H}_2\text{O}] + 1.142 \quad (12-4)$$

According to Tahara, Kobayashi, and Oka⁽³⁴⁾, this linear relation was strictly valid from 1.0 ppm up to 10^5 ppm at 45°C.

The interference by other gases (such as N_2 , H_2 , CO, CO_2 , NH_3 , or CH_4) was negligible. This is an example, but there are many other piezoelectric oxides and compounds: SiO_2 , $BaTiO_3$, ZnO, CdS, ZnS, and AlN. Therefore, other structures of the sensor with these compounds could be developed in future.

A few final remarks might be helpful to summarize this chapter. In the previous chapters, it has been repeatedly emphasized that the contents of electronic defects and crystal defects in the solid or liquid oxides depend heavily upon the chemical potential of oxygen gas. On the other hand, in catalyst chemistry, solid oxides are known to selectively adsorb various gases on the surface by chemical adsorption. The above two phenomena can be combined conceptionally to develop gas sensors based on the resistance change of the semiconductor oxides. The dissolution and adsorption of water vapor to acidic oxides can be used to develop a humidity sensor with the resistance change of alumina, silica and other oxides. When the above phenomena take place in the thin layers of oxides used in transistors and diodes, new groups of gas sensor can be developed. These are MOS gas sensors and Schottky-barrier-diode gas sensors. A humidity sensor can be developed by use of these microelectronic devices.

In this way, various microelectronic devices, such as optomagnetic and optoelectric devices, can conceivably be used as chemical sensors, as long as solid oxides are used as their parts.

REFERENCES TO CHAPTER 12

- (1) T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, *Analytical Chemistry*, Vol.34 (1962) pp. 1502-1503.
- (2) J.C. Loh, Japan. Patent 43-28560 (1967).
- (3) P.J. Shaver, General Electric Report No.67-C-293 (1967) and *Appl. Phys. Letters*, 11 (1967) 255.
- (4) *Proceedings of the International Meeting on Chemical Sensors*, edited by T. Seiyama et al., published by Elsevier (1983), Amsterdam (with 775 pages).
- (5) T. Oyabu, T. Kurobe, and T. Hidai, pp. 12-17 of the above proceedings of reference (4).
- (6) W.G. Wolber and K.D. Wise, *IEEE Trans. on Electron Devices*, ED-26 (1979), pp. 1864-1874.
- (7) K. Saji, H. Takahashi, H. Kondo, T. Takeuchi and I. Igarashi, pp. 171-176 of the proceedings given by reference (4).
- (8) Y.Yamamura, Y. Ninomiya and S. Sekido, pp. 187-192 of the proceedings of reference (4).
- (9) M. Iwamoto, Y. Yoda, M. Egashira and T. Seiyama, *J. Phys. Chem.*, 80 (1976) p. 1989.
- (10) M. Iwamoto, K. Maruyama, N. Yamazoe and T. Seiyama, *J. Phys. Chem.* 81 (1977) p. 622.
- (11) N. Yamazoe, J. Fuchigami, M. Kishikawa, and T. Seiyama, *Surface Science*, 86 (1979) pp. 335-344.
- (12) J.H. Anderson and G.A. Parks, *J. of Phys. Chem.*, 72 (1968) pp. 3662-3668.
- (13) C.M. Stover, *Rev. Sci. Instrum.*, 34 (1963) pp. 632-635.
- (14) K. Kanoh and K. Kawasaki, *Japanese J. of Electron.*, No.12 (1966) pp. 2172-2176.
- (15) T. Kawasaki, Z. Minowa and T. Inamatsu, *Oyo Butsuri* (a Japanese journal) 35 (1966) pp. 355-359.
- (16) T. Nitta, Z. Terada, and S. Hayakawa, *J. Amer. Ceramic Soc.*, 63 (1980) pp. 295-300.
- (17) Y. Nabeta, K. Suzuki and T. Inuzuka, *Proc. of Int. Meeting on Chem. Sensors*, edited by Seiyama et al., Elsevier Pub. Co., (1983) pp. 410-415.
- (18) T. Nitta, F. Fukushima and Y. Matsuo, pp. 387-392 of the proceedings given in reference (17).
- (19) H. Arai, S. Ezaki, Y. Shimizu, O. Shippo and T. Seiyama, pp. 393-398 of the proceedings (see ref.(17)).
- (20) F. Uchikawa, K. Miyao, H. Horii, and K. Shimamoto, pp. 445-450 of the proceedings given in ref.(17).
- (21) I. Lundström and C. Svensson, "Gas-Sensitive Metal Gate Semiconductor Devices", Chapter 1 of "Solid State Chemical Sensors" edited by J. Janata and R.J. Huber, Academic Press, INC (1985) London.
- (22) I. Lundström, S. Shivaraman, C. Svensson and L. Lundkvist, *Applied Physics Letters*, 26 (1975) pp. 55-57.
- (23) I. Lundström, S. Shivaraman, and C.M. Svensson, *J. of Appl. Physics*, 46 (1975) pp. 3876-3881.
- (24) M.C. Steele and B.A. MacIver, *Appl. Phys. Letters*, 28 (1976) pp. 687-688.
- (25) P.F. Ruths, S. Ashok, S.J. Fonash and J.M. Ruths, *IEEE Transactions of Electron Devices*, ED-28 (1981) pp. 1003-1009.
- (26) N. Yamamoto, S. Tonomura, T. Matsuoka and H. Tsubomura, *Surface Sci.*, 92 (1980) pp. 400-406.
- (27) K. Ito, *Surface Sci.*, 86 (1979) pp. 345-352.
- (28) M.S. Shivarman, I. Lundström, C. Svensson, and H. Hammarshin, *Electron. Lett.*, 12 (1976) pp. 483-484.
- (29) J.M. Ruths, S.J. Fonash, and T.E. Sullivan, *Extended Abstracts-154 the Meeting of Electrochem. Soc.*, Vol.78-2 (1978) pp. 648-

- 649.
- (30) R.S. Jachowicz and S.D. Sentuvia, J. of Sensors and Actuators, 2-2 (1981/82) p.171.
 - (31) R.S. Jachowicz, Proc. International Meeting on Chemical Sensors, (1983) Elsevier, pp. 399-404.
 - (32) G.J. Rogers, L.C. Westcott, R.A. Davies, H.O. Ali, G.H. Swallow, and E. Read, Proceedings Inter. Meet. on Chem. Sensors, Elsevier (1983) pp. 428-432.
 - (33) W.H. King Jr. Anal. Chem., 36 (1964) p. 1735 and U.S. Patent 3164004, January 5, 1965.
 - (34) S. Tahara, J. Kobayashi and S. Oka, Proceedings of Inter. Meet. on Chem. Sensors, Published by Elsevier (1983) pp. 405-409.

Chapter 13

VARIOUS OXIDES USED FOR ELECTRONIC DEVICES

13.1 PERSPECTIVE VIEW ON THE USE OF SOLID OXIDES FOR ELECTRONIC DEVICES

In this chapter, a perspective view is first given to show that a great number of oxides are used as component materials in electronic devices. Then, the procedure to make thin layers of oxides is discussed because oxides are usually used as thin layers in electronic devices. In the third section of this chapter, several electronic devices with solid oxides are introduced. The devices discussed demonstrate the application of solid state electrochemistry to metal oxides.

Generally speaking, the materials used in electronic devices are metals, semiconductors, and various inorganic compounds, including metal oxides, carbides, nitrides, and silicides. Therefore, many different materials are synthesized and the electronic devices are made with combinations of materials, usually in layered structures. Among these electronic materials, the metal oxides play an important role.

Table 13.1 shows examples of solid oxides used as electronic materials. This table was compiled from "The Encyclopedia of Functional Materials" written by Kitada⁽¹⁾ in 1984. In the previous chapter, the structure of MOS transistors was explained. The silicon oxide is used as the dielectric between the gate electrode and the channel. Alumina and other stable oxides with good heat conductivity are used in integrated circuits. SnO_2 and In_2O_3 are used as transparent conductors. SiO_2 is used as the insulator and as the dielectric in the integrated circuit. For the magnetic materials, various ferrites given in the table are used for magnetic memory devices. For optoelectronic devices, solid oxides are used as optical fibers, optical switches, and optical waveguide lenses.

In previous chapters, it was fully discussed how solid oxides are used for the chemical sensors. However, this group of sensor materials is further expanded in Table 13.2. In this table, thermosensors and infrared optical sensors are physical sensors. The change in electric resistivity of the oxides with temperature is used as the sensing principle of thermosensors. Infrared optical sensors are based upon photoelectric emission, the photoconductivity

TABLE 13.1

Examples of solid oxides used as electronic materials

Electronic materials	Solid oxide elements
Materials for IC, MOS-IC, LSI	SiO ₂ in Mo SiO ₂ Si Al ₂ O ₃ as substrate of IC PbO, In ₂ O ₃ , SiO ₂ in IC
Magnetic materials	Y-Fe ₂ O ₃ , BaO-6Fe ₂ O ₃ , MnO-ZnO-Fe ₂ O ₃ , MnO-MgO-Fe ₂ O ₃ , YFeO ₃ , YCoO ₃ , Y ₃ Fe ₅ O ₁₂ , BaM ₂ Fe ₁₂ O ₂₂ (M=Co, Zn, Mn, Ni, Fe)
Optoelectronic materials	Na ₂ O-B ₂ O ₃ -SiO ₂ , Na ₂ O-Li ₂ O-CaO-SiO ₂ for optical fibers LiNbO ₃ , LiTaO ₃ , PbTiO ₃ for optical switch CeO ₂ , Nb ₂ O ₅ , ZnO, LiNbO ₃ for optical wave- guide lens
Sensor materials	SnO ₂ , In ₂ O ₃ , ZnO, NiO, FeO, BaTiO ₃ for semiconductor gas sensors ZrO ₂ -MgO, ZrO ₂ -Y ₂ O ₃ , SrO-CeO ₂ -Yb ₂ O ₃ , Na ₂ O-11Al ₂ O ₃ , Na ₃ Zr ₂ Si ₂ PO ₁₂ for solid electrolyte gas sensors
Laser materials	Y ₃ Al ₅ O ₁₂ -Nd ₂ O ₃ , CaWO ₄ , YAlO ₃ , Al ₂ O ₃ -Cr ₂ O ₃ , Phosphate glass doped with Nd ₂ O ₃
Piezoelectric materials	PbTiO ₃ , PbZrO ₃ , LiNbO ₃ , LiTaO ₃
Ceramic superconductors	LiTi ₂ O ₄ , BaPb _{1-x} Bi _x O ₃ Perovskite of BaO-CuO-Y ₂ O ₃
Condenser	BaTiO ₃ , CaTiO ₃ , ZnTiO ₃ , SrTiO ₃ , Bi ₂ Ti ₂ O ₅ for condensers
Varistor	ZnO-Bi ₂ O ₃ for varistor
Resistor	RuO ₂ , RuO, Ru ₂ O ₃ for resistors
Others	In ₂ O ₃ -SnO ₂ for transparent conductor In ₂ O ₃ -Cu ₂ O for solar cell WO ₃ , NiO for electrochromic material BaO, CaO, SrO for oxide cathode to emit thermo-electrons

TABLE 13.2

Solid oxides used for sensor elements

Sensors	Examples of sensor elements
Thermo-sensors (Thermister)	NTC*: NiO, FeO, CoO, MnO, CoO-Al ₂ O ₃ PTC*: BaTiO ₃
Semiconductor gas sensors	SnO ₂ , In ₂ O ₃ , ZnO, WO ₃ , γ -Fe ₂ O ₃ , NiO, CoO, Cr ₂ O ₃ , LaNiO ₃ , BaTiO ₃ , TiO ₂ , CoO-MgO
Humidity sensors	Al ₂ O ₃ , P ₂ O ₅ , ZnO-Li ₂ O, NiFe ₂ O ₄ , TiO ₂ , MgCr ₂ O ₄ , Fe ₃ O ₄ , ZnO-Cr ₂ O ₃ , ZrO ₂ -MgO, SrSnO ₃ , SrTiO ₃
Infrared optical sensors	LiNbO ₃ , LaTaO ₃ , SrTiO ₃ , Ba ₂ NbNb ₅ O ₁₅
Solid electrolyte gas sensors	ZrO ₂ -MgO, ZrO ₂ -Y ₂ O ₃ , ZrO ₂ -CaO, ThO ₂ -Y ₂ O ₃ , Na ₂ O-11Al ₂ O ₃ (β -Al ₂ O ₃), SrO-CeO ₂ -Yb ₂ O ₃ , Bi ₂ O ₃ -MoO ₃ , Na ₃ Zr ₂ Si ₂ PO ₁₂

* NTC and PTC mean negative and positive temperature coefficient of electric resistivity with temperature increase, respectively.

effect, the photovoltaic effect, and the photoelectromagnetic effect. The oxides given in this table for the optical sensor are used with the photoconductivity effect.

Table 13.2 is compiled from "Dictionary of Sensors" written by Kitada⁽²⁾ in 1985.

The oxides used for gas and humidity sensors were discussed in previous chapters.

In Tables 13.1 and 13.2, the names of the electronic devices have been given first and then the various oxides used. However, the properties of the oxides can be given first and then various electronic devices can be shown. Table 13.3 is compiled from this view point and reported by Ichinose⁽³⁾ in "Advances of Functional Ceramics" in 1985.

In this table, the properties of the oxides are given at the left-hand side. The properties include, from the top, the insulating capability, the conductivity, the piezoelectric property, the semiconductivity, the magnetic property, the dielectric prop-

TABLE 13.3

Properties of solid oxides and their uses for electronic devices

Properties	Uses for devices		Examples of solid oxides used
Insulation	IC substrate		Al ₂ O ₃ , MgAl ₂ O ₄ , BeO
Conductivity	Heating elements and Lead wires		ZrO ₂ , MoSi ₂ , LaCrO ₃ , SiC Halides of Tl, Zr, Hf
Piezoelectric	Ignition device	Lighter	Pb(Zr, Ti)O ₃
	Piezoelectric filter	FM • TV	
	Surface wave device		
	Piezovibrator	Clock	Quartz, LiNbO ₃
Semiconductivity	Thermistor	Thermometer	Fe•Co•Mn•Si•O, BaTiO ₃
	Nonlinear semiconductor	Varistor	ZnO•Bi ₂ O ₃ , SiC
	Gas absorption semiconductor	Gas sensor	SnO ₂ , ZnO
Magnetic	Hard ferrites	Ferrites	(Ba, Sr)O•6Fe ₂ O ₃
	Soft ferrites	Transformer	(Zn, M)Fe ₂ O ₄ (M: Mn, Co, Ni, Mg)
		Memory device	Garnet ferrite
Dielectric	for Low frequency	Condenser	BaTiO ₃ + SnO ₂ + Bi ₂ O ₃
Ionic conductivity		Battery	β-Al ₂ O ₃ , ZrO ₂ (+ CaO, Y ₂ O ₃)

erty and the ionic property. In the center of this table is shown the kinds of electronic devices using these properties of solid oxides. Examples of the solid oxides are given on the right.

Needless to say, the industrial field of the microelectronics is now advancing very rapidly and thus the contents of Tables 13.1, 13.2, and 13.3 will change. Nevertheless, the essential parts of these tables will not change for a long time, because the oxides in the tables are chemically stable and their fabrication is generally not difficult.

In the previous chapters, the electrochemistry of solid oxides

has been intensively discussed. The scope of the discussion has included the insulating, ionic conducting and semiconducting properties in Table 13.3 but excluded the piezoelectric, magnetic and dielectric properties.

13.2 FABRICATION OF THIN FILMS OF SOLID OXIDES

The solid oxides used in electronic devices are usually in the form of thin films. The thin films are fabricated by physical vapor deposition, by chemical vapor deposition, by ion sputtering, by molecular beam epitaxy or by a combination of these methods.

These methods are reported in several proceedings⁽⁴⁾⁻⁽⁸⁾ of international meetings on solid state electrochemistry.

Among the various methods, the physical vapor deposition is most widely used to fabricate thin films of semiconductors, insulators, amorphous materials, metal leads and other components of electronic devices. Therefore, in the following discussion, only the physical vapor deposition of solid oxides is introduced. This method has been studied extensively by the present author and his coworkers.

Fig. 13.1 shows the sectional view of the vacuum chamber for physical vapor deposition. The chamber is evacuated by a diffusion pump and a rotary pump through a cold trap cooled by liquid nitrogen.

The object of the experiment by Zhang, Kobayashi, and Goto⁽⁹⁾ was to clarify the relation of the composition of the thin film, to the composition of the vaporizing source and to temperatures of both the source and the substrate, when binary oxides of $\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, and $\text{Li}_2\text{O}-\text{P}_2\text{O}_5$ are vaporized in vacuum. The industrial significance of the study lies in the potential use of the films of Li^+ conductors for thin batteries with a high energy density. This class of batteries is introduced in the next section.

During past ten years, it has been reported that amorphous solid oxides containing Li_2O exhibit a large ionic conductivity due to easy migration of Li^+ cations. Further, the thin film geometry is favored⁽¹⁰⁾⁻⁽¹³⁾ for miniaturization of devices as well as reducing the internal resistance. How to control precisely the composition of the thin films, however, has not been clarified. The object of an experiment by the author and his coworkers was to determine how to fabricate binary oxide films with precise compositions.

The experimental procedure was as follows; the complex oxide compounds $3\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}\cdot \text{P}_2\text{O}_5$ were synthesized by melting mixed chemical reagents in a platinum crucible. The melt was homog-

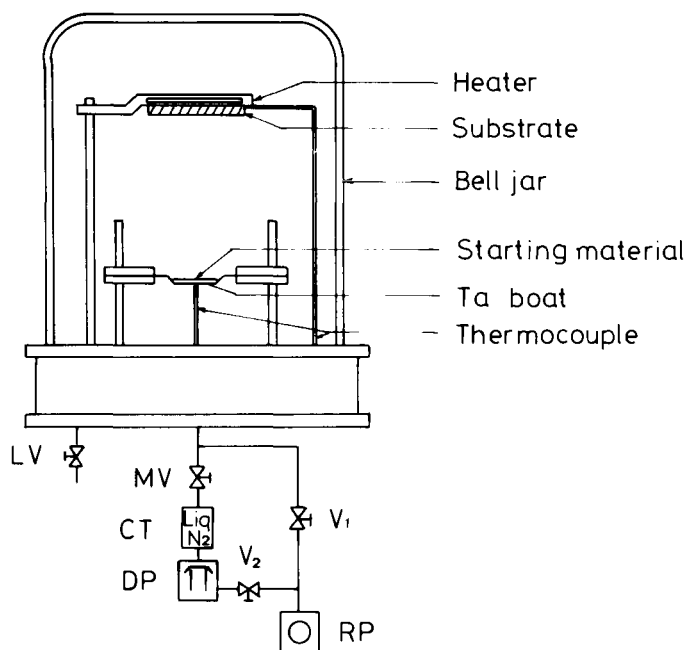


Fig. 13.1. Schematic diagram of experimental apparatus for "Physical Vapor Deposition" of binary oxide thin films (After Zhang, Kobayashi, and Goto (9) 1985).

enized for 20 hours and then quenched. The quenched oxide compounds were crushed and placed in the tantalum boat as the evaporation source. The temperature of the tantalum boat during the vaporization was precisely maintained at a constant temperature by controlling the current flowing through the boat.

Table 13.4 shows the conditions necessary to produce thin films. In the table, the starting material refers to the compounds charged into the tantalum boat as the vapor source. The temperature of the substrate was controlled by the heater attached to the backside of the substrate. The thickness of film and deposition rate were the experimental results. The thickness was measured by the "Taly Step" method. The deposition rates were calculated from the weight gain of the substrate. The evaporation quantity in the table indicates what percent of the original source by weight was vaporized.

A thin film of about one micron was determined to be completely amorphous by the X-ray diffraction analysis. The amorphous thin film of the binary oxide was imbedded in the resin with the substrate and the composition was determined by an ion microanalyzer.

TABLE 13.4

Conditions to fabricate the thin films of oxides and the experimental results (After Zhang, Kobayashi, and Goto (9) 1985)

Starting material	Initial vacuum (Torr)	Temp. of source (°C)	Temp. of substrate (°C)	Thickness of film (μm)	Deposition rate (μg/cm ² sec)	Evaporation quantity (%)
3Li ₂ O·2B ₂ O ₃	2 × 10 ⁻⁵	850	150, 400	0.8 - 1.0	0.1 - 0.2	20
Li ₂ O·B ₂ O ₃	2 × 10 ⁻⁵	850, 950, 1050	100 - 400	0.8 - 1.2	0.4 - 1.0	100
Li ₂ O·2B ₂ O ₃	2 × 10 ⁻⁵	920, 970, 1020	50 - 450	0.8 - 1.2	0.08 - 0.2	20
Li ₂ O·SiO ₂	2 × 10 ⁻⁵	1500	130	0.6	0.02 - 0.04	10
Li ₂ O·P ₂ O ₅	2 × 10 ⁻⁵	1000	400	0.8	0.13 - 0.16	10

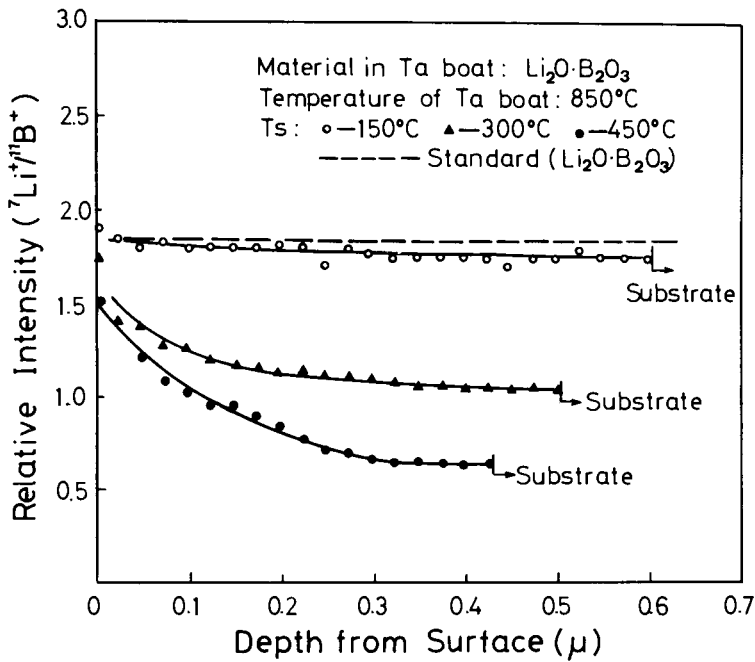


Fig. 13.2. Concentration distribution with depth for thin films of Li₂O·B₂O₃ for three substrate temperatures (After Zhang, Kobayashi, and Goto (9) 1985).

Fig. 13.2 gives the results of the analysis using an Ar^+ ion beam. The vertical axis is the relative intensity of sputtered ions of $^7\text{Li}^+$ and $^{11}\text{B}^{3+}$ and the horizontal axis is the depth from the surface of the thin film in microns. The position of the substrate is shown at the right hand side. The absolute composition is obtained by using the standard samples with known composition. The results in this figure tell us that the content of Li_2O in the film is increased by decreasing the temperature of the substrate. The temperature and the composition of the vaporizing source are fixed.

Also it is noted that there is a small concentration gradient in the oxide films when the temperature of the substrate is high. Thus, in the following discussion, the composition refers to that composition close to the substrate.

Fig. 13.3 shows the relation between the composition of the thin film and the temperature of the vaporizing sources. The vaporizing sources are from two different compositions. From this figure, it is noted that the composition of the thin film is always very

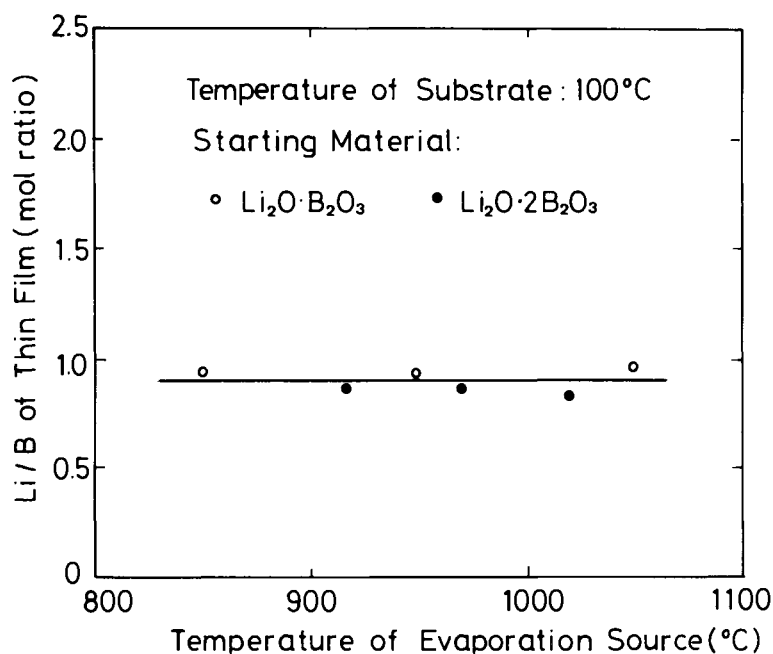


Fig. 13.3. Dependence of composition of thin film on temperature of evaporation source for two compositions of the vapor source (After Zhang, Kobayashi, and Goto (9) 1985).

close to $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ even with changes in the temperature of the source and its composition.

Fig. 13.4 indicates the relation between the composition of thin film and the temperature of the substrate for two vaporizing sources with different composition. The increase of the substrate temperature causes a decrease of Li_2O content in the oxide film. The composition of the film has no relation to that of the vaporizing source when it is changed from $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ to $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$.

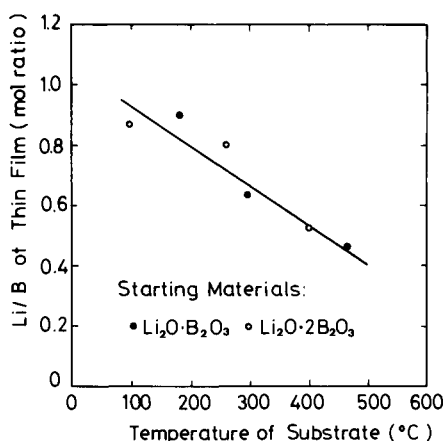


Fig. 13.4. Dependence of composition of thin film on temperature of substrate for two different compositions of the vapor source (After Zhang, Kobayashi, and Goto (9) 1985).

Fig. 13.5 shows the relation between the composition of the thin film and that of the vaporizing source expressed in gram-atom ratios of Li^+ and B^{3+} . The experimental results are given for three different temperatures of the substrate. Also, the results of Levasseur, Kballa, and Hagenmuller⁽¹⁴⁾ and Ito, Miyauchi, and Oi⁽¹⁵⁾ are given for comparison. The results in this figure tell us that the composition of the thin film is nearly constant when the vaporizing source contains Li_2O less than 0.5 mole fraction. The content of Li_2O in the film increases with a decrease in the temperature of the substrate in agreement with the results shown in the previous figure. When the source of the starting material contains more than 0.5 mole fraction of Li_2O , its content in the film increases as shown in the figure. The broken line crossing the diagram at a 45° angle represents the congruent relation between

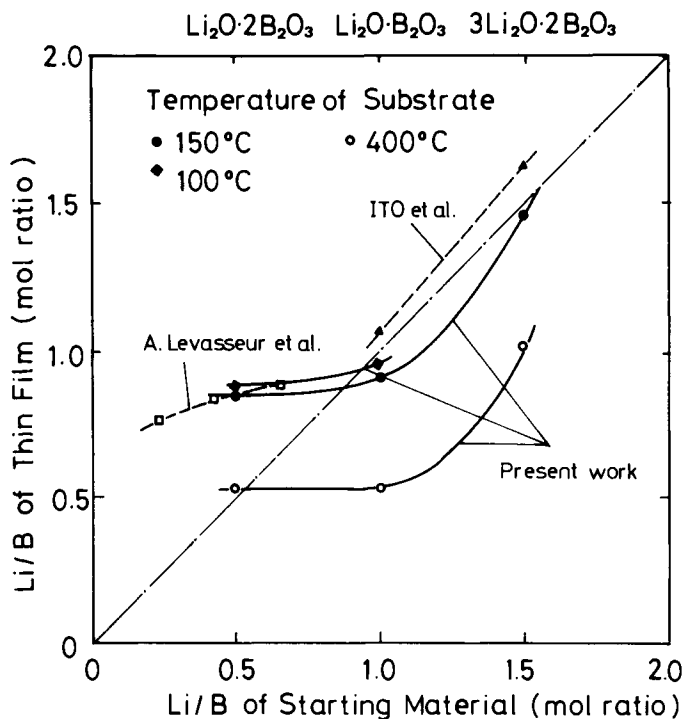


Fig. 13.5. Relationship between the compositions of thin film and starting material expressed by the ratio of Li content of B content (After Zhang, Kobayashi, and Goto (9) 1985).

the composition of the film and that of the source.

Fig. 13.6 shows the ratios of the compositions of the thin films and of the sources for three cases of the vaporizing sources of $\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3$, $\text{Li}_2\text{O}\cdot\text{P}_2\text{O}_5$, and $\text{Li}_2\text{O}\cdot\text{SiO}_2$. In this figure, the composition is expressed by the ratio of the gram-atom fractions of Li^+ against B^{3+} , P^{5+} , or Si^{4+} . Therefore, when the value of the vertical axis is 1.0, the composition of the thin film is equal to that of the source. According to this figure, the height of the vertical line for $\text{Li}_2\text{O}\cdot\text{B}_2\text{O}_3$ film is 0.85, which means the film has less Li_2O than the source. It is 2.74 for case of $\text{Li}_2\text{O}\cdot\text{P}_2\text{O}_5$ and thus, the film is much richer in Li_2O . In case of $\text{Li}_2\text{O}\cdot\text{SiO}_2$, the vertical line is 35.1 and thus, the film is extremely enriched by Li_2O . At the top of three vertical lines, temperatures of the source and the substrate are given.

In the above, the results of observations on the composition of the thin films of the oxides have been introduced. The intention

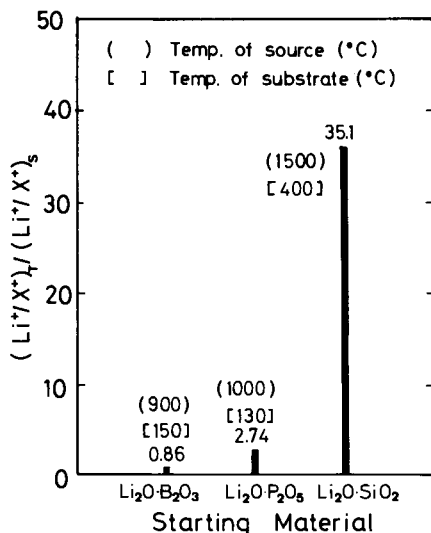


Fig. 13.6. Comparison of ratios of $(Li^+/X^+)_T$ of thin film ($X^+ = B^+, P^+, Si^+$) to that of starting material where (Li^+/X^+) is intensity ratio determined by an ion microprobe analyzer (After Zhang, Kobayashi, and Goto (9) 1985).

of this introduction is to demonstrate that the fabrication of thin films is by no means a simple phenomenon. Physical vapor deposition is generally considered to be the most simple method to fabricate thin films. The above observations suggest that the phenomenon should be more carefully studied, even for physical vapor deposition, in order to control precisely the composition of the film and thus its electronic and ionic properties.

To interpret the results shown in Figs. 13.3, 4, 5, and 6, one should know the absolute values of partial pressures of various gaseous species. Also, one should know the vaporization coefficients and the sticking coefficients of the various species. Otherwise, it can not be known why the films have taken the compositions shown in the figures.

Fig. 13.7 shows the equilibrium partial pressures of various gaseous species on $0.5Li_2O-0.5B_2O_3$ melt under an oxygen pressure of 10^{-8} atm. This figure was reported by Zhang, Yahagi, and Goto⁽¹⁶⁾ with other thermodynamic calculation on fused Na_2O-SiO_2 and $Na_2O-P_2O_5$ systems.

The oxygen pressure affects the pressures of Li, LiO and Li_2O_2 , and it was assumed to be 10^{-8} atm, which is not much different from

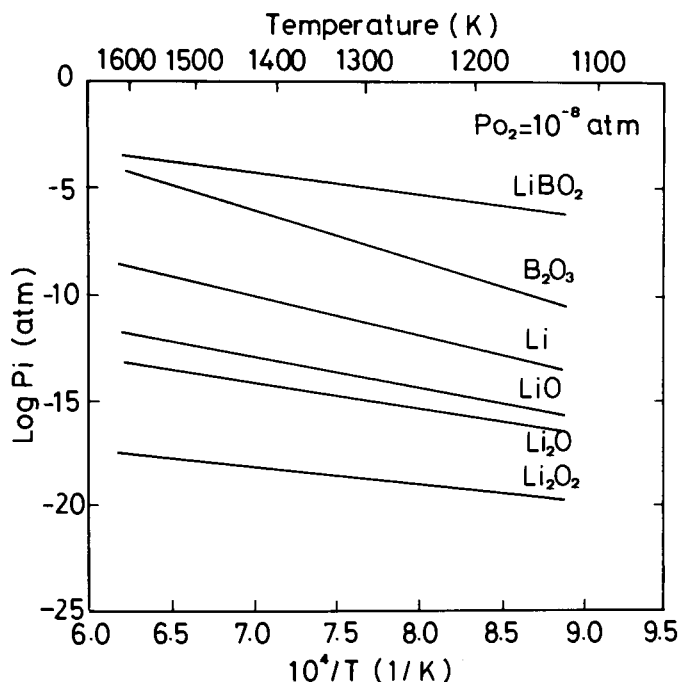


Fig. 13.7. Temperature dependence of partial pressures estimated for vapor species over molten $0.5\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3$ (After Zhang, Yahagi, and Goto (16) 1985).

that in ordinary vacuum chambers.

The calculation is based on the activities of Li_2O , and B_2O_3 in the melt. The procedure for the calculation is given in reference (16). According to the calculated results, the most predominant vapor species is LiBO_2 , in the composition range of 0 ~ 0.5 mole Li_2O . Therefore, the nearly constant composition of the thin film, shown in Fig. 13.5, can be interpreted from this predominant vapor species.

However, this is only an interpretation. The phenomenon of vaporization and condensation seems to be more complicated.

Fig. 13.8 shows the effusion of gas molecules from the opening of the Knudsen cell (left) and the free vaporization of the same molecules from the free surface of the liquid. The important characteristic of the Knudsen cell is its small hole on the top whose diameter must be smaller than the mean free path of the equilibrium vapor in the cell.

According to the gas molecular kinetics, the number of molecules

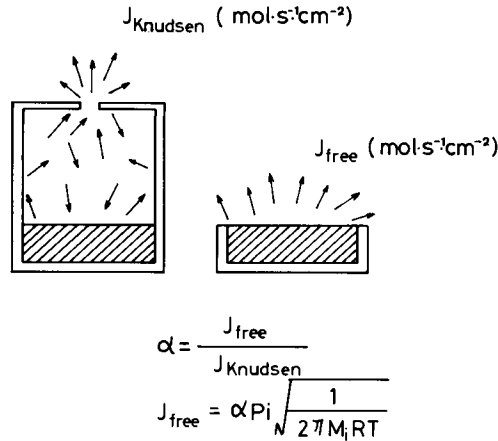


Fig. 13.8. A schematic picture to show direction of molecules in the Knudsen cell and for the case of free vaporization. α is defined as the vaporization coefficient.

hitting the unit area of the surface of the condensed phase per second is expressed by

$$J = P \sqrt{\frac{1}{2\pi mkT}} = 3.51 \times 10^{22} P_{\text{torr}} \sqrt{\frac{1}{MT}} \quad (13-1)$$

where J is given by number of molecules per second per cm^2 , P is pressure, m is mass of a single molecule, k is Boltzmann constant, T is absolute temperature, P_{torr} is the pressure expressed by torr (mmHg) and M is the molecular weight.

When some fraction of the molecules hitting the surface is condensed on the surface, the number of the condensing molecule is,

$$J_C = \alpha_C P \sqrt{\frac{1}{2\pi mkT}} \quad (13-2)$$

where α_C is called as the condensation coefficient.

When equilibrium is attained between the gas phase and its condensed phase, the rate of the condensation of Eq. (13-2) must be equal to the rate of vaporization, or

$$J_C = J_V, \quad (13-3)$$

where J_V is the rate of vaporization.

Inserting Eq. (13-2) into Eq. (13-3), one can have

$$J_v = \alpha_c P \sqrt{\frac{1}{2\pi mkT}} \quad (13-4)$$

Because this equation gives the rate of vaporization, α_c , is also called as the vaporization coefficient, usually expressed by α_v .

The vaporization coefficient is usually believed to be exactly equal to the condensation coefficient as long as the phenomenon is taking place under completely isothermal conditions.

As mentioned above, when the temperature of the gas molecules is exactly equal to the temperature of its condensed phase, the vaporization or condensation coefficient can be clearly defined. However, in the case of PVD, the temperature of the substrate is different from that of the hitting gas molecules. Under such conditions, it is usually very difficult to estimate the true surface temperature of the thin film on the substrate. Therefore, only an apparent "sticking coefficient" is sometimes used. However, its physical meaning is ambiguous. Thus, in the following section only the vaporization coefficient will be discussed.

Table 13.5 lists the enthalpy, entropy, and vaporization coefficient for various solid compounds⁽¹⁷⁾ (Reproduced from "Thin Film Handbook"). In the table, ΔH° and ΔH^* refer to the enthalpy of the equilibrium vaporization and the free vaporization, respectively.

The vaporization coefficient is given as $\bar{\alpha}_v$. From the table, the flux of the Knudsen effusion and of the free vaporization are given by

$$J_{\text{Knudsen}} = \left[\exp\left(\frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \right) \right] \sqrt{\frac{1}{2\pi mkT}} \quad (13-5)$$

and

$$J_{\text{free}} = \left[\exp\left(\frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \right) \right] \sqrt{\frac{1}{2\pi mkT}} \quad (13-6)$$

In the equations, the exponential terms in brackets, $[]$, are equal to P and $\alpha_c P$ in Eq. (13-1) and Eq. (13-2), respectively.

The lower part of Table 13.5 gives the vaporization coefficient for various oxides, such as ZnO , Al_2O_3 , Ga_2O_3 , In_2O_3 , SnO_2 , As_2O_3 , and As_4O_6 . The coefficients for these oxides are very much smaller than 1.0. The vaporization coefficients for LiBO_2 , B_2O_3 , LiO , Li_2O , and Li_2O_2 are not known for the liquid binary system of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$. However, from Table 13.5, the coefficients would be much smaller than unity, because the nature of bondings in solid oxides would not essentially change by melting them. The composition of the thin

TABLE 13.5

Enthalpy, entropy, and vaporization coefficient of various solids
(Reproduced from "Thin Film Handbook" (17) 1983)

Materials	Reactions for vaporization	Equil. vapor pressure		free vaporization		vaporization coefficient $\bar{\alpha}_v$	Temperature [K]
		ΔH_T° [$\frac{\text{kcal}}{\text{mol}}$]	ΔS° [eu]	ΔH_T^* [$\frac{\text{kcal}}{\text{mol}}$]	ΔS^* [eu]		
Graphite	$\text{C(s)} \rightarrow \Sigma \text{C}_i(\text{g})$	161(s) _{0*}		170 ₀		0.15	2400
P(red)	$4\text{P(s)} = \text{P}_4(\text{g})$	28(g)	49.4	52		$\sim 10^{-6}$	600
As	$4\text{As(s)} = \text{As}_4(\text{g})$	33.1(g) ₅₅₀	38.0	43.8 ₅₅₀	37.6	5×10^{-5}	550
Sb	$4\text{Sb(s)} = \text{Sb}_4(\text{g})$	47.4(g) ₆₅₀	35.7	49.5 ₆₅₀	35.5	0.2	650
I ₂	$\text{I}_2(\text{s}) = \text{I}_2(\text{g})$	14.96(g)		12.06		$\sim 10^{-2}$	217~308
AlN	$2\text{AlN(s)} = 2\text{Al(g)} + \text{N}_2(\text{g})$	153(s) ₂₉₈				$7 \times 10^{-4} \sim 3 \times 10^{-3}$	1600~1900
BN	$2\text{BN(s)} = 2\text{B(s)} + \text{N}_2(\text{g})$	60.2(s) ₂₉₈				$< 6 \times 10^{-3}$	1850~2160
GaN	$2\text{GaN(s)} = 2\text{Ga(l)} + \text{N}_2(\text{g})$	47(g) ₁₃₀₀		39 ₁₃₀₀		< 0.1	1200~1400
	$2\text{GaN(s)} = 2\text{Ga(g)} + \text{N}_2(\text{g})$	58(g) ₁₃₀₀		73 ₁₃₀₀		$\sim 10^{-3}$	1200~1400
Be ₃ N ₂	$\text{Be}_3\text{N}_2(\text{s}) = 3\text{Be(g)} + \text{N}_2(\text{g})$	361(s) ₁₈₀₀	124	409 ₁₈₀₀	~ 60	$\sim 10^{-5}$	1640~1960
CdS (single)	$2\text{CdS(s)} = 2\text{Cd(g)} + \text{S}_2(\text{g})$	75.2(s) ₁₀₀₀	45.4	75.3 ₁₀₀₀	38	$\sim 10^{-1}$	873~1133
CdSe (single)	$2\text{CdSe(s)} = 2\text{Cd(g)} + \text{Se}_2(\text{g})$	72.3(s) ₁₀₀₀	46.4	83.8 ₁₀₀₀	47	$\sim 10^{-1}$	873~1133
ZnO	$2\text{ZnO(s)} = 2\text{Zn(g)} + \text{O}_2(\text{g})$	111(s)	48	132	45	$\sim 10^{-3}$	~ 1400
Al ₂ O ₃	$\text{Al}_2\text{O}_3(\text{s}) \rightarrow \text{Al(g)}, \text{O}, \text{AlO} \dots$					0.3	2318 (at mp)
Ga ₂ O ₃	$\text{Ga}_2\text{O}_3(\text{s}) \rightarrow \text{Ga(g)}, \text{GaO}, \text{Ga}_2\text{O} \dots$					0.3	2068 (at mp)
In ₂ O ₃	$\text{In}_2\text{O}_3(\text{s}) \rightarrow \text{In(g)}, \text{In}_2\text{O}, \text{O}_2 \dots$	119(s) ₀				0.3	1500
SnO ₂	$2\text{SnO}_2(\text{s}) = 2\text{SnO(g)} + \text{O}_2$	143(s) ₂₉₈				< 0.1	1239~1485
As ₂ O ₃	$2\text{As}_2\text{O}_3(\text{s}) = \text{As}_4\text{O}_6(\text{g})$	24.2(g)	50	55.5	~ 74	$10^{-10} \sim 10^{-4}$	373~573
As ₄ O ₆	$\text{As}_4\text{O}_6(\text{s}) = \text{As}_4\text{O}_6(\text{g})$	24.9(g)		29.8		0.15(328K)	$< \sim 453$
NH ₄ Cl	$\text{NH}_4\text{Cl(s)} = \text{NH}_3(\text{g}) + \text{HCl(g)}$	39.5	61	27.0	4	3×10^{-5}	~ 600

* The small numbers in the table mean absolute temperature[K].

films shown in Figs. 13.3, 4, 5, and 6 would be naturally affected by the vaporization coefficients of various gaseous species.

However, the situation is complicated because the sticking coefficients of various gaseous species are also not known. Initially, the atoms or molecules from the evaporation source impinge on the substrate. Some are spontaneously reflected while the rest stick to the substrate. When the substrate temperature is high, some molecules that stick to the surface may re-evaporate a short time later.

Because the physical vapor deposition phenomenon is so complex, as discussed above, the composition of the oxide films shown in the figures can not be clearly interpreted at present.

The vaporization coefficient, α_v , can be expressed as follows, according to the absolute rate theory of vaporization⁽¹⁷⁾;

$$\alpha_v = \frac{F_I^*}{F_{Ig}} \exp\left[-\frac{E_o}{kT}\right] \quad (13-7)$$

where F_I^* is the internal partition function of the activated complex and F_{Ig} is the internal partition function of the gaseous molecule. E_o is the activation energy and k is the Boltzmann constant.

Fig. 13.9 illustrates the activated state and the gaseous molecule. The lower picture shows the energy of the molecule as a

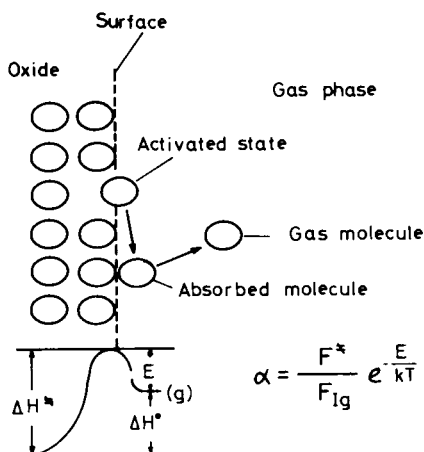


Fig. 13.9. A picture to show the mechanism of vaporization of a molecule with the vaporization coefficient, α , defined by the equation in the right hand side.

function of distance from the surface. In this picture, $\Delta H^{\ddagger}$ and ΔH° are equal to $\Delta H^{\ddagger}$ and ΔH° in Eqs. (13-5) and (13-6). The activation energy, E , can be considered nearly equal to E_0 of Eq. (13-7).

The above is a comment to demonstrate that the formation of thin films is a rather complex phenomenon. Nevertheless, many electronic devices are fabricated by combination of various technique. At the end of this section, as an example, the fabrication process will be introduced for the case of an electronic device, called an inverter, composed of two MOS transistors.

According to Ito and Ito⁽¹⁸⁾, the fabrication proceeds as follows. Fig. 13.10 shows how to make the MOS-IC. The four pictures are the sectional view of a p-type silicon wafer about 50 microns in length. First, a layer of about 100 Å of SiO_2 is formed by the dry oxidation of a silicon wafer at 1000°C and then a layer of about 100 Å of Si_3N_4 is formed at 650-900°C by CVD of

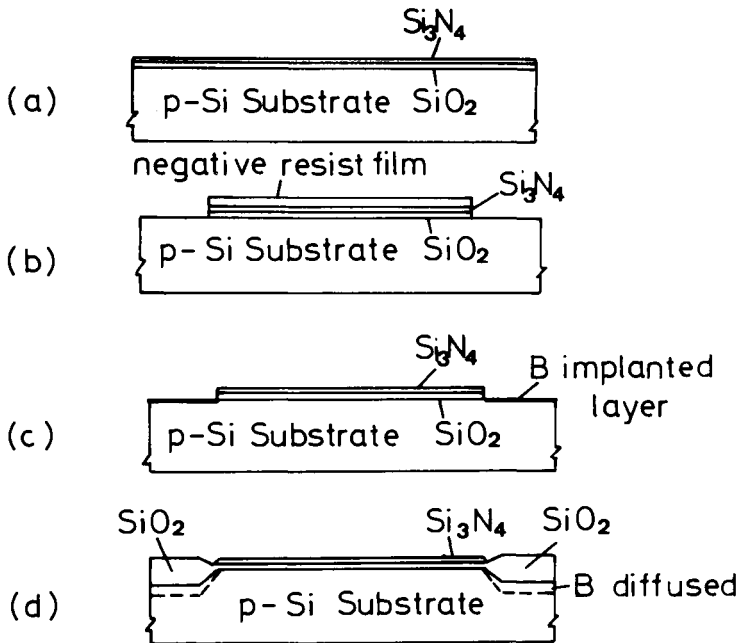
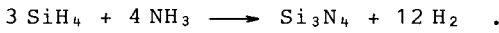


Fig. 13.10. Thin-layer processing to make functional layers on silicon wafer for MOS type transistor (After Ito and Ito (18) 1983).

The top figure marked by (a) shows the section after these processes.

The second figure marked by (b) shows the section after etching off Si_3N_4 and SiO_2 on the field region for insulation.

The ion implantation of Boron is made on the field region to avoid the induced "MOS" structure in this field. The third picture marked by (c) shows the section after the ion implantation.

Then, the field region is insulated by an SiO_2 film of about $1\text{ }\mu\text{m}$, which is produced by wet oxidation of silicon at 1100°C for 2 hours.

By repeating these processes, combined with local etching, the MOS-IC is finally produced after a total of 24 steps.

Fig. 13.11 is the sectional view of the IC of two MOS-transistors: One, at the left, is a depletion transistor and another, at the right, is an enhancement transistor. This IC is an inverter, which is an element of a logic circuit. The poly-crystal silicon is used as the metal electrode in this MOS-IC.

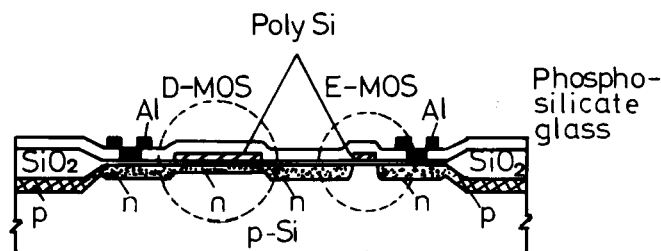


Fig. 13.11. Sectional view of an inverter with two MOS transistors (After Ito and Ito (18) 1983).

The fabrication procedure is changing with the rapid development of micro-electronic technology. Thus, the above should be understood only as an example used in the early 1980's.

If one examines carefully the sectional structure, he can find the interfaces of three phases, Al/ SiO_2 , poly Si/phospho-silicate glass and Si/ SiO_2 .

Because several steps of heating are involved in manufacturing the MOS-IC, it seems quite natural to expect electrochemical reactions at the interfaces. In fact, Iwata and his coworkers⁽¹⁹⁾⁻⁽²²⁾ have reported the experimental results on the reactions at the interfaces in the MOS-structure by using ESCA.

Books published on microelectronic devices are given at the end of this chapter for further information⁽²³⁾⁻⁽²⁸⁾.

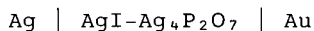
The author believes the electrochemical properties of the oxides used in electronic devices are important properties that are related to the rate of the contamination by impurities during processing as well as the rate of deterioration of the devices by moisture during their use.

13.3 APPLICATIONS OF SOLID STATE ELECTROCHEMISTRY OF OXIDES TO VARIOUS ELECTRONIC DEVICES

The electrochemical properties of solid oxides can be used in producing advanced electronic devices, such as small-size batteries, solid state timers, potential memory cells, variable resistors and display devices. These devices have been extensively developed by Ikeda and Tada⁽²⁹⁾ of Sanyo Electric Company, Kobe, Japan.

Electrochemical timing cell (Couliode)

Fig. 13.12 is the sectional view of the timer device, named "Couliode". The cell can be expressed by



where the solid electrolyte, $\text{AgI-Ag}_4\text{P}_2\text{O}_7$, may be replaced by AgI-RbI or $\text{AgI-Ag}_2\text{S-HgI}$. The charge carrier is exclusively Ag^+ .

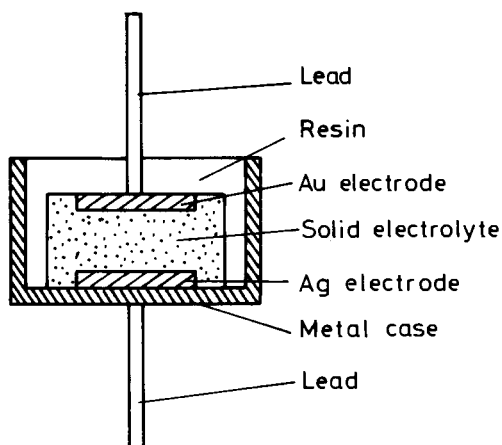


Fig. 13.12. The internal structure of Couliode (After Ikeda and Tada (29) 1980).

When electrons are supplied externally to the Au electrode, the cell is charged and silver is deposited on the Au electrode. When the current flow is reversed, the cell is discharged with a decrease in the amount of silver on the Au electrode. The current flows in both directions to satisfy Faraday's law.

When the cell is further discharged, the silver on the Au electrode is exhausted and the overpotential becomes suddenly very large due to the polarization of the Au electrode. The relation between the terminal voltage of this device and time is given in Fig. 13.13.

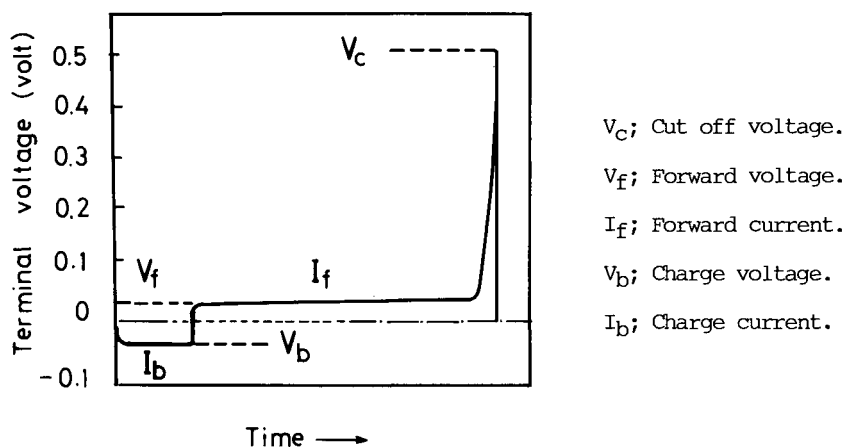
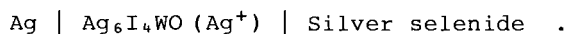


Fig. 13.13. Charge and discharge characteristic for Couliode (After Ikeda and Tada (29) 1980).

This sudden change in the terminal voltage can be used for switching and the interval of the discharge can be used for timing purposes. This device is produced commercially under the name "Couliode". It is only a few millimeters in diameter.

Electrochemical potential memory cell (Memoriode)

The potential memory cell can be expressed by



In this Galvanic cell, the activity of silver in silver selenide is controlled by the nonstoichiometric composition of the selenide. The electromotive force, E , is given by

$$E = - \frac{RT}{F} \ln a_{Ag} \tag{13-8}$$

where a_{Ag} is the activity of silver in the selenide.

The performance of this device can be explained by three separate processes: charging, holding, and discharging as shown in Fig. 13.14.

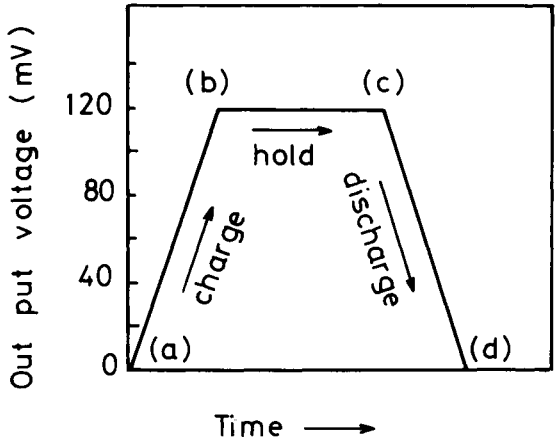


Fig. 13.14. Charge and discharge characteristics for Memoriode (After Ikeda and Tada (29) 1980).

During charging, the voltage, E , changes in proportion to the coulombs of the current externally supplied. When the charging is stopped, the voltage E is memorized for a long period. The potential memory device has been on market with the name "Memoriode". It is only a few millimeters in diameter.

Fig. 13.15 shows the sectional view of two types of the memoriode with two and three terminals to meet various requirements. The three terminal type has a reference electrode to detect the exact potential.

Table 13.6 shows the electrical characteristics of the six types of the commercial memoriodes. The frequency dependence is small for various input currents and an accuracy of ± 1 percent was achieved even at 1 MHz. The life-test characteristics show hardly any capacitance charge in more than 10^6 cycles of use, indicating a very high reliability.

These devices can be used as timers in integrating equipment and as automatic control units.

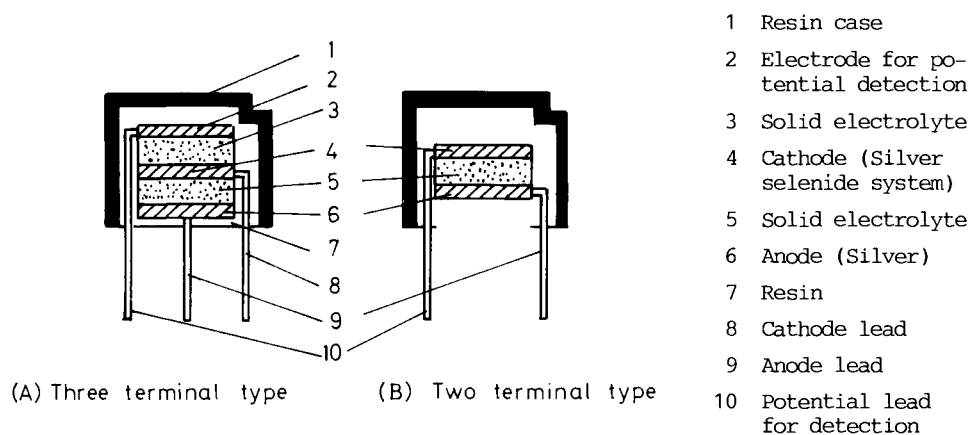


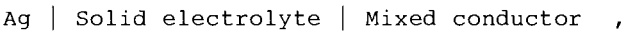
Fig. 13.15. The internal structure of Memoriode (After Ikeda and Tada (29) 1980).

TABLE 13.6 Ratings and electrical characteristics of Memoriode (After Ikeda and Tada (29) 1980)

Parameter	Type					
	MD-1B3	MD-1B2	MD-5C3	MD-5C2	MD-50E3	MD-50E2
Capacitance [μAh]	1	1	5	5	50	50
Capacitance tolerance [%]	± 15	+	+	+	+	+
Output voltage range [mV]	+120 0	+100 -100	+120 0	+100 -100	+120 0	+100 -100
Input current (max.) [mA]	10	10	20	20	40	40
Overvoltage (max.) [mV]	0.2 (1mA)	0.5 (0.1mA)	0.5 (2mA)	0.8 (0.1mA)	0.8 (2mA)	1 (0.1mA)
Change in holding voltage after 48hr. (max.) [mV]	± 0.3	+	+	+	+	+
Temperature coefficient of holding voltage (max.) [$\mu\text{V}/^\circ\text{C}$]	-10 ~ +40	± 25	-10 ~ +40	± 25	-10 ~ +40	± 25
Operating temperature range [$^\circ\text{C}$]	-20 ~ +60					
Storage temperature range [$^\circ\text{C}$]	-40 ~ +85					
Dimensions [mm]	10×7×8	10×7×8	15×11×12	15×11×12	20×16×13	20×16×13

Electrochemical variable resistor cell

The variable resistor cell can be expressed by



where the mixed conductor has both partial conductions due to migrations of both electrons and ions, as given in Table 13.7.

The cell structure and basic characteristics are shown in Fig. 13.16 and Fig. 13.17.

This device has a structure similar to the memoriode but it is different in that the device has two electrodes in contact with

TABLE 13.7
Silver ion mixed conductors (After Ikeda and Tada (29) 1980)

Substance	Temperature [°C]	Ionic conductivity [Ωcm] ⁻¹	Electronic conductivity [Ωcm] ⁻¹
(Ag ₂ Se) _{0.925} (Ag ₃ PO ₄) _{0.075}	25	4.2×10^{-1}	1.6×10^3
(Ag ₂ S) _{0.69} (Ag _{1.7} Te) _{0.285} (Ag ₄ P ₂ O ₇) _{0.025}	25	1.6×10^{-1}	8.5×10^2
(Ag ₂ S) _{0.50} (Ag _{1.7} Te) _{0.45} (Ag ₃ PO) _{0.05}	25	2.5×10^{-1}	4.3×10^2

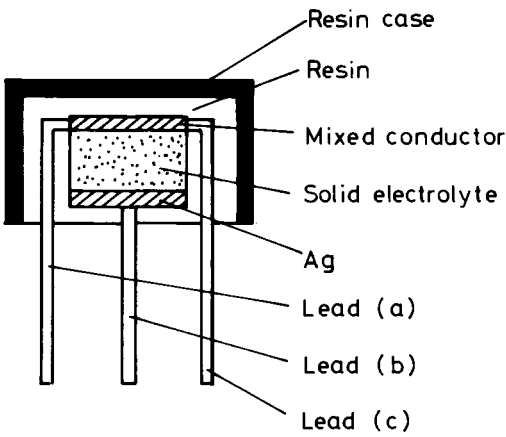


Fig. 13.16. The internal structure of variable resistor cell (After Ikeda and Tada (29) 1980).

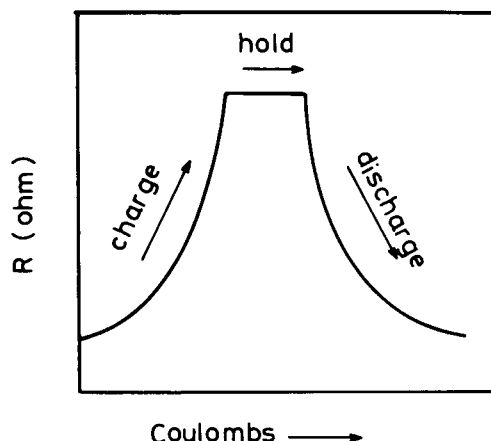


Fig. 13.17. Characteristics of the variable resistor cell (After Ikeda and Tada (29) 1980).

the mixed conductor. The resistance of the mixed conductor is controlled by the nonstoichiometric composition, which can be intentionally changed by the external current supply. This device functions for both integrating and memorizing.

Electrochemical switching device

The switching device is expressed by

Ag | Solid electrolyte | Mixed conductor .

This device has the same structure as the variable resistor cell but the upper two electrodes have point contacts with the mixed conductor, as shown in Fig. 13.18.

Fig. 13.19 shows the discharge characteristics. After the cell is overcharged, the mixed conductor contains a much larger quantity of silver. During the discharge of the overcharged cell, the resistance between lead a and b, expressed by R_{ab} , shows almost no change until the final high switching voltage caused by the depletion of movable silver ions in the mixed conductor.

This device has the unique function of integrating and memorizing the quantity of electricity with a very high switching voltage. Therefore, the device is suitable for indicating warranty time, maintenance time, and end-of-life time.

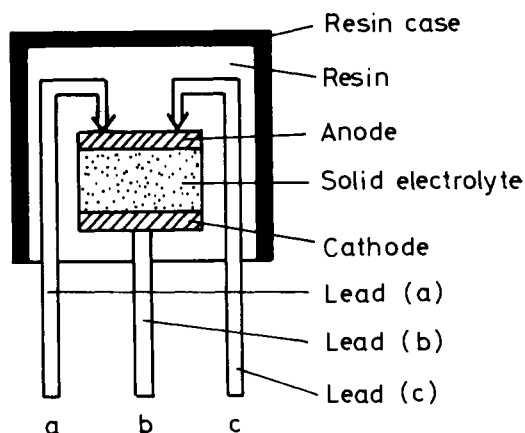


Fig. 13.18. The internal structure of the switching cell (After Ikeda and Tada (29) 1980).

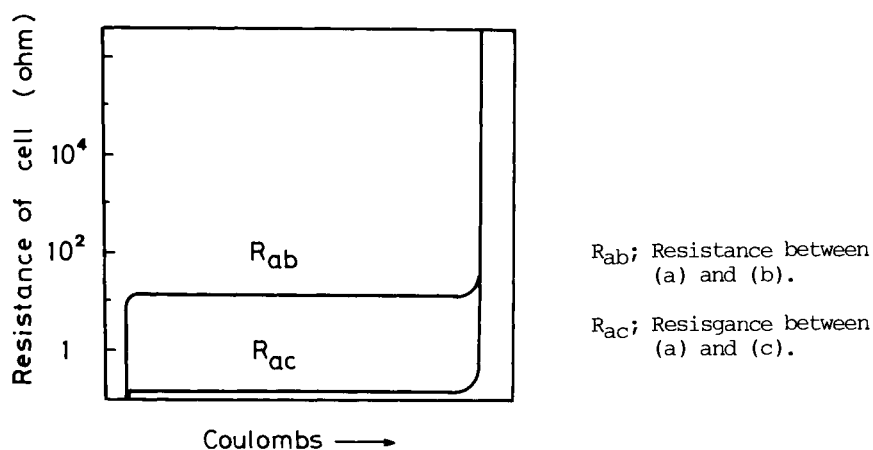
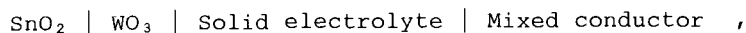


Fig. 13.19. Discharge characteristics for the switching cell (After Ikeda and Tada (29) 1980).

Electrochemical display device

The display device can be expressed by



where SnO_2 is the transparent-electrode conductor.

The structure of the display device is shown by Fig. 13.20. When cations and electrons are injected into WO_3 , coloration takes place.

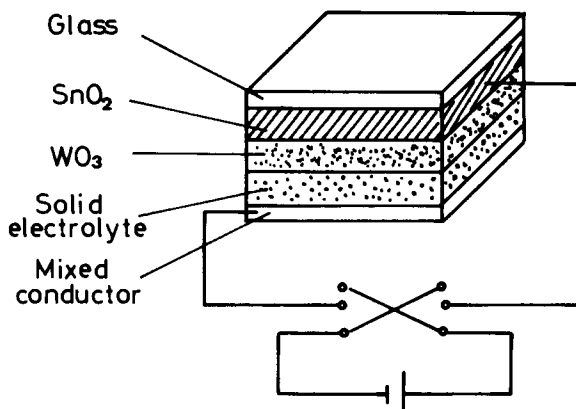
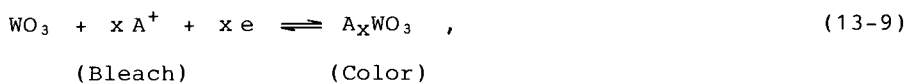


Fig. 13.20. Schematic diagram of the electrochromic display (After Ikeda and Tada (29) 1980).

When the current is reversed, it is bleached. This change may be described by



where A^+ stands for Li^+ , Na^+ , H^+ , Ag^+ , or K^+ .

This display device has the features of no optical angle and of low power consumption.

Solid state batteries with high energy density

In the 1970's, various types of small solid state batteries operatable at room temperature, were investigated. These batteries were designed for use as power sources for electronic devices and implantable cardiac pacemakers.

Among many studies, the investigations by Owens and his coworkers⁽³⁰⁾⁻⁽³²⁾ and by Liang and his coworkers⁽³³⁾⁻⁽³⁶⁾ have contributed to the development of reliable commercial batteries for these purposes.

Table 13.8 gives a list of the pacemaker batteries. The battery of $\text{Li}|\text{LiI}|\text{I}_2(\text{PVP})$ has been used in more than 300,000 units in U. S. A. between 1975 and 1980⁽³²⁾.

In all of the electrolytes in Table 13.8, the cation conductor and the electrode reactions may be represented as

TABLE 13.8

Lithium pacemaker batteries (After Owens (32) 1980)

Cell system	Electrolyte	Cell voltage [V]	Projected energy density** [wh/cc]
Li/I ₂ (PVP)*	LiI	2.8	0.5 ~ 0.8
Li/Br ₂ (PVP)	LiBr	3.5	1.25
Li/PbI ₂ , PbS	LiI(Al ₂ O ₃)	1.9	0.49
Li/Ag ₂ CrO ₄	LiClO ₄ in Org. solvent	3.4	0.5 ~ 0.7
Li/CuS	Li salts in Org. solvent	2.1	0.6
Li/SOCl ₂	LiAlCl ₄ in SOCl ₂	3.6	0.9

* PVP is poly-2-vinylpyridine.

** Values are projected because complete discharges at application rates are not completed.



Thus, the virtual cell reaction is



This cell reaction yields an open circuit potential of 2.803 Volts at 37°C in the human body.

The cathode is formed by combining I₂ with poly-2-vinylpyridine to form a polyphase, plastic product containing both a charge transfer complex PVP-I₂ and elemental I₂. Two important modifications to the cathode resulting from the addition of PVP are the decrease in electrical resistivity to 10³ Ωcm and an increase in plasticity of the cathode permitting ease of manufacture.

In Table 13.8, the LiI(Al₂O₃) electrolyte is also shown. This was developed by Liang and Barnette⁽³⁴⁾, in 1976. This electrolyte contains about 40mole% of a high surface area Al₂O₃ dispersed throughout the salt phase.

The conductivity is shown by Fig. 13.21 as reported by Liang et al.⁽³⁵⁾. The conductivity at 37°C is about 10⁻⁴ (Ωcm)⁻¹, 100 times more conductive than pure LiI.

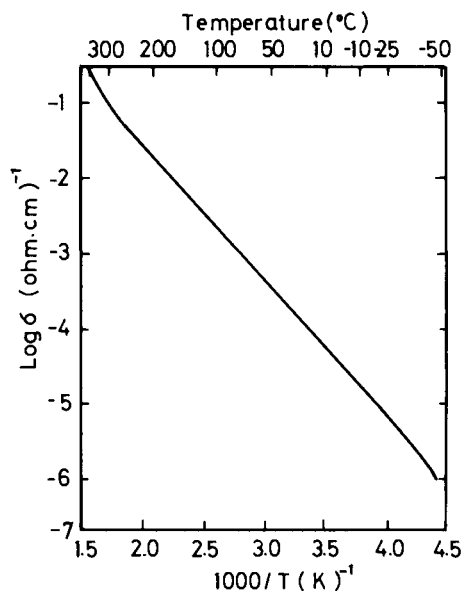
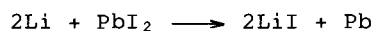
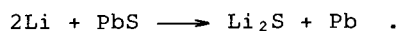


Fig. 13.21. Ionic conductivity of $\text{LiI}(\text{Al}_2\text{O}_3)$ as a function of temperature (After Liang et al. (35) 1978).

The cell reactions are



and



The major advantage of this cell is the absence of self-discharge losses. There are no volatile components in the cell and the electronic conductivity of the electrolyte is negligible.

The cells stored at 105°C for seven months, at 95°C for one year and at 25°C for two years, exhibited no change in discharge characteristics⁽³⁴⁾.

Fig. 13.22 shows the structure of the cardiac pacemaker cell developed by Liang⁽³⁶⁾. This is Model WG755 and has the following specifications:

Nominal dimension: 33mm × 9mm × 40mm
 Nominal weight : 33 grams
 Nominal volume : 9.5 cm³
 Nominal voltage : 2.8 V open circuit

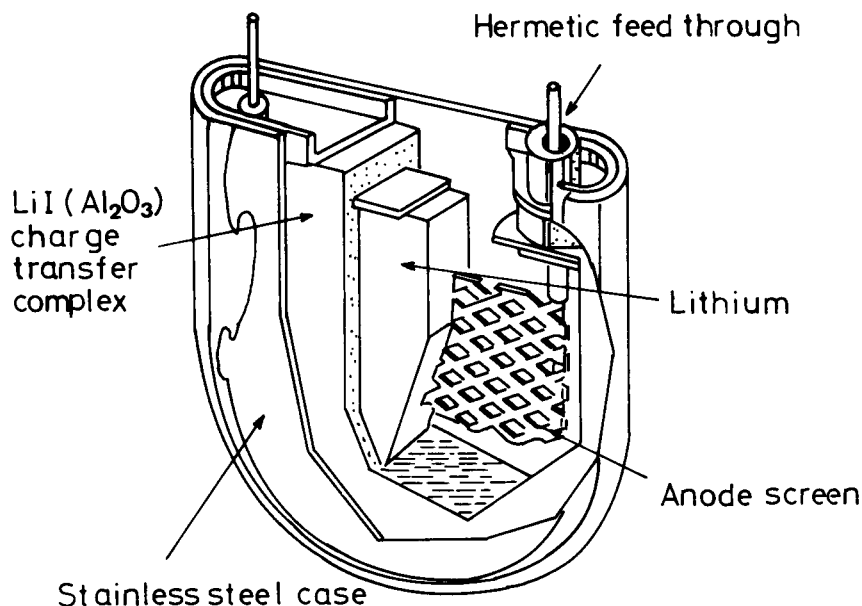


Fig. 13.22. Model WG755 $\text{Li}/\text{I}_2(\text{poly-2-vinylpyridine})$ cardiac pacemaker cell (After Liang (36) 1980).

Rate capacity	: 3 Ah
Rate current	: $30 \mu\text{A}$
Energy	: 7.5 Wh $\left\{ \begin{array}{l} \text{Calculated at 2.5 V mid-life} \\ \text{loaded voltage} \end{array} \right\}$
Energy density	: 227 Wh/kg $\left\{ \begin{array}{l} \text{Calculated at 2.5 V mid-life} \\ \text{loaded voltage} \end{array} \right\}$ 0.7 Wh/C

The total capacity of the cell is 3 Ah. Therefore, it would require a period of more than 15 years to complete the discharge at about $20 \mu\text{A}$ (140 kohm load).

After a discharge period of three years under 100 kohm load, the load voltage showed a decrease of less than 10 mV.

For a reliable performance, Liang⁽³⁶⁾ has developed a special technique to maintain a good contact between the electrodes and the electrolyte, even after the discharge of the battery.

The above battery is for use in the cardiac pacemaker but other types of solid state batteries are also proposed as power sources of various electronic devices.

Fig. 13.23, reported by Saito and Kashiara⁽³⁷⁾, is an example of such a battery and it can be expressed by

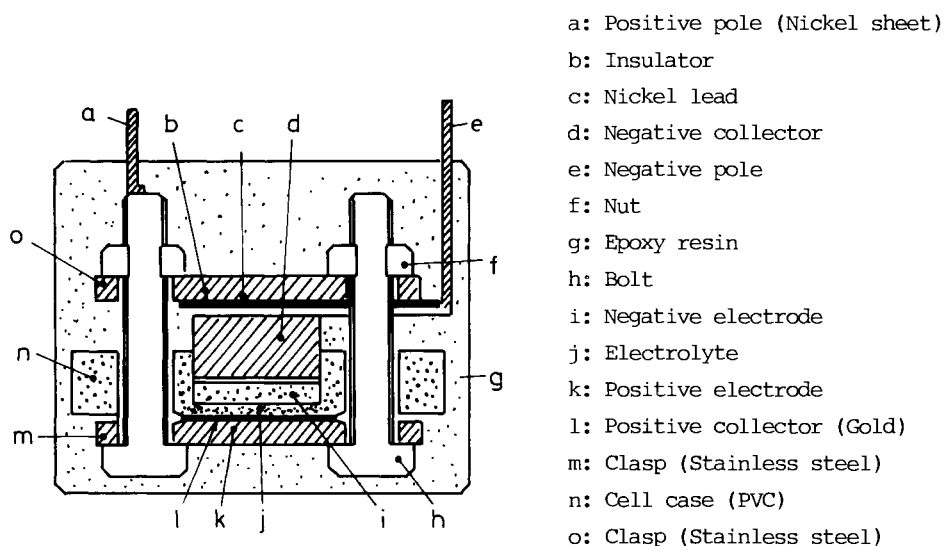


Fig. 13.23. Cross sectional view of test cell (After Saito and Kashihara (37) 1980).

$\ominus$ Ag powder + electrolyte | Electrolyte | Iodine + Phenothiazine $\oplus$.

In this cell, the negative electrode is a mixture of 80wt% silver powder of 325 mesh and 20wt% electrolyte powder.

The electrolyte is either silver rubidium iodide (RbAg_4I_5) or silver iodotungstate ($\text{Ag}_6\text{I}_4\text{WO}_4$). The positive electrode is a mixture of 60wt% iodine and 40wt% phenothiazine. This cell is 10 mm in diameter and 3 mm thick.

Fig. 13.24 shows the performance for various loads connected to

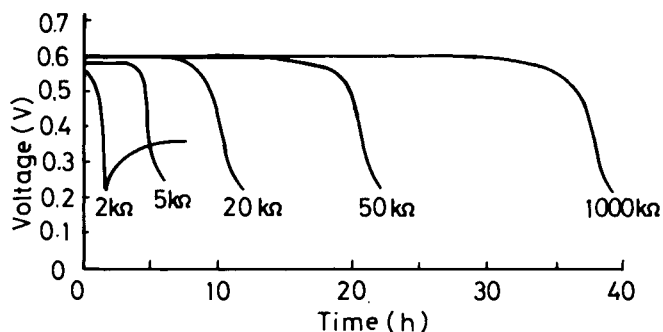
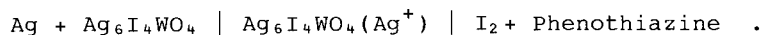


Fig. 13.24. Performance of the $\text{Ag}/\text{Ag}_6\text{I}_4\text{WO}_4/\text{I}_2+\text{Ph}$ (After Saito and Kashihara (37) 1980).

the cell of



The negative electrode weight was 70 mg/cell and the positive electrode weight was 50 mg/cell. The discharge voltage was especially stable for loads over 20 k Ω .

The details are not discussed above but a special structure is always needed to avoid any polarization at the interfaces between the electrodes and the electrolyte. Otherwise, the constant performance can not be maintained throughout the life of a solid state battery.

At the beginning of this chapter the perspective view was given to show how various solid oxides are used in many electronic devices.

In the second part, a phenomenological observation was introduced on the formation of thin films of binary oxides with amorphous structures by physical vapor deposition. This was discussed, as an example, to point out many problems in the fabrication of thin films, which are not yet scientifically well understood. The fabrication of an inverter with two MOS transistors has been introduced to give some information on how electronic devices are produced.

In the third section, various applications of solid state electrochemistry of oxides were discussed. The electronic devices covered were electrochemical timers, potential memory device, variable resistors, switching devices, display devices, and solid state batteries.

In the future, many more electronic devices will surely be developed to utilize the physical and chemical properties of solid oxides.

REFERENCES TO CHAPTER 13

- (1) M. Kitada, "Encyclopedia of Functional Materials", Kyoritsu-Shuppan Pub. Co. Ltd., Tokyo, Japan, (1984) (in Japanese).
- (2) M. Kitada, "Dictionary of Sensors", Agnes Pub. Co. Ltd., Tokyo, Japan, (1985) (in Japanese).
- (3) N. Ichinose, Chapter 1 of "Advance of Functional Ceramics" edited by S. Saito, H. Yanagida, and N. Ichinose, Techno-Plaza Co. Ltd., Tokyo, Japan, (1985) (in Japanese).
- (4) "Proceedings of the Third International Meeting on Solid Electrolytes — Solid State Ionics and Galvanic Cells", at Tokyo, edited by T. Takahashi et al., North-Holland Pub. Co., Amsterdam, (1980).
- (5) "Proceedings of the 4th International Conference on Solid State Ionics", at Grenoble, edited by M. Kleitz et al., North-Holland, Amsterdam, (1983).
- (6) "Proceedings of the 5th International Conference on Solid State Ionics", at Lake Tahoe, U. S. A., edited by J.B. Boyce et al., North-Holland, Amsterdam, (1985).
- (7) "Proceedings of the International Conference on Fast Ion Transport in Solids, Electrodes and Electrolytes", at Lake Geneva, Wisconsin, U. S. A., edited by P. Vashishta et al., North-Holland, New York, (1979).
- (8) "Proceedings of the International Conference on Fast Ionic Transport in Solids", at Gatlingburg, Tennessee, U. S. A., edited by J.B. Bates and G.C. Farrington, North-Holland, Amsterdam, (1981).
- (9) L-W. Zhang, M. Kobayashi, and K.S. Goto, "Micromechanism of Formation of Amorphous Thin Films of $\text{Li}_2\text{O-B}_2\text{O}_3$, $\text{Li}_2\text{O-SiO}_2$ and $\text{Li}_2\text{O-P}_2\text{O}_5$ by PVD", Solid State Ionics 18&19, (1986), pp. 741-746.
- (10) R.D. Shannon, B.E. Taylor, A.D. English, and T. Berzine, Electrochem. Acta, 22 (1977), p. 783.
- (11) H.L. Tuller, D.P. Button, and D.R. Uhlmann, J. of Non-crystalline Solids, 40 (1980), p. 93.
- (12) J.H. Kennedy, Thin Solid Films, 43 (1977), p. 41.
- (13) G.C. Farrington, Thin Solid Films, 83 (1981), p. 455.
- (14) A. Levasseur, M. Kbal, and P. Hagenmuller, Solid State Ionics 9&10, (1983), p. 1439.
- (15) Y. Ito, K. Miyauchi, and T. Oi, J. of Non-crystalline Solids, 57 (1983), p. 398.
- (16) L-W. Zhang, M. Yahagi, and K.S. Goto, "Vapor Species from Fused $\text{Li}_2\text{O-B}_2\text{O}_3$, $\text{Na}_2\text{O-SiO}_2$, and $\text{Na}_2\text{O-P}_2\text{O}_5$ Systems for Thin Film Manufacturing by PVD", Solid State Ionics 18&19, (1986), pp. 1163-1169.
- (17) "Thin Film Handbook", edited by the Japan Society for the Promotion of Science, 131st Committee, Ohm-Sha Pub. Co. Ltd., Tokyo, (1983) (in Japanese).
- (18) T. Ito and Y. Ito, "Basic Technology of Integrated Circuit", Shokodo Pub. Co. Ltd., Tokyo, (1983).
- (19) S. Iwata, N. Yamamoto, N. Kobayashi, T. Terada, and T. Mizutani, IEEE Trans. Electron Devices, ED-31 (1984), p. 1774.
- (20) S. Iwata, Ext. Abstracts of International Conferences on Solid State Devices and Materials, (1984), p. 15.
- (21) S. Iwata, A. Ishizaka, and H. Yamamoto, J. of Electrochem. Soc., 126 (1979), p. 110.
- (22) S. Iwata, "Many Problems on Reactions and Diffusion in Micro-electronic Devices", in Textbook on Diffusion, organized by Japan Institute of Metals, (1984), pp. 83-92.
- (23) A.S. Grove, "Physics and Technology of Semiconductor Devices",

- John Wiley and Sons, (1967).
- (24) W.N. Car and J.P. Mize, "MOS/LSI Design and Application", McGraw-Hill, (1972).
 - (25) B. Jaffe, W.R. Cook Jr., and H. Jaffe, "Piezoelectric Ceramics", Academic Press, London, (1971).
 - (26) Z.M. Jarzebski, "Oxide Semiconductors", Pergamon Press, Oxford, (1973).
 - (27) W. Koechner, "Solid State Laser Engineering", Springer-Verlag, New York, (1976).
 - (28) "Semiconductor Optoelectronics", edited by M.A. Herman, John Wiley and Sons, New York, (1980).
 - (29) H. Ikeda and K. Tada, "Sanyo's Couliodes and Memoriodes", in "Applications of Solid Electrolytes", edited by T. Takahashi and A. Kozawa, JES Press Inc., Cleveland, Ohio 44142, U. S. A., (1980), pp. 40-45.
 - (30) B.B. Owens, J.E. Oxley, and A.F. Sammells, "Applications of Halogenide Solid Electrolytes", in "Topics in Applied Physics", Vol. 21, Solid Electrolytes, edited by S. Geller, Springer-Verlag, Berlin, (1977), pp. 67-104.
 - (31) K. Fester and B. Owens, "Lithium Pacemaker Batteries", presented at Medtronic U. S. National Sales Conference, Colorado, January, (1977), R&D Document 77-D-002A.
 - (32) B.B. Owens, "Applications of Solid Electrolytes to Pacemaker Batteries", in the book given in reference (29), pp. 67-70.
 - (33) C.C. Liang, "Solid State Batteries", in "Applied Solid State Science", Vol. 4, edited by R. Wolfe, Academic Press, New York, N. Y., (1974), pp. 95-135.
 - (34) C.C. Liang and L.H. Barnette, J. Electrochem. Soc., 123 (1976), p. 453.
 - (35) C.C. Liang, A.V. Joshi, and N.E. Hamilton, J. Appl. Electrochem., 8 (1978), p. 445.
 - (36) C.C. Liang, pp. 60-66 of the book given in reference (29).
 - (37) S. Saito and S. Kashiara, pp. 46-50 of the book given in reference (29).

APPENDIX

List of Contents

(1)	Problems for discussion and calculation for Chapter 2 to Chapter 13 -----	406
(2)	Table of Standard free energy of reactions involving inorganic compounds as functions of temperature -----	434
(3)	Crystal structures of inorganic compounds -----	442

(1) PROBLEMS

PROBLEMS FOR CHAPTER 2

- (1) As given in Table 2.1, the charge carrier of the solid solution of $\text{ZrO}_2\text{-}0.15\text{CaO}$ is known to be O^{2-} anions. Calculate mobility of O^{2-} anions, when the conductivity is $10^{-2}/\text{cm}\cdot\Omega$ (see Fig. 2.12). Assume that the density of $\text{ZrO}_2\text{-}0.15\text{CaO}$ is 6.3 gr/cm^3 . Use Eq. (2-3) for the calculation.
- (2) Make the same calculation as the above problem for the mobility of Al^{3+} cations in pure Al_2O_3 , when the conductivity is $10^{-6}/\text{cm}\cdot\Omega$ (see Fig. 2.12). Assume the density of $\alpha\text{-Al}_2\text{O}_3$ to be 3.00 gr/cm^3 .
- (3) Convert the mobilities of O^{2-} and Al^{3+} obtained in Problems (1) and (2) into the absolute mobility according to Eq. (2-4). Discuss why the absolute mobility is very much different for two cases of O^{2-} and Al^{3+} , although the number of charge carriers per cm^3 is not much different.
- (4) The molar volume of $\text{K}_2\text{O-SiO}_2$ melts are $30.6 \text{ cm}^3/\text{mole}$ and $32.6 \text{ cm}^3/\text{mole}$ at 1400°C for 20 mole% K_2O and 30 mole% K_2O melts, respectively. The electrical conductivity is $0.446/\text{cm}\cdot\Omega$ and $0.795/\text{cm}\cdot\Omega$, respectively. Calculate the mobility of potassium cations in these two melts at 1400°C , assuming the charge carrier to be K^+ cations.
- (5) The numbers of Pb^{2+} ions per cm^3 of $\text{PbO-B}_2\text{O}_3$ melts are about 1.5×10^{22} and 1.03×10^{22} at 1050°C for 80 mole% and 60 mole% PbO melts, respectively. The mobilities defined by Eq. (2-3) are 2.8×10^{-4} and $1.75 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{sec}$. at 1050°C , respectively. Calculate the electrical conductivities of these two melts, provided that the charge carriers are Pb^{2+} cations.
- (6) Let us assume that only the lower reaction of Eq. (2-8) is taking place on a metal-deficient oxide. Namely, only the cation vacancies are predominant in the structure demonstrated by Fig. 2.5. Discuss the micromechanism of the virtual transfer of oxygen, when two gas compartments with different oxygen contents are separated by the wall made of this type of metal deficient oxide. Show the directions of migrations of the cation vacancies and the positive holes by a two dimensional diagram. Explain the reactions taking place at both surfaces of the wall.
- (7) Make the similar discussion as Problem (6), when only Eq. (2-20) is predominant in a metal excess oxide. Explain which

- direction the wall would be moving in cases of Problem (6) and (7).
- (8) H.H. Baumbach and C. Wagner measured the conductivity of pure solid ZnO at 500°C to 700°C (Z.physik.Chem.B22[1933] 199). The conductivity was proportional to $P_{O_2}^{-\frac{1}{4.5} \sim \frac{1}{5.0}}$. Assuming only interstitial zinc cations as the crystal defects, what theoretical relation do you expect between the conductivity and oxygen pressure. Discuss the probable reasons why the experimental results did not agree to the theory.
- (9) The experimental results given by Fig. 2.14 are suggesting that the solid solution of ThO_2 and Y_2O_3 would exhibit the p-type semiconduction at higher oxygen pressure and the ionic conduction at lower oxygen pressure. It is known from the conductivity measurement that at extremely lower oxygen pressure the solid solution exhibits the n-type semiconductivity. Draw a schematic diagram to show the relation between logarithm of the electrical conductivity and logarithm of oxygen pressure for three different contents of Y_2O_3 but at a constant temperature. Assume that the n-type and p-type semiconductivities are proportional to $P_{O_2}^{-\frac{1}{4}}$ and $P_{O_2}^{+\frac{1}{4}}$, respectively. This assumption is based on the large content of anion vacancies formed by doping of Y_2O_3 .
- (10) Draw a schematic diagram as the above problem (9) for one fixed composition but with three different temperatures. Do you expect that the range of the pure anion conduction would expand by increase of temperature. Assume the relative magnitude of ΔH° in Eq. (2-15) and the activation energy of the ionic conduction to answer this problem.
- (11) Draw a schematic diagram of $\log \sigma$ versus $(1/T)$, when an oxide exhibits the ionic conduction at higher temperature and the excess-electron conduction at lower temperature. Draw three lines for the excess-electron conduction for three different oxygen pressures. The ionic conductivity is independent of oxygen pressure.
- (12) Using Fig. 2.10, approximately make an equation to express the value of $\log \sigma$ as a function of $\log P_{O_2}$ at 1000°C. How much excess electrons are contained in 1 cm³ of TiO_2 at 1000°C under 10^{-8} atm of oxygen pressure. The density is about 4.23 gr/cm³.

- (13) Construct a diagram to show the relation between $\log \sigma$ and $1/T$ of Y_2O_3 at 10^{-12} atm and 10^{-4} atm of oxygen pressure using the data given in Fig. 2.11. What is the physical meaning of the slopes.
- (14) Discuss the probable experimental errors for determination of transference numbers of charge carriers by the electrolysis shown in Fig. 2.7 and by the blocking electrode method.
- (15) In Table 2.1, the references (2), (33) and (34) are given for β -Alumina, NASICON and LISICON. Read three papers and explain why these materials can exhibit superionic conduction.

PROBLEMS FOR CHAPTER 3

- (1) Equation (3-1) and (3-2) give the force exerting upon a particle placed in the gradient of electrical or chemical potential. Calculate the force, when an ion with the charge of $2e$ is placed under the field of 1.0 volt per 1.0 cm. Calculate also the force, when an atom is placed under the gradient of its partial molal free energy of 1 kilocalories per 1.0 cm. Show clearly the unit of the forces obtained. ($e=1.60 \times 10^{-19} \text{ A} \cdot \text{sec}$ or Coulombs, $1 \text{ erg} = 10^{-7} \text{ V} \cdot \text{A} \cdot \text{sec}$, $1 \text{ erg} = 1 \text{ dyne} \cdot \text{cm}$, $1 \text{ Joule} = 10^7 \text{ erg}$, $1 \text{ cal} = 4.18 \text{ Joule}$).
- (2) The tracer diffusivity of an ionic species in a solid oxide is measured to be $1.0 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 1000 K. what is the absolute mobility of this ionic species according to Equation (3-14)? The Boltzmann constant is $1.38 \times 10^{-23} \text{ V} \cdot \text{A} \cdot \text{sec}/\text{degree}$ or $1.38 \times 10^{-16} \text{ ergs/degree}$.
- (3) Assuming the charge to be $2+$, calculate the velocity of the ionic particle of Problem (2), when it is placed under the electrical- or chemical-potential gradient of Problem (1).
- (4) Calculate the current density according to Equation (3-6) for the velocity calculated in Problem (3) under electrical potential gradient of 1 volt/cm. The ionic species under consideration has the charge of $2+$. Assume the number of the ionic particle is $10^{23}/\text{cm}^3$.

- (5) Calculate the diffusion flux defined by Equation (3-12) for the velocity calculated in Problem (3) for the chemical potential gradient of 1.0 kilocalorie/cm. Assume n_i is $10^{23}/\text{cm}^3$.
- (6) According to Fig. 3.2, how much are the conductivity at 400 to 700°C by using Eq. (3-18)? Assume the density of solid NaBr roughly as 3.0 gr/cm³. Use the correlation factor in Table 3.1. Atomic weights are Na=23 and Br=80. (Faraday constant, $F=N_0 \times e = 96,495 \text{ A} \cdot \text{sec}/\text{equivalent}$ or 23,063 Cal/Volt·equivalent).
- (7) Construct a diagram to show the relation between logarithm conductivity of $\text{ZrO}_2\text{-}0.15\text{CaO}$ and reciprocal temperature by using Fig. 3.4. The number of O^{2-} are 7.24 per unit cell of the volume of $1.35 \times 10^{-24} \text{ cm}^3$.
- (8) The melting point of NaCl is 808°C. Using the data in Table 3.2, construct a diagram to show the relation between logarithm diffusivity of both Na and Cl in liquid NaCl and reciprocal temperature. Calculate the transference numbers of Na^+ and Cl^- at 850, 900 and 950°C, assuming the melt is a purely ionic conductor. The transference number is defined by

$$t_{\text{Na}^+} \equiv \frac{\sigma_{\text{Na}^+}}{\sigma_{\text{Na}^+} + \sigma_{\text{Cl}^-}}$$

- (9) Combine the diagram made in Problem (8) and Fig. 3.3 to produce a graph of $\log D_{\text{Na}}$ versus $1/T(\text{K})$ for the temperature range of 350°C up to 1000°C. Discuss why the diffusivity of Na^+ changes stepwisely at 808°C. Discuss why the activation energy is different for liquid and solid states.
- (10) Using data given in Table 3.4, construct a diagram to show the relation between $\log D_+$, $\log D_-$, and $\log D_p$ in liquid NaCl versus reciprocal temperature. Calculate the transference numbers of Na^+ and Cl^- at 850, 900, and 950°C. Compare them with the transference numbers obtained in Problem (8). Which are closer to the true values if the experimental errors are of the same magnitude?
- (11) In Table 3.5, ten values of the measured diffusivity are given for liquid 40wt%CaO-40wt%SiO₂-20wt%Al₂O₃ in the temperature range of 1350°C to 1500°C. Three values at 1350, 1400, and 1450°C are from three different literature sources. Using the Nernst-Einstein relation, calculate the electrical conductivities from these ten values. Construct the diagram

to show the relation between logarithm conductivity and reciprocal temperature. Assume the density is 2.8 gr/cm^3 in this temperature range and the charge carrier is Ca^{2+} . Atomic weights are $\text{Ca}=40$, $\text{Si}=28$, $\text{Al}=27$, and $\text{O}=16$.

- (12) Make the same calculation as Problem (11) but using four values of the calculated diffusivities for $40\text{wt}\%\text{CaO}-40\text{wt}\%\text{SiO}_2-20\text{wt}\%\text{Al}_2\text{O}_3$, given in Table 3.5. Plot the results on the same diagram obtained in Problem (11). Discuss why the results of Problems (11) and (12) are different.

PROBLEMS FOR CHAPTER 4

- (1) The intrinsic diffusivity in a binary system is defined by Equation (4-1) and the interdiffusivity, expressed by $\bar{D}_{1-2}$, is defined by Fick's First law of diffusion, Equation (4-12). From the conservation of matter, Fick's second law of diffusion is given by Equation (4-13). Drive the second law from the first law, considering the accumulation of component 1 in a thin slice of the diffusion medium.
- (2) The solution of Fick's second law of diffusion for the semi-infinite medium for a constant diffusivity is given by

$$\frac{C_1 - C_s}{C_0 - C_s} = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda \quad (4-30)$$

where C_1 is the concentration of component 1 at time = t and distance x from the surface, C_s is a constant surface concentration, and C_0 is the uniform initial concentration. λ is given by

$$\lambda = \frac{x}{2\sqrt{Dt}} \quad (4-31)$$

where D is the interdiffusivity, which was expressed by $\bar{D}_{1-2}$ in Problem (1). The right hand side of Eq. (4-30) is called the error function and its values are given below as a function of λ

λ	$\text{erf}(\lambda)$	λ	$\text{erf}(\lambda)$	λ	$\text{erf}(\lambda)$	λ	$\text{erf}(\lambda)$	λ	$\text{erf}(\lambda)$
0	0	0.20	0.2227	0.45	0.4755	0.70	0.6778	0.95	0.8209
0.025	0.0282	0.25	0.2763	0.50	0.5205	0.75	0.7112	1.0	0.8427
0.05	0.0564	0.30	0.3286	0.55	0.5633	0.80	0.7421	1.1	0.8802
0.10	0.1125	0.35	0.3794	0.60	0.6039	0.85	0.7707	1.2	0.9103
0.15	0.1680	0.40	0.4284	0.65	0.6420	0.90	0.7970	1.3	0.9340

1.4	0.9523	1.7	0.9838	2.0	0.9953	2.6	0.9998
1.5	0.9661	1.8	0.9891	2.2	0.9981	2.8	0.9999
1.6	0.9763	1.9	0.9928	2.4	0.9993		

Draw a diagram to show the relation between $(C-C_0)/(C_S-C_0)$ and x for $t=1000$ sec, and $\tilde{D}_{1-2}=10^{-10}$ cm²/sec.

- (3) For determination of the interdiffusivity, $\tilde{D}_{1-2}$, the diagram drawn as the solution of Problem (2) is experimentally obtained and then, the interdiffusivity is calculated. Draw the diagram to show the relation between $(x)/\sqrt{t\tilde{D}_{1-2}}$ and $(x)/\sqrt{t}$ from the diagram of the concentration distribution with help of the error-function table. The slope of the line obtained should be equal to $1/\sqrt{\tilde{D}_{1-2}}$ and thus should be equal to 10^{-10} cm²/sec. Prove the slope in your diagram equal to 10^{-10} cm²/sec.
- (4) Using the table of the error function, draw a diagram for the relation between $(C-C_0)/(C_S-C_0)$ and $(x)/\sqrt{t\tilde{D}_{1-2}}$. The curve obtained is called the master penetration-curve of 1 in a binary system of 1-2. Obtain the distance x for 0.5 of the vertical axis with $\tilde{D}_{1-2}=10^{-10}$ cm²/sec and $t=1000$ sec.
- (5) The treatment of a binary diffusion in the above problem is valid only in case of a constant interdiffusivity. When the diffusivity changes with the concentration, it can be obtained by a graphical integration of

$$\tilde{D}_{1-2}(C_1) = -\frac{1}{2t} \left(\frac{dx}{dC_1} \right) \int_0^{C_1} x dc \quad (4-32)$$

This treatment is called Boltzmann-Matano analysis (L. Boltzmann, Ann. Physik, 53, (1894) 960 and C. Matano, Japan Phys., 8 (1933) 109). Explain how $\tilde{D}_{1-2}$ can be obtained from the diagram of the relation between $(C_1-C_0)/(C_S-C_0)$ and x for a fixed time.

- (6) The relation between the intrinsic diffusivity D_1 and the tracer diffusivity D_1^{tr} is given by Eq. (4-21). Explain why the interdiffusivity $\tilde{D}_{1-2}$, tracer diffusivity D_1^{tr} , and intrinsic diffusivity D_1 become nearly equal to each other in the dilute range.
- (7) In a binary regular solution, the activity coefficient, γ_1 , can be expressed by

$$\ln \gamma_1 = \alpha/(1-N_1)^2 \quad (4-33)$$

where α is the constant experimentally obtained. Drive the relation among D_1 , D_1^{tr} , and D_{1-2} for the binary regular solution.

- (8) In Fig. 4.11, tracer diffusivities of Ca^{2+} and Fe^{2+} (with Fe^{3+}) are given. Obtain the equation of the quasi-binary interdiffusivity of Ca^{2+} and Fe^{2+} (with Fe^{3+}) for the fixed content of SiO_2 as a function of oxygen pressure, temperature and mole fractions of the components. Assume the ideal solution for this oxide melt.
- (9) Calculate the tracer diffusivities of Ca^{2+} in CaO , Co^{2+} in CoO , and Fe^{2+} (with Fe^{3+}) in Fe_{1-x}O at 1000°C , assuming that the data given in Table 4.1 is all valid at 1000°C .
- (10) Using Fig. 4.1 and Fig. 4.2, estimate approximate values of the oxygen pressures, under which the tracer diffusivities of Problem (9) would be measured in solid Fe_{1-x}O and CoO at 1000°C .
- (11) Draw the diagrams to show the relation between $(C-C_0)/(C_S-C_0)$ and x after the diffusion runs of 1000 sec at 1000°C for the case of Problem (9). Use the table of error function given in Problem (2). Discuss why the penetration curves for Ca^{2+} , Co^{2+} , and Fe^{2+} (with Fe^{3+}) are so different.
- (12) Draw a diagram to show the relation between $\log D^{\text{tr}}$ and $(1/T)$ for Na^+ in $\text{Na}_2\text{O}-11\text{Al}_2\text{O}_3$ (β -alumina, see Fig. 4.6!), O^{2-} in ZrO_2 - CaO (see Fig. 4.6!), Mg^{2+} in MgO (Table 4.1), Co^{2+} in CoO (Table 4.1) and Fe^{2+} (with Fe^{3+}) in Fe_{1-x}O (Table 4.1). At the end of this book, the crystal structures of the oxides are given as the appendix. Discuss the magnitude of the tracer diffusivities of these elements in relation to the crystal structure of the oxides with crystal and electronic defects.

PROBLEMS FOR CHAPTER 5

- (1) When carbon dissolved in γ -iron is diffusing both under temperature and concentration gradients, write the equations of diffusion fluxes of Fe and C, and heat flux according to Eq. (5-1) to Eq. (5-4) using an arbitrary internal reference frame. When the sublattice of iron is taken as the internal reference frame, the flux equations can be reduced to two as given Eqs. (5-40) and (5-41) because of $j_{\text{Fe}}=0$. Discuss the local velocity of this internal reference frame relative to the external reference frame. Would the inert marker discussed

in Chapter 4 shift or not in this case? If yes, then under what conditions it would shift?

- (2) The electrical potential, Ψ , can be experimentally measured but it is more convenient if it is eliminated in the flux equations. Explain the details of the derivation of Eq. (5-17) from the condition of the electrical neutrality expressed by Eq. (5-16).
- (3) According to Prigogine's book, the entropy production is equal to $\sum_k j_k X_k$. Because of the second law of thermodynamics, the entropy production must be always positive. Using Eqs. (5-40) and (5-41), prove Eq. (5-10) of $L_{ii} \geq 0$ and $L_{ii}L_{kk} \geq L_{ik}^2$.
- (4) Following Eq. (5-10), it is stated that the chemical potential of any ionic species can never be measured in a mixture. Then, explain why the activity of any ionic species can not be measured, using Ca^{2+} as an example contained in liquid solution of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system.
- (5) The assumption of the local equilibrium used to derive Eqs. (5-18) and (5-18') means that all kinds of reactions conceivable should be strictly in equilibrium. Namely



Sum up these three equations and write the equation to show the relation between chemical potentials of ionic species and neutral oxides. The obtained equation will not contain the chemical potential of oxygen anions. Explain that this is a suggestion why the chemical potential of oxygen anion can be eliminated from the flux equations.

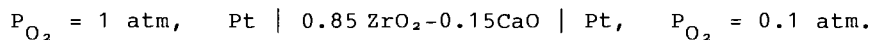
- (6) The thermodynamic factor Γ_{10} is defined by Eq. (5-22). How can the partial differential term be evaluated graphically when the iso-activity lines are given on a ternary composition triangle.
- (7) In Chapter 3, the Nernst-Einstein relation was derived. If one combines Eq. (5-27) and (5-28), he can derive the Nernst-Einstein relation for multicomponent systems. Derive this relation and discuss the difference of the relations in Chapter 3 and here derived.
- (8) Figs. 5.2 and 5.3 indicate that the uphill diffusions of SiO_2

and Al_2O_3 are not very large. Then, the diffusion phenomena shown by these two figures can be approximately treated as the interdiffusion of CaO and Al_2O_3 , or CaO and SiO_2 . Calculate approximately these interdiffusivities using the table of error function given in Problem (2) for Chapter 4.

- (9) Calculate the tracer diffusivities of Si, Ni, and Cr in liquid iron at temperatures and concentrations given in Table 5.5. Calculate the heat conductivity also from Table 5.5 and compare it with those of the oxide given in Fig. 5.22.
- (10) Using Fig. 5.12, estimate approximately the difference of chemical potential of oxygen gas with $P_{\text{O}_2} = 0.21$ atm at 900°C and 1200°C . Explain how this difference of the chemical potential can be calculated when the heat capacity of oxygen gas is known at a constant pressure.
- (11) Construct a diagram to show the relation between ΔT and $\ln t$ in Eq. (5-54) when q is 5 watts/m, 20 watts/m, 40 watts/m and 60 watts/m for a fixed heat conductivity of $1.0 \text{ W/m}\cdot\text{k}$. To have the temperature increase of 5 degrees at 10 sec, how much electric power should be supplied during 1 sec.
- (12) In Eq. (5-46), the difference of the chemical potential of CaO at two different temperatures is included. Explain how this term can be thermodynamically calculated if the heat capacities of solid and liquid pure CaO , heat of its fusion, and the activity of CaO at T_1 and T_2 are all known. Here, the standard state of the activity of CaO is its pure solid state.

PROBLEMS FOR CHAPTER 6

- (1) Calculate the Gibbs free energy change of the virtual cell reaction, according to Eq. (6-5), when a direct current of 4 Faradays flows through the following galvanic cell at 1000 K ;

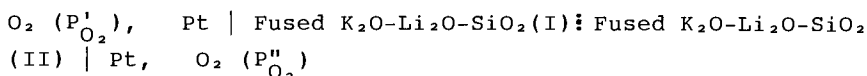


The direction of the current is such that the electrons enter the left-hand-side electrode and exit the right-hand-side electrode. The gas constant, R , is $1.98 \text{ cal/degree}\cdot\text{mole}$.

- (2) Calculate the equilibrium electromotive force of the galvanic cell of Problem (1) according to Equation (6-6). Faraday constant is $23,060 \text{ cal/volt}\cdot\text{equivalent}$.
- (3) Integrate Equation (6-7) when the value of the transference

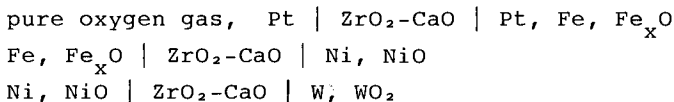
number of ions is assumed to be constant at 0.90 for fixed values of P'_{O_2} and P''_{O_2} at a constant temperature. The second logarithmic term of Eq. (6-16) can be neglected if the predominant electronic defects are excess electrons. The simplified equation is another expression of the electromotive force. Explain why the two equations are different. Also, show one method to evaluate the approximate value of P_{θ} at a constant temperature using the two equations and fixed values of P'_{O_2} and P''_{O_2} .

- (4) Derive the equation for the electromotive force of the following galvanic cell using Eq. (6-19);



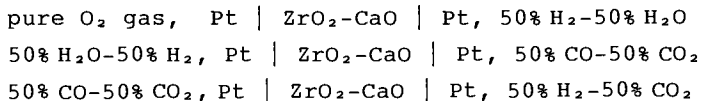
Assume that the value of the transference numbers of K^+ and Li^+ are comparable and that all other charge carriers can be neglected. Integrate the equation for constant transference numbers of K^+ and Li^+ . In the above galvanic cell, the composition of the ternary melts (I) and (II) are different.

- (5) Calculate the equilibrium electromotive forces of the following galvanic cells at 1000 K;



Use the standard Gibbs free energy of reactions given in the appendix of this book.

- (6) Derive the equations of the equilibrium electromotive forces as a function of temperature for the following galvanic cells;



Use the standard Gibbs free energy of reactions given in the appendix of this book.

- (7) Estimate the approximate electromotive force of the following galvanic cells at 1000°C;

pure Ni, NiO | ZrO₂•CaO | NiO, (0.5 Ni-0.5 Pt) alloy
 pure Pb, PbO | ZrO₂•CaO | pure Pb, fused oxide of (0.7 PbO-0.3 SiO₂)

Obtain the activities of Ni and PbO from Figs. 6.9 and 6.10, respectively.

- (8) Draw a diagram to show the equilibrium electromotive force and $\log \delta$ of Ni_{1- δ} O at 1200°C for the galvanic cell

Ni, NiO, Pt | ZrO₂•CaO | Pt, Ni_{1- δ} O.

Use the plots given in Fig. 6.12 and $\log P_{O_2}$ equal to -7.79 at equilibrium for Ni and NiO.

- (9) The reference electrode in commercial oxygen sensors for molten steel is made of mixtures of Mo and MoO₂, or Cr and Cr₂O₃. Derive the equations for the electromotive force as a function of the weight percent of oxygen in steel at 1600°C for the following oxygen sensors;

Mo, MoO₂ | ZrO₂•0.15 CaO | liquid Fe-O alloy
 Cr, Cr₂O₃ | ZrO₂•0.15 CaO | liquid Fe-O alloy.

Use the standard Gibbs free energy of formation of MoO₂ or Cr₂O₃ given in the appendix and the EMF equation of

$E(\text{volts}) = 0.571 - 0.186 \log [\text{wt}\% \text{O}]$ for air, Pt | ZrO₂•0.15 CaO | Fe-O alloy at 1200°C.

- (10) Calculate the equilibrium electromotive force of the following galvanic cells;

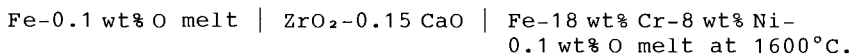
liquid Fe-0.1wt% O | ZrO₂-CaO | liquid Ni-0.1wt% O at 1600°C,
 and
 liquid Cu-0.1wt% O | ZrO₂-CaO | liquid Ag-0.1wt% O at 1200°C.

Use the equations for the electromotive forces given in the text for the galvanic cell of the type air, Pt | ZrO₂-CaO | M-O melt.

- (11) Calculate the activity of oxygen in Fe-18 wt% Cr-8 wt% Ni-0.1 wt% O melt at 1600°C with its standard state at infinitely dilute solution using wt% to express the composition. Use Eq.

(6-40) and the values of the interaction parameters given in Table 6.1.

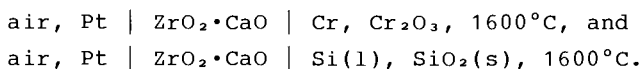
- (12) Calculate the equilibrium electromotive force for the following galvanic cells;



- (13) The parameter, P_Θ , is defined as the oxygen pressure at which the electronic conductivity becomes exactly equal to the ionic partial conductivity (see Eqs. (6-11) and (6-12)). This parameter is reported as

$$\log P_\Theta = 24.12 - \frac{70,500}{T(K)} \quad (\text{for ZrO}_2\text{-CaO})$$

by M. Iwase and T. Mori (Metall. Trans. B, 9B(1978) pp.365-367). Using Eq. (6-16) and the above equation, calculate the electromotive force of the galvanic cells;

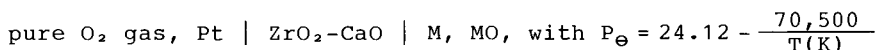


The EMF of the former galvanic cell would be nearly equal to

$$\frac{RT}{4F} \ln \frac{P_{\text{O}_2}(\text{Cr}_2/\text{Cr}_2\text{O}_3)}{P_{\text{O}_2}(\text{air})}.$$

The EMF calculation for the latter cell is not so simple.

- (14) The use of the solid-state galvanic cell with ZrO₂-CaO electrolyte is limited in low oxygen pressure range because of partial electronic conduction. Derive the equation for the oxygen pressure of the right electrode where the difference between the observed EMF and the theoretical EMF is 1% for



Here the theoretical EMF means the EMF according to Eq.(6-6).

PROBLEMS FOR CHAPTER 7

- (1) Calculate the activity of Na₂O in liquid Na₂CO₃ at 1500 K under a gas mixture of 50 Volume% O₂ and 50 Volume% CO₂. Use

the standard Gibbs free energy of reaction of Eq.(7-7') as 28.69 kCal. Assume that the activity of Na_2CO_3 is unity because the content of Na_2O is very small.

- (2) Calculate the electromotive force of the galvanic cell of Eq. (7-6) at 1500 K according to Eq. (7-7) with the following condition;

$$\Delta G_f^\circ = 28.69 \text{ kCal}, a'_{\text{Na}_2\text{O}} = 10^{-7}, P_{\text{CO}_2} = 0.5, P'_{\text{O}_2} = P''_{\text{O}_2} = 0.5.$$

- (3) Using Fig.7.6, calculate the free energy of mixing of liquid Na_2O - SiO_2 binary system at 1300°C according to

$$\Delta G^{\text{mix}} = RT (N_{\text{Na}_2\text{O}} \ln a_{\text{Na}_2\text{O}} + N_{\text{SiO}_2} \ln a_{\text{SiO}_2}),$$

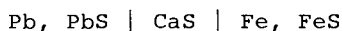
where ΔG^{mix} is the free energy of mixing, R is the gas constant, and $N_{\text{Na}_2\text{O}}$ and N_{SiO_2} are the mole fractions of Na_2O and SiO_2 , respectively. The activities of Na_2O and SiO_2 are $a_{\text{Na}_2\text{O}}$ and a_{SiO_2} , respectively. Construct a diagram of ΔG^{mix} versus $N_{\text{Na}_2\text{O}}$ at 1300°C.

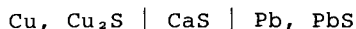
- (4) Compare the ΔG^{mix} versus $N_{\text{Na}_2\text{O}}$ curve obtained in the above problem with the ΔG^{mix} curve for the ideal binary solution given by

$$\Delta G^{\text{mix}} = RT (N_1 \ln N_2 + N_2 \ln N_1)$$

where N_1 and N_2 are the mole fractions of components 1 and 2 in the ideal binary solution. Discuss why the two curves are so different.

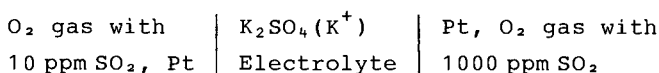
- (5) Explain the virtual cell reactions when 4 Faradays of electrons are supplied to the left-hand-side electrode of galvanic cells given by Eqs.(7-8) and (7-11). Explain why the solid electrolytes must be a mixture of two phases.
- (6) Explain both the electrode reactions and the virtual cell reaction of the galvanic cell given by Eq.(7-12) with the condition that the charge carriers of solid $4\text{CaO-P}_2\text{O}_5$ are exclusively Ca^{2+} ions. Prove Eq.(7-16) by your explanation of the virtual cell reaction.
- (7) Calculate the electromotive forces at 1000 K for the following galvanic cells;





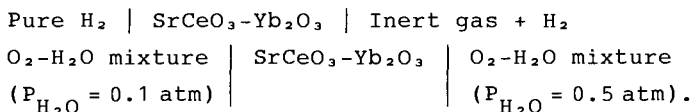
Use the standard free energies of formation for PbS, FeS, and Cu₂S given in the Appendix.

- (8) Explain the virtual cell reactions of the two galvanic cells given in Problem (7) when the charge carriers of the solid CaS electrolyte are Ca²⁺ ions or S²⁻ ions. Explain why the virtual cell reactions become the same for the two cases of charge carriers of Ca²⁺ or S²⁻ ions.
- (9) Calculate the equilibrium electromotive force for the galvanic cell



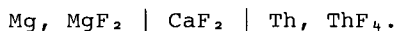
at 1000 K according to Eq.(7-25).

- (10) Discuss the virtual cell reactions of the following galvanic cells when 2 Faradays of electrons are supplied to the left-hand-side electrodes;



Assume that the charge carriers are H⁺ ions through the solid electrolyte. Would the virtual cell reaction be changed if the charge carriers are OH⁻ ions.

- (11) Construct a diagram to show the stable ranges of metallic Al, AlN, and Al₂O₃ at 1000°C, 1100°C, and 1200°C. The vertical axis is log P_{O₂} and the horizontal axis is log P_{N₂}. Compare the stability diagram you have constructed with Fig.7.24. Use the standard Gibbs free energies of formation for Al₂O₃ and AlN given in the appendix.
- (12) Explain the virtual cell reaction when 2 Faradays of electrons are supplied to the left-hand-side-electrode of the galvanic cell



Assume that the charge carriers are Ca²⁺ ions. What is the

theoretical equation for the electromotive force of this cell? Would this equation be changed if the charge carriers were F^- ions?

- (13) Derive the expression for the oxygen content outside the small opening of the cell given in Fig.7.25 as a function of the diffusion-limited currents shown in Fig.7.26. Express the diffusivity of oxygen gas by D_{O_2} in your equation and the Faraday constant by F .
- (14) A schematic diagram of the Knudsen cell is given in Fig.7.27. The diameter of the opening at the top must be smaller than the mean free path of the gaseous molecules within the cell. Calculate the diameter of the opening when it is 1/10 of the mean free path of O_2 gas molecules within the Knudsen cell at $20^\circ C$ and the pressure is 0.1 Torr. The mean free path, L , is given by

$$L = 0.08 \frac{T}{P\delta^2}$$

where L is in cm, P is in Torr, T is the absolute temperature, and δ is the diameter of gaseous molecules. (In this case, $\delta = 3.64 \times 10^{-8} \text{ cm}$ for O_2 gas).

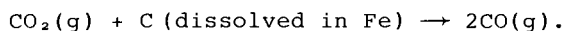
- (15) Calculate the effusion of oxygen per second from the Knudsen cell under the conditions of Problem (14) according to Eq. (7-30).

PROBLEMS FOR CHAPTER 8

- (1) Figure 8.1 shows a schematic diagram of the oxygen concentration change in the metal phase as a function of time and distance under a potentiostatic current flow. When a constant current is applied to this system instead of a constant potential, the concentration gradient at $x = 0$ must always be constant. Draw a schematic diagram of the oxygen concentration change for the case of polarization by a constant current density.
- (2) The transfer coefficient, α , is defined by using Fig.8.2. Explain the physical meaning of this coefficient. What factors would affect the value of the transfer coefficient.
- (3) The pictures (b) and (c) of Fig.8.5 show the concentration distribution of oxygen when one cycle of alternating current is supplied. Draw a schematic diagram that shows the concent-

ration distribution when two cycles of alternating current are supplied. Assume diffusion control for the electrode reaction.

- (4) According to Fig.8.10, the diffusivity of oxygen in liquid iron is about $2 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 1550°C . Construct quantitative diagram to show the relationship between current density, i , and the square root time, $\sqrt{t}$, according to Eq.(8-7) when C_0 and C_i are 500 ppm and 1000 ppm, respectively. Density of liquid iron is 7.0 g/cm^3 .
- (5) What is the value of the overpotential for the conditions given in Problem (4)? Use Eq.(8-2) for this calculation.
- (6) Derive Eq.(8-8) from Eq.(8-7) using Eq.(8-2).
- (7) According to Fig.8.10, the diffusivity of oxygen in liquid iron is about $2 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 1550°C . An alternating current is flowing through the interface between the electrolyte of $\text{ZrO}_2 \cdot \text{CaO}$ and liquid iron containing oxygen at 1550°C . Determine the Faradaic impedance when the oxygen content is 500 ppm and the frequency ($=2\pi\omega$) is 1 kHz. Use Eqs.(8-25) and (8-26) to calculate the ohmic and capacitive components. Then, insert these values in Eq.(8-27) to obtain the impedance.
- (8) Fig.8.8 shows the cell assembly for a polarization experiment. It is observed that the polarization at the interface of the powder mixture of Mo and MoO_3 with the solid electrolyte is negligible in comparison to that at the interface between liquid Fe-O alloy and the solid electrolyte. Explain why the polarization takes place only at the interface with the liquid iron-oxygen alloy. Define the buffering capacity of an electrode with respect to oxygen-potential change.
- (9) The experimental result shown in Fig.8.14 suggests that the rate of decarburization of liquid iron by CO_2 gas is controlled by diffusion in the stagnant gaseous layer. The reaction is

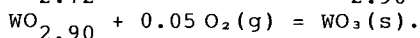
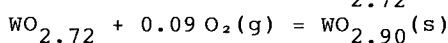
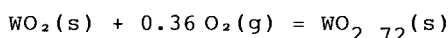


Write the rate equation that expresses the rate of decarburization as a function of the diffusivity of CO_2 in the gas phase, the bulk concentration of CO_2 , and the thickness of the stagnant gaseous layer.

- (10) The rate equation based on diffusion-control, as discussed in Problem (9), is known to be valid at 1550°C when liquid iron

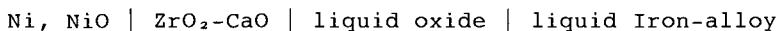
contains carbon in excess of 0.2 wt%. Construct a diagram (not to scale) that shows the relationship between [wt% C] in liquid iron and time, using your answer to Problem (9). The initial carbon content is 4.3 wt% and decreases to 0.2 wt% by decarburization with carbon dioxide gas. Discuss what factors would affect the rate of decarburization of liquid iron by carbon dioxide.

- (11) Explain how the standard free energies of the following reactions at 880°C can be calculated from the experimental results given by Fig.8.16;



The electromotive force given in Fig.8.16 is observed by using a reference electrode of the powder mixture of nickel and its oxide.

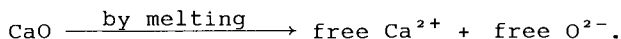
- (12) In Fig.8.17, three electromotive forces are expressed by E_1 , E_2 , and E_3 . Explain the virtual cell reaction for the cell given by Eq.(8-52), and derive Eq.(8-54). Explain the direction of migration of the ions in the electrolyte and the electrode reactions.
- (13) Explain the virtual cell reaction of the galvanic cell of Eq.(8-50) showing the direction of migration of the ions in the electrolyte and the electrode reactions. Derive Eq.(8-51) in accordance with your explanation.
- (14) The electromotive force expressed by E_2 in Fig.8.17 is considered to give the local oxygen pressure at the interface between the liquid oxide and liquid iron phases. Explain the virtual cell reaction of the galvanic cell of



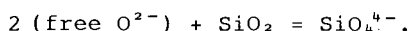
where the charge carriers in the liquid oxide can be assumed to be Na^+ ions.

PROBLEMS FOR CHAPTER 9

- (1) When a basic oxide is molten, it gives free cations and free oxygen anion. For example,



When an acidic oxide is added to the melt of a basic oxide, it makes anion complexes by consuming the free oxygen anion. For example,



Define and then calculate the ion fractions for the homogeneous melt of 3 moles CaO and 1 mole SiO₂. Assume that predominant ionic species are only Ca²⁺, O²⁻, and SiO₄⁴⁻.

- (2) Prove that the electrical neutrality is satisfied in the melt in Problem (1). Is the value of the horizontal axis of Fig. 9.1 proportional to the content of CaO in CaO-SiO₂-Fe_xO-CaF₂ slags? If not, why?
- (3) Why is the (O²⁻) negatively proportional to (SiO₄⁴⁺ + PO₄³⁻) in Fig. 9.2? How can the electrical neutrality be satisfied in this case?
- (4) Figure 9.4 shows the structure of the electrolytic cell for the liquid K₂O-SiO₂ system. How many moles of K₂O can be transferred to the left compartment when a direct current of 0.965 Amperes is supplied for 10,000 seconds? The direction of the current is such that the cations of K⁺ can be transferred from the right to the left compartment.
- (5) The charge carriers of the slag in Fig. 9.7 are believed to be cations of Ca²⁺ in CaO-SiO₂-Al₂O₃ melts. The direct current inducing the migration of Ca²⁺ cations toward the iron melt accelerate the desulfurization of iron melts. Explain why. Discuss the probable virtual electrode reaction at the interface between the liquid slag and the liquid iron.
- (6) Figures 9.9 and 9.10 indicate that the oxide melts containing iron oxides in large fractions exhibit an electronic conduction. In Chapter 2, the conduction mechanisms of solid FeO (Fig. 2.9) and Fe₃O₄ (Table 2.1) are given. Discuss the conduction mechanisms for the oxide melts reported in Fig. 9.11. Can you estimate the composition ranges for the

- predominant carriers by positive holes and excess electrons ?
- (7) Table 9.1 summarizes the transference numbers for liquid oxide systems. The predominant charge carriers are cations of alkaline and alkaline-earth metals. Explain why, considering Pauling's ionic radii and the sizes of silicate polymers, SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, ...
- (8) Theoretical equations for rates of electrode reactions have been given in Chapter 8. The observation shown by Fig. 9.14 seems to satisfy Equation (8-19). Explain the meanings of the slopes of lines marked 1, 2, 3 and 4 in Fig. 9.14. How can the exchange-current densities be estimated from Fig. 9.14 ? What are the ambiguities in the experiment reported by Figures 9.13 and 9.14 ?
- (9) Figure 8.5 is a diagram to explain the physical meaning of Faradaic impedance. Discuss the probable electrode reaction and the rate-controlling step for the cases illustrated in Figures 9.18 and 9.19.
- (10) Calculate the apparent interdiffusivity of SiO_2 , using the slopes of lines given in Fig. 9.24. Equation (9-8) gives the meaning of the slopes. In the equation, the constants are as follows:
 $R = 1.987 \text{ Cal/mole/degree}$, $T = \text{K}$, $i = \text{mA/cm}^2$, $t = \text{sec.}$,
 $Z = 4+$, $F = 23,060 \text{ Cal/Volt}$, $J = 4.183 \text{ Joul/cal}$, $k = 1.8 \times 10^{-3}$ (dimensionless).
- (11) In Chapter 4, the relation between the interdiffusivity and the tracer diffusivities has been given as Eq. (4-25). In Fig. 9.26, the quasi-binary interdiffusivity of CaO and SiO_2 is estimated. If both mole fractions of CaO and SiO_2 are assumed 0.5 and the thermodynamic factor is neglected, Eq. (4-25) can give very simply the interdiffusivity from tracer diffusivities. Estimate the interdiffusivity at 1400°C from tracer diffusivities of Ca and Si given in Fig. 9.26. Compare your estimation with the calculated value given in Fig. 9.26, which included thermodynamic factor.
- (12) Figures 9.29 and 9.30, and Eq. (9-12) explain the principle of the double pulse method. Using Fig. 9.30 and Eq. (9-12), explain the procedure to estimate the following quantities; the exchange current density of $\text{Ni} \rightleftharpoons \text{Ni}^{2+} + 2e$ at 450°C , the interdiffusivity of NiCl_2 in the KCl-LiCl melt at 450°C . Why are the slopes of the lines different in Figs. 9.30 and 9.31 ?

PROBLEMS FOR CHAPTER 10

- (1) When the local equilibrium prevails in a solid oxide expressed by MO, the following relation is satisfied in any place in the oxide;

$$\mu_M + \frac{1}{2} \mu_{O_2} = \mu_{MO} \quad \text{for} \quad M(s) + \frac{1}{2} O_2(g) = MO(s)$$

where μ_M , μ_{O_2} and μ_{MO} are the chemical potentials of a solid metal, oxygen gas and solid oxide, MO. Explain how the second line of Eq. (10-5) can be obtained from the first line using the above relation.

- (2) Explain why the virtual cell reaction of the cell of Eq. (10-4) is the same for the two cases of $t_{M^{2+}} = 1.0$ or $t_{O^{2-}} = 1.0$.
- (3) Eq. (10-10) must be used for the case of the Galvanic cell expressed by Eq. (10-3) where the solid electrolyte can be a solid solution of SiO_2 containing FeO and CaO. Explain the equation of the electromotive force when the predominant charge carriers are assumed to be Fe^{2+} cations. What is the virtual cell reaction?
- (4) Using Eq. (10-10), calculate the electromotive force of the following Galvanic cell at 1500 K;

$$P_{O_2} = 1.0 \text{ atm, Pt} \left| \begin{array}{c} Na_2O-SiO_2 \\ (a_{Na_2O} = 10^{-6}) \end{array} \right| \begin{array}{c} Na_2O-SiO_2 \\ (a_{Na_2O} = 10^{-10}) \end{array} \left| \text{Pt, } P_{O_2} = 0.1 \text{ atm.} \right.$$

Two liquid electrolytes with different activities of Na_2O are connected by a shallow liquid junction. Assume the charge carriers to be Na^+ cations.

- (5) When the liquid electrolyte of Na_2O-SiO_2 is always saturated with solid silica, the electromotive force can be expressed by Eq. (10-6). Explain the virtual cell reaction for the Galvanic cell of

$$P'_{O_2}, \text{ Pt} \left| \begin{array}{c} \text{liquid } Na_2O-SiO_2 \\ + \text{solid } SiO_2 \end{array} \right| \text{Pt, } P''_{O_2} .$$

- (6) The oxygen sensor expressed by Eq. (10-11) can give the equilibrium oxygen pressure at the temperature of the oxygen sensor. When the waste gas of a boiler contains 70 % N_2 , 28 % CO and 2 % O_2 at 25°C, how much is the electromotive force of the sensor of Eq. (10-11) at 1000 K? Use the standard Gibbs free energy of reaction given in the appendix.
- (7) Figure 10.12 shows the structure of the oxygen sensor with

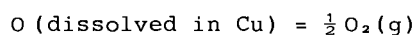
the diffusion-limited current. The constant currents shown in Fig. 10.13 are determined by the rates of steady state "diffuse-in" of oxygen gas through the leak aperture shown in Fig. 10.12. Derive an equation to express the diffusion-limited current as a function of diameter and length of the leak aperture, of diffusivity of oxygen gas and of oxygen content outside of the leak aperture.

- (8) When the applied potential increases beyond the decomposition potential of the solid electrolyte, the current increases again. Calculate the decomposition potential of a pure solid ZrO_2 at 350°C using the standard free energy of formation of ZrO_2 given in the appendix with the equation of

$$\Delta G^\circ = -4FE$$

where ΔG° is the Gibbs free energy, F is Faraday constant, and E is the decomposition potential.

- (9) When the gas contains both oxygen gas and water vapor, the current-voltage relations would be more complicated than those in Fig. 10.13. Calculate the decomposition potential of H_2O gas at 350°C in a gas mixture of 1.0 Volume % H_2O -5 % O_2 -94 % N_2 . The step "B" shown in Fig. 10.15 is reported to be due to the decomposition of moisture. Compare your decomposition potential and the on-set potential of "B" step.
- (10) In Fig. 10.16, the air theoretically needed for a gasoline engine has a 14.5 Air/Fuel ratio by weight. Explain why the electromotive force changes drastically at 14.5 of Air/Fuel ratio.
- (11) As shown in Fig. 10.18, the reference electrode is the inner electrode with air. Calculate the equilibrium ratio of $P_{\text{CO}_2}/P_{\text{CO}}$ at 700°C for the electromotive force of 900 mV.
- (12) In Fig. 10.16, the electromotive force is not so sensitive beyond an Air/Fuel ratio of 16. Why is the oxygen sensor of Fig. 10.19 more sensitive in this range of the Air/Fuel ratio? Use your answer to Problem (7).
- (13) Using the curve shown in Fig. 10.24, calculate the equilibrium constant, K , and the standard Gibbs free energy of the reaction at 1150°C for



where the equilibrium constant K is defined by

$$K \equiv \frac{P_{O_2}^{\frac{1}{2}}}{[\text{ppm } O]} .$$

The air is used for the reference electrode for Fig. 10.24.

Use the general relation of $\Delta G^\circ = -RT \ln K$.

- (14) According to the lowest picture of Fig. 10.28, the oxygen pressure in the matte seems nearly constant at 10^{-11} atm at 1200°C . Calculate the activity ratio of

$$\frac{a_{Fe_2O_3}^2}{a_{FeO}^4} , \text{ according to Eq. (10-13).}$$

Estimate the standard Gibbs free energy of the reaction of Eq. (10-12) from the free energy of various reactions given in the appendix.

- (15) Look for textbooks for refining of copper and other metals. Write chemical reactions taking place during the smelting of copper. Discuss the importance of the oxygen pressure and temperature for smelting. Give your comments to the observation on oxygen pressure and temperature shown in Fig. 10.30.

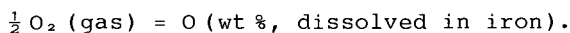
PROBLEMS FOR CHAPTER 11

- (1) The equilibrium constant, K for the dissolution of one half mole of oxygen gas into liquid iron is given by

$$\log_{10} K = \frac{6,120}{T} + 0.15$$

where T is absolute temperature and K is defined by

$$K \equiv \frac{[\text{wt \% } O \text{ in iron}]}{P_{O_2}^{\frac{1}{2}}} , \text{ for the reaction of}$$

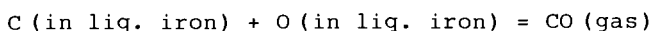


Construct a diagram to show the relation between the $[\text{wt \% } O]$ and the EMF of the oxygen sensor of Fig. 11.1 at 1550°C , 1600°C , and 1700°C . The range of $[\text{wt \% } O]$ must be between 0.0001 wt % and 0.1 wt %.

- (2) Discuss whether the molybdenum needle electrode of Fig. 11.2 would cause an error on the equilibrium oxygen pressure of the thin layer of mixture of Cr and Cr_2O_3 .
- (3) In section (4)-(c) of Chapter 5, the problem of non-isothermal electromotive force was fully discussed. Fig. 11.4 shows that the temperature of the outside of the solid electrolyte dipped in liquid iron is higher than that of the inside during the initial 6 seconds. Discuss the shape of the response curve of

the electromotive force during 15 seconds after dipping the sensor into liquid iron at 1600°C.

- (4) The carbon dissolved in liquid iron reacts with the dissolved oxygen producing carbon monoxide gas by



where the equilibrium constant, K , is defined by

$$K \equiv \frac{P_{\text{CO}}}{[\text{wt \% C}] \times [\text{wt \% O}]} .$$

The common logarithm of K is given by

$$\log_{10} K = \frac{1,168}{T} + 2.07$$

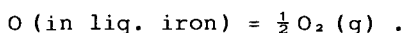
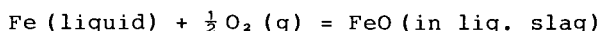
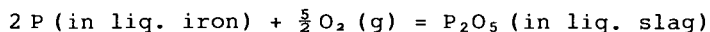
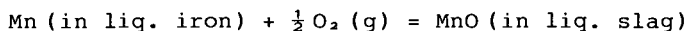
where T is absolute temperature.

Construct a diagram to show the relation between [wt % O] in the range of 0.0001% up to 0.1 wt % and [wt % C] at 1600°C.

Assume that the pressure of carbon monoxide is always 1.0 atm for simplicity in the calculation. Compare your result with the chained curve shown in Fig. 11.7.

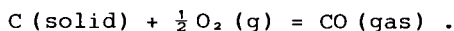
- (5) Concerning Fig. 11.12, one can estimate the electromotive force of the oxygen sensor dipped into liquid iron at the end of refining a steel. Estimate the electromotive force of the sensor when it is dipped into liquid steel containing 0.040 wt % oxygen at 1600°C at the end of refining. Use the equations given in Problem (1) or the diagram obtained in Problem (1).
- (6) In section 11.4.1, the following statement is given; "As long as the oxide melt does not contain any transition metals as impurities, it can be assumed that oxygen is physically dissolved as diatomic molecules". Discuss how oxygen gas would be dissolved if the oxide melt contains transition metal oxides. Comment about the above statement.
- (7) Find the paper in a library by Timucin and Morris published in Metallurgical Transactions of AIME, Vol. 1 (1970) p.3193. Read it and then explain how the broken line in Fig. 11.18 can be estimated. Estimate the magnitude of the error in calculating the broken line.
- (8) Fig. 11.20 shows that the oxygen pressure in the slag of the LD converter with top-blowing oxygen is generally higher than the oxygen pressure in the slag of the Q-BOP converter with bottom-blowing oxygen. Read the text of Chapter 11 concerned with these processes and discuss the difference.

- (9) Equation (11-7') gives the Gibbs free energy change of a refining reaction of Equation (11-7). Explain the derivation of Equation (11-12) and Equation (11-14) from Equation (11-7').
- (10) In Fig. 11.21, the Gibbs free energy changes are given in relation to [ppm O] in liquid steels for the following four chemical reactions;



What does the minus values of ΔG_i mean with respect to the direction of the chemical reactions? Why are the absolute values of ΔG_i decreasing with the increase of [ppm O]? The refining of steels end at about 500 ppm O. Are the above four reactions in thermodynamic equilibrium?

- (11) Fig. 11.23 gives the oxygen pressure in pig iron to be about 10^{-14} atm at about 1450°C. Calculate the equilibrium oxygen pressure in liquid iron saturated by solid carbon at 1450°C by the reaction;



Assume the pressure of CO gas to be 1.0 atm. Find the standard Gibbs free energy change for this reaction from the appendix. Compare your result with the result given by Fig. 11.23.

- (12) Fig. 11.24 shows that the oxygen pressure in the slag is generally higher than that in the pig iron for a long period of the observation. Discuss why. Explain what chemical reactions can be considered to control the oxygen pressure in the slag.

PROBLEMS FOR CHAPTER 12

- (1) In Chapter 2, the semiconductivity of various oxide was discussed in relation to temperature and oxygen pressure. In Fig. 12.1, zinc oxide, an n-type semiconductor, is used as the gas-sensing element. Various gases are adsorbing on the crystal grains of zinc oxide, changing the intergranular resistance. Why does adsorbed oxygen decrease the conductivity, and why do CO₂, benzene, and ethyl alcohol increase the

conductivity?

- (2) In the sensor shown in Fig. 12.4, tin dioxide is used as the sensing element. Give your speculation about the conduction mechanism of SnO_2 and its dependency on the oxygen pressure. The performance of this sensor is shown in Figures 12.5 and 12.6. Discuss whether these performance can be theoretically predicted or not.
- (3) Figure 12.10 shows the experimental results of desorption chromatograms of oxygen gas adsorbed on tin dioxide. Explain how the state of adsorption of oxygen on SnO_2 can be deduced from the results in Fig. 12.10 with help of the observation on the spectrum of electron spin resonance.
- (4) Explain why the resistivity of silica gel, as shown in Fig. 12.11, decreased with the increase of the adsorbed water. Explain the estimated states of the adsorption.
- (5) Explain the principle of determining the humidity in the air by the capacitance change as shown in Figures 12.13 and 12.14.
- (6) Explain the fabrication procedure for an MOS transistor as shown in Fig. 12.20. Explain the physical meaning of the threshold voltage of an MOS transistor.
- (7) The experimental results shown in Figs. 12.22 and 12.23 mean that the threshold voltage is decreased with the adsorption of hydrogen and ammonia. Explain why the decrease in the threshold voltage can be expected. (See Fig. 12.24).
- (8) Figures 12.25 and 12.26 show how the current-voltage characteristics of the diodes are changed by gas adsorption. Explain the principle of gas detection.
- (9) Explain the principle of the humidity sensor shown in Fig. 12.29.
- (10) Explain the principle of the humidity sensor with the piezoelectric oxide used as the sensing element.
- (11) In previous chapters, the sensors for oxygen, sulfur dioxide, and humidity with the solid electrolytes have been introduced. In the present chapter, the gas sensors with various sensing principles are introduced. Give your comments both on the sensors with the solid electrolytes and on the sensors of the present chapter concerning the difficulties in fabrication, the response time, the reproducibility of the electrical output of the sensors, chemical stability of the sensor components, and the life time.

PROBLEMS FOR CHAPTER 13

- (1) In Table 13.2, solid oxides used for sensor elements are summarized. Explain the principles of thermosensors, semiconductor gas sensors, humidity sensors, and solid electrolyte gas sensors. See Chapter 12 for the principles.
- (2) Fig. 13.1 is a sectional view of a vacuum chamber in which a vaporizing source and the substrate to accept the vaporized molecules are contained. The vapor source is contained in a tantalum boat to which an electric current is supplied to heat up the source to a desired temperature. Before the experiment, the chamber is evacuated down to 10^{-5} Torr (10^{-5} mm Hg). Calculate the mean free path of the gaseous molecules remaining, assuming that the remaining gas is oxygen. Use the equation;

$$L = \frac{1}{\pi\sqrt{2}} \times \frac{kT}{p\delta^2}$$

where L is the length of the mean free path, k is Boltzmann constant, T is absolute temperature, p is pressure and δ is the diameter of the gaseous molecule. The diameter of oxygen molecules is 3.64×10^{-8} cm (Problem (14) for Chapter 7 gives an approximate equation for the length of the mean free path).

- (3) According to Fig. 13.7, the vapor pressure of the gaseous species of LiBO_2 is in range of 10^{-5} atmosphere under the experimental conditions concerning this figure. Calculate the length of the mean free path of the molecules of LiBO_2 at 1200, 1300, and 1400 K, assuming the diameter of the molecules to be 10 Angstroms.
- (4) Discuss whether the molecules of LiBO_2 is directly translated to the surface of the substrate under the condition of Problem (3) if the distance between the vaporizing source and the substrate is 10 centimeters. Is there any possibility to have collisions between a LiBO_2 molecule and oxygen molecules leaked into the vacuum chamber?
- (5) Equation (13-1) gives the number of molecules hitting the unit area of the surface per second. Calculate the number of molecules of LiBO_2 per cm^2 per second under the conditions of Problem (3).
- (6) Fig. 13.8 shows the picture of the Knudsen cell. Discuss why the pressure in the cell can be maintained constant even if the gaseous molecules are going out from the small opening.

- (7) Discuss why the condensation coefficient defined by Equation (13-2) is believed equal to the vaporization coefficient. Discuss the probable reasons why these coefficients are sometimes smaller than unity.
- (8) For Fig. 13.7, the partial pressure of oxygen is assumed always to be 10^{-8} atm. Under this condition, the partial pressures of six gaseous species are estimated as functions of temperature. Discuss whether the oxygen pressure would affect the partial pressures of all six species?
- (9) Fig. 13.12 shows the structure of an electrochemical timing cell called "Coulodiode". Calculate the duration for the sudden increase in overpotential when a direct current of 10 mA is supplied to decrease the amount of the 10 mg of silver predeposited on the gold electrode.
- (10) Fig. 13.14 shows the charge-discharge characteristics for the Memoriode. How much is the activity of silver in the silver selenide when the hold voltage is 120 mV at 25°C as shown in Fig. 13.14. Assume the silver activity in silver selenide is uniform.
- (11) Table 13.6 gives the partial conductivities for three kinds of silver ion mixed conductors. Calculate the transference numbers of ions and electrons (or positive holes) for the three mixed conductors at 25°C.
- (12) Fig. 13.16 shows the structure of the valuable resistor cell in which the resistance between the electrodes (a) and (c) can be controlled by the supply of silver through the solid electrolyte. Fig. 13.17 implies that the resistance is increased by the supply of silver into the mixed conductor. Discuss the conduction mechanism assuming that the electronic conductivities given in Table 13.6 are mainly due to silver selenide (Ag_2Se) or silver sulfide (Ag_2S).
- (13) Calculate the standard Gibbs free energy of formation of LiI according to Equation (13-12) at 37°C.
- (14) Discuss what factors would affect the electrical energy contained in the cardiac pacemaker cell. What is the meaning of "high-energy density" for the pacemaker cell?

(2) TABLE

Standard Gibbs free energy of reactions

The table in following pages is reproduced with kind permissions of O. Kubaschewski and C.B. Alcock and Pergamon Press from "Metallurgical Thermochemistry" (1979) 5th edition. The references to the data are deleted for brevity.

The states of materials are expressed by: () = gaseous, { } = liquid, < > = solid, and [] = dissolved. The suffixes are denoting media.

TABLE
Standard Gibbs free energy of reactions
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$2\langle \text{Ag}_2\text{S} \rangle_\alpha = 4\langle \text{Ag} \rangle + (\text{S}_2)$	44,800	—	-22.1	1	298-452
$2\langle \text{Ag}_2\text{S} \rangle_\beta = 4\langle \text{Ag} \rangle + (\text{S}_2)$	41,980	—	-16.52	1	452-1115
$2\{\text{Ag}_2\text{S}\} = 4\{\text{Ag}\} + (\text{S}_2)$	51,800	—	-24.33	1.5	1234-1500
$2\langle \text{Al} \rangle + (\text{Cl}_2) = 2\langle \text{AlCl} \rangle$	-21,360	11.75	-76.5	3	298-933
$2\{\text{Al}\} + (\text{Cl}_2) = 2\{\text{AlCl}\}$	-25,860	11.8	-71.9	3	933-2000
$\langle \text{Al} \rangle + 1\frac{1}{2}(\text{Cl}_2) = \langle \text{AlCl}_3 \rangle$	-138,160	2.48	4.75	5	453-933
$\{\text{Al}\} + 1\frac{1}{2}(\text{Cl}_2) = \{\text{AlCl}_3\}$	-140,400	2.50	7.05	8	> 933
$2\langle \text{Al} \rangle + 3(\text{Cl}_2) = \langle \text{Al}_2\text{Cl}_6 \rangle$	-304,440	4.95	4.23	9	453-933
$\langle \text{Al}_2\text{O}_3 \rangle = 2\langle \text{Al} \rangle + 1\frac{1}{2}(\text{O}_2)$	400,810	3.98	-87.64	3	298-923
$\langle \text{Al}_2\text{O}_3 \rangle = 2\{\text{Al}\} + 1\frac{1}{2}(\text{O}_2)$	405,760	3.75	-92.22	4	923-1800
$2\langle \text{AlN} \rangle = 2\langle \text{Al} \rangle + (\text{N}_2)$	154,000	—	-44.5	16	298-923
$\langle \text{Al}_4\text{C}_3 \rangle = 4\langle \text{Al} \rangle + 3\langle \text{C} \rangle$	51,600	—	-10.0	2	298-932
$\langle \text{Al}_4\text{C}_3 \rangle = 4\{\text{Al}\} + 3\langle \text{C} \rangle$	63,700	—	-23.0	2	932-2000
$\{\text{Al}_2\text{Se}_3\} + 4\{\text{Al}\} = 3\{\text{Al}_2\text{Se}\}$	168,300	—	-97.1	5	1300-1500
$2\langle \text{BaO} \rangle = 2\langle \text{Ba} \rangle + (\text{O}_2)$	271,600	—	-46.4	8	298-983
$2\langle \text{BaO} \rangle = 2\{\text{Ba}\} + (\text{O}_2)$	278,000	—	-53.2	10	983-1600
$\langle \text{BaO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{BaSiO}_3 \rangle$	-26,800	—	+0.1	3	298-1600
$\langle \text{Ba}_3\text{N}_2 \rangle = 3\langle \text{Ba} \rangle + (\text{N}_2)$	87,000	—	-57.4	9	298-1000
$\langle \text{BeF}_2 \rangle = \langle \text{Be} \rangle + (\text{F}_2)$	243,200	15.4	-81.9	5	298-818
$\{\text{BeF}_2\} = \langle \text{Be} \rangle + (\text{F}_2)$	237,280	19.63	-87.0	5	818-1455
$(\text{BeF}_2) = \{\text{Be}\} + (\text{F}_2)$	178,000	5.65	-2.0	5	> 1557
$(\text{BeF}_2) + \langle \text{Be} \rangle = 2(\text{BeF})$	91,500	—	-44.3	—	1425-1675
$(\text{BeCl}_2) + \{\text{Be}\} = 2(\text{BeCl})$	89,100	—	-39.4	5	1573-1723
$2\langle \text{BeO} \rangle = 2\langle \text{Be} \rangle + (\text{O}_2)$	286,900	3.32	-56.1	10	298-1557
$2\langle \text{BeO} \rangle = 2\{\text{Be}\} + (\text{O}_2)$	291,900	3.32	-59.32	13	1557-2000
$\langle \text{Be}_3\text{N}_2 \rangle = 3\langle \text{Be} \rangle + (\text{N}_2)$	134,700	—	-40.6	12	298-1000
$\frac{2}{3}\langle \text{BiCl}_3 \rangle = \frac{2}{3}\langle \text{Bi} \rangle + (\text{Cl}_2)$	62,400	12.05	-66.6	3	298-503
$\frac{2}{3}\{\text{BiCl}_3\} = \frac{2}{3}\{\text{Bi}\} + (\text{Cl}_2)$	63,570	17.5	-83.4	4	544-714
$\frac{2}{3}(\text{BiCl}_3) = \frac{2}{3}(\text{Bi}) + (\text{Cl}_2)$	45,330	-3.96	+34.2	5	714-1500
$(\text{BiCl}_3) + 2\{\text{Bi}\} = 3(\text{BiCl})$	72,000	—	-54.0	5	873-973
$(\text{BiBr}_3) + 2\{\text{Bi}\} = 3(\text{BiBr})$	66,700	—	-54.0	5	870-980
$\langle \text{Bi}_2\text{S}_3 \rangle + 3(\text{H}_2) = 2\langle \text{Bi} \rangle + 3(\text{H}_2\text{S})$	24,500	27.73	-114.7	3	298-544
$\langle \text{Bi}_2\text{O}_3 \rangle = 2\{\text{Bi}\} + 1\frac{1}{2}(\text{O}_2)$	-137,890	—	+63.43	1	773-1093
$\langle \text{C} \rangle + 2(\text{H}_2) = (\text{CH}_4)$	-16,520	+12.25	-15.62	1	298-1200
$\langle \text{C} \rangle + 2(\text{F}_2) = (\text{CF}_4)$	-220,000	—	+36.0	5	298-1500
$\langle \text{C} \rangle + 2(\text{Cl}_2) = (\text{CCl}_4)$	-26,250	-5.16	49.32	1	350-800
$\langle \text{C} \rangle + \frac{1}{2}(\text{O}_2) = (\text{CO})$	-26,700	—	-20.95	1	298-2500
$\langle \text{C} \rangle + (\text{O}_2) = (\text{CO}_2)$	-94,200	—	-0.2	1	298-2000
$\langle \text{C} \rangle + \frac{1}{2}(\text{S}_2) = (\text{CS})$	59,000	—	-22.75	7	1873-2073
$\langle \text{C} \rangle + (\text{S}_2) = (\text{CS}_2)$	-3,100	—	-1.73	1	298-1600
$2(\text{CO}) + (\text{S}_2) = 2(\text{COS})$	-45,720	—	+37.4	3	298-1500
graphite = diamond	+310	—	1.13	0.2	298-1500
$\langle \text{CaF}_2 \rangle_\alpha = \langle \text{Ca} \rangle + (\text{F}_2)$	293,300	7.7	-64.4	5	298-1123
$\langle \text{CaF}_2 \rangle_\beta = \langle \text{Ca} \rangle + (\text{F}_2)$	297,600	16.9	-98.35	6	1123-1424
$\langle \text{CaF}_2 \rangle_\gamma = \langle \text{Ca} \rangle + (\text{F}_2)$	285,000	—	-35.0	7	1424-1756
$\langle \text{CaCl}_2 \rangle = \langle \text{Ca} \rangle + (\text{Cl}_2)$	189,900	—	-34.0	3	298-1055
$\{\text{CaCl}_2\} = \{\text{Ca}\} + (\text{Cl}_2)$	195,400	24.44	-112.6	5	1120-1900
$2\langle \text{CaO} \rangle = 2\langle \text{Ca} \rangle + (\text{O}_2)$	302,650	—	-47.32	3	298-1124
$2\langle \text{CaO} \rangle = 2\{\text{Ca}\} + (\text{O}_2)$	307,100	—	-51.28	3	1124-1760
$2\{\text{CaO}\} = 2\{\text{Ca}\} + (\text{O}_2)$	380,200	—	-93.24	5	1760-2500

TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + B T \log T + C T$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K.)
	A	B	C		
$2\langle \text{CaS} \rangle = 2\langle \text{Ca} \rangle_s + (\text{S}_2)$	258,870	—	-45.62	2	298-673
$2\langle \text{CaS} \rangle = 2\langle \text{Ca} \rangle_g + (\text{S}_2)$	259,100	—	-45.92	2	673-1124
$2\langle \text{CaS} \rangle = 2\langle \text{Ca} \rangle + (\text{S}_2)$	263,560	—	-49.88	3	1124-1760
$2\langle \text{CaS} \rangle = 2(\text{Ca}) + (\text{S}_2)$	336,710	—	-91.44	5	1760-2000
$\langle \text{Ca}_3\text{N}_2 \rangle = 3\langle \text{Ca} \rangle + (\text{N}_2)$	105,000	—	-50.0	11	298-1100
$\langle \text{Ca} \rangle_s + 2\langle \text{C} \rangle = \langle \text{CaC}_2 \rangle$	-13,600	—	-5.9	3	298-720
$\langle \text{Ca} \rangle_g + 2\langle \text{C} \rangle = \langle \text{CaC}_2 \rangle$	-11,620	—	-8.64	3	720-1123
$\langle \text{Ca} \rangle + 2\langle \text{C} \rangle = \langle \text{CaC}_2 \rangle$	-13,700	—	-6.80	3	1123-1963
$(\text{Ca}) + 2\langle \text{C} \rangle = \langle \text{CaC}_2 \rangle$	-51,210	—	+12.3	5	1963-2200
$\langle \text{CaCO}_3 \rangle = \langle \text{CaO} \rangle + (\text{CO}_2)$	40,250	—	-34.4	1	449-1150
$\langle \text{Ca} \rangle + \langle \text{Si} \rangle = \langle \text{CaSi} \rangle$	-36,000	—	-0.5	4	298-1123
$\langle \text{Ca} \rangle + \langle \text{Si} \rangle = \langle \text{CaSi} \rangle$	-25,750	—	-6.58	5	1520-1717
$2\langle \text{Ca} \rangle + \langle \text{Si} \rangle = \langle \text{Ca}_2\text{Si} \rangle$	-42,600	—	-4.65	5	1200-1717
$\langle \text{CaO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{CaSiO}_3 \rangle_s$	-21,300	—	+0.12	1	298-1483
$\langle \text{CaO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{CaSiO}_3 \rangle_g$	-19,900	—	-0.82	2	1483-1813
$2\langle \text{CaO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{Ca}_2\text{SiO}_4 \rangle$	-30,200	—	-1.2	2.5	298-1700
$2\langle \text{CdO} \rangle = 2(\text{Cd}) + (\text{O}_2)$	174,500	—	-99.9	—	1242-1379
$\langle \text{CeCl}_3 \rangle = \langle \text{Ce} \rangle + \frac{1}{2}(\text{Cl}_2)$	255,200	18.4	-114.9	4	298-900
$\langle \text{CeO}_2 \rangle = \langle \text{Ce} \rangle + (\text{O}_2)$	260,900	5.0	-65.25	3	298-1000
$2\langle \text{CeS} \rangle = 2\langle \text{Ce} \rangle + (\text{S}_2)$	267,000	—	-40.0	10	298-2200
$2\langle \text{CeN} \rangle = 2\langle \text{Ce} \rangle + (\text{N}_2)$	156,000	—	-57.5	17	298-1000
$\langle \text{CeC} \rangle = \langle \text{Ce} \rangle + \langle \text{C} \rangle$	27,900	—	-8.2	—	815-940
$2(\text{CoCl}_3) = 2(\text{CoCl}_2) + (\text{Cl}_2)$	33,800	—	-36.3	2	900-1100
$\langle \text{CoCl}_2 \rangle = \langle \text{Co} \rangle + (\text{Cl}_2)$	78,700	6.9	-54.12	3	298-1000
$\langle \text{CoCl}_3 \rangle = \langle \text{Co} \rangle + (\text{Cl}_2)$	72,200	9.2	-54.52	4	1000-1323
$(\text{CoCl}_3) = \langle \text{Co} \rangle + (\text{Cl}_2)$	31,700	-13.8	+47.8	4	1323-1786
$\langle \text{CoF}_2 \rangle = \langle \text{Co} \rangle + (\text{F}_2)$	158,000	—	-33.7	6	298-1450
$2\langle \text{CoO} \rangle = 2\langle \text{Co} \rangle + (\text{O}_2)$	111,800	—	-33.8	2	298-1400
$\langle \text{Co}_3\text{O}_4 \rangle = 3\langle \text{CoO} \rangle + \frac{1}{2}(\text{O}_2)$	43,800	—	-35.4	3	298-1300
$\frac{1}{2}\langle \text{Co}_9\text{S}_8 \rangle = \frac{3}{2}\langle \text{Co} \rangle + (\text{S}_2)$	79,240	—	-39.81	2	298-1048
$\frac{1}{2}\langle \text{Co}_9\text{S}_8 \rangle + (\text{S}_2) = \frac{3}{2}\langle \text{Co}_3\text{S}_4 \rangle$	-51,640	—	+34.03	3	600-750
$3\langle \text{CoS}_2 \rangle = \langle \text{Co}_3\text{S}_4 \rangle + (\text{S}_2)$	50,160	—	-50.41	3	600-900
$\langle \text{Co}_2\text{C} \rangle = 2\langle \text{Co} \rangle + \langle \text{C} \rangle$	-3950	—	+2.08	5	298-1200
$\langle \text{CrCl}_2 \rangle = \langle \text{Cr} \rangle + (\text{Cl}_2)$	93,900	8.7	-55.0	3	298-1088
$\langle \text{CrCl}_2 \rangle = \langle \text{Cr} \rangle + (\text{Cl}_2)$	86,900	8.36	-47.5	3	1088-1577
$(\text{CrCl}_2) = \langle \text{Cr} \rangle + (\text{Cl}_2)$	27,700	-6.26	+37.0	5	1577-2100
$\frac{3}{2}\langle \text{CrCl}_3 \rangle = \frac{3}{2}\langle \text{Cr} \rangle + (\text{Cl}_2)$	87,400	7.42	-58.4	5	298-1200
$\langle \text{Cr}_2\text{O}_3 \rangle = 2\langle \text{Cr} \rangle + \frac{3}{2}(\text{O}_2)$	277,190	—	-53.25	2	298-2100
$2\langle \text{Cr}_2\text{N} \rangle = 4\langle \text{Cr} \rangle + (\text{N}_2)$	51,900	11.5	-66.0	5	298-1400
$4\langle \text{CrN} \rangle = 2\langle \text{Cr}_2\text{N} \rangle + (\text{N}_2)$	64,000	11.5	-83.2	5	298-1400
$\frac{1}{2}\langle \text{Cr}_2\text{C}_6 \rangle = \frac{2}{3}\langle \text{Cr} \rangle + \langle \text{C} \rangle$	+16,380	—	+1.54	3	298-1673
$\frac{2}{3}\langle \text{Cr}_7\text{C}_3 \rangle = \frac{7}{3}\langle \text{Cr}_2\text{C}_6 \rangle + \langle \text{C} \rangle$	10,050	—	2.85	3	298-1673
$\frac{2}{3}\langle \text{Cr}_3\text{C}_2 \rangle = \frac{3}{2}\langle \text{Cr}_7\text{C}_3 \rangle + \langle \text{C} \rangle$	3200	—	0.20	3	298-1673
$(\text{CuCl}) + \frac{1}{2}(\text{H}_2) = \langle \text{Cu} \rangle + (\text{HCl})$	-43,660	-4.17	+31.81	2	298-1300
$(\text{Cu}_3\text{Cl}_3) + \frac{3}{2}(\text{H}_2) = 3\langle \text{Cu} \rangle + 3(\text{HCl})$	-4500	—	-9.4	2	1300
$\langle \text{Cu}_2\text{O} \rangle = 2\langle \text{Cu} \rangle + \frac{1}{2}(\text{O}_2)$	40,500	3.92	-29.5	1	298-1356
or $\langle \text{Cu}_2\text{O} \rangle = 2\langle \text{Cu} \rangle + \frac{1}{2}(\text{O}_2)$	39,800	—	-16.88	—	—
$2\langle \text{CuO} \rangle = \langle \text{Cu}_2\text{O} \rangle + \frac{1}{2}(\text{O}_2)$	46,700	3.92	-34.1	1.5	1356-1503
$2\langle \text{CuO} \rangle = \langle \text{Cu}_2\text{O} \rangle + \frac{1}{2}(\text{O}_2)$	34,950	6.1	-44.3	0.5	298-1300
$\langle \text{Cu}_2\text{S} \rangle_s = 2\langle \text{Cu} \rangle + \frac{1}{2}(\text{S}_2)$	35,655	4.34	-27.31	1	298-376
$\langle \text{Cu}_2\text{S} \rangle_s = \langle \text{Cu}_2\text{S} \rangle_g$	-490	-8.63	+23.53	1	—
$\langle \text{Cu}_2\text{S} \rangle_g = 2\langle \text{Cu} \rangle + \frac{1}{2}(\text{S}_2)$	34,150	6.22	-28.74	1	623-1360

TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$\langle \text{FeCl}_2 \rangle = \langle \text{Fe} \rangle_s + (\text{Cl}_2)$	82,770	6.98	-50.84	1	298-950
$\{\text{FeCl}_2\} = \langle \text{Fe} \rangle + (\text{Cl}_2)$	68,450	—	-15.22	1	950-1300
$(\text{FeCl}_2) = \langle \text{Fe} \rangle_s + (\text{Cl}_2)$	25,250	-23.0	+89.65	4	1300-1812
$2\langle \text{FeCl}_3 \rangle = 2\langle \text{FeCl}_2 \rangle + (\text{Cl}_2)$	25,900	—	-38.7	1	400-500
$2(\text{FeCl}_3) = (\text{Fe}_2\text{Cl}_6)$	-32,550	—	+31.65	1	778-978
$\langle \text{FeF}_2 \rangle = \langle \text{Fe} \rangle + (\text{F}_2)$	167,000	—	-31.8	6	298-1350
$2(\text{FeBr}_3) = 2(\text{FeBr}_2) + (\text{Br}_2)$	44,600	—	-33.7	2	750
$\langle \text{FeI}_2 \rangle = \langle \text{Fe} \rangle + (\text{I}_2)$	45,770	6.9	-51.2	5	298-867
$\{\text{FeI}_2\} = \langle \text{Fe} \rangle + (\text{I}_2)$	40,600	11.5	-58.6	6	867-1208
$2(\text{FeI}_3) = 2(\text{FeI}_2) + (\text{I}_2)$	32,000	—	-32.0	2	700-1000
$\langle \text{FeO} \rangle = \langle \text{Fe} \rangle + \frac{1}{2}(\text{O}_2)$	63,310	—	-15.62	3	298-1642
$\{\text{FeO}\} = \langle \text{Fe} \rangle + \frac{1}{2}(\text{O}_2)$	55,620	—	-10.83	3	1808-2000
$\langle \text{Fe}_3\text{O}_4 \rangle = 3\langle \text{FeO} \rangle + \frac{1}{2}(\text{O}_2)$	74,620	—	-29.9	3	298-1642
$3\langle \text{Fe}_2\text{O}_3 \rangle = 2\langle \text{Fe}_3\text{O}_4 \rangle + \frac{1}{2}(\text{O}_2)$	59,620	—	-33.62	8	298-1460
$\langle \text{Fe} \rangle + 2(\text{H}_2\text{O}) = (\text{Fe}(\text{OH})_2) + (\text{H}_2)$	42,700	—	-7.31	2	1573-1733
$2\langle \text{FeS} \rangle_s = 2\langle \text{Fe} \rangle_s + (\text{S}_2)$	74,320	—	-31.18	1	298-412
$2\langle \text{FeS} \rangle_f = 2\langle \text{Fe} \rangle_s + (\text{S}_2)$	71,820	—	-25.12	1	412-1179
$2\langle \text{FeS} \rangle_f = 2\langle \text{Fe} \rangle_s + (\text{S}_2)$	72,140	—	-25.48	2	1179-1261
$2\langle \text{FeS}_2 \rangle = 2\langle \text{FeS} \rangle + (\text{S}_2)$	86,700	—	-90.0	3	600-1100
$\langle \text{Fe}_3\text{N} \rangle = 4\langle \text{Fe} \rangle + \frac{1}{2}(\text{N}_2)$	200	-11.62	24.85	3	298-950
$\langle \text{Fe}_3\text{P} \rangle = 3\langle \text{Fe} \rangle + \frac{1}{2}(\text{P}_2)$	51,000	—	-11.3	8	298-1439
$3\langle \text{FeCO}_3 \rangle = \langle \text{Fe}_3\text{O}_4 \rangle + 2(\text{CO}_2) + (\text{CO})$	52,800	—	-11.22	14	298-700
$2\langle \text{Fe} \rangle + (\text{O}_2) + \langle \text{SiO}_2 \rangle = \langle \text{Fe}_2\text{SiO}_4 \rangle$	-135,300	—	+34.4	3	298-1478
$2\langle \text{Fe} \rangle + (\text{O}_2) + 2\langle \text{TiO}_2 \rangle = 2\langle \text{FeTiO}_3 \rangle$	-129,220	—	+25.86	2	1173-1400
$2\langle \text{Fe} \rangle + (\text{O}_2) + 2\langle \text{Cr}_2\text{O}_3 \rangle = 2\langle \text{FeCr}_2\text{O}_4 \rangle$	-131,600	—	+24.2	3	1173-1700
$2\langle \text{Fe} \rangle + (\text{O}_2) + 2\langle \text{Al}_2\text{O}_3 \rangle = 2\langle \text{FeAl}_2\text{O}_4 \rangle$	-150,000	—	+41.8	8	1100-1400
$\langle \text{Ga}_2\text{O}_3 \rangle = 2\{\text{Ga}\} + \frac{1}{2}\text{O}_2$	-259,340	—	+78.11	1	820-1073
$2\langle \text{GeI}_2 \rangle = \langle \text{Ge} \rangle + (\text{GeI}_4)$	32,500	18.4	-94.6	3	298-643
$(\text{GeO}) = \frac{1}{2}\langle \text{Ge} \rangle + \frac{1}{2}\langle \text{GeO}_2 \rangle$	-54,600	-6.9	+62.0	4	298-860
$\langle \text{GeO}_2 \rangle = \langle \text{Ge} \rangle + \text{O}_2$	-137,330	—	+44.86	1	600-1173
$2(\text{HF}) = (\text{H}_2) + (\text{F}_2)$	130,200	—	+1.9	—	298-2500
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}(\text{Cl}_2) = (\text{HCl})$	-21,770	0.99	-5.22	0.6	298-2100
$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$	-57,250	4.48	-2.21	0.3	298-2500
$(\text{H}_2) + \langle \text{S} \rangle = (\text{H}_2\text{S})$ or	-58,900	—	13.1	1	298-2500
$(\text{H}_2) + \langle \text{S} \rangle = (\text{H}_2\text{S})$	-3320	11.72	-44.55	0.6	298-392
$2(\text{H}_2) + (\text{S}_2) = 2(\text{H}_2\text{S})$	-40,210	7.25	-1.21	0.7	298-1750
or	-43,160	—	23.61	1	298-1800
$\frac{1}{2}(\text{N}_2) + \frac{1}{2}(\text{H}_2) = (\text{NH}_3)$	-10,400	7.1	3.79	0.5	298-1000
or	-12,050	—	+26.7	2	298-1000
$\langle \text{In}_2\text{O}_3 \rangle + 3(\text{H}_2) = 2\{\text{In}\} + 3(\text{H}_2\text{O})$	44,960	3.35	-49.63	3	430-1123
$\langle \text{In}_2\text{O}_3 \rangle = 2\{\text{In}\} + \frac{1}{2}\text{O}_2$	-215,550	—	+72.63	1	800-1123
$\langle \text{InS} \rangle + (\text{H}_2) = \{\text{In}\} + (\text{H}_2\text{S})$	41,900	2.75	-41.4	3	298-1000
$\langle \text{IrO}_2 \rangle = \langle \text{Ir} \rangle + (\text{O}_2)$	52,200	12.65	-77.25	4	298-1366
$\langle \text{Ir} \rangle + \frac{1}{2}(\text{O}_2) = (\text{IrO})$	4150	—	+10.8	—	1473-1673
$\frac{2}{3}\langle \text{Ir}_2\text{S}_3 \rangle = \frac{4}{3}\langle \text{Ir} \rangle + (\text{S}_2)$	64,500	—	-44.66	5	1000-1600
$\langle \text{KCl} \rangle = \{\text{K}\} + \frac{1}{2}(\text{Cl}_2)$	104,900	—	-24.0	1	298-1043
$\{\text{KCl}\} = (\text{K}) + \frac{1}{2}(\text{Cl}_2)$	116,600	—	-35.2	1.5	1043-1680
$(\text{KCl}) = (\text{K}) + \frac{1}{2}(\text{Cl}_2)$	66,000	-16.1	-46.84	2	1680-2300
$\langle \text{K}_2\text{O} \rangle = 2\langle \text{K} \rangle + \frac{1}{2}(\text{O}_2)$	86,600	-4.6	-44.6	3	298-

TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$\langle \text{La}_2\text{O}_3 \rangle = 2\langle \text{La} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	447,200	9.2	-96.9	4	298-1000
$\langle \text{LaN} \rangle = \langle \text{La} \rangle + \frac{1}{2}\langle \text{N}_2 \rangle$	72,100	—	-25.0	9	298-1000
$2\langle \text{LiOH} \rangle = \langle \text{Li}_2\text{O} \rangle + \langle \text{H}_2\text{O} \rangle$	34,940	—	-25.98	3	648-795
$\{\text{Li}_2\text{CO}_3\} = \{\text{Li}_2\text{O}\} + \langle \text{CO}_2 \rangle$	77,950	—	-69.0		m.p.-1125
$\langle \text{MgF}_2 \rangle = \langle \text{Mg} \rangle + \langle \text{F}_2 \rangle$	267,200	—	-40.2	3	298-923
$\langle \text{MgF}_2 \rangle = \{\text{Mg}\} + \langle \text{F}_2 \rangle$	269,300	—	-42.5	3	923-1276
$\langle \text{MgCl}_2 \rangle = \langle \text{Mg} \rangle + \langle \text{Cl}_2 \rangle$	154,440	9.88	-68.18	1	298-923
$\{\text{MgCl}_2\} = \{\text{Mg}\} + \langle \text{Cl}_2 \rangle$	147,850	13.58	-72.77	1.5	987-1376
$\{\text{MgCl}_2\} = \langle \text{Mg} \rangle + \langle \text{Cl}_2 \rangle$	184,100	20.71	-121.52	1.5	1380-1691
$\{\text{MgCl}_2\} = \langle \text{Mg} \rangle + \langle \text{Cl}_2 \rangle$	134,500	-2.29	-17.94	5	1691-2000
$\langle \text{MgO} \rangle = \langle \text{Mg} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	144,350	2.95	-33.95	1.5	298-923
$\langle \text{MgO} \rangle = \{\text{Mg}\} + \frac{1}{2}\langle \text{O}_2 \rangle$	145,350	0.24	-26.95	1.5	923-1380
$\langle \text{MgO} \rangle = \langle \text{Mg} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	181,600	7.37	-75.7	3	1380-2500
$\langle \text{Mg}(\text{OH})_2 \rangle = \langle \text{MgO} \rangle + \langle \text{H}_2\text{O} \rangle$	11,000	—	-24.0		653-923
$\langle \text{MgS} \rangle = \langle \text{Mg} \rangle + \frac{1}{2}\langle \text{S}_2 \rangle$	99,650	—	-22.8	5	298-923
$\langle \text{MgS} \rangle = \{\text{Mg}\} + \frac{1}{2}\langle \text{S}_2 \rangle$	101,800	—	-25.65	5	923-1380
$\langle \text{MgS} \rangle = \langle \text{Mg} \rangle + \frac{1}{2}\langle \text{S}_2 \rangle$	134,350	—	-48.75	5	1380-2000
$\langle \text{Mg}_3\text{N}_2 \rangle_s = 3\langle \text{Mg} \rangle + \langle \text{N}_2 \rangle$	109,600	—	-47.41	3	298-823
$\langle \text{Mg}_3\text{N}_2 \rangle_s = 3\{\text{Mg}\} + \langle \text{N}_2 \rangle$	115,970	—	-54.30	3	923-1061
$\langle \text{Mg}_3\text{N}_2 \rangle_s = 3\{\text{Mg}\} + \langle \text{N}_2 \rangle$	115,750	—	-54.09	3	1061-1300
$\langle \text{MgCO}_3 \rangle = \langle \text{MgO} \rangle + \langle \text{CO}_2 \rangle$	28,100	—	-40.6	4	298-1000
$\langle \text{MgO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{MgSiO}_3 \rangle$	-8900	—	+1.1	1	298-1600
$2\langle \text{MgO} \rangle + \langle \text{SiO}_2 \rangle = \langle \text{Mg}_2\text{SiO}_4 \rangle$	-15,120	—	0.0	2	298-1700
$\langle \text{MnCl}_2 \rangle = \langle \text{Mn} \rangle_s + \langle \text{Cl}_2 \rangle$	116,300	8.37	-56.0	1	298-923
$\{\text{MnCl}_2\} = \langle \text{Mn} \rangle_s + \langle \text{Cl}_2 \rangle$	107,970	9.11	-49.15	1	993-1373
$\{\text{MnCl}_2\} = \langle \text{Mn} \rangle_s + \langle \text{Cl}_2 \rangle$	105,930	4.07	-31.84	1.5	1400-1504
$\{\text{MnCl}_2\} = \{\text{Mn}\} + \langle \text{Cl}_2 \rangle$	53,450	-16.4	+68.2	2	1517-
$\langle \text{MnO} \rangle = \langle \text{Mn} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	91,950	—	-17.4	3	298-1500
$\langle \text{MnO} \rangle = \{\text{Mn}\} + \frac{1}{2}\langle \text{O}_2 \rangle$	95,400	—	-19.7	3	1500-2050
$\langle \text{MnS} \rangle = \langle \text{Mn} \rangle_s + \frac{1}{2}\langle \text{S}_2 \rangle$	64,000	—	-15.32	1.5	298-1000
$\langle \text{MnS} \rangle = \langle \text{Mn} \rangle_s + \frac{1}{2}\langle \text{S}_2 \rangle$	64,540	—	-15.86	1.5	1000-1374
$\langle \text{MnS} \rangle = \langle \text{Mn} \rangle_s + \frac{1}{2}\langle \text{S}_2 \rangle$	65,510	—	-16.56	1.5	1410-1517
$\langle \text{MnS} \rangle = \{\text{Mn}\} + \frac{1}{2}\langle \text{S}_2 \rangle$	69,010	—	-18.86	2	1517-1803
$\{\text{MnS}\} = \{\text{Mn}\} + \frac{1}{2}\langle \text{S}_2 \rangle$	62,770	—	-15.40	2	1803-2000
$\langle \text{Mn}_3\text{C} \rangle = 3\langle \text{Mn} \rangle + \langle \text{C} \rangle$	3330	—	+0.26	3	298-1010
$\langle \text{MnSiO}_3 \rangle = \langle \text{MnO} \rangle + \langle \text{SiO}_2 \rangle$	5920	—	-3.0	4	298-1600
$\langle \text{MoI}_2 \rangle = \langle \text{Mo} \rangle + 2\langle \text{I} \rangle$	25,000	—	9.5	2	1050-1500
$\langle \text{MoO}_2 \rangle = \langle \text{Mo} \rangle + \langle \text{O}_2 \rangle$	140,500	4.6	-56.8	6	298-1300
$\langle \text{MoO}_3 \rangle = \langle \text{MoO}_2 \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	38,700	—	-19.5	3	298-1300
$2\langle \text{Mo}_2\text{N} \rangle = 4\langle \text{Mo} \rangle + \langle \text{N}_2 \rangle$	34,400	9.2	-57.9	8	298-1300
$\frac{4}{3}\langle \text{Mo}_2\text{S}_3 \rangle = \frac{2}{3}\langle \text{Mo} \rangle + \langle \text{S}_2 \rangle$	85,700	—	-36.41	2	1123-1473
$\langle \text{NaF} \rangle = \{\text{Na}\} + \frac{1}{2}\langle \text{F}_2 \rangle$	137,000	—	-24.9	3	271-1156
$\langle \text{NaCl} \rangle = \{\text{Na}\} + \frac{1}{2}\langle \text{Cl}_2 \rangle$	99,000	—	-23.6	1.5	298-1073
$\{\text{NaCl}\} = \langle \text{Na} \rangle + \frac{1}{2}\langle \text{Cl}_2 \rangle$	114,300	—	-35.8	2	1183-1738
$\langle \text{Na}_2\text{S} \rangle = 2\{\text{Na}\} + \frac{1}{2}\langle \text{S}_2 \rangle$	105,250	—	-31.45	5	371-1187
$\langle \text{Na}_2\text{SiO}_3 \rangle = \langle \text{Na}_2\text{O} \rangle + \langle \text{SiO}_2 \rangle$	55,550	—	+1.40	8	298-1361
	43,080	—	10.55	10	1361-1600
$2\langle \text{NbCl}_4 \rangle = \langle \text{NbCl}_3 \rangle + \langle \text{NbCl}_5 \rangle$	28,300	—	-47.0	1	475-590
$2\langle \text{NbO} \rangle = 2\langle \text{Nb} \rangle + \langle \text{O}_2 \rangle$	198,700	11.5	-77.0	4	298-
$2\langle \text{NbO}_2 \rangle = 2\langle \text{NbO} \rangle + \langle \text{O}_2 \rangle$	185,100	11.5	-79.5	4	298-
$2\langle \text{Nb}_2\text{O}_5 \rangle = 4\langle \text{NbO}_2 \rangle + \langle \text{O}_2 \rangle$	149,700	11.5	-68.9	5	298-
$\langle \text{NbC} \rangle = \langle \text{Nb} \rangle + \langle \text{C} \rangle$	31,100	—	-0.4		1180-1370

TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$\langle \text{NdCl}_3 \rangle + (\text{H}_2\text{O}) = \langle \text{NdOCl} \rangle + 2(\text{HCl})$	20,910	—	-30.31	3	785
$\langle \text{NiCl}_2 \rangle + (\text{H}_2) = \langle \text{Ni} \rangle + 2(\text{HCl})$	29,075	6.15	-58.53	0.8	298-1260
$\langle \text{NiO} \rangle = \langle \text{Ni} \rangle + \frac{1}{2}(\text{O}_2)$	56,010	—	-20.37	2	298-1725
$\langle \text{NiO} \rangle = \langle \text{Ni} \rangle + \frac{1}{2}(\text{O}_2)$	62,650	—	-25.98	3	1725-2200
$\langle \text{Ni}_3\text{C} \rangle = 3\langle \text{Ni} \rangle + \langle \text{C} \rangle$	-8110	—	+1.70	3	298-1000
$\langle \text{Ni}_3\text{S}_2 \rangle = 3\langle \text{Ni} \rangle + (\text{S}_2)$	79,240	—	-39.01	2	650-800
$2\langle \text{NiS} \rangle = 2\langle \text{Ni} \rangle + (\text{S}_2)$	69,960	—	-34.41	3	670-850
$(\text{P}_4) = 2(\text{P}_2)$	53,860	4.35	-50.05	3	298-1200
$(\text{PCl}_3) = (\text{P}) + (\text{Cl}_2)$	22,850	4.37	-56.22	4	298-1000
$\langle \text{PbCl}_2 \rangle = \langle \text{Pb} \rangle + (\text{Cl}_2)$	85,000	—	-34.3	2	298-771
$\langle \text{PbCl}_2 \rangle = \langle \text{Pb} \rangle + (\text{Cl}_2)$	83,600	14.12	-73.3	3	771-1224
$(\text{PbCl}_2) = (\text{Pb}) + (\text{Cl}_2)$	37,800	-16.3	+57.92	3	1224-1500
$2\langle \text{PbO} \rangle = 2\langle \text{Pb} \rangle + (\text{O}_2)$	105,700	6.9	-68.86	4	298-600
$2\langle \text{PbO} \rangle = 2\langle \text{Pb} \rangle + (\text{O}_2)$	107,500	—	-52.6	4	600-760
$2\langle \text{PbO} \rangle = 2\langle \text{Pb} \rangle + (\text{O}_2)$	106,600	—	-51.4	4	760-1150
$2\langle \text{PbS} \rangle = 2\langle \text{Pb} \rangle + (\text{S}_2)$	72,710	—	-34.17	3	298-600
$2\langle \text{PbS} \rangle = 2\langle \text{Pb} \rangle + (\text{S}_2)$	75,160	—	-38.25	3	600-1380
$\langle \text{PbSe} \rangle = \langle \text{Pb} \rangle + \langle \text{Se} \rangle$	25,340	—	-3.8	2	473-573
$\langle \text{PdCl}_2 \rangle = \langle \text{Pd} \rangle + (\text{Cl}_2)$					
$\langle \text{PdCl}_2 \rangle = \langle \text{Pd} \rangle + (\text{Cl}_2)$					
$\langle \text{PdO} \rangle = \langle \text{Pd} \rangle + \frac{1}{2}(\text{O}_2)$	22,400	5.75	-36.9	2	298-1133
$\langle \text{PrCl}_3 \rangle + (\text{H}_2\text{O}) = \langle \text{PrOCl} \rangle + 2(\text{HCl})$	21,530	—	-30.07	3	785
$(\text{PtO}_2) = \langle \text{Pt} \rangle + (\text{O}_2)$	-39,270	—	+0.93	2	1373-1823
$2\langle \text{PtS} \rangle = 2\langle \text{Pt} \rangle + (\text{S}_2)$	66,100	—	-43.6	5	1000-1700
$2\langle \text{PtS}_2 \rangle = 2\langle \text{PtS} \rangle + (\text{S}_2)$	43,750	—	-43.8	5	700-1100
$\langle \text{ReS}_2 \rangle = \langle \text{Re} \rangle + (\text{S}_2)$	64,200	9.2	-68.6	5	298-1500
$(\text{RhO}_2) = \langle \text{Rh} \rangle + (\text{O}_2)$	-45,140	—	+4.94	1	1473-1773
$(\text{RuCl}_4) = \langle \text{Ru} \rangle + 2(\text{Cl}_2)$	21,650	-4.83	-8.4	2	298-1400
$\langle \text{RuCl}_3 \rangle = \langle \text{Ru} \rangle + \frac{1}{2}(\text{Cl}_2)$	61,800	10.35	-86.5		
$\langle \text{RuO}_2 \rangle = \langle \text{Ru} \rangle + (\text{O}_2)$	73,600	6.9	-62.4		298-1850
$(\text{S}_2) = \frac{1}{2}(\text{S}_4)$	-14,200	—	+15.94	2.5	298-1300
$(\text{S}_2) = \frac{1}{2}(\text{S}_4)$	-21,240	—	+23.1	1	298-1300
$(\text{S}_2) = \frac{1}{2}(\text{S}_4)$	-23,040	—	+25.3	2	298-1300
$(\text{S}_2) = 2(\text{S})$	+77,250	—	-29.7	10	298-2000
$2(\text{SO}) = (\text{S}_2) + (\text{O}_2)$	30,800	—	+2.8	7	298-2000
$(\text{S}_2) + 2(\text{O}_2) = 2(\text{SO}_2)$	-173,240	—	34.62	1	298-2000
$(\text{S}_2) + 3(\text{O}_2) = 2(\text{SO}_3)$	-218,440	—	77.34	3	318-1800
$\langle \text{Sb}_2\text{O}_3 \rangle = 2\langle \text{Sb} \rangle + \frac{1}{2}(\text{O}_2)$	-164,340	—	+57.62	1	773-900
$(\text{SiCl}_4) = \langle \text{Si} \rangle + 2(\text{Cl}_2)$	155,600	3.64	-43.9	3	298-1000
$\langle \text{Si} \rangle + (\text{SiCl}_4) = 2(\text{SiCl}_2)$	83,000	12.0	-89.4	3	298-1800
$\langle \text{SiO}_2 \rangle + \langle \text{Si} \rangle = 2(\text{SiO})$	169,600	12.9	-124.3	3	298-1700
$\langle \text{SiO}_2 \rangle = \langle \text{Si} \rangle + (\text{O}_2)$	215,600	—	-41.5	3	700-1700
$\langle \text{SiO}_2 \rangle = \langle \text{Si} \rangle + (\text{O}_2)$	227,700	—	-48.7	3	1700-2000
$\langle \text{Si}_3\text{N}_4 \rangle = 3\langle \text{Si} \rangle + 2(\text{N}_2)$	177,000	5.76	-96.3	6	298-1686

TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$\langle \text{Si}_3\text{N}_4 \rangle = 3\langle \text{Si} \rangle + 2\langle \text{N}_2 \rangle$	209,000	—	-96.8	1	1686-1973
$\langle \text{SiC} \rangle = \langle \text{Si} \rangle + \langle \text{C} \rangle$	14,000	1.3	-5.68	2.5	298-1686
$\langle \text{SiC} \rangle = \langle \text{Si} \rangle + \langle \text{C} \rangle$	27,100	2.73	-18.1	2	1686-2000
$\langle \text{SiS} \rangle = \langle \text{Si} \rangle + \frac{1}{2}\langle \text{S}_2 \rangle$	12,740	—	-19.18	2	863-1680
$\langle \text{SnCl}_2 \rangle = \langle \text{Sn} \rangle + \langle \text{Cl}_2 \rangle$	79,600	—	-28.3	4	520-925
$\langle \text{SnCl}_4 \rangle = \langle \text{Sn} \rangle + 2\langle \text{Cl}_2 \rangle$	122,500	—	-36.0	2.5	500-1200
$\langle \text{SnO}_2 \rangle = \langle \text{Sn} \rangle + \langle \text{O}_2 \rangle$	140,180	—	-51.52	1	770-980
$\langle \text{TaCl}_3 \rangle = \langle \text{TaCl}_4 \rangle + \frac{1}{2}\langle \text{Cl}_2 \rangle$	33,600	—	-31.3	—	—
$2\langle \text{TaCl}_4 \rangle = \langle \text{TaCl}_3 \rangle + \langle \text{TaCl}_5 \rangle$	27,000	—	-48.3	—	—
$3\langle \text{TaCl}_3 \rangle = 2\langle \text{TaCl}_4 \rangle + \langle \text{TaCl}_5 \rangle$	33,400	—	-32.3	—	—
$\langle \text{Ta}_2\text{O}_5 \rangle + 3\langle \text{TaCl}_3 \rangle = 5\langle \text{TaOCl}_3 \rangle$	99,000	—	-95.0	—	854-1026
$\langle \text{Ta}_2\text{O}_5 \rangle = 2\langle \text{Ta} \rangle + 2\frac{5}{2}\langle \text{O}_2 \rangle$	491,000	20.7	-168.4	5	298-2000
$2\langle \text{Ta}_2\text{N} \rangle = 2\langle \text{Ta} \rangle + \langle \text{N}_2 \rangle$	117,800	13.8	-79.7	7	298-2240
$\langle \text{TaC} \rangle = \langle \text{Ta} \rangle + \langle \text{C} \rangle$	34,900	—	-0.5	—	1250-1400
$\langle \text{TeO}_2 \rangle = \langle \text{Te} \rangle + \langle \text{O}_2 \rangle$	-75,120	—	+41.18	1	773-973
$\langle \text{ThO}_2 \rangle = \langle \text{Th} \rangle + \langle \text{O}_2 \rangle$	293,400	1.61	-47.7	5	298-1800
$\langle \text{Th}(\text{SO}_4)_2 \rangle = \langle \text{Th} \rangle + \langle \text{S}_2 \rangle + 4\langle \text{O}_2 \rangle$	645,150	33.2	-331.05	—	—
$\langle \text{Th}_3\text{N}_4 \rangle = 3\langle \text{Th} \rangle + 2\langle \text{N}_2 \rangle$	310,400	—	-89.7	20	298-2000
$\langle \text{ThC}_2 \rangle = \langle \text{Th} \rangle + 2\langle \text{C} \rangle$	45,000	—	-2.6	10	298-2300
$2\langle \text{TiCl}_3 \rangle = \langle \text{TiCl}_2 \rangle + \langle \text{TiCl}_4 \rangle$	40,500	18.4	-96.4	4	298-1000
$\langle \text{TiCl}_4 \rangle = \langle \text{Ti} \rangle + 2\langle \text{Cl}_2 \rangle$	180,700	1.8	-34.65	3	298-1700
$2\langle \text{TiI}_2 \rangle = \langle \text{Ti} \rangle + \langle \text{TiI}_4 \rangle$	50,600	13.8	-76.5	8	298-1000
$\langle \text{TiO} \rangle = \langle \text{Ti} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	122,300	—	-21.3	4	600-2000
$\langle \text{Ti}_2\text{O}_3 \rangle = 2\langle \text{TiO} \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	114,150	—	-19.05	4	298-2000
$2\langle \text{Ti}_3\text{O}_5 \rangle = 3\langle \text{Ti}_2\text{O}_3 \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	88,500	—	-19.7	3	700-2000
$3\langle \text{TiO}_2 \rangle = \langle \text{Ti}_3\text{O}_5 \rangle + \frac{1}{2}\langle \text{O}_2 \rangle$	73,000	—	-23.0	3	298-2123
$2\langle \text{TiN} \rangle = 2\langle \text{Ti} \rangle + \langle \text{N}_2 \rangle$	160,500	—	-44.4	4	298-1155
$2\langle \text{TiN} \rangle = 2\langle \text{Ti} \rangle + \langle \text{N}_2 \rangle$	161,700	—	-45.54	4	1155-1500
$\langle \text{TiC} \rangle = \langle \text{Ti} \rangle + \langle \text{C} \rangle$	43,750	—	-2.41	3	298-1155
$\langle \text{TiC} \rangle = \langle \text{Ti} \rangle + \langle \text{C} \rangle$	44,600	—	-3.16	3	1155-2000
$\langle \text{UF}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{F}_2 \rangle$	448,500	—	-67.4	—	298-1309
$\langle \text{UF}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{F}_2 \rangle$	433,100	—	-55.6	—	1309-1405
$\langle \text{UF}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{F}_2 \rangle$	—	—	—	—	1405-1730
$\langle \text{UF}_6 \rangle = \langle \text{UF}_4 \rangle + \langle \text{F}_2 \rangle$	73,000	—	-30.4	—	298-337
$\langle \text{UF}_6 \rangle = \langle \text{UF}_4 \rangle + \langle \text{F}_2 \rangle$	62,300	—	+2.8	—	298-1309
$\langle \text{UF}_6 \rangle = \langle \text{UF}_4 \rangle + \langle \text{F}_2 \rangle$	74,900	—	-7.1	—	1309-1730
$\langle \text{UCl}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{Cl}_2 \rangle$	253,100	14.3	-112.8	—	298-861
$\langle \text{UCl}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{Cl}_2 \rangle$	236,700	—	-52.0	—	861-1060
$\langle \text{UCl}_6 \rangle = \langle \text{UCl}_4 \rangle + \langle \text{Cl}_2 \rangle$	-2600	—	+1.5	—	450-900
$\langle \text{UBr}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{Br}_2 \rangle$	211,000	—	-70.9	—	298-792
$\langle \text{UBr}_4 \rangle = \langle \text{U} \rangle + 2\langle \text{Br}_2 \rangle$	194,000	—	-49.2	—	792-1050
$\langle \text{UO}_2 \rangle = \langle \text{U} \rangle + \langle \text{O}_2 \rangle$	258,000	—	-40.0	—	298-1405
$\langle \text{UO}_2 \rangle = \langle \text{U} \rangle + \langle \text{O}_2 \rangle$	269,700	15.4	-97.0	—	1405-2000
$2\langle \text{U}_4\text{O}_9 \rangle = 8\langle \text{UO}_2 \rangle + \langle \text{O}_2 \rangle$	86,700	23.0	-105.3	—	298-1395
$\langle \text{U}_3\text{O}_8 \rangle = 3\langle \text{UO}_2 \rangle + \langle \text{O}_2 \rangle$	75,800	—	-34.0	—	298-1395
$\langle \text{UN} \rangle = \langle \text{U} \rangle + \frac{1}{2}\langle \text{N}_2 \rangle$	70,000	—	-20.5	—	298-1405
$\langle \text{UN} \rangle = \langle \text{U} \rangle + \frac{1}{2}\langle \text{N}_2 \rangle$	71,200	—	-21.5	—	1405-2000
$\langle \text{UC} \rangle = \langle \text{U} \rangle + \langle \text{C} \rangle$	21,600	—	+1.5	1.5	298-m.p.

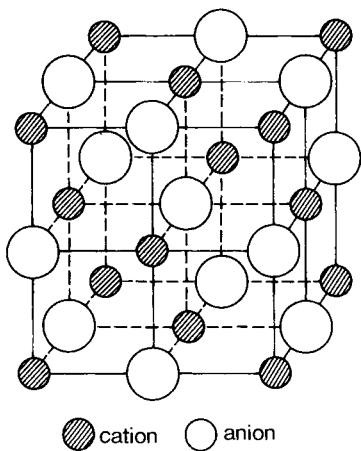
TABLE
Standard Gibbs free energy of reactions (continued)
 $\Delta G^\circ = A + BT \log T + CT$

Reaction	ΔG° in cal			$\pm$ kcal	Temp. range (°K)
	A	B	C		
$\langle UC \rangle = \langle U \rangle + \langle C \rangle$	24,600	—	-1.2	1.5	m.p.-2500
$\langle UC_2 \rangle = \langle U \rangle + 2\langle C \rangle$	27,700	—	-2.6	2	m.p.-2050
$2\langle VCl_3 \rangle = \langle VCl_2 \rangle + \langle VCl_4 \rangle$	38,000	—	-39.6	—	698-928
$2\langle VBr_3 \rangle + \langle Br_2 \rangle = 2\langle VBr_4 \rangle$	19,200	—	-32.9	—	523-873
$2\langle VO \rangle = 2\langle V \rangle + \langle O_2 \rangle$	205,900	—	-35.9	6	900-1800
$2\langle V_2O_3 \rangle = 4\langle VO \rangle + \langle O_2 \rangle$	175,300	—	-40.5	5	823-1385
$4\langle VO_2 \rangle = 2\langle V_2O_3 \rangle + \langle O_2 \rangle$	102,800	—	-33.5	4	1020-1180
$2\langle V_2O_5 \rangle = 4\langle VO_2 \rangle + \langle O_2 \rangle$	64,480	—	-45.6	3	298-943
$2\langle V_2O_5 \rangle = 4\langle VO_2 \rangle + \langle O_2 \rangle$	84,300	—	-40.3	4	943-1800
$\langle VC \rangle = \langle V \rangle + \langle C \rangle$	24,100	—	-1.5	—	1180-1370
$\langle WO_2 \rangle = \langle W \rangle + \langle O_2 \rangle$	138,500	—	-36.6	5	298-1500
$\langle WO_3 \rangle = \langle W \rangle + 1\frac{1}{2}\langle O_2 \rangle$	201,500	10.2	-91.7	5	298-1400
$\langle WS_2 \rangle = \langle W \rangle + \langle S_2 \rangle$	62,360	—	-23.0	10	298-1400
$\langle WC \rangle = \langle W \rangle + \langle C \rangle$	9000	—	-0.4	3	298-2000
$\langle ZnCl_2 \rangle = \langle Zn \rangle + \langle Cl_2 \rangle$	101,385	12.85	-75.45	3	298-586
$\{ZnCl_2\} = Zn + \langle Cl_2 \rangle$	93,950	—	-27.35	5	586-1005
$\langle ZnCl_2 \rangle = \langle Zn \rangle + \langle Cl_2 \rangle$	93,800	9.44	-38.6	5	1180-1800
$\langle ZnO \rangle = \langle Zn \rangle + \frac{1}{2}\langle O_2 \rangle$	84,100	6.9	-44.14	1.5	298-693
$\langle ZnO \rangle = \langle Zn \rangle + \frac{1}{2}\langle O_2 \rangle$	115,420	10.35	-82.38	2	1170-2000
$\langle ZnS \rangle = \langle Zn \rangle + \frac{1}{2}\langle S_2 \rangle$	63,650	4.6	-36.68	4	298-693
$\langle ZnS \rangle = \langle Zn \rangle + \frac{1}{2}\langle S_2 \rangle$	94,970	8.05	-74.92	5	1120-2000
$2\langle ZnO \rangle + \langle SiO_2 \rangle = \langle Zn_2SiO_4 \rangle$	-7130	—	+0.23	2	300-1300
$\langle ZrCl_4 \rangle = \langle Zr \rangle + 2\langle Cl_2 \rangle$	-233,250	—	+69.46	1	298-700
$\langle ZrO_2 \rangle_a = \langle Zr \rangle_a + \langle O_2 \rangle$	259,940	4.33	-59.12	4	298-1143
$\langle ZrO_2 \rangle_f = \langle Zr \rangle_f + \langle O_2 \rangle$	260,200	6.44	-65.99	4	1478-2138
$2\langle ZrN \rangle = 2\langle Zr \rangle_a + \langle N_2 \rangle$	174,000	—	-44.61	3	298-1135
$2\langle ZrN \rangle = 2\langle Zr \rangle_f + \langle N_2 \rangle$	175,850	—	-46.22	3	1135-1500
$\langle ZrC \rangle = \langle Zr \rangle + \langle C \rangle$	44,100	—	-2.2	3	298-2200

(3) CRYSTAL STRUCTURES OF INORGANIC COMPOUNDS

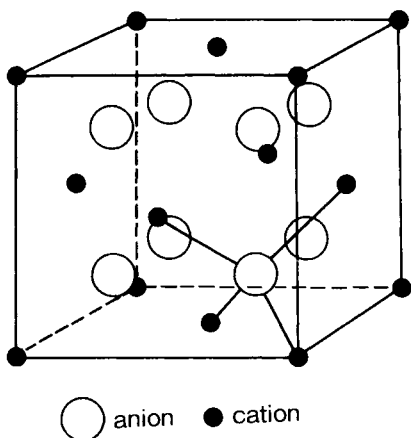
(a) FOUR COMMON CRYSTAL STRUCTURES OF OXIDES

Oxygen anion has a relatively large ionic diameter of 2.8 Å at 25°C in comparison to cations composing solid oxides. Thus, in the following common structures, oxygen makes the closed-packing sublattice and the cations are located at the interstitial sites. Only exception is fluorite structure.

Rock Salt Structure

$O^{2-} = \text{fcc}$, $M^{2+} = \text{at octahedral interstitial sites}$.

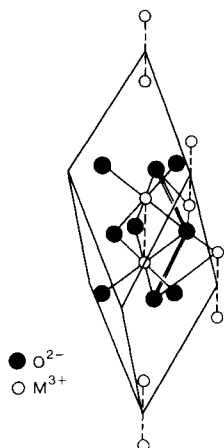
Examples: MgO, CaO, SrO, BaO,
CdO, CoO, NiO, FeO,
TiO, NbO, VO.

Fluorite Structure

$M^{4+} = \text{fcc}$, $O^{2-} = \text{at tetrahedral interstitial sites}$.

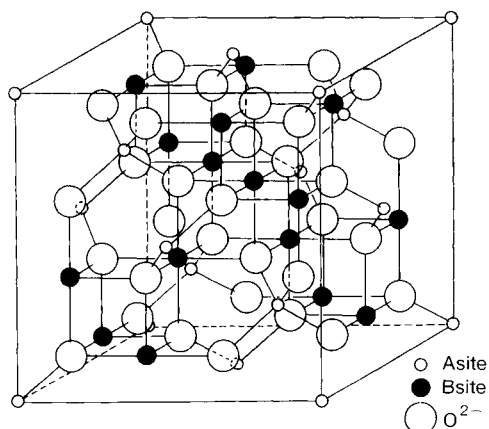
Examples: ZrO₂, HfO₂, CeO₂,
UO₂, ThO₂, PuO₂.

When the positions of cations and anions are reversed, it is called the antifluorite structure. Examples are Li₂O, Na₂O, K₂O, and Rb₂O.

Corundum Structure

O^{2-} = hcp, M^{3+} = at 2/3 of octahedral sites.

Examples: α - Al_2O_3 , α - Fe_2O_3 ,
 Cr_2O_3 , Ti_2O_3 , V_2O_3 .

Spinel Structure

O^{2-} = fcc, M^{2+} and M^{3+} = at tetrahedral sites and octahedral sites.

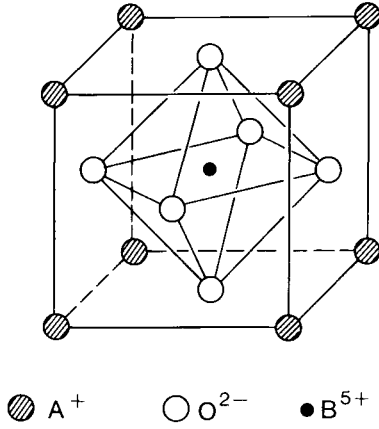
For example, $MgAl_2O_4$; O^{2-} = fcc,
 Mg^{2+} = at 1/8 of tetrahedral sites,
 Al^{3+} = at 1/2 of octahedral sites.

Examples: $MgAl_2O_4$, $MgTi_2O_4$, MgV_2O_4 , $MgCr_2O_4$,
 $MgMn_2O_4$, $MnTi_2O_4$, MnV_2O_4 , $MnCr_2O_4$,
 $FeCr_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$, $NiAl_2O_4$.

When eight tetrahedral sites of the unit cell with 32 oxygen anions are occupied by trivalent cations and the octahedral sites are shared by the trivalent and divalent ions, the structure is termed "inverse spinel". Examples are Fe_3O_4 , $MgIn_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $TiMn_2O_4$.

(b) OTHER CRYSTAL STRUCTURES OF COMPOUNDS

Perovskite Structure

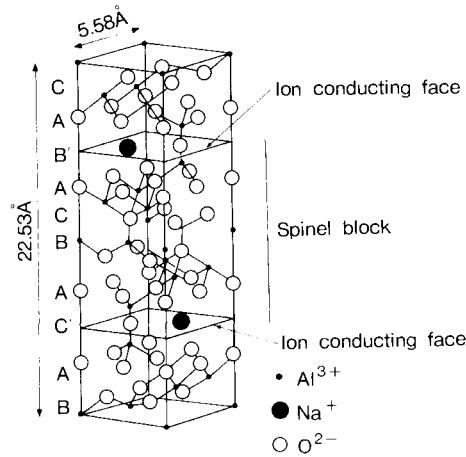


General formula = ABO_3

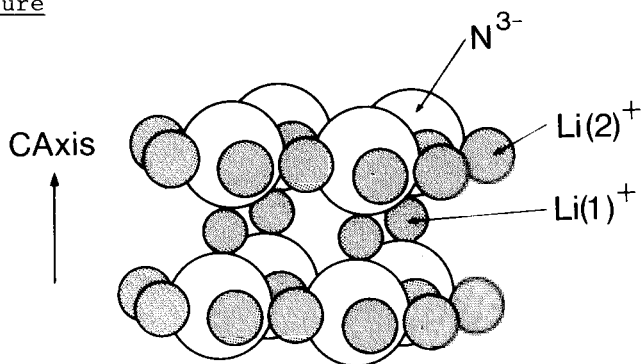
where $\text{A} = \text{A}^+$, $\text{B} = \text{B}^{5+}$, and $\text{O} = \text{O}^{2-}$,
 or $\text{A} = \text{A}^{2+}$, $\text{B} = \text{B}^{4+}$, and $\text{O} = \text{O}^{2-}$.

Examples: KTaO_3 , BaTiO_3 .

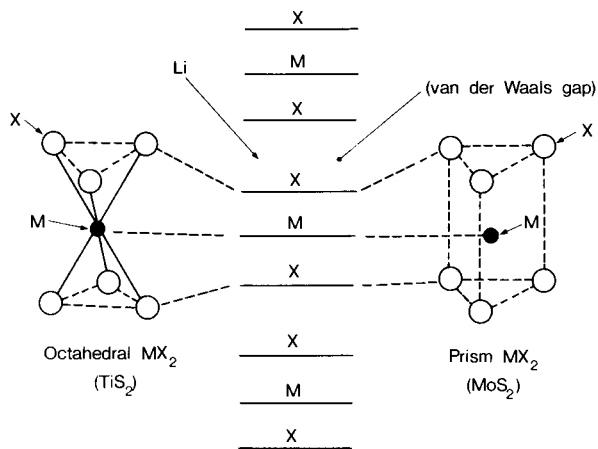
Beta-Alumina Structure



Examples: $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 5 \sim 11\text{Ga}_2\text{O}_5$.

Li₃N Structure

Examples: Li_3N , Li_5NI_2 , $\text{Li}_3\text{N} \cdot \text{LiCl}$,
 $\text{Li}_3\text{N} \cdot \text{LiI} \cdot \text{LiOH}$, Li_6NBr_3 .

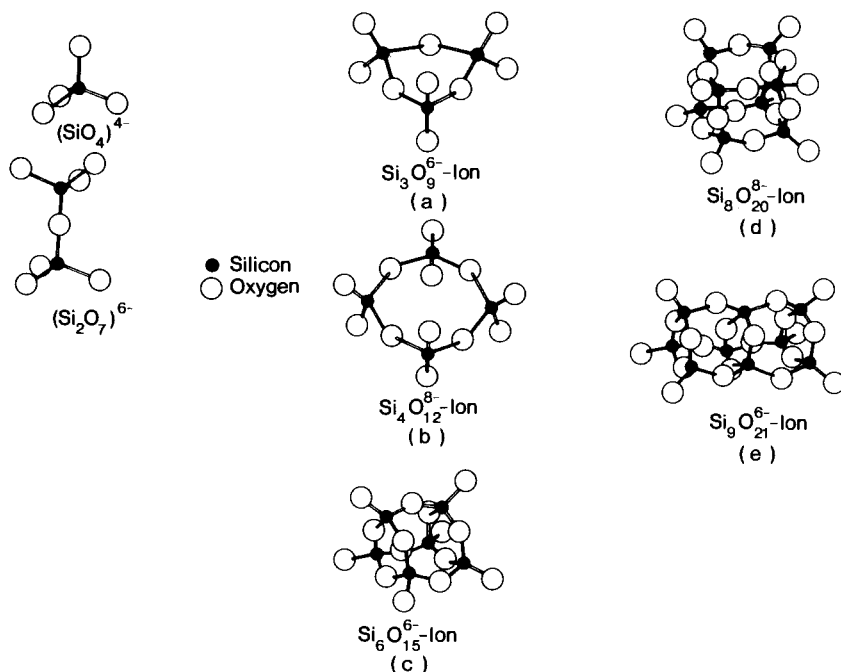
Intercalation Structure

Examples: TiS_2 , MoS_2 , Li_xTiS_2 , Li_xTaS_2 ,
 Li_xNiS_2 , Na_xTiS_2 , Na_xTaS_2 .

The sources of information on the above crystal structures are;
 1) M. Nakahira, "Crystal Chemistry" (1973), Kodansha Pub. Co., Tokyo
 (a Japanese monograph) and 2) K. Fueki and T. Kudo, "Solid State
 Ionics" (1986), Kodansha Pub. Co., Tokyo (a Japanese monograph).

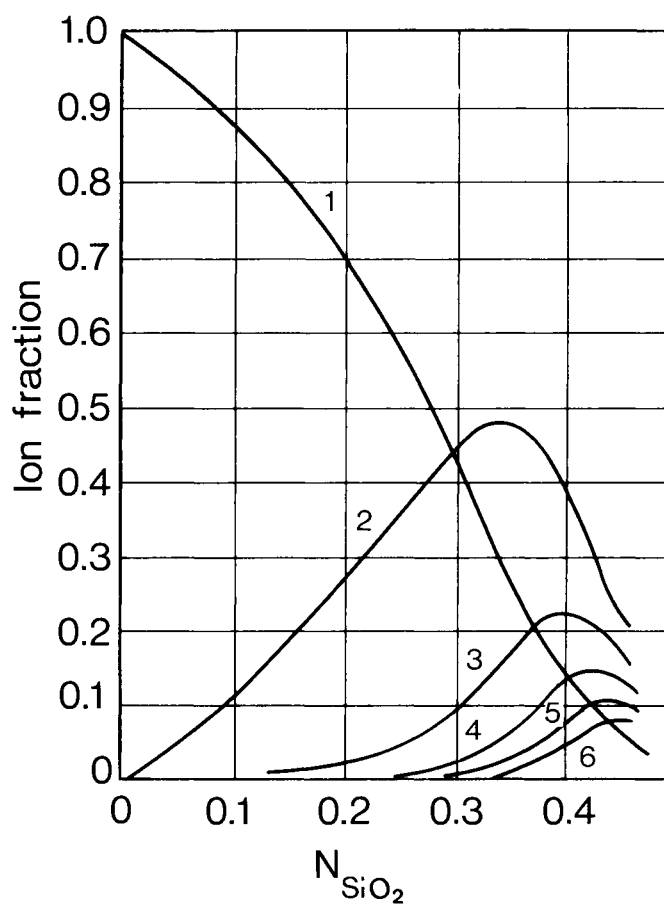
(c) PROBABLE IONIC STRUCTURE OF FUSED OXIDES

It is generally believed that basic oxides, such as K_2O , Li_2O , CaO , MgO , and PbO , are decomposed to free cations and oxygen anions by melting, while acidic oxides, such as SiO_2 , P_2O_5 , and B_2O_3 , yield anion polymers by melting as shown below:



In 1965, C.R. Masson proposed a theoretical model to estimate the anionic fractions of liquid silicates in Proc. Roy. Soc., 287 (1965), p. 201.

The following figure shows the anionic fractions of O^{2-} , SiO_4^{4-} , $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$, and $Si_5O_{16}^{12-}$. The calculation was made for $PbO-SiO_2$ melt at $1000^\circ C$ by assuming chain-like polymers according to the Masson's model.



Ion fraction of (1) NO_2^- , (2) NSiO_4^{4-} , (3) $\text{NSi}_2\text{O}_7^{6-}$, (4) $\text{NSi}_3\text{O}_{10}^{8-}$, (5) $\text{NSi}_4\text{O}_{13}^{10-}$, (6) $\text{NSi}_5\text{O}_{16}^{12-}$ plotted against mol fraction of SiO_2 for the system PbO-SiO_2 at 1000°C (After H. Saito, K.S. Goto, and M. Someno, Tetsu-to-Hagane, Japan, 55 (1969), pp. 539-549).

SUBJECT INDEX

- Absolute
 - mobility, 13
 - thermopotential of oxides, 114, 115
- Activity
 - coefficient, 66
 - measurement on alloys, 139
 - of oxide solutions, 141
 - of P_2O_5 in liquid oxide systems, 163, 164
 - of phosphorus in Fe-P binary melt, 170
 - of SiO_2 in liquid oxide systems, 162, 164
 - of silver in solid Ag_2S , 188
 - of soda, 157, 162, 163
- Adsorbed amount per unit area, 347
- Air/fuel ratio, 284
- Aliovalent ions, 16
- Alternating current polarization, 205
- Aluminum nitride electrolyte, 180, 181
- Amorphous oxide film, 377
- Amphoteric semiconductor oxides, 28, 32
- Annual consumption of oxygen sensors, 286, 300
- Anodic reaction, 200
- Arbitrary internal reference, 90
- Autocatalytic effect, 223
- Average crystal, 48 and appendix(3)
- Avogadro's number, 40
- Beta-alumina, 156
- Binary oxide film, 376
- Biosensors, 335
- Blast furnace, 4
- Blocking electrode method, 26
- Calcium
 - phosphate electrolyte, 169
 - sulfide electrolytes, 173-176
- Capacitive component, 208
- Capacity reactance, 206
- Carbonate electrolytes, 177
- Cardiac pacemaker, 400
- Caterpillar mechanism, 48
- Cathodic reaction, 200
- Ceramic superconductors, 373
- Channel, 358
- Charge
 - carriers, 12, 242
 - transfer control, 200
- Charge-up of double layer, 258
- Chemical
 - activity, 42
 - diffusivity, 68
 - sensors, 335
 - sensors for SO_2 , CO_2 , and NO_2 , 177
- Classification of sensors, 333-335
- Cole-Cole plot, 262
- Combustion control
 - of boilers, 280
 - of car engines, 284, 285
- Commercial
 - humidity sensor, 354
 - oxygen sensor for molten steel, 300
- Complex impedance plot, 262
- Component diffusivity, 68
- Composite film sensors, 356
- Concentration change of AC polarization, 205
- Condensation coefficient, 384
- Conduction mechanism of oxides, 24, 28, 29
- Conductivity equation for liquid oxides, 240
- Conservation of mass, 62
- Control of aluminum content, 308
- Converter, 5
- Correlation factor, 44
- Corundum structure, 69 and appendix(3)
- Coulhode, 390
- Coulometric titration using solid electrolytes, 144
- Counter electrode, 246
- Coupling effect, 90
- Crystal defects, 16
- Current
 - density, 41
 - density equation of DC polarization, 199
 - efficiency, 237
- CVD- SiO_2 , 367
- Decarburization of iron, 219
- Decomposition of H_2O in air, 283
- Definition of sensor, 266
- Deoxidation control by oxygen sensor, 308-312
- Dephosphurization of iron by soda, 224
- Deposition rates, 378
- Desorption chromatogram (DCT), 346
- Desulfurization
 - ratio, 233, 234
 - with current supply, 237-239
- Detection limits of H_2 , H_2S , and NH_3 , 364
- Determination
 - of activity of alumina by EMF method, 172
 - of activity of silica by EMF method, 172
 - of nonstoichiometric composition of oxides, 144

- Dielectric
 - layer sensor, 366
 - silica layer, 358
- Diffusion
 - constant of oxygen in fused oxides, 315
 - controlled overpotential, 196
 - couple, 100, 101
 - impedance, 208
- Diffusion-limited current, 184, 185
- Diffusivities in fused oxides by polarization, 256, 257
- Diffusivity of oxygen in liquid iron, 212
- Dipole moment of hydrogen, 362
- Direct current polarization, 196
- Display device, 396
- Dissolved oxygen in steels, 306
- Distribution of CO₂ gas, 220
- Double
 - layer capacitance, 207
 - pulse method, 257
- Drain current, 358, 360
- Einstein relation, 43
- Electric conductivity, 12
- Electrical conductivity of liquid oxides, 235
- Electrochemical
 - display device, 396
 - Knudsen cell, 183
 - potential memory cell, 391
 - reactions in MOS-IC, 389
 - switching cell, 395
 - timing cell, 390
 - variable resistor, 394
- Electrolysis of liquid oxides, 235-238
- Electron spin resonance, 347
- Electroneutrality in oxides, 93
- Electronic
 - conductivity, 12, 241
 - defects, 18
 - materials, 6, 373
- EMF
 - of Galvanic cells with electrolyte of binary liquid oxides, 131
 - of Galvanic cells with sulfate electrolytes, 176
 - of hydrogen concentration cell, 179
 - of oxygen sensors, 271
 - of water vapor concentration cell, 179
- Energy density, 398
- Entropy
 - of gaseous species of sulfur, 191
 - of vaporization, 386
 - production, 91
- Equilibrium
 - constant, 20
 - distribution of oxygen, 232
 - oxygen pressure in pig iron, 327
- Equivalent circuit, 207
- Exchange current density, 202, 261
- Exhaust gas composition, 284
- External
 - coordination, 62
 - transference number, 96
- Eyring theory of absolute reaction rate, 70
- Fabrication
 - of MOS-transistor, 388
 - of SnO₂ sensors, 339
- Faradaic impedance, 207, 248
- Fast
 - bleader reactor, 294
 - charge-transfer reaction, 258
- Ferric/ferrous equilibrium in slag, 318
- Fick's
 - first law of diffusion, 43
 - second law of diffusion, 64
- Fluorite structure, 69 and appendix(3)
- Forsterite solid electrolyte, 166
- Fourier's second law of heat conduction, 119
- Free
 - oxygen anion, 232
 - vaporization, 384
- Frequency
 - dependence of impedance, 208-210
 - shift by water adsorption, 368
 - shift piezoelectric crystal, 368
- Functional elements, 5, 372
- Galvanic
 - cells, 125
 - cell with electrolyte beta-alumina, 158
 - cells with oxides electrolytes, 137, 141, 147
- Galvanostatic overpotential of silicon electrode, 253-255
- Gas
 - sensing system for apartment house, 340
 - sensors, 335
- Gaseous species
 - from Li₂O-B₂O₃ system, 383
 - of sulfur, 191
- Generalized force, 90
- Gibbs-Duhem relation, 67
- Grain boundary resistance, 336

Haven ratio, 44

Heat

- conductivity of CaF_2 , 119
- conductivity of silicates, 120-122
- conductivity of solid and liquid oxides, 118-122
- of transfer, 111, 116

Helmholz double layer, 201

Herasymenko's ionic theory, 232

Heterogeneous potential, 114

Hittorf

- experiment, 239
- transference number, 96

Homogeneous thermal potential, 114

Hot wire method, 118

Humidity

- sensitive capacitor, 367
- sensors, 335
- sensor with capacitance, 352
- sensor with MgCr_2O_4 , 350
- sensor with SiO_2 , 348
- sensor with $\text{ZrO}_2\text{-MgO}$, 353

Hygroscopic dielectric, 368

Impedance

- of chemical reaction control, 209
- of mixed-control, 209

Induction reactance, 206

Inert marker, 61, 65

Infrared optical sensor, 374

Interaction parameter, 151, 152, 153

Interdiffusivity, 64, 92

- data for liquid oxides, 85
- matrices for ternary system, 92
- of oxygen in metals, 211

Internal

- partition function, 387
- reference, 63, 92

International convention of EMF expression, 126

Interstitial diffusion, 68

Intra-particle oxygen pressure, 221, 222

Intrinsic diffusivity, 62

Ion

- intensity of mass spectrometer, 190
- sensors, 335

Ionic

- conductivity, 12
- conductors, 15
- fraction, 232, 233

Iron oxide content in slag, 328

Iso-activity lines diagrams, 163, 164

Isotopic effect of resistance, 349

Kirkaldy's method, 102

Kirkendall effect, 61, 65

Knudsen cell, 185, 186, 384

Laser materials, 373

Layered

- oxygen sensor, 287
- structure of gas sensors, 339, 340

Lean gas mixture, 286

Levich's equation, 249

Life time of oxygen sensors for car, 284

Liquid oxides electrolyte, 170, 171, 172

Liquid-like structure, 48 and appendix(3)

Local

- equilibrium, 94
- oxygen pressure at interface, 217
- velocity of marker, 62

Magnesium aluminate electrolyte, 167

Magnetic

- materials, 373-375
- sensors, 334

Magnitude of nonequilibrium, 322-324, 328-329

Mass spectrometer, 189

Matano interface, 101, 102

Mechanism of vaporization, 387

Memoriode, 391

Metal-deficient oxide, 18

Metal-excess oxide, 18

Microelectronics, 6, 372

Microelectronic devices, 373-375

Mineralogical names of oxide ores, 3

Mixed conductor sensor, 345

Mobility

- of charge carriers, 12
- of electrons, 20

Mole fraction, 63

Monitor of polluted water, 283

MOS-sensor

- for ammonia, 361
- for hydrogen, 360

MOS-transistor, 8, 359

Multicomponent oxide systems, 90

Needle sensor, 301

Nernst-Einstein relation, 40, 44

Nitrate electrolyte, 177

NO_x content in waste gases, 279

Noble metal catalyst in gas sensors, 338

Nondiagonal terms, 91

Nonisothermal diffusion, 90

Nonstoichiometric oxides, 18, 22

NTC, 7

Ohmic

- component, 208
- potential drop, 213

Onsager's reciprocal relation, 91

Optical sensors, 334

Optoelectric materials, 373

Overpotential of galvanostatic polarization, 200

Oxidation of silicon, 252

Oxide inclusions in steels, 306

Oxides used for devices, 373-375

Oxygen

- concentration cell, 125
- content in liquid metals, 146
- control in heat-treatment furnace, 281
- coverage on active sites, 218
- permeation through electrolyte, 213
- pressure and diffusivity
 - in n-type semiconductor oxides, 23, 31
 - in p-type semiconductor oxides, 21, 30, 31
 - in solid oxides, 79, 80
- pressure in liquid oxides, 314
- sensors for atomic reactors, 294
- sensors for copper refining, 289
- sensor
 - for copper smelting blast furnace, 291
 - for matte, 291
 - for self-fluxing furnace, 293
 - with semiconducting TiO_2 , 343

P-type semiconductors, 17

Pacemaker batteries, 398

Palladium-doped SnO_2 sensors, 339

Partial

- conductivities, 12
- molal Gibbs free energy, 42

Permeability of oxygen through fused oxides, 315

Perovskite oxygen sensor, 344

Phase difference of current and potential, 206

Phenomenological linear-equations, 91

Physical

- sensors, 334
- vapor deposition (PVD), 376

Piezoelectric

- compounds, 369
- gas sensor, 368

Platinum catalyst, 285

Polarization at Pt/liquid-oxide interface, 245, 247, 252

Power source for devices, 401

Pressure sensors, 334

Proton conductor electrolyte, 178-180

PTC, 7

Radioactive tracer technique, 237

Rate

- equations for oxidation and reduction, 218, 222

- of effusion from Knudsen cell, 186

Reference electrode, 246

Relation between

- compositions of source and film, 381-382
- current and potential for charge transfer control, 202, 203
- interdiffusivity and tracer diffusivity, 67
- intrinsic diffusivities and interdiffusivity, 64
- intrinsic diffusivity and tracer diffusivity, 67
- overpotential and time, 254, 255
- threshold voltage and hydrogen pressure, 360
- tracer diffusivities and temperature, 76, 77, 78
- transport coefficients
 - and electrical conductivity, 95
 - and heat conductivity, 96
 - and heats of transfer, 117
 - and interdiffusivities, 92-95
 - and tracer diffusivities, 96
 - and transference number, 96

Resistivity of commercial zirconia electrolytes, 275

Response

- curves of oxygen sensors, 302
- of zinc oxide sensor, 338

Rock salt structure, 69 and appendix(3)

Rotating disk electrode, 249

Schmalzried parameter, 128

Schottky barrier

- diode, 365
- sensor, 364

Seebeck coefficient, 111, 112

Self diffusivity, 61, 68

Semiconductor gas sensors, 336-348

Sensitive dielectric layer, 367

Sensor

- elements, 7, Chapters 10, 11, 12
- for lean gas mixtures, 288
- of diffusion-limited current, 281, 282
- with zinc oxide film, 337

- Silver iodide solid electrolyte, 183, 187
- Sodium-sulfur battery, 157
- Solid
 - electrolytes of cation conduction, 156
 - fluorite electrolytes, 182, 183
 - halide electrolytes, 183
 - state battery, 397
- Soret effect, 97
- Source, 358
- Spinel structure, 69 and appendix(3)
- Stability range diagram, 182
- Standard Gibbs free energy of formation
 - of interoxide compounds, 138
 - of pure oxides, 136
 - of sodium carbonate, 159
 - of sulfides, 174
- State of adsorbed gases, 346
- Stationary current of electrochemical
 - Knudsen cell, 188
- Steelmaking converter, 310
- Sticking coefficient, 385
- Strictly-stoichiometric oxides, 15
- Structures of semiconductor sensors, 339
- Substrate, 376
 - temperature, 380
- Sulfate solid electrolytes, 175, 177
- Sulfur
 - content in liquid copper, 176
 - dioxide content in air, 177
- Sulfide electrolytes, 173, 176
- Super ionic conductors, 29
- Supersaturation of oxygen in slag and iron, 304, 327
- Switching device, 395
- Symmetrical cell assembly, 214
- Tafel curve, 204
- Taly step method, 377
- Taylor series expression of activity coefficient, 151
- Temperature dependence of ionic conductivity, 17
- Ternary phase reaction zone, 222
- Tetrahedral site, 69
- Thermal SiO_2 , 367
- Thermodiffusion
 - in liquid iron-base alloys, 109, 110
 - in liquid oxides, 105-108
- Thermodynamic factor, 94
- Thermo-electromotive force
 - of liquid oxides, 117
 - of perovskite oxides, 355
 - of solid oxides, 110-114
- Thermosensors, 334
- Thermosensor for car engine, 288
- Thin film fabrication, 376
- Threshold voltage, 359
- Timer device, 390
- Total
 - carbon (TC), 284
 - oxygen demand (TOD), 283
 - oxygen in steels, 306
- Tough pitch billets, 289
- Tracer diffusivity, 43
- Tracer diffusivities
 - in liquid halides, 50
 - in liquid oxides, 54, 55, 80, 81, 82, 83
 - in solid halides, 45-47
 - in solid oxides, 70, 71, 72
- Transfer coefficient, 202
- Transference
 - number, 24
 - numbers in liquid oxides, 239-243
- Transparent conductor, 373
- Transport
 - coefficients, 90, 99
 - properties, 91
- Two phase mixture for electrolyte, 167
- Unidirectional diffusion of oxygen, 212
- Unit charge, 13
- Up-hill diffusion, 102
- Uses of oxygen sensors in industry, 278
- Vacancy
 - mechanism, 44
 - pairs, 46, 52
- Valence, 13
- Validity
 - of Levich's equation, 250
 - of Nernst-Einstein relation, 45, 49
- Vapor pressure of sodium, 226
- Vaporization coefficients, 385, 386
- Vaporizing source, 376
- Variable resistor, 394
- Varister, 373-375
- Vertically movable oxygen concentration cell, 220
- Virtual
 - cell reaction, 125
 - electrochemical reactions at electrode interfaces, 126
- Wagner's general equation of EMF, 133, 134
- Wirebar casting, 289
- Working electrode, 246
- ZrO_2 -base solid electrolytes, 135