A COMPARISON OF REFERENCE ELECTRODES IN
MOLTEN SODIUM SULFATE

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ABSTRACT

Four commonly used electrodes in molten sulfate melts have been combined to form six interrelatable galvanic cells. The dependencies of cell emf on sodium oxide activity and oxygen activity of a pure Na₂SO₄ melt at 1200K have been studied and interpreted. Only a platinum wire immersed in the melt provided behavior inconsistent with a simple interpretation, in this case, an equilibrium of molecular oxygen and oxide ions in the melt. An interference of superoxide and peroxide ions, and the formation of corrosion products on the platinum electrode, are suggested as the cause of the inconsistent electrode behavior.

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Introduction

The study of the effect of molten sodium sulfate on the hot corrosion of superalloys makes extensive use of electrochemical measurements. Previously several reference-and indicator-electrodes have been used, but apparently no systematic study of the electrodes has been published.

The electrodes examined in this study are (1) the Ag/Ag^+ electrode, (2) the ZrO_2/oxygen electrode, (3) the SO_2/O_2 gas electrode, and (4) bare Pt wire and/or foil electrodes in the melt (in some instances Pt was substituted by Au). These four electrodes combine to give six different electrochemical cells.

Experiment

The basic experimental setup is shown in Fig. 1. The molten Na_2SO_4 was contained in an alumina crucible inside a 15cm OD mullite tube in a vertical electric furnace. The mullite tube had a water-cooled brass flange sealed by epoxy. Brass O-ring couplings were sealed to the flange, and the electrodes were inserted into the melt through these couplings. Also gas inlet and outlet tubes were passed through the brass flange. The electrodes were positioned so that they were inside the alumina crucible and immersed in the Na_2SO_4 when the cell was brought to temperature (1200K). The Na_2SO_4 was dried for several days at 200°C prior to use, and was added to the Al_2O_3 crucible through a quartz or Al_2O_3 addition tube that was inserted through a coupling in the brass flange.

The construction of the electrodes is shown in Fig. 2. Figure 2a shows the Ag/Ag^+ electrode which consisted of a mullite tube (McDaniel MV30) containing a solution of 10% Ag_2SO_4, 90% Na_2SO_4. Into this solution was immersed a 1 mm silver wire spot-welded to a platinum wire that served as the lead wire. Rahmel reported that evacuation of the tube is not necessary. However, to minimize drift which would be caused by loss of SO_3 from decomposition exchange.

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of the salt, the tube was sealed with a piece of Tygon tubing and a pinch clamp. The ease of fabrication and stability of this electrode, make it well suited for use with molten sodium sulfate. One negative aspect of this electrode is evidence for transport of Ag through the mullite tube. The part of the tube that contained the Ag$_2$SO$_4$/Na$_2$SO$_4$ mixture became dark in color, and silver could be detected in the Na$_2$SO$_4$ in the crucible. Transport of silver through a Na ion conductor has been reported previously at lower temperatures with Pyrex$^7$ and at high temperatures with mullite$^9$.

The ZrO$_2$ oxygen electrode, shown in Fig. 2b was prepared by platinizing the inside of the ZrO$_2$ tube at the bottom. The reference gas on the inside of the tube was air. Electrical contact with the platinized area is obtained by placing a Pt/Pt$\cdot$10Rh thermocouple in an alumina protection tube and spring loading it inside the ZrO$_2$ tube to ensure positive electrical contact. The tubes used were either partially stabilized 3.5 w/o CaO or fully stabilized 7.5 w/o Y$_2$O$_3$ zirconia manufactured by Zircoa. They would break easily from thermal shocks, and great care had to be exercised when heating and cooling the tubes.

The SO$_2$/O$_2$ gas electrode is basically the same as used by Stroud and Rapp$^1$, and is shown schematically in Fig. 2c. A small amount of Na$_2$SO$_4$ was placed in a mullite tube (McDaniel MV30). An equilibrated mixture of SO$_3$, SO$_2$ and O$_2$ was passed over the salt, and a 20 mil Pt wire was inserted into the Na$_2$SO$_4$ as an electrode. The SO$_2$/O$_2$ gas preliminarily passed over a catalyst of platinized ceramic material so that by fixing the P$_{SO_3}$ in the gas phase, the basicity of the Na$_2$SO$_4$ was fixed and the electrode should maintain a fixed potential.

The gas used in the electrode was SO$_2$ (Matheson) containing 1 ppm O$_2$. This small amount of O$_2$ made the electrode potential very sensitive to small
changes in flow rate, indicating that it was difficult to establish the $SO_3/\text{SO}_2/O_2$ equilibrium. Several arrangements were tried in order to ensure establishment of equilibrium within the gas phase. The arrangement used for most of the experiments was that shown in Fig. 2c. Some of the platinized material was crushed into small particles and filled into the gas inlet tube of the electrode. This should have ensured better gas/catalyst contact, but the flow rate dependence still persisted.

Figures 3a and 3b show how the Pt (and Au) electrodes were arranged for large amounts of melt (a) and for small amounts and thin films of sodium sulfate (b). When large amounts of salt were used, one electrode was completely submerged in the melt while the other was about half submerged and half extending out of the melt.

The sodium sulfate electrolyte decomposes according to the reaction

$$Na_2SO_4 = Na_2O + SO_3$$

and the basicity of the melt can therefore be fixed by fixing the $P_{SO_3}$ in the gas phase over the melt.

The gas compositions used and the corresponding basicities (activity of $Na_2O$) in the melt are shown in Table I. To extend further the range of $\alpha_{Na_2O}$, $Na_2O_2$ was added to the melt when pure oxygen was used as the gas; some additions of $Na_2S_2O_7$ were made to reduce the oxide activity. $Na_2O_2$ was used rather than $Na_2O$ because of the hygroscopic nature of $Na_2O$. The thermal decomposition was assumed to be rapid, so that the $Na_2O_2$ addition actually became $Na_2O$.

The solid materials dipping into the salt have a finite solubility in the salt. The molten salt will consequently not be completely pure and it is impossible to control accurately the composition of the melt.

**Electrochemical cells and proposed cell reactions**

The four electrodes can be combined into six different cells. These cells and their proposed
Nernst equations are:

**Cell A** The cell arrangement is

\[
\begin{array}{c|c|c|c|c|c}
O_2(r) & ZrO_2 & Na_2SO_4' & (Na_2O') & Mullite & 10m/o Ag_2SO_4'' \\
(-) Pt & (O_2^-) & SO_2O_2' & (Na^+) & Na_2SO_4'' & Ag (+)
\end{array}
\]

and the proposed reactions are:

\[
\begin{align*}
O_2^- (ZrO_2) &= \frac{1}{2} O_2(r) + 2 e^- \quad \text{(anode/ZrO}_2) \\
O_2'^- &= O_2^- (ZrO_2) \quad \text{(ZrO}_2'/\text{solution)} \\
Na_2O' &= O_2'^- + 2Na^+ \\
2 Na^+ &= 2 Na^+ \quad \text{(mullite)} \quad \text{('solution/mullite)} \\
2 Na^+ (mullite) &= 2 Na^+'' \quad \text{(mullite/'solution)} \\
2 Na^+'' + Ag_2SO_4'' + 2 e^- &= Na_2SO_4'' + 2 Ag \quad \text{(cathode)} \\
Na_2O' + Ag_2SO_4'' &= \frac{1}{2} O_2(r) + Na_2SO_4'' + 2 Ag \quad \text{(A-1)}
\end{align*}
\]

From the overall reaction involving two electrons one obtains:

\[
E_A = E_A^0 - \frac{2.3RT}{2F} \log \frac{a_{Na_2SO_4''}}{a_{Na_2O'} a_{Ag_2SO_4''}}
\]

(A-2)

since \( a_{Ag} = 1 \) for pure Ag. Upon combining the activities of the salt in the Ag/Ag+ electrode and the \( P_{O_2}(r) \) term we obtain

\[
E_A = E_A^0' + \frac{2.3RT}{2F} \log a_{Na_2O'}
\]

(A-3)

where

\[
E_A^0' = E_A^0 - \frac{2.3RT}{2F} \log \frac{a_{Na_2SO_4''}}{a_{Ag_2SO_4''}} - \frac{2.3RT}{4F} \log P_{O_2}(r)
\]

(A-4)

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and $E^\circ_A$ can be calculated from

$$E^\circ_A = \frac{1}{2F} \left[ \Delta G^\circ_f (\text{Na}_2\text{SO}_4) - \Delta G^\circ_f (\text{Na}_2\text{O}) - \Delta G^\circ_f (\text{Ag}_2\text{SO}_4) \right]$$  \hspace{1cm} (A-5)

if the thermodynamic data are known. Table II gives the thermodynamic data that are appropriate for these calculations. Most of the data is obtained from JANAF, but $\Delta G^\circ_f (\text{Ag}_2\text{SO}_4)$ is not available at 1200K. Extrapolation of low temperature data gives for $\Delta G^\circ_f (\text{Ag}_2\text{SO}_4)$ at 1200 K the value 78,736 cal/mol (-328.4kJ/mol) in reasonable agreement with the data reported for cell E. The thermodynamic data indicate that $E^\circ_A = 1.63$ volts and $E^\circ_A' = 1.56$ volts. $E^\circ_A'$ is calculated assuming the 10 m/o Ag$_2$SO$_4$/Na$_2$SO$_4$ mixture is an ideal solution.

**Cell B** The cell arrangement is

(-) $\text{O}_2(r)$, Pt $\parallel \text{ZrO}_2 (\text{O}^{2-}) \parallel \text{Na}_2\text{SO}_4'$, $\text{O}^{2-}$, Pt (+)

and the electrode reactions and equilibria are

$$\text{O}^{2-}(\text{ZrO}_2) = 2 \text{ e}^- + 1/2 \text{ O}_2(r) \quad \text{(anode/ZrO}_2)$$

$$\text{O}^{2-}' = \text{O}^{2-}(\text{ZrO}_2) \quad \text{(ZrO}_2/'\text{solution})$$

$$1/2 \text{ O}_2' + 2 \text{ e}^- = \text{O}^{2-}' \quad \text{(cathode/solution)}$$

$$1/2 \text{ O}_2' = 1/2 \text{ O}_2(r) \quad \text{(B-1)}$$

and

$$E_B = \frac{-2.3RT}{4F} \log P_{O_2}(r) + \frac{2.3RT}{4F} \log P_{O_2'}$$  \hspace{1cm} (B-2)

For $P_{O_2}(r) = 0.21$ atm at 1200K

$$E_B = 0.040 + 0.0595 \log P_{O_2'} \quad \text{(B-3)}$$
Cell C This cell combines the gas electrode and ZrO₂ electrode

\[ (-) \text{SO}_2^{m}, O_2^{m}, \text{Pt, Mullite} \mid \text{Na}_2\text{SO}_4^{i} | \text{ZrO}_2 | \text{Pt, O}_2(\text{r})(+) \]

\[ \text{Na}_2\text{SO}_4^{i} \]

\[ 2\text{Na}^{+} + \text{SO}_2^{m} = 2\text{Na}^{+} + \text{Na}_2\text{SO}_4^{m} + 2e^- \quad \text{(anode)} \]

\[ 2\text{Na}^{+} (\text{mullite}) = 2 \text{Na}^{+} \quad \text{('solution/mullite)} \]

\[ 2 \text{Na}^{+} (\text{mullite}) = 2 \text{Na}^{+} \quad \text{(mullite/solution)} \]

\[ 2 \text{Na}^{+} + \text{O}_2^{m} = 2 \text{Na}_2\text{O}^{m} \quad \text{('solution)} \]

\[ \text{O}_2^{m}(\text{ZrO}_2) = \text{O}_2^{m} \quad \text{('solution/ZrO}_2) \]

\[ 1/2 \text{O}_2(\text{r}) + 2e^- = \text{O}_2^{m}(\text{ZrO}_2) \quad \text{(ZrO}_2/\text{cathode)} \]

\[ 2\text{Na}_2\text{SO}_4^{m} + 1/2 \text{O}_2(\text{r}) = \text{Na}_2\text{SO}_4^{m} + \text{Na}_2\text{O}^{m} \tag{C-1} \]

for which the Nernst equation is

\[ E_C = E_C^o - \frac{2.3RT}{2F} \log \frac{a_{\text{Na}_2\text{SO}_4^{m}} a_{\text{Na}_2\text{O}^{m}}}{a_{\text{Na}_2\text{O}^{m}} a_{\text{SO}_2^{m}}^{1/2}} \tag{C-2} \]

Upon rearranging (C-2) one obtains

\[ E_C = \left( E_C^o + \frac{2.3RT}{2F} \log \left( \frac{a_{\text{Na}_2\text{O}^{m}} a_{\text{SO}_2^{m}}^{1/2}(\text{r})}{a_{\text{Na}_2\text{O}^{m}} a_{\text{SO}_2^{m}}^{1/2}(\text{r})} \right) \right) - \frac{2.3RT}{2F} \log a_{\text{Na}_2\text{O}^{m}} \tag{C-3} \]

with \( a_{\text{Na}_2\text{SO}_4^{m}} = 1 \), where

\[ E_C^o = -\frac{1}{2F} \left[ \Delta G_F^{o} (\text{Na}_2\text{SO}_4) - \Delta G_F^{o} (\text{Na}_2\text{O}) - \Delta G_F^{o} (\text{SO}_2) \right] \tag{C-4} \]

From the thermodynamic data of Table II, \( E_C^o = 1.91 \) volts. The second term in Eq. (C-3) depends on the composition of the gas in equilibrium with the molten \( \text{Na}_2\text{SO}_4 \).
Cell D combines the Ag/Ag⁺ electrode and the Pt electrode in the melt.

\[ \begin{array}{c|c|c}
\text{O}_2^{'}, \text{SO}_4^{'}, \text{Pt} & \text{mullite} & \\
\text{(-)Na}_2\text{SO}_4 & \text{Na}^+ & 10\% \text{Ag}_2\text{SO}_4^{^{''}}, \text{Na}_2\text{SO}_4^{^{''}}, \text{Ag (++)} \\
\end{array} \]

0\textsuperscript{2-}' = 2e\textsuperscript{-} + 1/2 O\textsubscript{2}'

\( \text{Na}_2\text{O}' = 2 \text{Na}^{+} + o\textsuperscript{2-}' \) (solution)

2 Na\textsuperscript{+} = 2 Na\textsuperscript{+} (mullite)

2Na\textsuperscript{+} (mullite) = 2 Na\textsuperscript{+}'

2Na\textsuperscript{+}' + Ag\textsubscript{2}SO\textsubscript{4}' + 2e\textsuperscript{-} = 2 Ag + Na\textsubscript{2}SO\textsubscript{4}'

(\text{cathode})

\( \text{Na}_2\text{O}' + \text{Ag}_2\text{SO}_4^{^{''}} = 1/2 \text{O}_2' + 2 \text{Ag} + \text{Na}_2\text{SO}_4' \) (D-1)

And the resultant equation for the above equilibrium reaction is

\[ E_D = E_D^\circ - \frac{2.3RT}{2F} \log \frac{a_{Na^2SO_4^{^{''}}}}{a_{Na_2O'}a_{Ag_2SO_4^{^{''}}}} \] (D-2)

where \( a_{Ag_{2}} = 1 \). Upon rearranging

\[ E_D = \left\{ E_D^\circ - \frac{2.3RT}{2F} \log \frac{a_{Na^2SO_4^{^{''}}}}{a_{Ag_2SO_4^{^{''}}}} \right\} + \frac{2.3RT}{2F} \log \frac{a_{Na_2O'}}{a_{Ag_2SO_4^{^{''}}}} \] (D-3)

and

\[ E_D^\circ = \frac{1}{2F} \left[ \Delta G_F^\circ(\text{Na}_2\text{SO}_4') - \Delta G_F^\circ(\text{Na}_2\text{O}) - \Delta G_F^\circ(\text{Ag}_2\text{SO}_4') \right] \] (D-4)

When the thermodynamic data given in Table II are employed, \( E_D^\circ = 1.63 \) volts, and if the solution of 10 m/o \( \text{Ag}_2\text{SO}_4 \) and 90 m/o \( \text{Na}_2\text{SO}_4 \) is an ideal solution then the second term of Eq. (D-3) is 0.114 volts at 1200K and the term

\[ E_D^\circ - \frac{2.3RT}{2F} \log \frac{a_{Na^2SO_4^{^{''}}}}{a_{Ag_2SO_4^{^{''}}}} = 1.52 \] volts.
Cell E  Cell E is an important cell because it should be independent of the gas and salt compositions of the test melt. The cell is a combination of the gas electrode and the Ag/Ag⁺ electrode:

\[
\begin{align*}
\text{(-) } & \text{SO}_2^{II}, \text{O}_2^{I}, \text{Pt} & \text{Mullite} & \text{Na}_2\text{SO}_4^{II}, \text{O}_2^{I}, \text{SO}_2^{II} & \text{Mullite} & \text{Ag}_2\text{SO}_4^{II}, \text{Ag} \\
\text{(Na⁺)} & \text{(Na⁺)} & \text{(Na₂O')} & \text{Na}_2\text{SO}_4^{II} & \text{(Na⁺)} & \text{Na}_2\text{SO}_4^{II} \quad (+)
\end{align*}
\]

\[
\begin{align*}
2 \text{Na}_2\text{O}^{III} + \text{SO}_2^{II} & = 2 \text{Na}^+^{III} + \text{Na}_2\text{SO}_4^{II} + 2e^- \quad \text{(anode)} \\
2 \text{Na}^{IV} = 2 \text{Na}^+^{III} & \quad (\text{solution/mullite}) \\
2 \text{Na}^+^{IV} (\text{mullite}) = 2 \text{Na}^+ & \quad (\text{mullite}/\text{solution}) \\
2 \text{Na}^+^{IV} = 2 \text{Na}^+^{III} & \quad (\text{solution/mullite}) \\
2 \text{Na}^+^{III} (\text{mullite}) = 2 \text{Na}^+^{IV} & \quad (\text{mullite}/\text{solution}) \\
2 \text{Na}^{IV}^{IV} + \text{Ag}_2\text{SO}_4^{II} + 2e^- & = \text{Na}_2\text{SO}_4 + 2 \text{Ag} \quad \text{(cathode)} \\
2\text{Na}_2\text{O}^{III} + \text{SO}_2^{II} + \text{Ag}_2\text{SO}_4^{II} & = \text{Na}_2\text{SO}_4^{II} + 2 \text{Ag} + \text{Na}_2\text{SO}_4^{II} \quad (E-1)
\end{align*}
\]

\[
E_E = E^\circ_E - \frac{2.3RT}{2F} \log \left( \frac{a_{\text{Na}_2\text{SO}_4^{II}} a_{\text{Na}_2\text{SO}_4^{II}}}{a_{\text{Ag}_2\text{SO}_4^{II}} a_{\text{Na}_2\text{O}'} a_{\text{SO}_2^{II}}} \right) \quad (E-2)
\]

where

\[
E^\circ_E = -\frac{1}{2F} \left[ \Delta G^\circ_f (\text{Na}_2\text{SO}_4) - \Delta G^\circ_f (\text{Na}_2\text{O}) - \Delta G^\circ_f (\text{SO}_2) \right] - \frac{1}{2F} \left[ \Delta G^\circ_f (\text{Na}_2\text{SO}_4) - \Delta G^\circ_f (\text{Na}_2\text{O}) - \Delta G^\circ_f (\text{Ag}_2\text{SO}_4) \right] \quad (E-3)
\]

The first term in Eq. (E-3) is equivalent to \( E_C^\circ \) and the second term is equivalent to either \( E_A^\circ \) or \( E_D^\circ \). Thus

\[
E^\circ_E = E_C^\circ + E_A^\circ \quad (E-4)
\]

Based on the given thermodynamic data, \( E_C^\circ = 3.54 \) volts. If the \( \text{Ag}_2\text{SO}_4/\text{Na}_2\text{SO}_4 \) is ideal, then \( a_{\text{Na}_2\text{SO}_4^{II}} / a_{\text{Ag}_2\text{SO}_4^{II}} \) remains constant and Eq. (E-2) can be written as
\[ E_E = \left\{ E^\circ_E - \frac{2.3RT}{2F} \log \frac{a_{\text{Na}_2\text{SO}_4}}{a_{\text{Ag}_2\text{SO}_4}} \right\} + \frac{2.3RT}{2F} \log \left( \frac{a_{\text{Na}_2\text{O}^+}^2 \text{P}_{\text{SO}_2}}{p_{\text{O}_2}} \right) \] (E-5)

where the first term is constant and the second will vary if the flow rate in the gas electrode varies. If the silver sulfate/sodium sulfate solution is ideal, the constant term becomes 3.43 volts.

Cell F Cell F is equivalent to the cell used by Stroud and Rapp:\textsuperscript{14}

\[
\begin{array}{cccc}
\text{SO}_2^{\text{III}}, \text{O}_2^{\text{III}} & \text{Mullite} & \text{Na}_2\text{SO}_4^{\text{IV}}, \text{(Na}_2\text{O)} & \text{Pt} (+) \\
\text{Na}_2\text{SO}_4^{\text{IV}} & \text{(Na}^+) & \text{O}_2', \text{SO}_2' & \text{Pt} (+)
\end{array}
\]

The equilibrium reactions are

\[
2 \text{Na}_2\text{O}^{\text{IV}} + \text{SO}_2^{\text{III}} = \text{Na}_2\text{SO}_4^{\text{IV}} + 2 \text{Na}^{+\text{III}} + 2\text{e}^-
\] (anode)

\[
2 \text{Na}^{+\text{III}} = 2 \text{Na}^+ \text{ (mullite)}
\]

\[
2 \text{Na}^+ \text{ (mullite)} = 2 \text{Na}^+
\]

\[
2 \text{Na}^+ + \text{O}_2^- = \text{Na}_2\text{O}^-
\]

1/2 \text{O}_2 = \text{Na}_2\text{O}^-

2 \text{Na}_2\text{O}^{\text{IV}} + \text{SO}_2^{\text{III}} + 1/2 \text{O}_2 = \text{Na}_2\text{SO}_4^{\text{IV}} + \text{Na}_2\text{O}^-

(F-1)

\[
E_F = E_F^\circ - \frac{2.3RT}{2F} \log \frac{a_{\text{Na}_2\text{SO}_4}}{a_{\text{Na}_2\text{O}^+}^2} \frac{a_{\text{Na}_2\text{O}^-}}{a_{\text{Na}_2\text{O}^+}^2 \text{P}_{\text{SO}_2}^{1/2}}
\] (F-2)

and upon rearranging

\[
E_F = \left\{ E_F^\circ + \frac{2.3RT}{2F} \log \frac{a_{\text{Na}_2\text{O}^+}^2 \text{P}_{\text{SO}_2}}{a_{\text{Na}_2\text{O}^+}^2 \text{P}_{\text{SO}_2}^{1/2}} \right\} - \frac{2.3RT}{2F} \log \frac{a_{\text{Na}_2\text{O}^-}}{p_{\text{O}_2}^{1/2}}
\] (F-3)

where \(a_{\text{Na}_2\text{SO}_4} = 1\) and
\[ E_F^o = - \frac{1}{2F} \left[ \Delta G_f^o(Na_2SO_4) - \Delta G_f^o(Na_2O) - \Delta G_f^o(SO_2) \right] \]  

(F-4)

which is the same as \( E_C^o \).

Since the reactions in Cells A through F are all consistent, the emfs of the cells are related and can be used to check the internal consistency of the measurements. Some of the relationships are

\[ E_A - E_B = E_D \]  
(1)

\[ E_F - E_C = E_B \]  
(2)

\[ E_A + E_C = E_E \]  
(3)

\[ E_D + E_F = E_E \]  
(4)

In all cases that have been checked these relationships were always satisfied to within 2 - 3 mV, which is well within the accuracy of measurement. No matter what electrode reactions are postulated, so long as they are consistent for all cells, the above relationships are valid and will be obeyed. Of course, satisfying the above interrelationships in no way confirms the validity of the proposed chemical and electrochemical equilibria.

Results

Open-circuit potential measurements (OCM) were made using either an Esterline-Angus recorder or a digital voltmeter (Data Precision), each of which have input impedances of 10 megohms. Figures 4 - 8 show how the emf of the various cells changed with time as the gas phase over the molten Na_2SO_4 was changed. The gas compositions utilized are listed in Table I. Figures 9-11 show the effect of additions of Na_2O_2 and Na_2S_2O_7 to the melt when the gas phase was maintained as pure O_2 or Ar (which also contained 20 ppm O_2).

Examination of the cell emfs for gases D ("pure" Ar) and E (Ar with 100 ppm SO_2) indicate that these gases were very similar in their effect. Gas B (SO_2)
caused a large sudden change in emf for cells A, B and C while cells D and F exhibited very little change. This result occurs because cells D and F should respond to changes in both $a_{\text{Na}_2\text{O}}$ and $P_{\text{O}_2}$, while cells A, B and C respond to only one of these parameters. Frequently a fairly large change occurred when the gas flow was first started, with a slow increase or decrease from that extreme value. This response indicates that reactions were taking place that slowly changed the $a_{\text{Na}_2\text{O}}$ in the salt. Figure 5 shows that changes in $P_{\text{O}_2}$ in the gas phase caused rapid response for cell B. Because of the low solubility of $\text{O}_2$ in $\text{Na}_2\text{SO}_4$, the rapid equilibration of the Pt electrode contacting the melt does not, however, infer that the bulk melt is so rapidly equilibrated with the gas.

With pure $\text{O}_2$, cell B should have had an emf of 0.040 V, and with gas G, 0.033 V. The steady-state values for cell B for these gases differed from the ideally expected values, and repeated measurements of these gases did not give repeatable results. The emf of cell B remained constant after reaching a steady-state value, while cells D and F continued to change over a longer period of time. This indicates that reactions were occurring at the Pt electrode in the melt which involved $\text{Na}_2\text{O}$ or $\text{SO}_3$ rather than $\text{O}_2$.

When the gas phase was fixed (gas D or F) and additions of $\text{Na}_2\text{O}_2$ and $\text{Na}_2\text{S}_2\text{O}_7$ were made, the cells responded rapidly, followed by a slower variation with time. Again, this indicates a consumption of the addition, probably by corrosion of some ceramic components in the melt.

In Fig. 12, measured values of $E_F$ obtained during the addition of $\text{Na}_2\text{O}_2$ and $\text{Na}_2\text{S}_2\text{O}_7$ to the melt are plotted as a function of the mol fraction of $\text{Na}_2\text{O}$ in the melt after the additions. The addition of $\text{Na}_2\text{S}_2\text{O}_7$ is considered to consume $\text{Na}_2\text{O}$ in accordance with the reaction

$$\text{Na}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_7 = 2 \text{Na}_2\text{SO}_4$$

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and the amount of Na$_2$O consumed was thus calculated to get the value of N$_{Na_2O}$ resulting from the addition of the pyrosulfate. Complete consumption of the added Na$_2$S$_2$O$_7$ was assumed. Additions 1, 2 and 3 were of Na$_2$O$_2$ while 4, 5, 6, 7 and 8 were Na$_2$S$_2$O$_7$. A line of expected slope is drawn through the data points and the fit is reasonable for the data points 1 to 5; however, points 6 to 8 deviate sharply from the expected slope. The E$_F$ values correspond to the steady-state values shown on Figure 11.

Discussion

As already mentioned, the behavior of cell B in Fig. 9 did not correspond reasonably to known (or possible) values for P$_{O_2}$ according to Eq. (B-3). After the initial addition of Na$_2$O$_2$, the indicated P$_{O_2}$ reached a value of several atmospheres, and after addition #2, the cell indicated a steady-state of about 3.8 atm. The interpretation of cell B as discussed in Eqs. (B-1) to (B-3) must be questioned, at least when the melt basicity is high. Similar problems were experienced when attempts were made to measure P$_{O_2}$ of gas A.

To avoid this difficulty and be able to check the validity of other proposed cell reactions, the following interpretation is offered. We assume that the manufacturer's analysis of gas G is correct, and that therefore P$_{O_2}$ equals 0.76 atm for this gas. Further, we assume that equilibrium is established in the gas phase between SO$_2$, SO$_3$ and O$_2$, and at the Pt electrode between the gas phase and the salt. The sodium oxide activity of the salt can then be calculated to give $\log a_{Na_2O} = -12.93$ for gas G. Next, we assume that the proposed equation for E$_F$ is correct, and we can then calculate E$_F^O$, i.e., the bracketed part of Eq. (F-3).
The result of this calculation gives for the emf of cell F:

\[ E_F = -1.22 -0.119 \log \frac{a_{Na_2O}}{P_{O_2}^{1/2}} \]

The emf of cell E (with gas G) is then used to calculate the term

\[ E_A^{''} = E_A - 0.119 \log \frac{a_{Na_2SO_4''}}{a_{Ag_2SO_4''}} \]

Because the relationship

\[ E_E = E_F^{''} + E_A^{''} \]

is valid, we get the result

\[ E_A = 1.46 + 0.119 \log a_{Na_2O} \]

Then \( E_D \) and \( E_C \) can be calculated

\[ E_D = 1.42 + 0.119 \log \frac{a_{Na_2O}}{P_{O_2}^{1/2}} \]

\[ E_C = -1.26 - 0.119 \log a_{Na_2O} \]

Then \( E_F^{''} \) can be used to calculate the basicity \( a_{Na_2O}^{''''} \) of the salt inside the mullite tube, which, when assuming \( P_{SO_2}^{'''} = 1 \), amounts to \( \log a_{Na_2O}^{''''} = -13.15 \), \( \log P_{SO_3}^{'''} = -3.48 \) and \( \log P_{O_2}^{''''} = -5.80 \). Finally, the measured emfs for cells F and B are used to calculate \( \log \frac{a'_{Na_2O}}{P_{O_2}^{1/2}} \)
and \( \frac{1}{2} \log P_{O_2} \). The results of these calculations are shown in Figs. 13-15. The data points fall very close to lines with slope equal to that predicted by the Nernst equations given previously. In fact Figs. 13-15 are demonstrations of the internal consistency of the measurements.

There can be several reasons for the discrepancy between some measured and expected emfs - especially those mentioned for cell B which indicated unreasonably high oxygen pressures. As shown in Fig. 3a, two platinum electrodes were used when working with deep melts. The emf between the two Pt foils should be zero when the salt was equilibrated with the gas phase. This was not the case, however. Even after long times (more than a week), a 10mv difference existed between the electrodes. The foil that was partially immersed in the melt was attacked by the sulfate. Gold is relatively inert to molten sodium sulfate, and the platinum foils and lower parts of the lead wires were substituted with gold foils and wires. The results of these measurements are shown in Table III. Although the two gold foils reached the same potential (in the course of 5-6 days), they failed to indicate correctly the oxygen pressure. For example, the emf given for cell B and gas F in Table III, corresponds to a \( P_{O_2} = 2.7 \) atm, which is quite unrealistic.

A possible explanation consistent with this discrepancy is the formation of higher oxides such as peroxide and the superoxide ions in the melt. These oxides have been reported by several investigators\(^{15,16}\) and are especially stable for basic melts under high oxygen pressures. For cell B, then

\[
E_B = - \frac{2.3RT}{4F} \log P_{O_2} (r) + \frac{2.3RT}{4F} \log P_{O_2} (melt)
\]

Since superoxide is the predominant species\(^{10}\) compared to the peroxide

\[
Na_2O + \frac{3}{2} O_2 = 2 NaO_2 \quad \log K = 2.21
\]

and \( P_{O_2} (r) = 0.21 \) (air), we get

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\[ E_B = 0.128 + 0.0397 \log \frac{a^{2}_{\text{Na}_2\text{O}}}{a_{\text{Na}_2\text{O}}} \]

\[ \log a_{\text{Na}_2\text{O}} \] can be calculated from cell A and \[ \log a_{\text{Na}_2\text{O}} \] from the above equation. The results for gases F and G are shown in Fig. 16. The line drawn through the points has a slope of 0.59, while it should have 0.50 according to the equation above. This calculation only takes into consideration the superoxide and ignores the peroxide, and the agreement is therefore considered satisfactory. In effect, this explanation suggests that in basic melts, especially at high \[ P_{\text{O}_2} \], an immersed Pt electrode may respond to a redox potential involving the superoxide and peroxide instead of the dissolved molecular oxygen content. In such melts, a Pt\text{O}_2 film is also observed to form.

There are undoubtedly several possible reactions contributing to the electrode potential of a base Pt metal electrode in \( \text{Na}_2\text{S}_4\text{O}_4 \).

Conclusion

The most common electrodes used in molten sulfate research have been investigated and compared and the Nernst equations for the possible electrochemical cells formulated. All of the emfs exhibited the dependences on sodium oxide activity and oxygen as proposed, except the cell B consisting of the zirconia electrode and the platinum electrode. This behavior is rationalized in terms of corrosion of the platinum and formation of higher oxides in the melt. As the anomaly persists when the Pt electrodes are substituted with gold (which is recommended for subsequent work) the most probable explanation is the formation of oxides of sodium.

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Table I  Gas compositions and corresponding salt basicity.

| Gas  | Manufacturer | Composition | -log $a_{\text{Na}_2\text{O}}$ |
|------|--------------|-------------|-------------------------------|
| A SO₂ | Matheson     | 99.9%       | 14.00                         |
| B SO₂ | Liquid Carbonic | 99.8%       | 13.16                         |
| C SO₂ | Matheson     | 99.9%       | 14.00                         |
| D Ar  |              | 20-50 ppm O₂ |                               |
| E Ar/SO₂ | Matheson     | 100 ppm SO₂ | 11.30                         |
| F O₂  | Cols. Oxygen | 99.6% O₂    |                               |
| G O₂/SO₂/N₂ | Matheson | 76% O₂, 0.1% SO₂ | 12.90 |

Table II  Thermodynamic Data

| Compound       | $\Delta G_f^\circ (1200K)$ (cal/mole) | Source                          |
|----------------|--------------------------------------|--------------------------------|
| Na₂SO₄(l)      | -213,612                             | JANAF¹⁰                         |
| Na₂O (s)       | -59,832                              | "                              |
| Na₂O₂ (s)      | -60,642                              | "                              |
| NaO₂ (s)       | -23,848                              | "                              |
| SO₂ (v)        | -65,495                              | "                              |
| SO₃ (v)        | -62,283                              | "                              |
| Ag₂SO₄(l)      | -78,736                              | extrapolated from data at lower temperature |

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| Gas     | $E_A$ | $E_B$ | $E_C$ | $E_D$ | $E_E$ | $E_F$ |
|---------|-------|-------|-------|-------|-------|-------|
| C $\text{SO}_2$ | 0.155 | -0.326 | 0.152 | 0.481 | 0.306 | -0.174 |
| F $\text{O}_2$  | -0.0034 | 0.066  | 0.117 | -0.100 | 0.083 | 0.184  |
| G $\text{SO}_2, \text{O}_2, \text{N}_2$ | -0.184 | 0.012  | 0.372 | -0.195 | 0.185 | 0.382  |
Fig. 1 Schematic drawing of experimental setup. The ceramic tubes (electrodes) are lowered into the salt after it is molten.
Fig. 2a Schematic drawing of the Ag/Ag⁺ electrode
2b Schematic drawing of the ZrO₂ electrode.
2c Schematic drawing of the SO₂/O₂ gas electrode.
Fig. 3a Arrangement of the platinum electrodes in the melt when a bulk melt was used.

Fig. 3b Arrangement of platinum foil on bottom of crucible when a thin salt film was used.
Fig. 4  Emf of cell A as function of time
the various gases of Table I passed
over a thin Na₂SO₄ film electrolyte.

Fig. 5  Emf of cell B as function of time
for the various gases passed over thin
Na₂SO₄ film electrolyte.
Fig. 6  Emf of cell C as function of time for the various gases passed over thin Na$_2$SO$_4$ film electrolyte.

Fig. 7  Emf of cell D as function of time for the various gases passed over thin Na$_2$SO$_4$ film electrolyte.
Fig. 8  Emf of cell F as function of time for the various gases passed over thin Na\textsubscript{2}SO\textsubscript{4} film electrolyte.

Fig. 9  Emf of cell B as function of time with additions of Na\textsubscript{2}O\textsubscript{2}. Gas phase is maintained as pure O\textsubscript{2} (gas F).
Fig. 10 Emf of cell B as function of time with additions of Na$_2$O$_2$. Gas phase is maintained as Ar (gas D).

Fig. 11 Emf of cell F as function of time with additions of Na$_2$O$_2$ and Na$_2$S$_2$O$_7$. Gas phase is maintained as pure O$_2$ (gas F).
The full drawn line has the slope predicted by Eq. (A-4).

Fig. 13 Emf of cell A as function of log $a_{Na_2O}$. The full drawn line has the slope predicted by Eq. (A-4).
Fig. 14 Emf of cell C as function of log $a_{\text{Na}_2\text{O}}$. The slope of the full drawn line is that predicted by Eq. (C-3).

Fig. 15 Emf of cell D as function of log $a_{\text{Na}_2\text{O}/\text{P}_{\text{O}_2}}$ calculated from emfs measured with cell F. The full drawn line has the slope predicted by Eq. (D-3).
Fig. 16 Log $a_{NaO_2}$ plotted as function of log $a_{Na_2O}$ calculated from $E_A$ for gases F (pure $O_2$) and G (76% $O_2$, 0.1% $SO_2$, bal. $N_2$).