THE CHEMICAL BEHAVIOR
OF ACIDIFIED CHROMIUM (III) SOLUTIONS

(NASA-CR-172997) The Chemical Behavior of Acidified Chromium (III) Solutions  B.S.
Thesis (Spring Arbor Coll., Mich.) 29 F
HC A03/MF A01 CSCI 07D Unclas G3/25 15007

Thesis Submitted in Partial Fulfillment
for Honors in Chemistry
to the
Faculty of Spring Arbor College

by
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May 1981
APPROVAL OF EXAMINING COMMITTEE

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ACKNOWLEDGEMENTS

The author wishes to express her sincere gratitude to Dr. David A. Johnson for his guidance, encouragement, and for his unending patience throughout the length of this research.

The author also wants to express appreciation to the National Aeronautics and Space Administration at Lewis Research Center who provided funding for this research through the Energy Directorate, Solar and Electrochemistry Division.

The author also wishes to express a special thank-you to Jeffrey R. Gingrich for his untiring dedication to the research, his much-needed help, and for his special friendship and patience during the course of the research.

Lastly, the author wishes to express her appreciation to Leland M. Coffman for his support and understanding throughout the research and especially in the preparation of this paper.
INTRODUCTION

A unique energy-storage system has been developed at NASA's Lewis Research Center called REDOX. This NASA-REDOX system is an electrochemical storage device that utilizes the oxidation and reduction of two fully soluble redox couples for charging and discharging. The redox couples now being investigated are acidified chloride solutions of chromium (Cr\(^{2+}/Cr^{3+}\)) and iron (Fe\(^{2+}/Fe^{3+}\)). Figure 1 shows the system in its simplest form.\(^9\)

The basic flow cell consists of two porous carbon-felt electrodes separated by a sheet of membrane material. The membrane is a highly selective ion exchange membrane. It is engineered to almost completely prohibit the passage of iron and chromium ions but allow easy passage of chloride and hydrogen ions (fig. 2).\(^9\) In the development of the electrodes, it was found that the rates of oxidation and reduction of ferrous and ferric ions were rapid enough that a catalyst was not needed. However, the chromium side did require a catalyst. Therefore, gold and lead were added to the chromium electrode. The lead has long been known as an effective catalyst for reduction of Cr\(^{3+}\). The presence of small amounts of gold are needed to provide a surface on which the lead plates during charging.\(^7\)

The REDOX solutions are pumped through the porous electrodes. As the system is being charged, the chromium solution is mostly chrome.
PRINCIPLE OF OPERATION OF NASA-REDOX CONCEPT

ANODE FLUID

CATHODE FLUID

Cr^{+2} \rightarrow Cr^{+3} + e^-

INERT ELECTRODES

SELECTIVE MEMBRANE

Fe^{+3} + e^- \rightarrow Fe^{+2}

CHARGE

Fe^{+2} \rightarrow Fe^{+3} + e^-

POWER CONVERSION SECTION

PUMPS

FIGURE 2
POWER CONVERSION SECTION

CELL TERMINALS

Inlet

Inlet

Inert Electrode

Inert Electrode

Anion Selective Membrane

Outlet

Outlet

FIGURE 3
ion, and the iron solution is mostly ferrous ion. During discharge, chloride ions move from the cathode compartment to the anode compartment while hydrogen ions move in the opposite direction. The discharge process is summarized as follows:

At anode: \( \text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e^- \)

At cathode: \( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \)

As discharge continues, there comes a point as in any battery where recharging is necessary. Therefore, to recharge, a power supply is connected to the terminals, and the reverse electrochemical reactions occur.

This REDOX energy storage system has some significant potential uses. For utilities, it could provide electric power companies with an efficient means of load levelling; that is, the storing of thousands of kilowatt-hours of energy during low demand periods for use later during periods of maximum power consumption. Also, REDOX systems could help to speed up the growth of solar electric (photovoltaic) and wind-energy systems where the cost of electrical storage has important considerations. Storage is necessary when the sun is not shining or the wind not blowing.

The fully functioning system has had some minor problems. One is that in the chromium side small amounts of hydrogen gas are evolved. This can reduce the efficiency of the system by one to two percent each discharge cycle if uncorrected. However, this gas has been found to be easily captured and recombined with the iron reactant in a special rebalancing cell built into the system.

The second problem involves differences in the open circuit voltage and rates of charge and discharge. It has been noticed that
color changes occur during the charge and discharge cycles. It is also evidenced by open circuit voltage versus depth of discharge plots. Distinctive differences in the colors of the chromium solutions, the open circuit voltages and rates of charge or discharge are observed at the same state-of-charge depending on whether the cell is in the charge mode or the discharge mode (fig. 4). It therefore appears that the chromium solution involves several complex ion species. Research was carried on to determine the identity of these chromium species and to investigate the mechanisms of the oxidation and reduction reaction at the chromium electrodes. 3

In a previous study, the reactions at the chromium electrode were followed spectrophotometrically. A single cell was taken through two charge-discharge cycles, and a one millimeter flow-cell was connected to the REDOX cell and placed in a spectrophotometer. The spectrum was recorded at selected states of charge from 350 nm to 1000 nm. A look at the spectra showed two broad bands with maxima at 410-430 nm and 575-610 nm.

A literature search indicated the following complex ions could exist in acidified chromium chloride solutions.

<table>
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<th>Complex</th>
<th>Maxima</th>
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<tr>
<td>Cr(H₂O)₆³⁺</td>
<td>407 nm</td>
</tr>
<tr>
<td>Cr(H₂O)₅Cl²⁺</td>
<td>430 nm</td>
</tr>
<tr>
<td>Cr(H₂O)₄Cl₂⁺¹</td>
<td>450 nm</td>
</tr>
</tbody>
</table>

The spectral peaks were thus resolved into component peaks using a DuPont 310 Curve Resolver (fig. 5). The data clearly showed that oxidation and reduction both
OPEN-CIRCUIT VOLTAGE HYSTERESIS OF IRON/CHROMIUM REDOX CELL

CHARGING CURRENT = 20 AMPS/FT²

REACTANT VOLUME = 0.65 CM³/CM²

MEMBRANE AREA

FIGURE 4
involved \( \text{Cr(H}_2\text{O)}_5\text{Cl}^{2+} \). The charging process in which \( \text{Cr}^{3+} \) is reduced involves reduction of \( \text{Cr(H}_2\text{O)}_6\text{Cl}^{2+} \) indicated by a marked decrease in the concentration of \( \text{Cr(H}_2\text{O)}_6^{3+} \). The discharge process also involves \( \text{Cr(H}_2\text{O)}_5\text{Cl}^{2+} \) in which \( \text{Cr}^{2+} \) is oxidized to \( \text{Cr}^{3+} \). This reaction:
\[
\text{Cr(H}_2\text{O)}_5\text{Cl}^{2+} + \text{e}^- \rightarrow \text{Cr(H}_2\text{O)}_5\text{Cl}^{3+}
\]
is reversible and occurs through a chlorido-bridged, inner sphere pathway as demonstrated by Anson. 4

Because the spectrophotometric studies involved resolving the composite peaks into the component peaks it seemed judicious to see if the complex ions present in cell solutions could be separated and identified.

**EXPERIMENTAL**

A literature search indicated that three complex ions could be expected to be in aqueous solutions of acidified chromic chloride. The three complex ions are hexaaquochromium (III), chloropenta-aquochromium (III), and trans-dichlorotetraaquochromium (III). Figures six and seven show their structures.

Robert J. Angelici has prepared and separated the complexes using ion-exchange chromatography. The column used was prepared with a Dowex 50W-X8, cation exchange resin, 50-100 mesh, \( \text{H}^+ \) form (fig. 8). A buret approximately sixty centimeters long and one centimeter in diameter was plugged with glass wool and then filled to fifty centimeters with a slurry of the Dowex resin. 1

A 1 M \( \text{CrCl}_3 \cdot 6\text{H}_2\text{O} \) solution was made by dissolving 26.6434 grams in 100 milliliters of 0.02 M \( \text{HClO}_4 \). The first complex to be prepared and separated was the trans-dichlorotetraaquochromium (III). Five
\[ \text{Cr(H}_2\text{O)}_5\text{Cl}^{+2} \]

\[ \text{Cr(H}_2\text{O)}_6^{+3} \]

FIGURE 7
Cotton Exchange Beam
(Corner mesh, 10 turn)

Figure ii
milliliters of the 1 M \(\text{CrCl}_3 \cdot 6\text{H}_2\text{O}\) solution was transferred directly to the resin column. The solution was drained to resin level and then 0.1 M \(\text{HClO}_4\) was added continuously using a syphon. The eluant was allowed to flow about one drop per second. The progress of the green-colored solution was followed down the column and was collected at its most intensely colored portion (table 1). The visible spectra was run and maximum absorption peaks were obtained at 450 nm and 635 nm (fig. 9).

The chloropentaquaquochromium (III) was prepared by warming ten milliliters of the 1 M \(\text{CrCl}_3 \cdot 6\text{H}_2\text{O}\) solution in a water bath at fifty-five degrees celsius for a minute and a half. It was then diluted with ten milliliters of distilled water and transferred directly to a fresh resin column. The solution was drained to resin level and 0.1 M \(\text{HClO}_4\) was syphoned onto the column to elute out the unreacted \(\text{Cr(H}_2\text{O})_4\text{Cl}_2^{+1}\). This was followed down the column and collected. Then 1.0 M \(\text{HClO}_4\) was passed through the column to elute the \(\text{Cr(H}_2\text{O})_5\text{Cl}^{+2}\). This solution was also green, and its progress was easily followed down the column and collected at its most intensely colored portion (table 2). The spectra of this solution showed maximum absorption peaks at 430 nm and 605 nm (fig. 10).

The last complex, hexaquochromium (III), was prepared also using the same 1 M \(\text{CrCl}_3 \cdot 6\text{H}_2\text{O}\) in 0.002 M \(\text{HClO}_4\). Ten milliliters was diluted with ten milliliters of distilled water and then boiled for five minutes. Ten more milliliters of distilled water was added and the resulting solution transferred to a fresh resin column. Again the solution was drained to resin level. The 1.0 M \(\text{HClO}_4\) was added first to elute off any unreacted \(\text{Cr(H}_2\text{O})_4\text{Cl}_2^{+1}\) or \(\text{Cr(H}_2\text{O})_5\text{Cl}^{+2}\). Finally 3.0 M
TRANs - CrCl₂(OH₂)₄⁺

CrCl₃ · 6H₂O dissolved in 0.002M HClO₄

Eluted with 0.2M HClO₄

Visible Spectra

Maxima 450 nm, 635 nm
\[ \text{Cr(H}_2\text{O)}_5\text{Cl}^{2+} \]

\[ \text{CrCl}_3 \cdot \text{6H}_2\text{O dissol} \text{ved in 0.002M HClO}_4 \]

Warmed 1½ minutes in 55°C water bath

Eluted with 1.0 M HClO₄

Visible Spectra

Maxima 430 nm, 605 nm.

Table 2
WAVELENGTH (MILLIMICRONS)

CHLOROPENTA-AQUOCHROMIUM (III)

FIGURE 10
HClO₄ was added to elute the Cr(H₂O)₆⁺³. This solution was a distinct blue color in contrast to the other species which were green. This, too, was collected at its most intensely colored portion and the spectra obtained (table 3). The maximum absorption peaks were obtained at 407 nm and 575 nm (fig. 11).¹

It should be noted that the absorption peaks obtained were identical to those found by Thomas W. Swaddle, Edward L. King, ⁸ and Philip J. Elving in their preparation and identification of these complexes.²

The acidified CrCl₃ solution used in the NASA-REDOX cell was analyzed to determine the identity of the complexes present. The cell solution was prepared by dissolving 26.3896 grams of CrCl₃·6H₂O in 100 milliliters of 1 M HCl. Ten milliliters was pipetted directly into a fresh resin column. The sample was first eluted with 0.1 M HClO₄. The green-colored solution was collected until the fraction was clear. Twenty-five milliliters were collected. The next elution was with 1.0 M HClO₄. Again, a green-colored solution was collected until the column fraction was clear. This time 195 milliliters was collected. Lastly, 3.0 M HClO₄ eluted off 172 milliliters of a blue-colored solution. The spectra of fractions were obtained using the Bausch and Lomb Spectronic 20. The spectra of the first fraction showed maximum absorption peaks at 430 nm and 605 nm. The second fraction had absorption peaks also at 430 nm and 605 nm. The last fraction had maximum absorption peaks at 407 nm and 575 nm, characteristic of the Cr(H₂O)₆⁺³. From these spectra it can be concluded that no Cr(H₂O)₆Cl⁺⁺⁺ was present in the cell solution, and only Cr(H₂O)₅Cl⁺⁺ and Cr(H₂O)₆⁺³ existed (table 4).
$\text{Cr(OH}_{2}}\text{)}_6^{+3}$

$\text{CrCl}_3 \cdot \text{6H}_2\text{O dissolved in 0.002M HClO}_4$

Boiled for 5 minutes

Eluted with 3.0M HClO$_4$

Visible Spectra

Maxima 407 nm, 575 nm.

TABLE 3
ORIGINAL PHOTOGRAPH OF POOR QUALITY

WAVELENGTH (MILLIMICRONS)

HEXAAQUOCHROMIUM (III)

FIGURE 11
CELL SOLUTION

1M CrCl₃ • 6H₂O in 1M HCl

A. Elution with 0.1M HClO₄

Spectra maxima 430 nm, 605 nm

B. Elution with 1.0M HClO₄

Spectra maxima 430 nm, 605 nm

C. Elution with 3.0M HClO₄

Spectra Maxima 407 nm, 575 nm

D. CrCl(OH₂)₅⁺²/Cr(OH₂)₆⁺³

4:3:1 (2 HF); 1.2:1 (9 days)

TABLE 4
Next, the cell solution which had been run through two charge-discharge cycles was analyzed to identify the ions present.

A solution of 1 M CrCl$_3$·6H$_2$O was prepared by dissolving 133.326 grams in 500 milliliters of 1 M HCL. This solution was then placed in the battery and run through two charge-discharge cycles at .32 amps. Immediately upon the second discharge, ten milliliters was pipetted out and transferred directly to a fresh resin column. Again began with 0.1 M HClO$_4$ followed by 1.0 M HClO$_4$ and 3.0 M HClO$_4$. Thirty milliliters, 267 milliliters, and 380 milliliters respectively were collected. Three solutions were collected and the spectra obtained using the Spectronic 20. The first two solutions again had the same maximum absorption peaks at 430 nm and 605 nm characteristic of the Cr(H$_2$O)$_5$Cl$^{+2}$. The last fraction again had maximum absorption peaks at 407 nm and 575 nm showing the presence of Cr(H$_2$O)$_6$$^{+3}$ (table 5). This procedure using the solution from the two charge-discharge cycles was performed twice. Data obtained coincided as far as the species present was concerned. The ratio of the two complexes differed slightly (table 5). Another difference between the two trials is that the first procedure resulted in some dimers formed and remaining in the column. No dimers were present the second time.

CONCLUSION

The data clearly shows that the three complex ions, trans-dichlorotetraaquochromium (III), chloropentaaquochromium (III), and hexaaquochromium (III) have been prepared, separated using ion exchange chromatography, and identified spectrophotometrically. In the original cell solution, Cr(H$_2$O)$_5$Cl$^{+2}$ and Cr(H$_2$O)$_6$$^{+3}$ have been
CELL SOLUTION AFTER 2 CHARGE-DISCHARGE CYCLES (.32 AMPS)

1M CrCl₃ • 6H₂O in 1M HCl

A. ELUTION WITH 0.1M HClO₄

Spectra maxima 430 nm, 605 nm

B. ELUTION WITH 1.0M HClO₄

Spectra maxima 430 nm, 605 nm

C. ELUTION WITH 3.0M HClO₄

Spectra maxima 407 nm, 575 nm

D. Cr(OH₂)₆³⁺/CrCl(OH₂)₅⁺²  2.4:1 (2 hrs.)

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identified as the principle chromium species with $\text{Cr(h}_2\text{o)}_5\text{Cl}^{+2}$ predominating (table 4). In the cell solution after two charge-discharge cycles, the principle species were $\text{Cr(h}_2\text{o)}_5\text{Cl}^{+2}$ and $\text{Cr(h}_2\text{o)}_6^{+3}$ with $\text{Cr(h}_2\text{o)}_6^{+3}$ the predominating species (table 5). This data correlates with the resolved peaks collected earlier.

The experiment with the cell solution after two charge-discharge cycles was performed twice. The first time a dimer was formed in the column; however, the second time no dimer was found. Why the dimer was formed the first time and not the second is not known and should be the subject of further study.
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