Lawrence Berkeley National Laboratory
Recent Work

Title
DESIGN CRITERIA FOR SOLID ELECTROLYTE ELECTROCHEMICAL CELLS

Permalink
https://escholarship.org/uc/item/23f4p29x

Author
Headrick, Richard Wyant.

Publication Date
1972-07-01
DESIGN CRITERIA FOR SOLID ELECTROLYTE ELECTROCHEMICAL CELLS

Richard Wyant Headrick
(M.S. Thesis)

July 1972

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room
This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Table of Contents

Abstract ................................................................. v

I. Introduction ......................................................... 1

II. Review of Solid Electrolyte Galvanic Cells .................. 6

III. Theory of Electrochemical Measurements with Ion-Selective Electrolytes .................................................. 21
   A. Cationic Model ...................................................... 22
   B. Anionic Model ...................................................... 23
   C. General Transport Equation ...................................... 24
      1. Electronic Transport ........................................... 26
      2. Ionic Transport ................................................ 27
      3. Total Current .................................................. 28

IV. Electrolyte Materials-Criteria and Review ................... 35

V. Reference Electrodes .............................................. 40

VI. Experimental Studies ............................................. 43
   A. Materials .......................................................... 43
      1. Metal-Metal Oxide Powders .................................... 43
      2. Electrolyte ..................................................... 43
      3. Alumina Tubes ................................................ 43
   B. Equipment ........................................................ 43
      1. Furnace ......................................................... 43
      2. Furnace Temperature Controller ................................ 44
      3. Cell Temperature ............................................... 44
      4. EMF Measurement ............................................... 44
C. Construction of Cell #1 ........................................ 45
D. Construction of Cell #2 ........................................ 47
E. Construction of Cell #3 ........................................ 51
F. Construction of Cell #4 ........................................ 52
G. Construction of Cell #5 ........................................ 52

VII. Experimental Results and Discussion .............................. 53
A. The Ni(s) + Cu_2O(s) \rightleftharpoons NiO(s) + 2Cu(s) Reaction ..... 53
   1. Cell #1 .................................................. 53
   2. Cell #2 .................................................. 57
   3. Cell #3 .................................................. 59
   4. Cell #4 .................................................. 59
B. The Ni(s) + 3Fe_2O_3(s) \rightleftharpoons 2Fe_3O_4(s) + NiO(s) Reaction ... 64
   1. Cell #5
C. Calculated Thermodynamic Properties from Experimental
   Results ......................................................... 65
D. Discussion of the H_2O Effect on Cell EMF ......................... 65

VIII. Summary and Recommendations .................................... 70
ACKNOWLEDGEMENTS .................................................. 72
REFERENCES .......................................................... 73
DESIGN CRITERIA FOR SOLID ELECTROLYTE ELECTROCHEMICAL CELLS

Richard Wyant Headrick

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Chemical Engineering; University of California Berkeley, California

ABSTRACT

Factors affecting the accuracy of galvanic cells involving solid electrolytes in thermochemical measurements were studied with regard to cell design and operation. Because coexistence electrodes are particularly well suited for determining free energies of formation of metal oxide compounds, the cells

\[ \text{Cu, Cu}_2\text{O|Zr}_0.85\text{Ca}_{0.15}\text{O}_{1.85|Ni, NiO} \]

and

\[ \text{Fe}_{2}\text{O}_3, \text{Fe}_3\text{O}_4|\text{Zr}_0.85\text{Ca}_{0.15}\text{O}_{1.85|Ni, NiO} \]

exhibiting low and high entropies of reaction, respectively, were examined for critical parameters.

The galvanic cells studied were based on the closed cell concept involving sealed electrode compartments. Design improvements include (1) interior thermocouples for accurate measurement of the electrolyte interface temperature, (2) individual gas and vacuum manifolds on the isolated half-cell compartments, (3) elimination of stray emf in potential leads, and (4) tapered alumina to glass wax seals to facilitate
rapid electrode replacement and resealing.

The improvements introduced in galvanic cell structure led to standard free energy change determinations for the following reactions:

\[ \text{Ni}_2(\text{s}) + \text{Cu}_2\text{O}(\text{s}) \rightarrow \text{NiO}(\text{s}) + 2\text{Cu}(\text{s}) \]

\[ \text{Ni}_2(\text{s}) + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{NiO} \]

The most significant error in cell voltage (emf) measurements was found to arise from secondary electrode reactions with water vapor. Proper outgassing of the half-cells was determined to be extremely important, as even a slight amount of retained moisture caused higher cell emfs. Secondary electrode reactions with retained water vapor are proposed as a mechanism whereby emf data from earlier studies, particularly those using "open cell" techniques, on the above systems is higher than that measured in this study. Incorrect temperature measurement due to thermal gradients around the electrolyte, was also shown to be a source of error.
I. INTRODUCTION

The pioneering work of Kiukkola and Wagner in the mid 1950's stimulated considerable interest in the use of galvanic cells employing solid electrolytes for the measurement of thermodynamic properties of inorganic compounds. This technique is particularly useful for the metal oxides since several solid electrolytes have been developed which are essentially pure ionic conductors and furthermore, are selective oxygen anion electrolytes. Several different electrolytes have been used by various investigators and include solid solutions of ThO$_2$ + LaO, ThO$_2$ + CaO, and ZrO$_2$ + CaO; however, ZrO$_2$ + 5-15% w CaO has been the preferred electrolyte because its electronic conductivity has been to be found virtually constant (about 1.6 x 10$^{-1}$ ohm$^{-1}$ cm$^{-1}$) over an extremely wide oxygen partial pressure range (1 atm - 4 x 10$^{-2}$ atm)\textsuperscript{1,23} and temperature range (up to $\sim$ 1000$^\circ$C).\textsuperscript{23}

Thermodynamic properties measured with solid electrolyte electrochemical cells are not always in agreement with measurements by traditional calorimetric methods. It is suspected that these differences can be traced in part to errors introduced by the solid electrolyte cell technique. It is appropriate, then, to assess the possible error sources inherent in the solid electrolyte cell methods and to develop guidelines for future cell design in thermodynamic studies using this promising new technique.

Two basic methods of cell construction have been used. The first consists of a stacked assembly of electrode and electrolyte pellets which are exposed to a common inert gas environment. This method was used by Kiukkola and Wagner in their pioneering work and has been used
extensively by several other investigators.\textsuperscript{1-4,6,16-19} The second method consists of isolating the electrodes so that the problem of interelectrode oxygen transfer around the electrolyte is eliminated. This method was primarily developed by Charette and Flengas\textsuperscript{5} and was used in this study.

The overall cell reaction of a solid oxide electrochemical cell can be described using both a cationic model and an anionic model. For the cationic model, the overall cell reaction is $M_1 + M_2O \rightarrow M_2 + M_1O$. The cell potential $E_a$ is given by the well known expression:

$$E_a = -\left[\frac{\Delta G_f^{\circ} M_1O - \Delta G_f^{\circ} M_2O}{2F}\right]$$

where $\Delta G_f^{\circ} M_1O$ and $\Delta G_f^{\circ} M_2O$ are the standard free energies for the formation of the oxides $M_1O$ and $M_2O$ at the temperatures of the measurement.

In the anionic model the overall cell reaction is $1/2 \ 0_2 P_0^{\circ}'' = 1/2 \ 0_2 P_0^{\circ'}$, where $P_0^{\circ}''$ and $P_0^{\circ'}$ are the partial pressure of oxygen present over the oxide phases $M_2O$ and $M_1O$, respectively. The cell potential $E_b$ is given by

$$E_b = \frac{RT}{nF} \ln \left[\frac{P_0^{\circ}''}{P_0^{\circ'}}\right]^{1/2}$$

where $F$ is the Faraday constant (23,061 cal/V), $R$ the gas constant (1.987 cal/°C), $T$ the absolute temperature, and $n$ equals 2, the number of electrons transferred in the cell reaction.
The two Equations (1 and 2) represent the same potential only when the oxygen pressures over the oxide phases are at their equilibrium values. From the above analysis it can readily be seen that for electrochemical measurements made using this technique to be accurate, it is important that the cells be operated under truly equilibrium conditions. Non-equilibrium oxygen partial pressures above either electrode will cause either oxidation of the metal or reduction of the oxide and will result in erroneous equilibrium electrode potential differences.

The open-cell method has several inherent drawbacks. Chief among them is that the measured cell potential is not necessarily the thermodynamic potential of the system if the oxygen content of the atmosphere surrounding each electrode is not at equilibrium with the metal-metal oxide system present.

A flowing inert gas atmosphere can affect the cell potential by carrying away oxygen from the electrodes and by promoting oxygen diffusion between the two electrode atmospheres. Also, if the flowing gas is not in thermal equilibrium with the electrodes, thermal gradients are introduced which cause errors in cell temperature. Impurities in the inert gas are also a potential source of error.

Thermionic emission has also been reported to be a source of error, especially at high temperatures. The emission produces electronic currents through the gas phase, causing short-circuiting of the cell.

Despite the obvious deficiencies of the open cell technique, Bugden and Pratt showed that if the proper reference electrodes were chosen
satisfactory results could be obtained using the open cell concept providing certain criteria were maintained. The conditions which were shown to be significant were (1) that both electrodes have oxygen partial pressures of the same order of magnitude (2) that both electrodes be exposed to the same static atmosphere of inert gas and (3) that crucibles of electrolyte material be used to separate the two electrodes, thereby increasing the oxygen diffusion path between them.

Recognizing the inherent problems in the open cell technique, Charette and Flengas developed a "closed system" solid electrolyte electrochemical cell. Their cell consisted basically of two half-cell compartments separated by a calcium oxide stabilized zirconia diaphragm, both sealed under vacuum. The work of Charette and Flengas is well done and is recognized by many investigators as being the best to date.

Other than recognizing the fact that the accuracy of electrochemical measurements made with galvanic cells using solid oxide electrolytes is dependent on whether or not equilibrium oxygen pressures are maintained above each electrode, very little has been said about other factors which cause error in emf measurement or which effect the oxygen pressures at the electrodes e.g. impurities in the electrode materials, electronic conduction in the electrolyte, thermal gradients at the electrolyte interface, and tarnishing reactions between the electrodes and the electrolyte. Also, little has been said about design criteria or cell assembly procedure which can reduce the number of error sources. The following discussion will deal with some of these factors and their significance, as well as recommendations for future cell design with the
intent of improving both the accuracy of measurement and ease of cell construction.
II. REVIEW OF SOLID ELECTROLYTE GALVANIC CELLS

The following review is by no means a complete documentation of all solid electrolyte cells constructed or all studies made. However, the different basic approaches to cell design and construction are discussed along with an analysis of potential sources of error in emf measurements.

Kluukkanla and Wagner, who pioneered the use of galvanic cells utilizing ion selective solid electrolytes for the measurement of thermodynamic properties, developed the cell configuration shown in Fig. 1. The cell consisted of a compressed tablet of a mixture of metal A and its oxide, a tablet of the electrolyte (ZrO₂ - CaO), and a compressed tablet of a mixture of metal B and its oxide. The cell was operated under the flow of an inert gas common to both electrodes.

Although conceptually quite simple, considerable work was required in constructing the cell. The electrode powders were first compressed into tablets and sintered. The tablets were then coated with either thin Au layers applied by vacuum vaporization or with thin platinum films obtained by cathodic sputtering to minimize contact resistance. A continuous flow of highly purified inert gas also had to be provided inside the sealed cell.

Remembering that the cell potential is defined by Eq. (2) where \( P'' \) and \( P' \) are the equilibrium oxygen pressures at the cathode and anode, respectively, it can readily be observed that the emf measured using this cell arrangement is not necessarily the thermodynamic potential difference of the system. The cell emf would be dependent on the flow rate of inert gas.
Fig. 1. Cell design and construction used by Kiukkola and Wagner.
gas (which would affect the inter-electrode oxygen diffusion rate) and on any residual oxygen contaminant present in the gas.

Several other investigators have utilized the "open cell" technique developed by Kiukkola and Wagner with some modifications. Roeder and Smeltzer\textsuperscript{16} utilized cells containing embedded electrodes of the reaction metals to determine dissociation pressures for wustite, magnetite, and nickel oxide. Their cell assembly, Fig. 2, is very similar to Kiukkola and Wagner's. The cell could be run in vacuum (to $10^{-6}$ mm Hg) or utilize an inert gas flow. The galvanic cell used is shown in Fig. 3. Roeder and Smeltzer state that by using this configuration, where the electrolyte tablet (0.4 in. diameter and 0.15 in. thick) is larger than the metal-metal oxide tablets (0.3 in. diameter and 0.1 in. thick), oxygen short circuiting of the electrolyte is prevented. However, this author as well as others\textsuperscript{2,5,17} doubt this is true. The scattering of their cell emf is considerably greater than that of later investigators who used more plausible methods to minimize oxygen short-circuiting of the electrolyte\textsuperscript{2,6,18,19} or used cells utilizing independently sealed electrodes.\textsuperscript{5}

Bidwell and Speiser\textsuperscript{18} developed a similar cell design to determine thermodynamic properties of solid nickel-palladium alloys (Fig. 4). A helium atmosphere was used in their cell. The authors claim good cell stability with equilibration times varying from 1 – 2 hours at the higher temperatures (> 800°C) to 4 – 8 hours at the lower temperatures (< 800°C). The data scatter, however, is considerably greater than that obtained in this study (0.1%) or in others where a "closed system"
Fig. 2. Cell design and construction used by Roeder and Smeltzer.
Fig. 3. Galvanic cell assembly used by Roeder and Smeltzer.
cell was used. Data scatter ranged from 1 to 2.5%. Once again the accuracy of the measurements is questionable because of probable oxygen short-circuiting of the electrolyte.

Rizzo, et al made a significant improvement in the "open cell" technique by using an impervious, closed-end calcia-stabilized zirconia tube instead of a flat tablet of electrolyte to separate the electrodes (Fig. 5). This design would tend to reduce leakage between the two electrode atmospheres by increasing the diffusion path. However, Rizzo did not operate this cell design using a flow of purified helium common to both electrodes. He was investigating cells of the type Ni, NiO|ZrO₡-CaO|O₂ (air) and Cu, Cu₂O|ZrO₂-CaO|O₂ (air) with the open end of the zirconia tube exposed to ambient air. The anode compartment was evacuated during heating and closed off upon reaching the experimental temperature with a vacuum of approximately 10⁻³ Torr. By so doing, Rizzo, et al became the first investigators (to this author's knowledge) to operate a galvanic cell under truly equilibrium conditions—both electrode atmospheres being completely independent from one another. The standard molar free energy of formation of Cu₂O was determined from the cell emf and compared with results obtained using an "open flow" type cell Ni, NiO|ZrO₂-CaO|Cu, Cu₂O based on Bidwell and Speiser's design. The two independently determined values of ΔG°Cu₂O were in remarkably close agreement (30 to 80 cal/mole difference over the temperature range investigated) and indicated that either type of cell design is appropriate—at least in some cases. However, it remained for Bugden and Pratt to further investigate the conditions under which
Fig. 4. Schematic diagram of galvanic cell and holder used by Bidwell and Speiser.
Fig. 5. Schematic of cell design used by Rizzo et al.
satisfactory results can be obtained using the "open-cell technique.

The cell design used by Bugden and Pratt is shown in Fig. 6. The metal-metal oxide electrodes, compacted from high purity materials, were separated by an electrolyte crucible, and the cell was held together firmly on a boron nitride or alumina support by spring pressure inside a gastight silica vessel containing a static atmosphere of purified argon. Based on results obtained on several different cells they concluded that satisfactory operation of the solid oxide electrolyte "open cell" technique can be achieved by using a static inert gas atmosphere common to both electrodes and a crucible of electrolyte to separate the electrodes. Gas-phase oxygen transfer between the two electrodes is minimized by the static inert atmosphere and by the electrolyte crucible which separates the electrodes more effectively than a simple disc of electrolyte.

Lacy and Pask used a modification of this cell to measure the activities of the transition metal oxides in disilicate glass. Their cell assembly, Fig. 7, was operated using a static argon atmosphere common to both electrodes; however, the metal-metal oxide mixture (outer electrode) was sealed from the ambient atmosphere by covering it lightly with a powdered sodium disilicate glass containing 7.55% NiO + excess Ni metal. The emf of the cell was not altered by this procedure and the cells were stabilized for longer times, thus increasing the precision of the measurements.

Although considerable work has been done using the "open-cell" technique as evidenced from the above review, most of the investigators
Fig. 6. Basic cell design used by Bugden and Pratt.
Fig. 7. Schematic diagram of cell assembly used by Lacy and Pask.
experienced cell stability problems, relatively wide scattering of data points, and emf dependency on the flow rate of inert gas (if a flowing system was used). Such difficulties became particularly severe when the difference in oxygen pressures above the two metal-metal oxide electrodes was large. Recognizing that these difficulties were probably due to oxygen short-circuiting of the electrolyte disc or crucible by gas diffusion, Steele and Alcock\textsuperscript{19} developed a cell whereby the two electrodes were exposed to separate gas streams (Fig. 8). The electrolyte pellet was pressed against the polished end of an alumina tube to help prevent the gas surrounding one electrode from coming into contact with the other electrode. They found that this cell arrangement was essential when the two metal-metal oxide electrodes had very different oxygen potentials (e.g., Ni, NiO, and Nb, NbO). However, it is doubtful whether the electrolyte to alumina contact could make the gas atmospheres over the two electrodes truly independent of each other. It remained for Charette and Flengas\textsuperscript{5} to develop a cell designed to operate under truly equilibrium oxygen pressure conditions.

The cell design used by Charette and Flengas, Fig. 9, consisted of two half-cell compartments separated by a calcium oxide stabilized zirconia diaphragm, both sealed under vacuum. The electrolyte diaphragm was a tube 2\textsuperscript{1/2} in. long, closed one end, and served to contain the inner reference electrode, which in their case consisted of a loosely packed mixture of nickel-nickel oxide powder. The top of this tube was closed using a tight fitting bell-shaped Pyrex tube and sealed with De Khotinsky cement. The assembled Ni-NiO half-cell was then evacuated using side
Fig. 8. Cell design and construction used by Steele and Alcock.
arm tubes incorporated into the Pyrex cover and flame sealed under vacuum. The cell was assembled by inserting the Ni-NiO reference half-cell into a small thoria or alumina crucible, which contained a Pt foil electrode, and pressing it against the Pt electrode. The free volume of the crucible was then packed with the oxide mixture under investigation. A spring type arrangement was used to insure good contact with the Pt foil. The completed cell was then placed into a fused quartz tube (alumina was used at temp > 1150°C) which was then sealed in the same manner as the zirconia tube. The outer half-cell was then evacuated and flame sealed.

The design approach taken by Charette and Flengas undoubtedly represents a near complete solution of the problem of gas-phase inter-electrode transfer.
Fig. 9. Cell design and construction used by Charette and Flengas.
III. THEORY OF ELECTROCHEMICAL MEASUREMENTS
WITH ION-SELECTIVE ELECTROLYTES

An understanding of the basic theory of electrochemical measurements is important when galvanic cells are used to obtain thermodynamic data. Most of the design criteria for such cells, such as the choice of and limitations on solid electrolytes, and the maintenance of equilibrium partial pressures at the electrodes have sound theoretical bases, and degradation of cell potentials can be assessed in terms of the theory. In the presentation below, simple thermodynamic relationships are first used to derive expressions for the cell potential considering both the cationic and anionic cell models. A general transport equation is then developed which takes into account both ionic and electronic conduction. Boundary conditions are then applied to the generalized equation to obtain the working equation for galvanic cells utilizing solid ion-selective electrolytes.

The free energy of a spontaneous exchange reaction of the type

\[ M_1 + M_2^0 \rightleftharpoons M_1^0 + M_2 \]  

where \( M_1^0 \) and \( M_2^0 \) are the metal saturated phases of the two oxides, may be obtained directly from the emf of the following solid oxide electrochemical cell:

\[
\text{(-) \, } M_1, M_1^0 \quad \text{ion-selective electrolyte} \quad \text{M}_2^0, M_2 \, (+) \\
\text{P}_0^2, \text{(anode)} \quad \text{(ZrO}_2-\text{CaO)} \quad \text{(cathode), } P_0^2''
\]
A. Cationic Model

Using a cationic model, we have the following charge transfer operations:

at the anode,

\[ M_1(\text{metal}) \rightarrow M_1^{2+} (M_1^0) + 2e^- , \quad (\text{oxidation}) \quad (4) \]

and at the cathode,

\[ M_2^{2+} (M_2^0) + 2e^- \rightarrow M_2(\text{metal}) \quad , \quad (\text{reduction}) \quad (5) \]

There is also a transfer of oxygen anions from the cathode to the anode through the electrolyte,

\[ O^{2-} \quad (M_2^0) \rightarrow O^{2-} \quad (M_1^0) \quad . \quad (6) \]

The overall cell reaction is, therefore,

\[ M_1 + M_2^0 \rightarrow M_2 + M_1^0 \quad . \quad (7) \]

The cell potential, \( E \), for this reaction is given by a form of the Nernst equation,

\[ E = - \left[ \frac{\Delta G^0}{2F} \right] \quad , \quad (8) \]

where \( \Delta G^0_{M_1^0} \) and \( \Delta G^0_{M_2^0} \), are the standard free energies for the formation of the oxides \( M_1^0 \) and \( M_2^0 \) at the temperature of measurement.
B. Anionic Model

If an anionic model is used, we have the following half-cell reactions:

at the anode,

\[ \frac{1}{2} O_2 (P'_0) + 2e^- \rightarrow O^{2-}_{(M_1O)} \]  

(9)

and at the cathode,

\[ \frac{1}{2} O_2 (P''_0) + 2e^- \rightarrow O^{2-}_{(M_2O)} \]  

(10)

There is also a net transfer of oxygen ions through the electrolyte,

\[ O^{2-}_{(M_2O)} \rightarrow O^{2-}_{(M_1O)} \]  

(11)

The overall cell reaction is, therefore,

\[ \frac{1}{2} O_2 (P''_0) \rightarrow \frac{1}{2} O_2 (P'_0) \]  

(12)

where \( P''_0 \) and \( P'_0 \) are the equilibrium oxygen partial pressures at the cathode and anode, respectively.

From the anionic model and overall cell reaction we can derive a simple working equation. For the overall cell reaction,

\[ K = \frac{\left[ P'_0 \right]^{1/2}}{\left[ P''_0 \right]^{1/2}} \]  

(13)
Therefore, the standard free energy change is

\[ \Delta G_f^0 = -nFE = RT \ln K = RT \ln \left[ \frac{P_{O_2}'}{P_{O_2}''} \right]^{1/2} \]  

(14)

and the cell voltage is

\[ E = \frac{RT}{nF} \ln \left[ \frac{P_{O_2}''}{P_{O_2}'} \right]^{1/2} \]  

(15)

It must be remembered that Eq. (23) is valid only if the oxygen pressures over the oxide phases correspond to the true equilibrium values and if the transport number of oxygen anions through the electrolyte is unity, as shown in the following analyses given by Heyne. 10

C. General Transport Equation

In terms of charged point defects, the partial current density flowing through the electrolyte under an applied potential gradient is

\[ j_k = -n_k \left| z_k \right| q v_k \text{grad} V - D_k z_k q \text{grad} n_k \]  

(16)

where \( j_k \) = electrical current density for the flow of charge carriers of type \( k \) having a charge \( z_k q \)

\( q \) = absolute value of electronic charge

\( n_k \) = concentration of particles of type \( k \)

\( v_k \) = mobility of particles of type \( k \)
\[ D_k = \text{Diffusion coefficient of particles of type } k \]
\[ V = \text{electrical potential.} \]

This relationship assumes that, apart from the interaction through the electrical field, the currents and gradients of one particle species do not influence the flow of other species. Furthermore, only isothermal conditions are considered. The electrochemical potential, \( \eta_k \), is related to the chemical potential, \( \mu_k \), and to the electrical potential by

\[ \eta_k = \mu_k + z_k q V \quad \text{(17)} \]

where

\[ \mu_k = \mu_k^o + kT \ln n_k \quad \text{(18)} \]

Using the Einstein equation for diffusion,

\[ D_k = \frac{kT v_k}{|z_k| q} \quad \text{(19)} \]

we obtain the k-carrier current density as a function of the electrochemical potential gradient:

\[ j_k = -\frac{\sigma_k}{z_k q} \text{grad } \eta_k \quad \text{(20)} \]

Here \( \sigma_k \) is the partial conductivity associated with carrier species \( k \).

If the particles considered are not lattice defects, but lattice ions themselves, Eq. (20) is still valid; \( \eta_k \) is in that case not the virtual electrochemical potential of the defects, but the real
electrochemical potential of the corresponding ions. Since both
electrochemical potentials differ only by a constant (not considering
the sign) their gradients are equal.

1. Electronic Transport

The electronic component, $J_e$, of the total current is composed of
contributions from both electrons and holes:

$$J_e = J_n + J_p.$$  \hspace{1cm} (21)

Therefore, in terms of the electrochemical potential,

$$J_e = \frac{\sigma_n}{q} \text{grad} \eta_n - \frac{\sigma_p}{q} \text{grad} \eta_p.$$  \hspace{1cm} (22)

This expression can be re-written in the form

$$J_e = \frac{\sigma_n + \sigma_p}{q} \text{grad} \eta_n - \frac{\sigma_p}{q} (\text{grad} \eta_n + \text{grad} \eta_p).$$  \hspace{1cm} (23)

Assuming the thermodynamic equilibrium between electrons and holes
is not disturbed by the current flow, we can write the following
equilibrium constraint:

$$\text{grad} \eta_n + \text{grad} \eta_p = 0.$$  \hspace{1cm} (24)

Therefore, the electronic current density has the form:

$$J_e = \frac{\sigma_n + \sigma_p}{q} \text{grad} \eta_n = \frac{\sigma_e}{q} \text{grad} \eta_n = - \frac{\sigma_e}{q} \text{grad} \eta_p.$$  \hspace{1cm} (25)
where $\sigma_e$ is the electronic conductivity, $\sigma_n + \sigma_p$.

2. Ionic Transport

Assuming there are two ionic species (1 and 2) which contribute to the current transport, the total ionic current density can be defined as follows:

$$J_i = J_1 + J_2.$$  \hspace{1cm} (26)

Carrying out the same procedure as above, we can define the ionic current as,

$$J_i = -\frac{\sigma_1 + \sigma_2}{z_1 q} \text{grad } \eta_1 + \frac{\sigma_2}{q} \left( \frac{1}{z_1} \text{grad } \eta_1 - \frac{1}{z_2} \text{grad } \eta_2 \right).$$  \hspace{1cm} (27)

Assuming that the thermodynamic equilibrium between the ionic species is undisturbed by the current flow, an analogy similar to that for electronic transport can be made. The thermodynamic equilibrium can be expressed by a reaction equation of the form

$$|z_2| M |z_1|^+ + |z_1| X |z_2|^- = M|z_2| X |z_1|. \hspace{1cm} (28)$$

The equilibrium condition requires that the sums of the chemical potentials be equal on both sides of this equation, therefore,

$$|z_1| \mu_2 + |z_2| \mu_1 = \mu_{MX}. \hspace{1cm} (29)$$
This equation is also valid for the gradients:

\[ |z_1| \text{grad } \mu_2 + |z_2| \text{grad } \mu_1 = \text{grad } \mu_{MX}. \]  

(30)

For small defect concentrations \( \mu_{MX} \) is constant and, therefore,

\[ \text{grad } \mu_{MX} = 0. \]  

(31)

Furthermore, the gradients in the chemical potentials may be replaced by gradients in electrochemical potentials since the electrical terms balance. We thus obtain the following constraint:

\[ |z_1| \text{grad } \eta_2 + |z_2| \text{grad } \eta_1 = 0. \]  

(32)

Therefore, the ionic current density can be written in the form,

\[ J_1 = J_1 + J_2 = -\frac{\sigma_1 + \sigma_2}{z_1q} \text{grad } \eta_1 = -\frac{\sigma_1}{z_1q} \text{grad } \eta_1 = -\frac{\sigma_1}{z_2q} \text{grad } \eta_2. \]  

(33)

3. **Total Current**

The total electrical current density, \( J_t \), is simply the sum of the electronic and ionic currents, from Eqs. (25) and (33),

\[ J_t = j_e + J_1 = \frac{\sigma_e}{q} \text{grad } \eta_n - \frac{\sigma_1}{z_1q} \text{grad } \eta_i \]  

(34)
where $\eta_n$ and $\eta_i$ are the sums of electronic and ionic electrochemical potentials, respectively. A more convenient form of Eq. (34) is

$$ j_t = \frac{\sigma_e + \sigma_i}{q} \text{grad} \eta_n - \frac{\sigma_i}{q} \left( \frac{1}{z_i} \text{grad} \eta_i + \text{grad} \eta_n \right). \quad (35) $$

If the thermodynamic equilibrium between ions and electrons is locally undisturbed, the following equilibrium reaction equations can be considered:

$$ \begin{align*}
X^{|z_2|^-} + |z_2|h & \Rightarrow X^* \quad (36) \\
M^{|z_1|^+} + |z_1|e & \Rightarrow M^* \quad (37)
\end{align*} $$

where

- $M^*$ = a neutral metal atom
- $X^*$ = a neutral anionic atom
- $h$ = an electron hole
- $e$ = an electron.

Equilibration of chemical potentials for the above equations then requires

$$ \mu_2 + |z_2|\mu_p = \mu_X, \quad (38) $$

and

$$ \mu_1 + |z_1|\mu_n = \mu_M. \quad (39) $$

When written in terms of gradients, electrochemical potentials can be introduced resulting in the following expressions:
Finally, substituting these expressions into Eq. (35) we obtain

\[
\begin{align*}
\mathbf{j}_t &= \frac{\sigma_t}{q} \nabla n - \frac{\sigma_i}{qz_1} \nabla \mu_M = - \frac{\sigma_t}{q} \nabla \eta_p - \frac{\sigma_i}{qz_2} \nabla \mu_X. \\
\end{align*}
\]  

In a galvanic cell employing an oxygen selective electrolyte, the electrolyte acts as an oxygen membrane which separates two regions where constant (equilibrium) oxygen partial pressures are maintained. Under the condition that no external electric current is supplied to the system, \( \mathbf{j}_t \) in Eq. (42) is zero. Using Eq. (24) and setting \( z_2 = -2 \) (valence of oxygen ion) we obtain:

\[
\begin{align*}
\nabla \eta_n &= - \frac{\sigma_i}{2\sigma_t} \nabla \mu_0 = - \frac{1}{2} t_1 \nabla \mu_0 \\
&= - \frac{t_1}{4} \nabla \mu_0.2
\end{align*}
\]

where \( t_1 \) is the ionic transference number. A value for the difference in the electrochemical potential of the electrons at both sides can be obtained by integrating between the two boundaries. This difference is just \(-q\) times the value of the voltage that can be measured between two identical metal electrodes (the chemical potentials and derived quantities are expressed per atom here instead of the usual gram atom). We thus
obtain:

\[ E = -\frac{1}{q} \int_{\eta_n}^{\eta_n} d\eta_n = \frac{1}{4q} \int_{\eta_0}^{\eta_0} t_1 d\mu_{02} \quad (44) \]

where, for reversible electrodes,

\[ t_1 = \frac{\sigma_i}{\sigma_i + \sigma_e} = \frac{j_i}{j_1 + j_e} \quad . \quad (45) \]

If the oxygen potential difference is small, so that \( t_1 \) can be considered to be constant (equal to an average value \( \bar{t}_1 \)) we obtain simply:

\[ E = \frac{1}{4q} \bar{t}_1 (\mu_{02}^{II} - \mu_{02}^I) \quad , \quad (46) \]

or, since \( \mu_{02} = \mu_{02}^0 + kT \ln P_{02} \)

\[ E = \bar{t}_1 \frac{kT}{4q} \ln \frac{P_{02}^{II}}{P_{02}^I} \quad , \quad (47) \]

which is the working equation for galvanic cells given by Wagner\textsuperscript{21} in his pioneering work.

The average ionic transfer number, \( \bar{t}_1 \), between the oxygen pressures imposed at the electrodes, as given in Eqs. (46) and (47), is defined as the ratio of the measured cell emf, \( E_m \), to the thermodynamic emf, \( E_t \):\textsuperscript{14}

\[ \bar{t}_1 = \frac{E_m}{E_t} \quad . \quad (48) \]
The thermodynamic emf, $E_t$, of an oxygen concentration cell having a stabilized zirconia electrolyte and oxygen pressures of $P_{O_2}'$ and $P_{O_2}''$ at the anode and cathode, respectively, $(P_{O_2}'' > P_{O_2}')$ is given by

$$E_t = \frac{RT}{4F} \ln \frac{P_{O_2}''}{P_{O_2}'}.$$  \hspace{1cm} (49)

The measured emf, $E_m$, is defined as

$$E_m = \frac{RT}{F} \ln \frac{P_{O_2}''_{1/4}}{P_{O_2}^{1/4} + P_0^{1/4}}.$$  \hspace{1cm} (50)

providing $P_{O_2}'' > P_0$. \textsuperscript{14,15} $P_0$, a characteristic of the electrolyte, is a parameter accounting for finite n-type conductivity, \textsuperscript{14,15} and is defined as the oxygen pressure at which $t_e = 0.5$ (where $t_e$ is the transport number of excess electrons). In the derivation of Eq. (50) it is assumed that the n-type conductivity, $\sigma_n$, follows the theoretical $P_{O_2}^{-1/4}$ dependence predictable from the electrolyte reaction

$$O_0 = \frac{1}{2} O_2(g) + V_o^{+2} + 2e^-$$ \hspace{1cm} (51)

where $O_0$ is an oxygen ion on a normal lattice site, $V_o^{+2}$ is a doubly ionized oxygen vacancy, and $e^-$ is a conduction electron.

The mass action equation for Eq. (51) is

$$K = [V_o^{2+}] \ [e^-]^2 P_{O_2}^{1/2}$$ \hspace{1cm} (52)
which, solving for $[e^-]$ yields,

$$[e^-] = \left[ \frac{K}{v_{2^+}} \right]^{1/2} p_{O_2}^{-1/4}. \quad (53)$$

From Eq. (53) and the definition of $\sigma_n$,

$$\sigma_n = \eta_n |z_n| q v_n, \quad (54)$$

the $p_{O_2}^{-1/4}$ dependence can be readily seen.

Also, in conjunction with Eq. (45), the ionic transference number, $t_i$, can be readily shown to be

$$t_i = \frac{p_{O_2}^{1/4}}{p_{O_2}^{1/4} + p_0^{1/4}} \quad (55)$$

for low partial pressures of oxygen. A knowledge of $p_0$, therefore, suffices for calculating the ionic transport number at any required oxygen pressure. Equation (55) indicates that the electrolyte can be used without significant electronic conduction error only when $p_{O_2} \gg p_0$.

Equation (47) can be further reduced if the electrolyte is principally an ionic conductor, $(\bar{t}_i \approx 1)$, to

$$E = \frac{kT}{4q} \ln \frac{P_{II}}{P_I}. \quad (56)$$

Equation (56) is equivalent to Eq. (15) derived earlier using simple thermodynamic relationships and making the assumptions of equilibrium oxygen partial pressures at the electrodes and a pure ionic conducting
electrolyte. The validity of Eq. (56) can be verified by a sample calculation of $t_1$ at the temperature and partial pressure of interest. As an example, at 1000°C, the oxygen partial pressure at the anode (assuming a Ni-NiO mixture is used) is $10^{-10.35}$ atm. The oxygen partial pressure at the cathode (assuming a Cu-Cu$_2$O mixture is used) is $10^{-6.29}$ atm. $P_0$ for CSZ based on data developed by Etsell and Flengas is $10^{-29}$ atm. Substituting these values into Eq. (48), (49) and (50), $t_1$ is found to be 0.99999.$^+$.
IV. ELECTROLYTE MATERIALS—CRITERIA AND REVIEW

In designing an electrochemical cell, one of the most important factors to be considered is the proper choice of electrolyte. Wagner has shown that the cell voltage of an electrochemical cell utilizing a solid oxide electrolyte is related to the oxygen partial pressures at the electrode-electrolyte interfaces and the ionic transference number by the following equation:

\[ E = \frac{RT}{4F} \int \ln \frac{P_{O_2}^n}{P_{O_2}^0} t_i \, d\ln P_{O_2} \]  \hspace{1cm} (57)

Equation (57) is identical to the expression for cell voltage derived previously (Eq. 44). In this equation, the ionic transference number, \( t_i \), is generally a function of the oxygen activity within the electrolyte. An expression for \( t_i \) obtained from a point defect model was given previously in Eq. (45) and the dependency of \( t_i \) on the oxygen pressure and n-type conductivity in the electrolyte was presented in Eq. (55). Whenever \( t_i \) differs appreciably from unity, it is necessary to relate the measured cell voltage to the integral of Eq. (57). However, by properly choosing an electrolyte with a broad ionic range where \( t_i \) is approximately unity, Eq. (57) can be integrated to give Eq. (2). If electronic conductivity is significant (\( t_i < .99 \)) the thermodynamic quantities calculated from the measured voltages will be inaccurate since any electronic conductivity has the effect of shorting out the cell, thus causing the measured cell voltages to be smaller than those...
predicted from Eq. (2).

Considerable effort has been made to find and develop ion selective electrolytes which exhibit pure ionic conductivity and are stable over relatively wide ranges of temperature and pressure. A list of solid oxide electrolytes used or studied by other investigators is presented in Table 1.

The two most commonly used oxygen electrolytes are calcia stabilized zirconia (CSZ) and yttria doped thoria (YDT). The variation of ionic transference number with temperature and oxygen pressure for both these electrolytes can be easily inferred from a comparison of the measured cell voltages with those calculated from the known oxygen pressures using Eq. (2). A comparison of CSZ and YDT has been made by Patterson, using published results of equilibrium oxygen pressure measurements for both electrolytes. This data is presented in Figs. 10 and 11. The electrolytic domains for both CSZ and YDT increase toward lower oxygen partial pressures with decreasing temperature. The ionic range, as defined by \( t_1 > 0.99 \), for YDT lies some five orders of magnitude lower in oxygen partial pressure than that for CSZ.

CSZ is usually used whenever possible because it is lower in cost than YDT, less susceptible to thermal shock, and is non-radioactive. However, YDT must be chosen when exploring equilibria exhibiting very low oxygen partial pressures. A thorough study of CSZ as an electrolyte has been made by Estell and Flengas. The choice of CSZ as the electrolyte for this study was based on their work as well as work done by Charette and Flengas and other investigators.
<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Stabilizing Component</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>Pyrex (SiO₂)</td>
<td>Na₂O</td>
<td>69</td>
</tr>
<tr>
<td>Thüringer glass</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>CeO₂-Y₂O₃</td>
<td>32</td>
</tr>
<tr>
<td>&quot;</td>
<td>Y₂O₃</td>
<td>24, 25</td>
</tr>
<tr>
<td>&quot;</td>
<td>CaO</td>
<td>14, 22, 23</td>
</tr>
<tr>
<td>ZrO₂ (Monoclinic)</td>
<td>-</td>
<td>26 - 29</td>
</tr>
<tr>
<td>ZrO₂ (Tetragonal)</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>HfO₂</td>
<td>CaO</td>
<td>31</td>
</tr>
<tr>
<td>&quot;</td>
<td>Y₂O₃</td>
<td>32</td>
</tr>
<tr>
<td>ThO₂</td>
<td>-</td>
<td>26, 33, 34</td>
</tr>
<tr>
<td>&quot;</td>
<td>Y₂O₃</td>
<td>19, 35 - 39</td>
</tr>
<tr>
<td>CeO₂</td>
<td>-</td>
<td>40 - 42</td>
</tr>
<tr>
<td>&quot;</td>
<td>La₂O₃</td>
<td>43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>44 - 47</td>
</tr>
<tr>
<td>BeO</td>
<td>-</td>
<td>48 - 59</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>47, 60 - 66</td>
</tr>
</tbody>
</table>
Fig. 10. Electrolytic domain and related data for CSZ (from Ref. 22).
Fig. 11. Electrolytic domain and related data for YDT (from Ref. 22).
V. REFERENCE ELECTRODES

In the emf technique, measurements of oxygen activity in a given material must be referenced to a known oxygen partial pressure. The reference oxygen partial pressure can be supplied by a mixture of phases such as a metal and its oxide in equilibrium, or by a gas mixture which establishes an equilibrium oxygen partial pressure by gas phase reaction. CO, CO$_2$ and H$_2$, H$_2$O gas mixtures have been used as reference electrodes in earlier open cell studies; however, metal-metal oxide coexistence electrodes are more appropriate for closed-cell studies.

To qualify as a reference electrode, the phases in the coexistence electrode must be stable over the temperature range of interest and be stoichiometric. However, there is another criteria that is often overlooked. In deriving Eqs. (54) through (56), we assumed that the oxygen potential difference between the two electrodes was relatively small so that $t_i$ could be considered as a constant (equal to an average value $\bar{t}_i$). If the relative oxygen partial pressure difference at the two electrodes is large this assumption cannot always be made. Therefore, in choosing a reference electrode, it is desirable to select a system which has an equilibrium oxygen partial pressure close to that of the unknown system throughout the temperature range of interest. However, if the electrolyte is chosen such that $t_i > 0.99$ at both electrodes (see Eq. (55)) so that $\bar{t}_i$ is approximately unity over the temperature range of interest, the above stipulation is not necessary. A large oxygen potential difference can also result in higher slopes when plotting cell emf vs. T. This increases the effect of temperature gradients and can lead to erroneous emf readings.
Several different metal-metal oxide systems have been used as reference electrodes for solid electrolyte galvanic cell studies; however, Ni-NiO, Cu-Cu$_2$O, and Fe-FeO are the most common. The dependence of RT log $P_{O_2}$ vs. temperature for many of the more stable coexistence electrode reactions is shown in Fig. 12. The equilibrium oxygen partial pressure for a given system can be found by passing a straight line from the point marked $O_x$ (corresponding to $\Delta G^0 = 0$) through the electrode reaction at the required temperature to the scale at the right. Superimposed on the diagram are the minimum oxygen partial pressures within the ionic range ($t_1 > .99$) for CSZ and YDT.

Ni-NiO was chosen as the reference electrode for this study based on work done by Bugden and Pratt, Charette and Flengas, and Rizzo and co-workers. The Ni-NiO system is ideal as a reference electrode for use with solid electrolytes at temperatures between 500 and 1400°C because Ni-saturated NiO is known to be stoichiometric, and solid Ni metal dissolves very little oxygen up to 1438°C. Considerable work has been done on the Ni-NiO system and the standard free energy of formation, $\Delta G^0_{NiO}$, has been well documented by the aforementioned researchers and was taken to be represented by the equation:

$$\Delta G^0_{NiO} = -55,884 + 20.290 T \pm 50 \text{ cal.} \quad (58)$$

as experimentally determined by Charette and Flengas. To illustrate how well this value is known, Rizzo and co-workers given the following equation for the temperature range 900-1400°C

$$\Delta G^0_{NiO} = -55,995 + 20.36 T \pm 130 \text{ cal.} \quad (59)$$
Fig. 12. The standard free energy of formation of compounds commonly used as reference electrodes as a function of temperature. From Ref. 80 and 81.
VI. EXPERIMENTAL STUDIES

A. Materials

1. Metal-Metal Oxide Powders

The Ni, NiO, Cu and Cu$_2$O powders used were all high purity materials obtained from the Atomergic Chemical Co. and analyzed 99.99, 99.9, 99.99 and 99.9% purity, respectively. The Fe$_2$O$_3$ and Fe$_3$O$_4$ powders were obtained from Research Organic, Inc. and analyzed 99.9% and 99% purity, respectively.

2. Electrolyte

The electrolyte used was ZrO$_2$ doped with 7 1/2% CaO and was obtained from the Zirconium Corporation of America. The electrolyte was in the form of a closed end tube 1/2 in. O.D. x 3/8 in. I.D. x 24 in. long and was certified He leak tested.

3. Alumina Tubes

Two sizes of alumina tubes were used. Crucibles 1 1/4 in. high x 3/4 in. O.D. were used to contain the outer electrode metal-metal oxide mixture and the electrolyte tube containing the Ni, NiO mixture (reference electrode). An impervious alumina tube 1 1/4 in. O.D. x 1 in. I.D. x 24 in. long, closed one end, was used to contain the cell assembly. The alumina tubes and crucibles were obtained from Morganite, Inc. and were triangle RR grade purity.

B. Equipment

1. Furnace

A platinum wound furnace 1 3/4 in. I.D. x 10 in. high was used for all experimental work. The furnace was closed at the bottom and was
metal jacketed having overall dimensions of 10 in. O.D. × 14 in. high. The temperature profile was such that a relatively constant temperature zone (ΔT < 2°C) 1-1\(\frac{1}{2}\) in. in length existed throughout the temperature range investigated.

2. **Furnace Temperature Controller.**

The furnace temperature was controlled using a Leeds and Northrup Speedomax® H temperature controller in conjunction with an external potentiometer circuit. The thermocouple used in conjunction with the controller was Pt-Pt 10% Rh and was positioned inside the furnace alongside the alumina tube containing the galvanic cell at the level of the electrolyte interface. Furnace temperature was maintained within ± 0.5°C of set point using this apparatus.

3. **Cell Temperature.**

The temperature of the cell was measured using a Leeds and Northrup K-3 potentiometer. In initial work, the cell temperature was measured using a Pt-Pt 10% Rh thermocouple positioned alongside the alumina tube containing the cell at the level of the electrolyte interface (same position as the furnace controller thermocouple). However, in later work the thermocouple was incorporated into the cell design and positioned alongside the zirconia tube in the alumina crucible containing the outer electrode mixture (see Fig. 14).

4. **EMF Measurement**

The cell emf was measured using either a Keithley Model 640 Vibrating Capacitor Electrometer or a PAR Model 134 Electrometer. A potentiometer was connected in series between the cell and the
electrometer so that part of the cell emf could be suppressed, thereby permitting the full scale setting of the electrometer to be reduced to 10 millivolts. This allowed the true cell emf to be read with an accuracy greater than ± 0.1 millivolt.

C. Construction of Cell #1

Believing the design approach devised by Charette and Flengas to be well conceived, the cell design they developed was used as a pattern for the first cell we constructed.

This cell design (Fig. 13) consisted of two half-cell compartments separated by a calcium stabilized zirconia diaphragm. The electrolyte diaphragm, a Zr $O_2 + 7.5\% w\ CaO$ tube, closed one end, served as a container for the inner electrode material. Both half-cells were individually sealed under vacuum ($10^{-3}$ mm Hg He). The half-cells were flushed out with helium and sealed after approximately five minutes of vacuum degassing at room temperature. The inner reference electrode consisted of the closed end zirconia tube, discussed previously, containing a loosely packed Ni-NiO powder. The top of this tube was sealed using a tight fitting Pyrex glass tube. The Pyrex tube was sealed to the zirconia with wax. Since the zirconia and alumina tubes used were 24 inches long, and only the bottom eight inches or so, were in the furnace, the upper portion of the tubes remained at room temperature and no special sealants were required. The wax used was capable of maintaining a good seal up to about 200°F. Small diameter Pyrex side arm tubes were sealed into the Pyrex top allowing the platinum wire leads to pass through. The wires were sealed into the small tubes
Fig. 13. Schematic diagram of the cell design used for cell #1.
using wax. This eliminated having to seal tungsten electrode connections into the glass and then welding the tungsten to the platinum lead wires as done by other investigators, resulting in thermal emfs which had to be corrected for when measuring the cell emf. Other investigators used spring type arrangements to maintain a constant pressure on the electrode to make sure of good electrode contact; however, the weight of the inner half-cell seemed sufficient to guarantee contact, so no springs were used. An alumina rod, closed on one end, was placed inside the inner zirconia tube on top of the Ni-NiO powder to further enhance contact of the powder and the electrode and also to cut down on the available air space above the powder.

The outer half-cell contained a mixture of Cu-Cu$_2$O. A ten mil perforated foil platinum electrode was placed at the bottom of a small alumina crucible and the Ni, NiO reference half-cell was inserted into the alumina crucible and pressed against the platinum foil electrode. The free volume of the crucible was then packed with the Cu-Cu$_2$O powder mixture (approx. 50/50 weight ratio). The entire cell was then placed inside an alumina tube 24 in. long x 1 in. I.D., which was then sealed in the same manner as the inner zirconia tube. The total time actually spent in assembly was less than two hours. As will be shown later, too many short cuts were taken in cell construction resulting in stabilization problems and high emf readings.

D. Construction of Cell #2

Considerable effort was taken in the construction of this cell to assure that the high purity metals and metal oxides used as electrodes
were free of volatile impurities e.g., H$_2$O. Also, the cell was constructed in such a manner as to assure good contact between the platinum electrode leads and the metal-metal oxide powders at the electrolyte interface.

Glass stop cocks incorporating high vacuum grease were designed into the Pyrex half cell covers so that the vacuum could be checked at the end of each experiment. This design feature made it easy to determine if any leaks had developed without dismantling the entire cell (Fig. 14).

Since considerable time was involved in sealing the first cell because of the relatively large clearances between the tubes and the glass covers, the zirconia and alumina tubes used were tapered to fit ground Pyrex glass joints which were designed into the Pyrex glass covers. This permitted the half cells to be sealed quickly and easily. Once the taped joints were connected, the junctions were heated using a flameless heater (rapid local heating with a flame caused the zirconia tube to fracture). The wax was then applied and flowed up into the ground glass joint by capillary action forming a vacuum tight seal.

Cell construction was similar to that of the first cell. The inner half cell consisted of a zirconia tube 24 in. long × 3/8 in. I.D. containing a Ni-NiO powder mixture. Considerable care was taken to assure good contact of the platinum electrode lead with the Ni-NiO mixture at the electrolyte interface. Platinum wire .020 in. in diameter was fashioned into a spiral conforming to the inside diameter of the zirconia tube. A flattened piece of platinum wire was welded across the bottom of the spiral to maintain its shape. An alumina tube, open at both ends, having an outside diameter just under the
Fig. 14. Schematic diagram of the cell design used for cells 2-5.
inside diameter of the zirconia tube was then used to insert the
platinum spiral lead into the zirconia tube and hold it in position
at the bottom. The desired amount of Ni-NiO mixture was then added
through the alumina tube.

The outer half cell was similarly prepared. A second piece of
platinum wire was formed into a spiral for the Cu-Cu₂O electrode lead.
The inner half cell was then placed onto the spiral lead. A portion of
the platinum wire leaving the spiral was wrapped around the lower 1/2 in.
of the zirconia tube and held firmly in place by another piece of
platinum wire wrapped once around the tube, twisted tightly, and
welded to the spiral lead. This procedure gave good contact over the
bottom portion of the electrolyte tube (interface). The completed
inner half cell was then placed into a small (1 1/16 in. × 25/32 in. I.D.)
alumina crucible which was then filled with a powder mixture of Cu-Cu₂O.

A sheathed Pt, Pt-10% Rh thermocouple was placed alongside the
zirconia tube, embedded in the Cu-Cu₂O mixture and touching the bottom
of the alumina crucible. Positioning the thermocouple inside the cell
in this manner assured accurate temperature measurement and gave a
positive method of determining when the cell temperature had stabilized;
the furnace temperature stabilized much more rapidly.

The completed cell was then placed into a large alumina tube 2½ in.
long × 1 in. I.D. The tapered Pyrex tubes designed to close the tops
of the zirconia tube and the large alumina tube were then placed in
position. The joints were then heated and sealed with wax as described
previously. The platinum electrode leads and the thermocouple leads
were also sealed through the glass using wax. This procedure eliminated
the generation of thermal emfs experienced by other investigators who sealed tungsten wires through the glass (glass seal) and then welded the platinum electrode leads to the tungsten wire before sealing the cell.

The assembled cell was then flushed with helium and heated to approximately 230°C for two hours while being evacuated to approximately 10^{-3} \text{mm Hg He} using a standard floor pump. Both half cells were evacuated together using a tee on the vacuum pump line. The individual half cells were refushed several times during the heating and evacuation procedure. The cell was then evacuated over night (with the heater off) to assure removal of all volatile contaminants. In the morning the cell was flushed again with helium and evacuated once again while being heated to 230°C. After one hour of heating and evacuation, the heater was turned off and the cell allowed to cool to room temperature (while being evacuated) at which time the stop cocks were closed.

E. Construction of Cell #3

This cell was constructed in the same manner as cell #2. However, due to carelessness, a considerable excess of material was placed in each electrode. The inner electrode, Ni-NiO, was filled to a height of 3-4 in., and the small alumina crucible containing the outer electrode, Cu-Cu_2O, was filled to the top. The cell was flushed with helium and heated for five hours at a temperature of 230°C will being degassed under a vacuum of \sim 10^{-5} \text{mm Hg}. A diffusion pump was used to evacuate the cell. After the five hour period, the cell was sealed (stop cocks closed) under a vacuum 10^{-5} \text{mm Hg He}.
F. Construction of Cell #4

The construction procedure was identical to that of cell #2 and #3. This time 2-4 grams of material were placed in each electrode. The cell was flushed with argon and then heated for 1 hour at a temperature of 230°C while being evacuated under a vacuum of $10^{-7}$ mm Hg. After the heating period, the cell was evacuated for 60 hours using an oil diffusion pump. The final cell vacuum was $10^{-7}$ mm Hg Ar.

G. Construction of Cell #5

The construction procedure was identical to that of cells #2 - #4 with the exception that a quartz tube was used in place of the alumina tube to contain the cell assembly. The use of a quartz tube limits the maximum cell operating temperature to about 1100°C. However, temperatures above 1100°C were not investigated in this study and, therefore, the choice of quartz or alumina was arbitrary. Also, a mixture of $\text{Fe}_2\text{O}_3$-$\text{Fe}_3\text{O}_4$ was used as the cathode in place of the Cu-Cu$_2$O mixture used in the previous cells. Each electrode consisted of 2-4 grams of material. The cell was flushed with high purity argon (0.99998+) and heated for 45 minutes at a temperature of 230°C while being evacuated under high vacuum. After the heating period, the cell was further evacuated for another 45 minute period. The final cell vacuum was $10^{-5}$ mm Hg Ar.
VII. EXPERIMENTAL RESULTS AND DISCUSSION

A. The $\text{Ni}_\text{(s)} + \text{Cu}_2\text{O} \rightarrow \text{NiO}_\text{(s)} + 2\text{Cu}_\text{(s)}$ Reaction

The standard free energy change of this reaction was determined from the measured emf of the cell,

$$\Theta \text{ Cu, Cu}_2\text{O} | \text{ZrO}_0.85 \text{Ca}_0.15 \theta_{0.85} | \text{ Ni, NiO } \Theta.$$  

This cell was chosen for initial study with regard to galvanic cell design primarily because it has been studied previously by numerous authors$^{1,2,5,6,19}$ employing a wide variety of galvanic cell structures. The galvanic cells constructed in the present study, and the experimental results obtained from them could be compared with the earlier studies to determine factors which account for variations in experimental data.

1. Cell #1

The initial galvanic cell studied consisted of individually evacuated and sealed electrode compartments modeled after the cell developed by Charette and Flengas.$^5$ The cell structure is shown schematically in Fig. 13. The emf of the cell is presented in Fig. 15 as a function of cell temperature, and represent data taken over a three week period. Shortly after the cell was initially heated to operating temperature, a considerable amount of water condensate was noticed inside the Pyrex covers of both electrode compartments. The condensate remained throughout the entire time the cell was in operation moving up and down the Pyrex tube cover with cell temperature. To this writer's
Fig. 15. Temperature dependence of emf for the system Ni, NiO - Cu, Cu₂O.
knowledge, no other investigator has reported the appearance of water condensate during cell operation. The appearance of water condensate would have to be attributed to one or a combination of the following causes:

a) Adsorbed water on the tube surfaces (a large tube surface area was involved)

b) Adsorbed water within the Pyrex glass tubes used to seal the electrode compartments.

c) Adsorbed water on the metal-metal oxide powders used in the cell construction

Since the emf data obtained from this cell was ~ 3-5 mV higher than other data reported by reputable investigators, it was assumed that the water in some way affected the cell emf. Also, instead of being linear, the plot of emf vs. T was concave upward. De-gassing procedures were subsequently introduced causing a pronounced effect on the cell emf. Based on work by other investigators we know that short-circuiting of the electrolyte causes lower and concave downward plots of emf vs. T. We can preclude any significant short circuiting by transport between the electrode atmospheres, even if there was a leak in the inner electrode seal, by virtue of the cell design. Two factors, therefore, remain to explain the high, non-linear data

a) a leak in the cathode compartment

b) water contamination causing an additional reaction at one or both of the electrodes.
The cell emf was repeatable within ±1 mV over this time period at temperatures greater than 900°C. However, the repeatability of the data became progressively worse as the temperature was lowered.

The cell was cycled repeatedly through the temperature range from approximately 680°C to 1030°C. However, during the final run a drastic change in measured emf occurred, corresponding to curve D in Fig. 15. The measured emf was not linearly decreasing with temperature, and was not stable with respect to time at a given temperature. The cell was checked for vacuum by heating a small area of each Pyrex tube glass cover with a pin point flame until the glass softening point was reached. Since the glass wall was not drawn in, it was concluded that the vacuum was lost in both electrode compartments.

The presence of water vapor on electrodes during galvanic cell operation has not been reported previously. Most previous investigators used "open cell" techniques using sintered two-phase electrode tablets in a flowing inert purge gas, and in this technique, any volatile would be transported by the carrier gas stream. The "closed cell" designed by Charette and Flengas probably was susceptible to the problem of condensed water vapor since no reported precautions were taken to eliminate moisture from their electrode materials. However, with their particular cell design, any condensate formed in the inner electrode compartment was hidden from view, while the large Pyrex surface on the outer electrode compartment would tend to distribute any condensate in the outer cell over a large area, making it more difficult to detect.
Two design objectives became evident from this first cell. The first was that some method should be incorporated into the cell design to enable the vacuum in each compartment to be readily checked without dismantling the cell. The second objective was to eliminate the water condensate which appeared during operation. Degassing procedures were instigated for subsequent cells tested, and design modifications were made to allow independent residual gas monitoring of the electrode compartments.

2. Cell #2

The data obtained from this cell is presented in Fig. 16. Shortly after cell #2 was heated to operating temperature a slight amount of condensate formed on the Pyrex cover of the inner electrode. The condensate remained throughout the entire cell operation (~10 days). The cell emf was repeatable within ~± 0.2 mV going either up or down in temperature for temperatures > ~ 800°C.

It is interesting to note that the presence of water in the cell does not noticeably effect the linearity of the emf vs. temperature plot at high temperatures. Non-linearity occurs at low temperatures only. Also, the data obtained for cell #2 is approximately 2 mV higher than that reported by Charette and Flemgas. 5

Cell #2 was designed so the thermocouple used to monitor the cell reaction temperature was positioned alongside the zirconia tube and buried in the Cu, Cu₂O electrode mixture. Positioned in this manner, the reaction temperature could be more accurately measured and furthermore, allowed a more reliable determination of the time required for the cell temperature to stabilize—the furnace temperature stabilizes
much more rapidly. Using the interior thermocouple, a significant temperature difference of 10°C was discovered between the outside of the cell (where Charatte and Flengas had measured their cell temperature) and the temperature at the electrolyte interface. This temperature difference was relatively constant over the temperature range investigated, 660-1000°C, with the temperature inside the cell being consistently less than that outside the cell. Assuming that a similar temperature difference existed in Charette and Flengas' cell, we can conclude that the data they report is approximately 0.5 mV too high throughout the reported temperature range. Data from cell #2 is therefore, approximately 2.5 mV higher than the corrected data of Charette and Flengas. At temperatures less than 800°C, the repeatability grew increasingly worse and the plot of emf vs. temperature was no longer linear. After several days of operation the continued increase with time of the cell emf at a constant temperature indicated that a leak had developed in the cathode compartment of the cell (curve A), since cell \( \text{emf} \) is directly proportional to \( \ln \frac{P_{02}}{P_{02}'} \), as shown by Eq. (2).

Notably, the emf data for cell #2 under most stable conditions was considerably lower than that for cell #1. Since the preparative conditions tended to reduce the initial water vapor present in the electrodes for cell #2, the hypothesis that residual water vapor raises the cell potential is again supported.
3. **Cell #3**

Cell #3 was constructed in a manner similar to cell #2. Considerable condensate formed as soon as cell operation started. As the data show in Fig. 16, curve C, the cell emf was significantly greater than that obtained from cell #2. In an effort to determine just what was causing the high cell emf, the cell was de-gassed for 15 hours under a vacuum of $10^{-5}$ mm Hg. The degassing process was carried out at room temperature.

The result was significant in that the cell emf dropped significantly, as shown in Fig. 16, curve D. It was assumed that not all of the moisture initially present in the metal-metal oxide powders was removed by the degassing process because of the large amount of materials used at each electrode (see cell construction). This large volume and depth of powder would make it extremely difficult to remove volatile impurities by pore diffusion without extended heating under vacuum.

With this knowledge in hand, another cell was constructed.

4. **Cell #4**

Soon after this cell was put in operation, a light mist of condensate was noticed on the Pyrex cover of the inner electrode. However, the presence of this small amount of water seemed to not effect the linearity of the cell emf vs. temperature plot as mentioned previously (see Fig. 16, curve B and Table 2). Also, the data was considerably lower than any previously obtained and compared well with that reported by Charette and Flengas\(^5\) (about 1 mV higher throughout the temperature range). The cell emf was extremely repeatable at all temperatures whether the cell temperature was increased or decreased.
To observe the effect of a small amount of water on the cell emf, the cell was heated to 230°C for 4 hours while being evacuated under a vacuum of 10⁻⁷ mm Hg. At the end of this time, the cell vacuum was ~ 10⁻⁷ mm Hg. The cell was then re-tested and the result is presented in Fig. 16, curve E, and Table 2. The cell emf dropped slightly but significantly and now agree well with the data reported by Charette and Flengas (Fig. 17).

The results of this study in conjunction with the work of other investigators mentioned previously, indicate that as more and more refinements in cell design are made, the lower the cell emfs will become. This is evident from Fig. 17. Also, the experimentally determined values and calculated values are in better agreement (Fig. 17).

Most data reported,²,₆,₁⁹ was obtained using the open cell technique or modifications thereof. Since short-circuiting of the electrolyte can never be completely eliminated using the open-cell design, one would expect values determined in this manner to be lower than those determined using a closed cell design since short-circuiting of the electrolyte lowers the ratio of \( P''_{\text{O}_2} / P'_{\text{O}_2} \) which is proportional to the cell emf. However, this is not evident from Fig. 17; in fact, the opposite occurs. The cell emfs obtained using open cells are higher than those obtained from closed cells. Based on the results of this study, we can conclude that the presence of water vapor can result in high cell emfs. Because of cell designs and the use of flowing streams of inert gas, other investigators were possibly not aware of this problem (water vapor was continuously flushed from the system).
Fig. 16. Temperature dependence of emf for the system Ni, NiO - Cu, Cu₂O.
Table 2. Experimental Voltages, Cu-Cu₂O|Ni-NiO System

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cell No. 4</th>
<th>Cell No. 4 Degassed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp, °K</td>
<td>E.M.F. (mV)</td>
</tr>
<tr>
<td>1</td>
<td>1263.85</td>
<td>259.20</td>
</tr>
<tr>
<td>2</td>
<td>1192.88</td>
<td>263.75</td>
</tr>
<tr>
<td>3</td>
<td>1119.70</td>
<td>268.90</td>
</tr>
<tr>
<td>4</td>
<td>1047.42</td>
<td>274.05</td>
</tr>
<tr>
<td>5</td>
<td>970.15</td>
<td>279.05</td>
</tr>
<tr>
<td>6</td>
<td>1009.15</td>
<td>276.58</td>
</tr>
<tr>
<td>7</td>
<td>942.29</td>
<td>280.95</td>
</tr>
<tr>
<td>8</td>
<td>1156.28</td>
<td>266.15</td>
</tr>
<tr>
<td>9</td>
<td>1083.02</td>
<td>271.06</td>
</tr>
</tbody>
</table>
Fig. 17. A comparison of the published temperature dependence of EMF for the system Ni, NiO - Cu, Cu₂O with this work.
B. The \( \text{Ni}(s) + 3 \text{Fe}_2 \text{O}_3(s) \neq 2 \text{Fe}_3 \text{O}_4 + \text{NiO}(s) \) Reaction

Only one other investigator\(^5\) has reported the change in free energy for this reaction using emf techniques. This system was chosen for study to corroborate the aforementioned work and to determine cell design parameters affecting systems where the difference in oxygen pressures above the two electrodes is large or when one of the electrodes has a relatively high equilibrium oxygen pressure. The following cell was used:

\[ \oplus \text{Fe}_2 \text{O}_3, \text{Fe}_3 \text{O}_4 \mid \text{Zr}_{0.85} \text{Ca}_{0.15} \text{O}_{1.85} \mid \text{Ni}, \text{NiO} \oplus \]

1. Cell #5

Based on the information obtained from the earlier cells it was determined to prepare this cell in such a manner as to be able to determine the effect of volatile impurities on the cell emf. As described previously, the completed cell was heated for 45 minutes at 230°C and evacuated for a total of 1 1/2 hours to eliminate most of the volatile impurities. Final cell vacuum was \(10^{-5}\) mm Hg Ar. However, shortly after the cell was put in operation a light mist of condensate was noticed on the Pyrex cover of the inner electrode. This small amount of condensate did not appear to effect the linearity of the cell emf vs. temperature plot or the repeatability of the measurements (Fig. 18). After completing measurements under these conditions, the cell was evacuated again for 19 hours using an oil diffusion pump. During this time, the cell was heated for 3 1/2 hours at 230°C (while being evacuated). Final cell vacuum was \(10^{-7}\) mm Hg Ar. The cell was then re-tested.
The complete results of this study are presented in Table 3 and Fig. 18. Contrary to earlier observations with the Cu, Cu₂O || Ni, NiO system, the presence of water vapor in the cell had no noticeable effect on the cell emf.

C. Calculated Thermodynamic Properties from Experimental Results

The thermodynamic properties calculated from the results of this study, using the Nernst Equation, are presented in Table 4. Data generated by Charette and Flengas⁵ are given for comparison since they used a similar cell design in their work and their data is considerably more consistent than that obtained by other investigators. As can readily be observed, the two sets of data are in good agreement. However, the consistency of the data and estimated accuracy of the calculated thermodynamic properties from this study makes it the most consistent to date.

D. Discussion of the H₂O Effect on Cell EMF

If water is present in an electrode compartment and a temperature gradient is imposed along the compartment, a thermomolecular diffusion flux toward the colder end (T₁) will oppose the flux produced by ordinary diffusion. The vapor pressure of water at the electrode (T₂), neglecting convective transport effects, is related to that at T₁ by

\[ \frac{P_{H₂O}(T₂)}{P_{H₂O}(T₁)} \approx \frac{T₂}{T₁} \]  

(60)

where T₁ and T₂ are °K. The vapor pressure of condensed water at 25°C is 23.7 torr. If this vapor is in dynamic equilibrium with an electrode mixture at 1000°C, the water vapor pressure is approximately 49 torr
<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cell No. 5</th>
<th>Cell No. 5 Degassed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp, °K</td>
<td>E.M.F. (mV)</td>
</tr>
<tr>
<td>1</td>
<td>984.39</td>
<td>219.90</td>
</tr>
<tr>
<td>2</td>
<td>1066.33</td>
<td>243.00</td>
</tr>
<tr>
<td>3</td>
<td>1156.98</td>
<td>269.85</td>
</tr>
<tr>
<td>4</td>
<td>1245.76</td>
<td>297.52</td>
</tr>
<tr>
<td>5</td>
<td>1201.15</td>
<td>284.20</td>
</tr>
<tr>
<td>6</td>
<td>1373.15</td>
<td>337.20</td>
</tr>
<tr>
<td>7</td>
<td>1304.89</td>
<td>316.40</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 18. A comparison of the published temperature dependence of emf for the system Ni, NiO - Fe₂O₃, Fe₃O₄ with this work.
at the electrode ($T_2$). Furthermore, the dissociation of water vapor (at 1000°C) creates an oxygen partial pressure of $10^{-5.8}$ atm, which is sufficient to oxidize both the Cu, Cu$_2$O electrode ($P_{O_2}^{eq} = 10^{-6.29}$ atm) and the Ni, NiO electrode ($P_{O_2}^{eq} = 10^{-10.35}$ atm) while leaving the Fe$_2$O$_3$, Fe$_3$O$_4$ electrode unaffected. However, since both electrodes are coexistence electrodes (a two phase mixture of either a metal and its oxide on two oxides) the presence of the water vapor should cause dynamic effects, but not disturb the equilibrium of oxygen over the electrodes, provided that sufficient amounts of each phase are present in the electrode. The complete answer to this phenomena is still unresolved.
Table 4. Thermodynamic Data.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Investigator</th>
<th>Temperature Range, °K</th>
<th>Cell Potential $E^\circ + RT \ln (a)$ (mV)</th>
<th>Standard Error of Estimate (mV)</th>
<th>Data Correlation Coefficient</th>
<th>Standard Free Energy Change ($\Delta G^\circ$) (Cal)</th>
<th>Estimated Accuracy (Cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2 \text{(g)} + \text{Cu}_2 \text{O} \text{(s)} = \text{NiO(s)} + 2 \text{Cu(s)}$</td>
<td>This Work (Cell #4 Degassed)</td>
<td>942-1285</td>
<td>343.8224, -0.0575165</td>
<td>0.16850</td>
<td>0.99965</td>
<td>-15,057.7767</td>
<td>3.113997</td>
</tr>
<tr>
<td>$\text{Ni} \text{(s)} + 3 \text{Fe}_2 \text{O}_3 \text{(s)} = 2 \text{Fe}_3 \text{O}_4 \text{(s)} + \text{NiO} \text{(s)}$</td>
<td>Charette and Flengas</td>
<td>929-1328</td>
<td>346.68, -0.07046</td>
<td>0.19</td>
<td>---</td>
<td>-15,089</td>
<td>3.149</td>
</tr>
<tr>
<td>$\text{Ni} \text{(s)} + 3 \text{Fe}_2 \text{O}_3 \text{(s)} = 2 \text{Fe}_3 \text{O}_4 \text{(s)} + \text{NiO} \text{(s)}$</td>
<td>This Work (Cell #5 Degassed)</td>
<td>984-1373</td>
<td>-78.9457, 0.3027502</td>
<td>0.61474</td>
<td>0.99981</td>
<td>3,641.1797</td>
<td>-13,9634</td>
</tr>
<tr>
<td>$\text{Ni} \text{(s)} + 3 \text{Fe}_2 \text{O}_3 \text{(s)} = 2 \text{Fe}_3 \text{O}_4 \text{(s)} + \text{NiO} \text{(s)}$</td>
<td>Charette and Flengas</td>
<td>967-1373</td>
<td>-69.445, 0.29425</td>
<td>1.00</td>
<td>---</td>
<td>3,203</td>
<td>-12,571</td>
</tr>
</tbody>
</table>
VIII. SUMMARY AND RECOMMENDATIONS

Galvanic cells incorporating a solid electrolyte (CSZ) and based on the closed cell design of Charette and Flengas have been examined to determine potential error sources and design criteria.

Several refinements and improvements in galvanic cell design were made. In particular, the temperature recording thermocouple was placed inside the cell so the actual reaction temperature could be measured; glass stop cocks were designed into the Pyrex half-cell covers to facilitate measurement of residual vacuum and analysis of residual gas if desired; tapered joints were used to facilitate sealing of the half-cell compartments; and the generation of extraneous thermal emfs was eliminated by using black wax to seal all electrode and thermocouple wires passing through the Pyrex covers.

A comparison of the published data from several investigations using open-cell designs with that resulting from this study indicates a contradiction to the usual explanation for cell emf variability. Any short-circuiting of the electrolyte by oxygen transport from the high pressure side, cathode, to the low pressure side, anode, would result in a lowering of the cell emf. One would, therefore, expect the data obtained from the open cell method to be lower than that generated using the closed cell method. The published data indicates the opposite. A possible explanation for this deviation from the theory was presented based on data obtained in this study in which it was shown that a small amount of water contamination results in high cell emfs.

Based on the problems experienced and data generated during this study, the following recommendations are made for the use of solid
electrolyte electrochemical cells in the determination of thermodynamic properties:

1. The closed cell design developed by Charette and Flengas and improved upon in this study can be successfully used to generate accurate data only if precautions are taken to assume that coexistence electrodes consisting of high purity materials (metals and metal oxides) are free of any and all retained moisture or other sources of secondary reactions.

2. The modifications in cell structure used on this study are recommended in order to facilitate ease of construction since they are simple, inexpensive, and enable visual observance of some problems which may develop, e.g., formation of condensate.

3. The cell apparatus, furnace and vacuum system should be connected in series so that the cell can be heated to its highest operating temperature while being evacuated. This would assure the removal of all volatile contaminates and significantly reduce the time required to prepare the cell for operation.
ACKNOWLEDGEMENTS

The author would like to thank Professor Lee F. Donaghey for the help, inspiration and guidance he provided throughout the duration of this study.

The constructive criticism and recommendations given by Professors Robert A. Pask and Charles W. Tobias in writing the thesis is also gratefully acknowledged.

The author would like to express a special kind of thanks to Dane Anderberg and Paul Hendrickson of the LRL Glass Shop for their help and suggestions in cell design and construction and for their friendship.

Thanks also go to Shirley Ashley, Alice Ramirez and Jean Wolslegel for their patience in typing the manuscript and to Nancy Monroe for drafting the numerous figures. Finally, the author would like to thank his wife for her patience and love throughout this study and for sustaining him in all his endeavors ever since that lucky day, August 24, 1968.

This work was done under the auspices of the U. S. Atomic Energy Commission.
REFERENCES

46. R. W. Cooper, quoted by F. A. Kröger, ref. [39].
68. F. Haber and A. Moser, Z. Elektrochem., 11, 593-609, 1905.
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.