THE STANDARD ELECTRODE POTENTIAL OF THE
  BROMATE - PERBROMATE COUPLE

A Thesis
Presented to
the Department of Chemistry
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of the Requirements for the Degree
Master of Science in Chemistry

by
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Approved for the Graduate Council

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CHAPTER I

INTRODUCTION

Since 1894 there have been several unsuccessful attempts to synthesize perbromates. The strongest oxidizing agents known had been used and it was generally accepted that perbromates could not exist. Some suggested that BrO$_4^-$ was unstable and decomposed upon formation.$^1,2$

Recently, several successful methods for the preparation of BrO$_4^-$ have been reported.$^3,4$ The method used in this research involves the oxidation of an alkaline solution of sodium bromate by molecular fluorine.

There is a question of whether thermodynamic or kinetic effects are responsible for the difficulty in forming BrO$_4^-$. There is also no satisfactory thermodynamic explanation for the apparent failure of oxidants such as peroxydisulfate$^4$ and ozone$^5$ to cause perbromate formation. Determination of the $E^\circ$ value for the BrO$_3^-$/BrO$_4^-$ electrode would help solve the problem of what energy effects are responsible for this difficulty in formation. A large negative $E^\circ$ value would suggest a thermodynamic barrier, whereas, a smaller value would indicate a kinetic barrier.

The research reported here is an attempt to determine the standard electrode potential of the BrO$_3^-$/BrO$_4^-$ couple. The basic procedure proposed by Zeilen$^6$ involves the determination of cell potentials by direct electrode measurements.
A definite $E^0$ value for the $\text{BrO}_3^-/\text{BrO}_4^-$ electrode has not been determined because of the failure of the cell data to completely obey the Debye-Hückel relationship.
Preparation of Perbromate

Sodium perbromate was prepared by the fluorination of a solution that consisted of one part 50% sodium hydroxide and three parts 1.3M sodium bromate. The reaction vessel, which was a 500 ml teflon bottle, was placed in an ice bath and cooled before fluorination commenced.

The fluorination apparatus consisted of a fluorine tank and regulator (Matheson Co.) to which copper tubing was connected. This apparatus was constructed for use in a well ventilated hood. A teflon tip provided an exit for the fluorine gas to be bubbled through the alkaline bromate solution. Nitrogen was used to flush fluorine from the system before handling the reaction vessel.

It was found that high fluorine flow rates produced small fires and explosions at the surface of the solution. A regulated flow of two bubbles per second was found to be satisfactory in that no violent side effects were observed. The system was never left unattended while fluorination was in progress. No additional perbromate was formed after the solution became acidic. This usually occurred after five to six hours of fluorination.

The acidic solution was placed in a teflon-lined container and concentrated on a hot plate and then was cooled. The chilled solution was centrifuged and the liquid was decanted from the solid NaF and excess NaBrO₃. This decantate was treated with a concentrated silver
fluoride solution which was prepared by dissolving silver oxide in hydrofluoric acid and filtering. The silver oxide was freshly prepared by adding 50% NaOH to a concentrated silver nitrate solution. Before the addition of hydrofluoric acid, the silver oxide was washed repeatedly with deionized water.

The silver bromate precipitate was removed by centrifuging. Excess calcium hydroxide was stirred overnight with the perbromate solution to remove the remaining silver as silver oxide and fluoride as calcium fluoride. This mixture was, again, centrifuged. At this point, the slightly basic decantate contained NaBrO₄ along with very slight amounts of Ca²⁺, BrO₃⁻, and F⁻.

This solution was stirred with an acid-form cation exchange resin until it became neutral or slightly acidic. It was then passed through a column of the same resin to form perbromic acid, HBrO₄. Complete elimination of Na⁺ and Ca²⁺ was proven by a negative flame test. The HBrO₄ was neutralized with potassium hydroxide to form aqueous KBrO₄. The potassium perbromate solution was concentrated and chilled to precipitate KBrO₄, which has a solubility of less than .2M in ice cold water. The KBrO₄ was then filtered and recrystallized twice before analyses.

**Analysis of Potassium Perbromate**

Three methods of analysis were used to determine the purity of the potassium perbromate: (1) elemental analysis, (2) determination of oxidizing power, (3) infrared and Raman spectra.
The oxygen content was determined by heating KBrO₄ to KBr and taking the difference in weight as oxygen lost. The procedure involved heating a weighed sample of KBrO₄ slowly up to 410-430°C for approximately 1 - 2 hours. This proved to be very difficult because sample loss due to splattering was hard to control, even with covered crucibles. The oxygen content of the KBrO₄ was found to be 35.03% which compares with the theoretical value of 34.97% (Table I).

The residue, which was assumed to be 100% KBr, was analyzed for bromide. This residue was dissolved in water and titrated with a standardized silver nitrate solution. The percentage of bromide was found to be 43.63% (Table II). The theoretical percentage is 43.66%.

Since there is a 1:1 ratio of bromide to potassium, the bromide data was used to find the potassium content. This was found to be 21.36% which compares with the actual value of 21.36% (Table II).

Tests were performed to detect possible bromate and silver ion impurities. Dilute HBr was added to a small amount of aqueous KBrO₄. If bromate were present, Br₂ would have been formed and would have been visible as Br₃⁻. No 275nm Br₃⁻ peak was found in the UV absorption spectrum. Therefore, bromate had been removed by the recrystallization procedure.

The lack of silver bromide precipitate indicated that no silver ion was carried through the recrystallization.

The determination of the oxidizing power is also an indication of purity. The theoretical number of electrons transferred in the reduction of perbromate to bromide is eight. Therefore, the ratio of equivalents of reducing agent to one mole of pure perbromate will be
TABLE I

OXYGEN DETERMINATION IN KBrO$_4$

<table>
<thead>
<tr>
<th>Weight of crucible</th>
<th>Weight of crucible and KBrO$_4$</th>
<th>Weight of KBrO$_4$</th>
<th>Weight of crucible and contents after heating</th>
<th>Weight loss</th>
<th>% Oxygen in sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.2215g</td>
<td>14.4377g</td>
<td>.2162g</td>
<td>14.3617g</td>
<td>.0760g</td>
<td>35.15%</td>
</tr>
<tr>
<td>14.2258g</td>
<td>14.4348g</td>
<td>.2090g</td>
<td>14.3617g</td>
<td>.0731g</td>
<td>34.98%</td>
</tr>
<tr>
<td>14.2299g</td>
<td>14.3627g</td>
<td>.1328g</td>
<td>14.3162g</td>
<td>.0465g</td>
<td>35.02%</td>
</tr>
<tr>
<td>14.2218g</td>
<td>14.4009g</td>
<td>.1791g</td>
<td>14.3381g</td>
<td>.0628g</td>
<td>35.06%</td>
</tr>
<tr>
<td>14.1620g</td>
<td>14.3298g</td>
<td>.1678g</td>
<td>14.2711g</td>
<td>.0587g</td>
<td>34.98%</td>
</tr>
</tbody>
</table>

average = 35.03%

standard deviation = +.23%
TABLE II

BROMIDE AND POTASSIUM DETERMINATION IN KBrO₄

<table>
<thead>
<tr>
<th>Weight of KBrO₄</th>
<th>ml. of .0312N AgNO₃ sol</th>
<th>Moles of Br⁻ x 10⁴</th>
<th>Moles of K⁺ x 10⁴</th>
<th>Grams of Br⁻</th>
<th>Grams of K⁺</th>
<th>% Br⁻</th>
<th>% K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2090g</td>
<td>31.48</td>
<td>1.1421</td>
<td>1.1421</td>
<td>.0913g</td>
<td>.0447</td>
<td>43.67</td>
<td>21.37</td>
</tr>
<tr>
<td>.1328g</td>
<td>20.07</td>
<td>.7246</td>
<td>.7246</td>
<td>.0579g</td>
<td>.0283g</td>
<td>43.60</td>
<td>21.33</td>
</tr>
<tr>
<td>.1791g</td>
<td>27.07</td>
<td>.9774</td>
<td>.9774</td>
<td>.0781g</td>
<td>.0382g</td>
<td>43.61</td>
<td>21.34</td>
</tr>
<tr>
<td>.1678g</td>
<td>25.40</td>
<td>.9173</td>
<td>.9173</td>
<td>.0733g</td>
<td>.0359g</td>
<td>43.66</td>
<td>21.39</td>
</tr>
</tbody>
</table>

average = 43.64%; 21.36%

standard deviation = +.04%; +.09%
eight to one.

This study confirms a previous report\textsuperscript{3,4} that perbromate is very stable in the presence of ordinary reducing agents. The reduction of perbromate directly with thiosulfate occurs so slowly that accurate potentiometric titration data cannot be obtained. For this reason the determination of oxidizing power must be done by an indirect method.

Concentrated hydrobromic acid (12M HBr) was added to a weighed amount of KBrO\textsubscript{4} dissolved in water in at least a 5:1 ratio by volume. The 12M HBr was prepared by bubbling HBr gas through reagent grade 48\% HBr. The containers had to be covered at all times to prevent loss of Br\textsubscript{2}. Excess potassium iodide and enough monosodium phosphate to neutralize the acid were added. The mixture was stirred for ten minutes. The Br\textsubscript{2} oxidizes I\textsuperscript{-} to I\textsubscript{3}\textsuperscript{-}, and the I\textsubscript{3}\textsuperscript{-} is then titrated with a standard thiosulfate solution. The oxidizing power was found to be 7.97\textpm0.03 (Table III).

The infrared and Raman spectra were compared with those of Appelman\textsuperscript{4} to detect possible impurities. In this study the infrared spectrum was taken both with nujol and a KBr pellet.

The infrared spectrum of a nujol mull of KBrO\textsubscript{4} between sodium chloride plates was recorded with a Perkin-Elmer Infracord between 4000 and 700 cm\textsuperscript{-1} (Figure 1). The two major peaks at about 880 cm\textsuperscript{-1} and 800 cm\textsuperscript{-1} agree rather well with the previously recorded infrared spectrum\textsuperscript{4} (Figure 2). A better spectrum of KBrO\textsubscript{4} in a KBr pellet was obtained with a Perkin-Elmer 457 from 4000-250 cm\textsuperscript{-1} (Figure 3).
FIGURE 1

INFRARED SPECTRUM OF KBrO$_4$ IN NUJOL
FIGURE 2

COMPARISON INFRARED SPECTRUM OF $\text{KBrO}_4$ IN NÜJOL
FIGURE 3

INFRARED SPECTRUM OF $\text{KBrO}_4$ IN A $\text{KBr}$ PELLET
TABLE III  

DETERMINATION OF OXIDIZING POWER OF BrO$_4^-$

<table>
<thead>
<tr>
<th>Grams of KBrO$_4$</th>
<th>Vol. of .1012N Thiosulfate</th>
<th>Oxidizing Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0058g</td>
<td>2.51 ml</td>
<td>7.94</td>
</tr>
<tr>
<td>.0208g</td>
<td>8.98 ml</td>
<td>7.99</td>
</tr>
<tr>
<td>.0203g</td>
<td>8.73 ml</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>average: 7.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>standard deviation: +.03</td>
</tr>
</tbody>
</table>

This spectrum gives all four of the major peaks of KBrO$_4$ previously reported$^4$ (Figure 2).

The peaks at about 1100 cm$^{-1}$ in figures 1 and 3 would suggest an impurity since they are absent in the comparison spectra. These peaks remained even after repeated recrystallization of the KBrO$_4$. Infrared spectra of all possible impurities, including other oxidation states of bromine, teflon, and of each material used in the separation and purification procedure produced no such peaks. An infrared spectrum of KBrO$_4$ made from later fluorinations, also, gave no peaks at 1100 cm$^{-1}$.

All the KBrO$_4$ that was synthesized was mixed together and the elemental and chemical analyses were performed. Since these analyses
indicated that the KBrO₄ was of very high purity, it was concluded that the presence of the extraneous peaks could be ignored. This KBrO₄ was used to prepare perbromic acid.

The Raman spectrum (Figure 4) of a single crystal of KBrO₄ was recorded with a laser-excited Spex spectrophotometer. This spectrum compares well with the previously recorded Raman spectrum (Figure 5).

Preparation and Analysis of Perbromic Acid

The stock perbromic acid solution was prepared by use of Bio-Rad AG 50x12 acid-form cation exchange resin. Aqueous KBrO₄ was mixed with the resin until the solution became slightly acidic. It was then passed through a column of more of the resin.

The eluent was analyzed for perbromate by an iodimetric titration. The hydrogen ion concentration was determined by a pH titration of aliquots of eluent with a primary standard of THAM (Tris (hydroxymethyl) aminomethane). Also, a potassium flame test was performed to detect remaining potassium ion. If the hydrogen ion concentration was less than the perbromate concentration, the solution was passed through more of the same resin and reanalyzed until the two concentrations became equal and a negative potassium flame test was obtained.

Later in this study, a better method of analyzing for perbromate was obtained by modification of a procedure used to detect perchlorate. This technique involved a spectrophotometric determination of a perbromate-crystal violet complex by solvent extraction with chlorobenzene. UV-visible spectra were obtained with a Bausch and Lomb
FIGURE 4

RAMAN SPECTRUM OF CRYSTALLINE KBrO₄
FIGURE 5

COMPARISON RAMAN SPECTRUM OF CRYSTALLINE KBrO$_4$
Model 600 recording spectrophotometer.

This technique had the advantages that there was no chance of error due to volatilization of Br$_2$ and that very little perbromate was destroyed during the analysis.

This analysis was performed to find the concentration of HBrO$_4$ used in making cell #9. Using a stock KBrO$_4$ solution, a calibration curve was constructed by plotting absorbance versus concentration (Figure 6). The data produces a straight line which indicates Beer's law is obeyed (Table IV).

### TABLE IV

SPECTROPHOTOMETRIC DATA FOR BrO$_4^{-}$ DETERMINATION AT 595 nm

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Concentration</th>
<th>Aliquot Size (µl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.28</td>
<td>.198 x 10$^{-5}$M</td>
<td>10</td>
</tr>
<tr>
<td>.58</td>
<td>.396 x 10$^{-5}$M</td>
<td>20</td>
</tr>
<tr>
<td>1.46</td>
<td>.998 x 10$^{-5}$M</td>
<td>50</td>
</tr>
</tbody>
</table>

In this procedure 2 ml of 1 x 10$^{-3}$M crystal violet solution are added to five ml of pH 7 buffer and a small aliquot of 4.99 x 10$^{-3}$M perbromate (Table IV). This mixture is diluted to 25 ml. Ten ml of this solution was added to ten ml of chlorobenzene and was shaken for at least one minute. The chlorobenzene layer was drawn off, centrifuged
CALIBRATION CURVE FOR $\text{BrO}_4^-$ DETERMINATION BY CRYSTAL VIOLET METHOD$^7$
and analyzed spectrophotometrically at 595 nm (Figure 6).

Attempts to analyze for bromate by this method were unsuccessful, since Beer's law was not obeyed. For this reason, analysis of perbromate in presence of bromate was not attempted because of the possible interference from bromate.

**Preparation and Analysis of Bromic Acid**

Like perbromic acid, bromic acid was prepared on an ion exchange column. A solution of sodium bromate was stirred with the cation resin and passed through a column of more of the same resin until a sodium flame test of the eluent was negative.

The bromate was analyzed by titration with a standard arsenious acid solution using methyl red for an indicator. Since methyl red is an irreversible indicator in this reaction, the arsenious acid solution was titrated with the bromic acid to the disappearance of the red color.

This same procedure was used in an attempt to analyze for perbromate, but it was found that arsenious acid will not reduce perbromate. An excess of perbromic acid was added to an aliquot of arsenious acid and stirred overnight at temperatures up to boiling. The indicator showed no sign of reaction. This procedure was found to be a useful way of analyzing for bromate in presence of perbromate.
CHAPTER III

EXPERIMENTAL PROCEDURES FOR THE DETERMINATION
OF THE STANDARD E.M.F. OF THE

$\text{BrO}_3^-/\text{BrO}_4^-$ ELECTRODE

Preparation of Cell Solutions

The electrode cell solutions were prepared by mixing weighed amounts of the bromic and perbromic acid stock solutions. The densities of these stock solutions were also determined to allow the use of the molal concentration unit. The ionic strengths were then calculated.

Dilutions of the cell solutions were done gravimetrically. Certain weights of each cell solution were diluted with weighed amounts of water. All weighings were corrected to vacuum, and the ionic strengths were adjusted accordingly.

Analysis of a cell after a series of dilutions was done to check for any change in concentration of bromate and perbromate from the values calculated from the dilutions. The bromate was determined by titration with a standard solution of As(III). The perbromate concentration was determined indirectly by the calculated difference between the total acid concentration and the bromate concentration. The acid was titrated with a standard solution of THAM. The error found (0.0006M) was not large enough to produce a significant change in the Debye-Hückel correction factor.
Measurements of Cell Potentials

The cell may be represented in the form:

\[
\text{Pt} \mid \text{H}_2(\text{g}) \ (1 \ \text{atm}), \ \text{H}^+(\text{aq}) \mid \text{BrO}_5^-(\text{aq}), \ \text{BrO}_4^-(\text{aq}), \ \text{H}^+(\text{aq}) \mid \text{Pt}
\]

The standard electrode potential of this cell will be that of the reaction:

\[
\text{HBrO}_3 + \text{H}_2\text{O} = \text{HBrO}_4 + \text{H}_2(\text{g})
\]

The electrode cell temperature was maintained at 25 ± 0.01°C and 50 ± 0.01°C using a Forma refrigerated and heated water bath and circulator. Potentials were measured with a Beckman Research pH meter which operated with a precision and accuracy of ± 0.1 millivolts.

The hydrogen used for the hydrogen electrode was passed through a Deoxo cartridge and then through tubes of Drierite and Ascarite. All gas lines were made of glass tubing and a minimum of tygon tubing to reduce oxygen contamination.

Nitrogen was bubbled through the BrO$_3^-$/BrO$_4^-$ cells to sweep out oxygen and to act as a stirring agent. It was also passed through tubes of drierite and ascarite. For cell #17, the N$_2$ was passed through a chromous scrubber to insure absence of oxygen. No difference in cell behavior occurred indicating no oxygen electrode interference.

Both gases were bubbled through presaturators of water which were immersed in the thermostatted water bath. This helped to reduce evaporation of the cell solutions.

The working electrodes were glass and platinized platinum electrodes. The platinum electrodes were platinized according to a
procedure in Ives and Janz. The platinum electrodes were anodized in 0.01M \( \text{H}_2\text{SO}_4 \) and allowed to stand in deionized water for thirty minutes before each use. Both electrodes were stored in deionized water.

Attempts to use a gold electrode were abandoned due to irreversibility which evidently was a result of the lack of ample surface area. An unplatinized platinum electrode showed similar signs of irreversibility.

To insure that the electrode material was reacting in no way with the bromate or perbromate, a piece of platinum was placed in contact with one of the cell solutions. Daily, small aliquots were analyzed with a Beckman DB-G grating spectrophotometer at 230 nm to observe changes in the bromate and perbromate absorbance. The same procedure was followed with a piece of gold. No change in absorbance was observed with either the platinum or gold. This indicates no change in concentration of bromate and perbromate. These results show that the platinum and gold electrodes did not promote decomposition of the perbromate.

The cell measurements were recorded as a function of time. Once the hydrogen electrode cell potential established a linear drift, the glass electrode was transferred to the \( \text{BrO}_3^-/\text{BrO}_4^- \) cell, the potential of which is represented by \( E_{\text{V}/\text{VII}} \). After a short time, this cell would establish a linear drift that was equal in magnitude but of the opposite sign if the electrode was operating reversibly. Extrapolation of these lines to the time of transfer gave \( E'_{\text{H}_2} \) and \( E'_{\text{V}/\text{VII}} \) where:
At this point, reproducibility and reversibility were checked by transferring the glass electrode back to the hydrogen cell. The plots of potential versus time are represented in Figure 7. Extrapolation to the second time of transfer gives $E''_{H2}$ and $E''_{V/VII}$ where:

$$E''_{V/VII} - E''_{H2} = E''_{obs}$$

If the cell is reversible, then $E'_{obs} = E''_{obs}$.

The Standard E.M.F. of the $BrO_3^-/BrO_4^-$ Electrode

The reaction to be considered in the cell is:

$$HBrO_3 + H_2O = HBrO_4 + H_2(g)$$

The potential in the cell can be represented by the Nernst equation in this form:

$$E = E^0 - 0.05916 \frac{a_{VII} \cdot p_{H2}}{a_V} \log \frac{a_{VII} \cdot p_{H2}}{a_V}$$

(1)

where $a_{VII}$ and $a_V$ represent the activities of $HBrO_4$ and $HBrO_3$, respectively. $p_{H2}$ was corrected to a barometric pressure of 1 atm. $^{10}$

Making a thermodynamic substitution for $a_{VII}$ and $a_V$, equation (1) becomes:

$$E = E^0 - 0.05916 \frac{a_{VII} \cdot p_{H2}}{a_V} \log \frac{M^2_{VII} \cdot \gamma^2_{VII}}{M^2_V \cdot \gamma^2_V}$$

(2)

The Debye-Hückel limiting law $^{11}$ now may be introduced for use in equation (2):
FIGURE 7

POTENTIAL VS TIME PLOT OF CELL DATA
\[
\log \gamma = \frac{-0.511\mu^{1/2}}{1 + \mu^{1/2}} + B\mu
\]  

(3)

where \( \mu \) = ionic strength and \( B \) is the ionic interaction coefficient.

Substituting for \( \gamma \) in equation (2), the observed potential can be expressed as:

\[
E_{\text{obs}} = E^0 - \frac{0.05916}{2} \log \frac{M^2_{\text{VII}}}{M^2_{\text{V}}} - \frac{0.05916}{2} \bar{B}\mu
\]

(4)

where \( \bar{B} = 2(B_{\text{VII}} - B_{\text{V}}) \). Rearranging equation (4) and letting:

\[
E' = E_{\text{obs}} + \frac{0.05916}{2} \log \frac{M^2_{\text{VII}}}{M^2_{\text{V}}}
\]

we have:

\[
E' = E^0 - \frac{0.05916}{2} \bar{B}\mu
\]

(5)

From equation (5), it is evident that if \( E' \) is plotted versus ionic strength, a straight line should be obtained for electrodes that behave reversibly and obey the Nernst relation. The standard electrode potential, \( E^0 \), is found by extrapolation of this line to infinite dilution.
CHAPTER IV

RESULTS AND DISCUSSION

The $E'$ values of Table V obtained with the platinized platinum electrode were plotted as a function of ionic strength (Figure 8). The platinized platinum electrode was used since it achieved equilibrium much better than the gold electrode. These data were found to deviate seriously from the expected straight line. This large deviation prevents the determination of an accurate $E^0$ value.

The expected slope of this line was estimated by using the tabulated $B$ values\textsuperscript{11} for HClO$_3$ and HClO$_4$. This slope is represented by:

$$\text{Slope} = \frac{-0.05916}{2} \bar{B}$$

where:

$$\bar{B} = 2(B_{\text{VII}} - B_{\text{V}})$$

$B_{\text{VII}}$ and $B_{\text{V}}$ are the ionic interaction coefficients of HClO$_4$ and HClO$_3$, respectively.

$B_{\text{VII}}$ is .26 and $B_{\text{V}}$ is calculated from the difference in $B$ values of NaClO$_3$ (.09) and NaClO$_4$ (.11). This proportional difference would indicate $B_{\text{V}}$ to be .24. Therefore:

$$\bar{B} = .04$$

and

$$\text{Slope} = -1.18 \times 10^{-3}$$
TABLE V

DATA FROM THE MOST REVERSIBLE CELLS AT 25° C

<table>
<thead>
<tr>
<th>Cell</th>
<th>Molality of HBrO₃</th>
<th>Molality of HBrO₄</th>
<th>Ionic Strength</th>
<th>Observed Potential (v)</th>
<th>Debye-Hückel Correction (v)</th>
<th>E' (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell #9</td>
<td>.1582</td>
<td>.0060</td>
<td>.1642</td>
<td>-1.4675</td>
<td>-.0843</td>
<td>-1.5518</td>
</tr>
<tr>
<td>Cell #10</td>
<td>.2674</td>
<td>.0102</td>
<td>.2776</td>
<td>-1.4757</td>
<td>-.0843</td>
<td>-1.5600</td>
</tr>
<tr>
<td>Cell #11</td>
<td>.1187</td>
<td>.0045</td>
<td>.1232</td>
<td>-1.4499</td>
<td>-.0843</td>
<td>-1.5342</td>
</tr>
<tr>
<td>Cell #12</td>
<td>.0734</td>
<td>.0028</td>
<td>.0762</td>
<td>-1.4336</td>
<td>-.0843</td>
<td>-1.5179</td>
</tr>
<tr>
<td>Cell #13</td>
<td>.0659</td>
<td>.0405</td>
<td>.1064</td>
<td>-1.4390</td>
<td>-.0125</td>
<td>-1.4515</td>
</tr>
<tr>
<td>Cell #14</td>
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<td>.0440</td>
<td>.1014</td>
<td>-1.4376</td>
<td>-.0069</td>
<td>-1.4445</td>
</tr>
<tr>
<td>Cell #15</td>
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<td>.0241</td>
<td>.2517</td>
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<td>-.0577</td>
<td>-1.5172</td>
</tr>
<tr>
<td>Cell #16</td>
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<td>.0025</td>
<td>.1469</td>
<td>-1.4526</td>
<td>-.1040</td>
<td>-1.5566</td>
</tr>
<tr>
<td>Cell #17</td>
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<td>.0135</td>
<td>.1303</td>
<td>-1.4444</td>
<td>-.0555</td>
<td>-1.4999</td>
</tr>
</tbody>
</table>

average = -1.5148v

standard deviation = ± .0424v
DEBYE-HÜCKEL PLOT OF CORRECTED CELL DATA

FIGURE 8
Since this slope denotes a nearly horizontal line, all values of $E'$ can be averaged and an $E^0$ value obtained. From the data in Table V, $E^0$ is found to be -1.5148v with a standard deviation of $\pm 0.0424v$.

It should be remembered that extreme oxidizing conditions are necessary to form perbromate from bromate. The results of this research also agree with previous observations that perbromate is a very sluggish oxidizing agent as it appeared not to react at all with As(III). It would, therefore, not be surprising if this electrode did not behave reversibly. The raw data indicate the electrode is behaving reversibly, but the Nernst equation is not obeyed. It is possible that some sort of kinetic barrier exists in the $\text{BrO}_3^-/\text{BrO}_4^-$ electrode reaction, and that complete reversibility cannot be obtained.

The data in Table V and Figure 8 indicate that although the electrode potential responded linearly to changes in ionic strength, the response to changes in the $\text{BrO}_3^-/\text{BrO}_4^-$ ratio was less satisfactory. In each case, the slope was more negative than expected. These facts suggest the possibility that activation energy requirements must be satisfied in the bromate-perbromate reaction, and further suggests that these oxidation states are not in equilibrium.
BIBLIOGRAPHY


