Magnesium and Copper (II) Chloride: A Curious Redox Reaction

Moira E. Mannard
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MAGNESIUM AND COPPER (II) CHLORIDE:
A CURIOUS REDOX REACTION

A Thesis
Submitted to the School of Graduate Studies and Research
in Partial Fulfillment of the
Requirements for the Degree
Master of Science

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December 2013
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The focus of this research is to follow the oxidation-reduction reaction of solid magnesium metal and an aqueous solution of copper (II) chloride (CuCl$_2$), both with and without the addition of hydrochloric acid (HCl), and separately with sodium chloride (NaCl). When magnesium is added to CuCl$_2$, the reaction does not occur in the predicted straightforward single displacement model to produce magnesium chloride and copper metal. A single displacement reaction may occur, but the reaction first goes through some transitions (including competing side reactions) before the final product of elemental copper is formed. An important purpose of this project is to identify different intermediates through which copper proceeds as this reaction takes place. Copper hydroxide chloride compounds, belloite (Cu(OH)Cl) and paratacamite (Cu$_2$(OH)$_3$Cl), are intermediates that form when the two reactants combine, with and without a chloride source, respectively. Elemental copper forms when magnesium reacts with Cu$_2$(OH)$_3$Cl.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td><strong>1.1</strong> Copper Metal</td>
<td>1</td>
</tr>
<tr>
<td><strong>2</strong> OXIDATION REDUCTION REACTIONS</td>
<td>7</td>
</tr>
<tr>
<td><strong>2.1</strong> Introduction</td>
<td>7</td>
</tr>
<tr>
<td><strong>2.1.1</strong> Basic Definitions</td>
<td>7</td>
</tr>
<tr>
<td><strong>2.1.2</strong> Redox Reaction Example</td>
<td>7</td>
</tr>
<tr>
<td><strong>2.1.3</strong> Copper Redox Reactions in Industry</td>
<td>8</td>
</tr>
<tr>
<td><strong>2.2</strong> Diagrams</td>
<td>9</td>
</tr>
<tr>
<td><strong>2.2.1</strong> Latimer Diagrams</td>
<td>9</td>
</tr>
<tr>
<td><strong>2.2.2</strong> Pourbaix Diagrams</td>
<td>10</td>
</tr>
<tr>
<td><strong>3</strong> EXPERIMENTAL PLAN</td>
<td>11</td>
</tr>
<tr>
<td><strong>3.1</strong> Introduction</td>
<td>11</td>
</tr>
<tr>
<td><strong>3.2</strong> Design of the Experiment</td>
<td>11</td>
</tr>
<tr>
<td><strong>3.3</strong> Chemicals and Equipment</td>
<td>12</td>
</tr>
<tr>
<td><strong>3.4</strong> Experimental Procedure</td>
<td>13</td>
</tr>
<tr>
<td><strong>3.4.1</strong> Reaction of Magnesium and CuCl$_2$ (with HCl)</td>
<td>13</td>
</tr>
<tr>
<td><strong>3.4.2</strong> Reaction of Magnesium and CuCl$_2$ (without HCl)</td>
<td>14</td>
</tr>
<tr>
<td><strong>3.4.3</strong> Reaction of Magnesium and CuCl$_2$ (with NaCl)</td>
<td>14</td>
</tr>
<tr>
<td><strong>3.5</strong> Separation and Characterization</td>
<td>14</td>
</tr>
<tr>
<td><strong>3.5.1</strong> Purification and Recrystallization</td>
<td>15</td>
</tr>
<tr>
<td><strong>3.5.2</strong> Ultraviolet-Visible Spectroscopy</td>
<td>15</td>
</tr>
<tr>
<td><strong>3.5.3</strong> X-ray Powder Diffraction</td>
<td>16</td>
</tr>
<tr>
<td><strong>4</strong> RESULTS</td>
<td>18</td>
</tr>
<tr>
<td><strong>4.1</strong> Analysis of Reactions</td>
<td>18</td>
</tr>
<tr>
<td><strong>4.1.1</strong> Color Change Observations</td>
<td>18</td>
</tr>
<tr>
<td><strong>4.1.1.1</strong> Reaction of Magnesium and CuCl$_2$ (with HCl)</td>
<td>18</td>
</tr>
<tr>
<td><strong>4.1.1.2</strong> Reaction of Magnesium and CuCl$_2$ (without HCl)</td>
<td>19</td>
</tr>
<tr>
<td><strong>4.1.1.3</strong> Reaction of Magnesium and CuCl$_2$ (with NaCl)</td>
<td>19</td>
</tr>
</tbody>
</table>
Chapter 5.2

5.1 Summary and Conclusions

5.2 Future Research Directions

REFERENCES
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDICES .................................................................</td>
<td>46</td>
</tr>
<tr>
<td>Appendix 1 Calculation of % Copper by Mass in Cu$_2$(OH)$_3$Cl..........................</td>
<td>46</td>
</tr>
<tr>
<td>Appendix 2 Calculation of % Chloride by Mass in Cu$_2$(OH)$_3$Cl........................</td>
<td>47</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1.1 Chemicals and Manufacturers</td>
<td>12</td>
</tr>
<tr>
<td>1.2 Equipment and Manufacturers</td>
<td>12</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Diagram of splitting of the $d$-orbital energies that result from the Jahn-Teller effect</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Latimer diagrams for copper (in acidic solution) and chlorine (in basic solution)</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Pourbaix diagram of copper in a chloride solution</td>
<td>10</td>
</tr>
<tr>
<td>3.1</td>
<td>Diagram of a filtration setup using the Büchner funnel</td>
<td>15</td>
</tr>
<tr>
<td>3.2</td>
<td>Diagram of a UV-Vis spectrum</td>
<td>16</td>
</tr>
<tr>
<td>3.3</td>
<td>Photograph of a desktop X-ray diffractometer</td>
<td>17</td>
</tr>
<tr>
<td>4.1</td>
<td>UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (with HCl, recrystallized)</td>
<td>22</td>
</tr>
<tr>
<td>4.2</td>
<td>UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (without HCl, recrystallized)</td>
<td>22</td>
</tr>
<tr>
<td>4.3</td>
<td>UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (with NaCl, recrystallized)</td>
<td>23</td>
</tr>
<tr>
<td>4.4</td>
<td>XRD diffractogram of the magnesium and CuCl$_2$ reaction (with HCl, recrystallized)</td>
<td>25</td>
</tr>
<tr>
<td>4.5</td>
<td>XRD diffractogram of the magnesium and CuCl$_2$ reaction (without HCl, recrystallized)</td>
<td>26</td>
</tr>
<tr>
<td>4.6</td>
<td>XRD diffractogram of the magnesium and CuCl$_2$ reaction (with NaCl, recrystallized)</td>
<td>27</td>
</tr>
<tr>
<td>4.7</td>
<td>UV-Vis spectrum of the diluted CuCl$_2$ solution</td>
<td>29</td>
</tr>
<tr>
<td>4.8</td>
<td>UV-Vis spectrum of the diluted, powdered Cu$_2$O</td>
<td>29</td>
</tr>
<tr>
<td>4.9</td>
<td>XRD diffractogram of the powdered Cu$_2$O</td>
<td>30</td>
</tr>
<tr>
<td>4.10</td>
<td>Absorbance vs. concentration calibration curve of five standard solutions of CuSO$_4$•5H$_2$O with (0, 0) point</td>
<td>33</td>
</tr>
<tr>
<td>4.11</td>
<td>UV-Vis spectrum of the solution of Cu$_2$(OH)$_3$Cl</td>
<td>34</td>
</tr>
<tr>
<td>4.12</td>
<td>IR spectrum of the synthesized Cu$_2$(OH)$_3$Cl</td>
<td>35</td>
</tr>
<tr>
<td>4.13</td>
<td>UV-Vis spectrum of the synthesized Cu$_2$(OH)$_3$Cl</td>
<td>37</td>
</tr>
<tr>
<td>4.14</td>
<td>XRD diffractogram of the synthesized Cu$_2$(OH)$_3$Cl</td>
<td>38</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>4.15 UV-Vis spectrum of the magnesium and Cu$_2$(OH)$_3$Cl reaction</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>4.16 XRD diffractogram of the magnesium and Cu$_2$(OH)$_3$Cl reaction</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF COMPOUNDS AND THEIR CHEMICAL FORMULAS

Copper (II) chloride, CuCl₂

Hydrochloric acid, HCl

Ethanol, CH₃CH₂OH

Acetone, CH₃COCH₃

Dichloromethane, CH₂Cl₂

Hexane, C₆H₁₄

Benzene, C₆H₆

Belloite, Cu(OH)Cl

Bischofite, MgCl₂•6H₂O

Paratacamite, Cu₂(OH)₃Cl

Copper chloride hydroxide hydrate, Cu₁₁Cl₈(OH)₁₄•6H₂O

Halite, NaCl

Cuprite, Cu₂O

Copper (II) chloride dihydrate, CuCl₂•2H₂O

Sodium hydroxide, NaOH

Copper (II) sulfate pentahydrate, CuSO₄•5H₂O

Ammonia, NH₃

Nitric acid, HNO₃

Silver nitrate, AgNO₃

Magnesium chloride hydroxide hydrate, Mg₂(OH)₃Cl•4H₂O
CHAPTER 1
INTRODUCTION

1.1 Copper Metal

A transition metal, copper is the second to last member of the first-row transition metals. Transition metals typically have more than one common oxidation state: copper forms compounds with oxidation states +1 (cuprous) and +2 (cupric). Copper is a known exception to the Aufbau principle; copper would have the expected ground-state valence configuration of 4s^23d^9, but one electron is “borrowed” from the 4s orbital to completely fill the 3d orbitals, making the configuration 4s^13d^{10}. For the copper ions, the electron configuration of the cuprous ion (Cu^+) is 4s^03d^{10}, while the configuration for the cupric ion (Cu^{2+}) is 4s^03d^9. Cu^+ is stabilized in the solid phase, in which its compounds are generally colorless or white. The +2 state of copper dominates its aqueous chemistry, and it is more stable in that phase. Many Cu^{2+} compounds are blue due to the presence of the hexaaquacopper (II) ion, Cu(H_2O)_6^{2+}.

Oxidation and reduction chemistry of transition metals is a complex process. Cu^+ and Cu^{2+} are compared by observing redox properties that involve precipitation and complex ion formation. A complex ion is an ion that contains a metal cation connected to one or more small molecules or ions (such as NH_3, CN-, or OH-) with lone pairs of electrons. Forming a complex ion occurs in steps and each step has its own characteristic equilibrium constant. In order to insure that complexation is complete, significant excesses of ligands need to be added. The reactions in the demonstration by Ophardt compared and contrasted the relative stabilities of the Cu^+ and Cu^{2+} oxidation states with different ligands attached. The following reduction potentials show that Cu^+ is a stronger oxidizing agent than Cu^{2+}:

\[ \text{Cu}^{2+} (\text{aq}) + e^- \rightleftharpoons \text{Cu}^+ (\text{aq}) \quad E^0 = +0.16 \text{ V} \quad (1.1) \]
\[
\begin{align*}
\text{Cu}^+_{(aq)} + e^- & \rightleftharpoons \text{Cu}_{(s)} \quad E^0 = +0.52 \text{ V} \quad (1.2) \\
\text{Cu}^{2+}_{(aq)} + 2e^- & \rightleftharpoons \text{Cu}_{(s)} \quad E^0 = +0.34 \text{ V} \quad (1.3)
\end{align*}
\]

This behavior is different than most other transition metals because very few of them have common states of both +1 and +2. Also, the larger oxidation state of a transition metal often has the largest reduction potential value, but for copper, the smaller oxidation state has the largest value. Iron is one of a few transition metals that has common states of +2 and +3. The transition of the +3 state to the +2 state has a much larger potential value (+0.77 V) than the value for the transition of the +2 state to the elemental state (-0.44 V).

Compounds or ions at intermediate oxidation states can undergo disproportionation, a process in which a compound undergoes an autoredox reaction (where the same substance is simultaneously oxidized and reduced) to produce higher and lower oxidation states than the original. Combining equations 1.1 and 1.2, copper disproportionates when in the +1 state:

\[
2\text{Cu}^+_{(aq)} \rightleftharpoons \text{Cu}^{2+}_{(aq)} + \text{Cu}_{(s)} \quad E^0 = +0.36 \text{ V} \quad (1.4)
\]

The reverse of this equation, where Cu and Cu\textsuperscript{2+} are converted to 2Cu\textsuperscript{+}, is called comproportionation. When equation 1.4 is reversed, the following equation is represented by an equilibrium constant, \(K_r\):

\[
\text{Cu(II)}_{(aq)} + \text{Cu}_{(s)} \rightleftharpoons 2\text{Cu(I)}_{(aq)} \quad K_r = \frac{C_{\text{Cu(I)}}^2}{C_{\text{Cu(II)}}} \quad (1.5)
\]

According to Malyszko and Kaczor\textsuperscript{4}, the equilibrium constant is determined by measuring the equilibrium concentrations of Cu(I) and Cu(II). The equilibrium in equation 1.5 \((K_r = 10^6)\) favors the formation of Cu\textsuperscript{2+} under standard aqueous conditions. If the concentration of Cu\textsuperscript{+} is decreased, the equilibrium (Equation 1.5) is expected to shift to the right. If the concentration of
Cu$^{2+}$ is decreased, then the equilibrium is expected to shift to the left.$^4$ Changing the ligands attached to copper changes the distribution of the equilibrium concentrations of Cu$^+$ and Cu$^{2+}$.

Cu$^+$ is diamagnetic because the electron configuration results when electrons in elemental copper are lost first out of the 4s orbital.$^1$ Cu$^{2+}$ has an electron configuration resulting when a second electron is removed, rendering it paramagnetic.$^5$ The geometries of these copper ions can vary depending on the complexes they form with attached ligands. The complexes that form can also have different crystal structures. Compounds with Cu$^+$ often have tetrahedral geometry: copper (I) chloride (CuCl) has a zinc blende structure,$^6$ which has tetrahedral coordination. In this structure, each atom is surrounded by four atoms of the opposite type; all of them are positioned together at the four vertices of a regular tetrahedron. Cu$^{2+}$ often forms complexes with a distorted octahedral geometry: anhydrous CuCl$_2$ has a distorted cadmium iodide structure.$^6$ In this structure, the iodide anions are arranged in a hexagonal close-packed assembly, while the cadmium cations interchange layers in order to fill the octahedral sites. This distortion occurs because of the Jahn-Teller effect,$^7$ which describes the geometrical distortion of molecules and ions that is associated with certain electron configurations. The effect is most evident in complexes that have the configuration d$^9$, when an odd number of electrons occupy the $e_g$ orbitals. Since Cu$^{2+}$ has this configuration, three electrons are in the two degenerate $e_g$ orbitals, which leads to a doubly degenerate electronic ground state. Figure 1.1 illustrates the results of the Jahn-Teller effect on the electron configuration for this ion.
The most common oxidation states of copper are +1 and +2, but some Cu$^{3+}$ complexes do exist.\textsuperscript{1} As higher oxidation states of transition metals are difficult to stabilize, Burdett and Sevov\textsuperscript{8} suggested that adding an electropositive element might stabilize these states. The approach of adding electropositive elements was based on charge density calculations by the linear-muffin-tin-orbital (LMTO) method on Cu$^{3+}$ halides.\textsuperscript{8} The experiments also focused on the interactions between the copper and oxygen orbitals. Because silver and gold are in the same group as copper, the interactions in their orbitals were also calculated. All three metals were calculated in binary compounds with oxidation states as high as +3. The strength of their interactions with oxygen increases in the order Cu $<$ Ag $<$ Au. Of these three metals, only gold has a common oxidation state of +3, so it forms a well-known and stable binary compound with the formula Au$_2$O$_3$.\textsuperscript{8} While no binary copper (III) oxide (Cu$_2$O$_3$) exists, the calculations found that Cu$^{3+}$ was likely to be stabilized by potassium (as KCuO$_2$) or some other electropositive element. Ligands that are highly basic are capable of stabilizing metal ions in high oxidation states. Cu$^{3+}$ and Cu$^{4+}$ complexes that have fluoride ligands include K$_3$CuF$_6$ and Cs$_2$CuF$_6$, which have electropositive elements (potassium and cesium, respectively).\textsuperscript{1}

\textbf{Figure 1.1.} Diagram of splitting of the d-orbital energies that result from the Jahn-Teller effect.\textsuperscript{7}
Palomino et al.\textsuperscript{9} discussed how temperature can affect the different oxidation states of copper, in that more ions of Cu\textsuperscript{2+} transformed to ions of Cu\textsuperscript{+} as the temperature increased. Various spectroscopic techniques (infrared, ultraviolet-visible, electron-paramagnetic resonance) have shown the redox behavior of Cu/ZSM-5 zeolites prepared by ion exchange from aqueous solutions. This is an analysis of the dehydration-thermal reduction of Cu\textsuperscript{2+} between room temperature and 673 K and the reverse process under different conditions.\textsuperscript{9} Reduction of Cu\textsuperscript{2+} to Cu\textsuperscript{+} is not involved in the early stages of dehydration, which ranges from room temperature to around 470 K. Cu\textsuperscript{+} is not directly oxidized to Cu\textsuperscript{2+} even when samples that contain Cu\textsuperscript{+} are rehydrated. Molecular oxygen (O\textsubscript{2}) can be used as an oxidant for this process, but if it makes contact with the dehydrated material, the oxidation will not happen at room temperature.

Beutel et al.\textsuperscript{10} studied the redox chemistry of elemental copper in zeolite ZSM-5 using Fourier transform infrared spectroscopy (FTIR), temperature-programmed reduction (TPR), electron paramagnetic resonance (EPR), and extended X-ray absorption fine structure (EXAFS). The studies identified isolated ions, Cu\textsuperscript{2+}, oxocations, [Cu – O – Cu]\textsuperscript{2+}, and oxide particles. At room temperature, oxocations are reduced by carbon monoxide (CO) and nitric monoxide (NO); both molecules are used as probes to identify Cu\textsuperscript{+} in FTIR. Cu\textsuperscript{0} is thermodynamically unstable around Cu\textsuperscript{2+}, which makes Cu\textsuperscript{+} the first detectable product; Cu\textsuperscript{0} is detected when the Cu\textsuperscript{2+} is gone.\textsuperscript{10} In CO, only oxide particles and oxocations are reduced, but when Cu\textsuperscript{2+} ions are present, they react with Cu\textsuperscript{0} to form Cu\textsuperscript{+}. A complex between Cu\textsuperscript{+} and CO is formed when the CO accelerates the process of zeolite protons oxidizing Cu\textsuperscript{0} to Cu\textsuperscript{+}.

Fox et al.\textsuperscript{11} have stated that singly charged transition metals are unstable in aqueous media; in turn, their aqueous chemistry is unknown whenever they have no attached ligands. This instability happens partially because metal ions that have a 2+ charge have a much higher
hydration energy than the same metal ions with a 1+ charge. In the case of copper, this leads to a rapid disproportionation, as shown in equation 1.4. It is possible that the +1 state can be stabilized by complexation, and the Cu^{II}/Cu^{I} couple has significance in electron-transfer processes within enzymes and proteins.\textsuperscript{11} The first row transition metals (Sc → Zn) display several different oxidation states, and copper is an exception to a rule that states that these elements do not form stable uncomplexed metal (I) ions in aqueous solutions. When Mg\textsuperscript{2+}, Al\textsuperscript{3+}, and V\textsuperscript{3+} react with HCl, it leads to oxidation and the release of atomic (H) or molecular hydrogen (H\textsubscript{2}).\textsuperscript{11} But the ions of copper (along with those of manganese, cobalt, and iron) react without changing their oxidation states even in the presence of corrosive HCl.

According to Liu et al.\textsuperscript{12}, Cu\textsuperscript{2+} centers may be important functional units in a variety of multicopper blue oxidases, including laccase and ascorbate oxidases; the latter has a purpose in catalyzing the reduction of oxygen to water. These two multicopper blue oxidases, along with nitrous oxide reductase, are capable of existing in fully reduced Cu\textsuperscript{+} states.\textsuperscript{12} Halides or thiocyanate anions, such as Cl\textsuperscript{−} and SCN\textsuperscript{−}, function both as reducing agents and as ligands. These anions are included in polynuclear species of Cu\textsuperscript{+} or Cu\textsuperscript{2+}, where oxidation occurs for Cu\textsuperscript{+} centers while partial reduction occurs for Cu\textsuperscript{2+}. 


CHAPTER 2
OXIDATION REDUCTION REACTIONS

2.1 Introduction

The reactants of magnesium and CuCl₂ are an elemental metal and a binary compound, respectively. When they react, a single displacement reaction is expected to occur.

2.1.1 Basic Definitions

Redox reactions are chemical reactions that involve the shift or transfer of electrons between ions, atoms, or molecules. Within these reactions, however, there may not always be an actual transfer of electrons; oxidation and reduction are best considered as changes in an oxidation state. Hence, oxidation is characterized as an increase in oxidation state, while reduction is known as a decrease in oxidation state.

2.1.2 Redox Reaction Example

Redox reactions typically occur in single displacement reactions, which are also known as substitution reactions. In these reactions, an atom or ion changes its oxidation state as it moves from one compound to another, switching places with another atom that exhibits the same type of charge (e.g., a metal switches places with another metal). The reactants are commonly an element and a compound, as seen in the example reaction of elemental nickel and copper (II) sulfate (CuSO₄) solution. This is a single displacement reaction that includes an oxyanion in the compound rather than a single anion:

\[ \text{Ni}_\text{(s)} + \text{CuSO}_4\text{(aq)} \Leftrightarrow \text{NiSO}_4\text{(aq)} + \text{Cu}_\text{(s)} \] (2.1)
The net ionic equation for the reaction is:

\[
\text{Ni}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Ni}^{2+}(aq) + \text{Cu}(s) \quad (2.2)
\]

This reaction is represented by two half-equations. In them, nickel is oxidized at the same time that copper is reduced:

\[
\text{Ni}(s) \rightleftharpoons \text{Ni}^{2+}(aq) + 2e^- \quad (2.3)
\]

\[
\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad (2.4)
\]

### 2.1.3 Copper Redox Reactions in Industry

Examples of redox reactions of copper are found in the industry. One such type is smelting; its main purpose is to produce a metal from its ore. This includes copper extraction from copper ore and other base metals from their ores.\(^\text{13}\) Smelting uses heat and carbon, which acts as a reducing agent, to change the oxidation state of the metal in the ore. The carbon removes oxygen from the ore to leave the elemental metal behind.

When metals are destroyed over a period of time due to a chemical reaction that occurs within the atmosphere, the process is known as corrosion. Aluminum corrosion is an important topic for industry; studies have indicated that aluminum corrodes more quickly in seawater or when it makes contact with copper (metallic or as \(\text{Cu}^{2+}\) in solution).\(^\text{14}\) \(\text{Cu}^{2+}\) has a positive reduction potential and aluminum has a smaller, negative reduction potential,

\[
\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^0 = +0.34 \text{ V} \quad (2.5)
\]

\[
\text{Al}^{3+}(aq) + 3e^- \rightleftharpoons \text{Al}(s) \quad E^0 = -1.66 \text{ V} \quad (2.6)
\]

so a spontaneous electrochemical reaction can occur easily, which promotes aluminum oxidation. Accelerated aluminum corrosion in seawater is caused by the “chloride-acceleration
effect,” which is well established; however, comparison of this effect with other halides has not yet been reported.\textsuperscript{14}

2.2 Diagrams

There are a few different types of diagrams that analyze the oxidation states of a given element using the standard reduction potentials, which can provide useful redox information.\textsuperscript{15} Some of the most useful of these are the Latimer and Pourbaix diagrams.

2.2.1 Latimer Diagrams

Latimer diagrams summarize the standard electrode potential data of a particular element.\textsuperscript{15} All of the known oxidation states of the element are written as an extended equation with arrows between them. The most highly oxidized form of the element is found on the left, which is then followed by all of the lower oxidation states towards the right. The numerical values of the standard reduction potentials are written over the arrows located between the oxidation states of the element.\textsuperscript{15} Figure 2.1 gives the Latimer diagram representations for both copper and chlorine, where copper is in acidic solution and chlorine is in a basic solution. For the copper diagram, the given data is the same as those in equations 1.1 through 1.3.

![Latimer diagrams for copper (in acidic solution) and chlorine (in basic solution).](image)

\textbf{Figure 2.1.} Latimer diagrams for copper (in acidic solution) and chlorine (in basic solution).\textsuperscript{16}
2.2.2 Pourbaix Diagrams

The Pourbaix diagram shows the thermodynamically stable form of an element as a function of standard reduction potential and pH. The pairs (pH, $E_{\text{red}}^0$) are used to map the boundaries between the various oxidation states; the stable states are shown at different pH values. The neutrality point on the diagram is defined at 7 and $E_{\text{red}}^0$ at a value of +0.40 V. The diagram shows the most thermodynamically stable compounds of the chosen element at any potential and pH condition. The Pourbaix diagram contains three different types of lines that show the equilibrium conditions for the given element. Vertical lines indicate an equilibrium that is dependent only on pH and not a redox process. Horizontal lines represent pure redox transformations, so the boundaries are dependent on potential and not pH. The diagonal lines represent redox potentials of a solution in equilibrium which involves hydroxide or hydrogen ions. More specifically, the dashed lines represent boundaries within which reactions in aqueous solution are possible. Figure 2.2 displays the Pourbaix diagram of copper in a chloride solution.

![Pourbaix diagram of copper in a chloride solution](image)

Figure 2.2. Pourbaix diagram of copper in a chloride solution.
CHAPTER 3
EXPERIMENTAL PLAN

3.1 Introduction

In this chapter, the techniques of this research are clarified, including the original design of the experiment, the experimental steps, equipment, and materials and methods used in this thesis. The basic purposes of recrystallization, ultraviolet-visible spectroscopy, and powder X-ray diffraction are also explained.

3.2 Design of the Experiment

Magnesium metal reacted with an aqueous solution of CuCl$_2$ and a single displacement reaction was expected to happen. Instead, a variety of colors and transitions through which the copper was going were observed.$^{18}$ The reaction was originally investigated by undergraduate student Brittany Buterbaugh$^{19}$ to see specifically what happened as the reaction took place.

The main reaction investigated in this project is one of magnesium with a CuCl$_2$ solution, which was expected to follow a single displacement model to form aqueous magnesium chloride (MgCl$_2$) and elemental copper metal. The reaction also included the addition of HCl. Addition of HCl decreases the quantity of intermediate hydroxides that may form during the reaction. It also produces a supplementary amount of the green tetrachlorocuprate ion, CuCl$_4^{2-}$. After the initial reaction was performed, a few more reactions were run for comparison. Using approximately the same amounts of magnesium and CuCl$_2$ that were used in the initial reaction, these other reactions included repeating the initial reaction twice: one without an inclusion of HCl, and another with NaCl instead of HCl.
3.3 Chemicals and Equipment

The main chemicals used in this research were magnesium metal and CuCl$_2$ solution, along with the occasional usage of HCl and NaCl. All of the reactions were performed in and used standard glassware, which included beakers, test tubes, and flasks. Because there were various steps that used many different chemicals and equipment within the project, all of the major materials are tabulated in Table 1.1, while all of the major pieces of equipment are tabulated in Table 1.2.

<table>
<thead>
<tr>
<th>Materials</th>
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<tbody>
<tr>
<td>Magnesium</td>
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</tr>
<tr>
<td>CuCl$_2$</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>HCl</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>NaCl</td>
<td>Fisher Scientific and EMD</td>
</tr>
<tr>
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<td>Fisher Scientific</td>
</tr>
<tr>
<td>CH$_3$COCH$_3$</td>
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</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
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</tr>
<tr>
<td>C$_6$H$_6$</td>
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</tr>
<tr>
<td>Cu$_2$O</td>
<td>Sigma-Aldrich</td>
</tr>
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<td>Fisher Scientific</td>
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<tr>
<td>HNO$_3$</td>
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</tr>
<tr>
<td>AgNO$_3$</td>
<td>Baker and Adamson</td>
</tr>
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</table>

<table>
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<th>Equipment</th>
<th>Manufacturer</th>
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<td>Balance</td>
<td>Mettler Toledo</td>
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<td>Ocean Optics</td>
</tr>
<tr>
<td>X-ray Diffractometer</td>
<td>Rigaku</td>
</tr>
<tr>
<td>IR Spectrophotometer</td>
<td>PerkinElmer</td>
</tr>
<tr>
<td>MDI Jade (software)</td>
<td>Materials Data</td>
</tr>
</tbody>
</table>

Table 1.1. Chemicals and Manufacturers

Table 1.2. Equipment and Manufacturers


3.4 Experimental Procedure

3.4.1 Reaction of Magnesium and CuCl₂ (with HCl)

When magnesium metal reacts with the CuCl₂ solution, this single displacement reaction is expected:

\[ \text{Mg}_{(s)} + \text{CuCl}_2_{(aq)} \rightarrow \text{MgCl}_2_{(aq)} + \text{Cu}_{(s)} \]  \hspace{1cm} (3.1)

These two starting materials were expected to react stoichiometrically; however, a larger amount of magnesium than CuCl₂ was used: 1.50 g (0.0622 mol) of magnesium was added to 40 mL (0.0400 mol) of 1.0 M CuCl₂. The reaction mixture turned from blue to dark green almost immediately; bubbling also resulted since \( \text{Cu(H}_2\text{O)}_6^{2+} \) in the CuCl₂ solution can act as an acid.

Magnesium reacts exothermically with most acids, and including HCl in the reaction released hydrogen gas. The addition of HCl caused the solution to change colors a few more times. Extra magnesium was added, a little at a time, to control how the reaction proceeded. The specific color changes to the solution and the magnesium were noted. When the reaction ended (no new bubbles or colors appeared in the beaker), the solution was centrifuged to collect the precipitates.

The different color changes visible in the solution during the main reaction are possibly the results of different competing side reactions. The reactions below are the probable competing side reactions that occurred:

\[ \text{CuCl}_2_{(aq)} + 6\text{H}_2\text{O}_{(l)} \rightarrow \text{Cu(H}_2\text{O)}_6^{2+}{}_{(aq)} + 2\text{Cl}^-{}_{(aq)} \]  \hspace{1cm} (3.1.1)

This reaction is what gives the initial solution its blue color.²⁰

\[ \text{Cu}^{2+}{}_{(aq)} + 4\text{Cl}^-{}_{(aq)} \rightarrow \text{CuCl}_4^{2-}{}_{(aq)} \]  \hspace{1cm} (3.1.2)

Because this ion is yellow, combining it with CuCl₂ resulted in a green color at the start of the reaction. This would lead to an increase due to the addition of HCl or removal of Cu²⁺ ions, resulting in an excess of Cl⁻ ions.²⁰
3.4.2 Reaction of Magnesium and CuCl₂ (without HCl)

The next reaction performed was between 1.50 g (0.0622 mol) of magnesium and 40 mL (0.0400 mol) of CuCl₂, without the addition of HCl. Even without HCl, the solution changed color as the magnesium was added, including different shades of light green. But without the presence of an acid, the color changes that did occur, along with the appearance of bubbles, did not correspond to those in the initial reaction.

3.4.3 Reaction of Magnesium and CuCl₂ (with NaCl)

The initial reaction was repeated with 1.50 g (0.0622 mol) of magnesium added to 40 mL (0.0400 mol) of CuCl₂, but this time, NaCl was added instead of HCl. Adding a salt instead of an acid caused a few different color changes to the solution and precipitate, including yellow and yellow green. Upon the addition of NaCl, bubbles did not appear as much or as fast. Some NaCl remained in the precipitate and did not dissolve completely when the reaction ended.

3.5. Separation and Characterization

Because the reactions are not expected to form elemental copper immediately, the intermediates formed were characterized to determine the species’ identities. These species could be used to see if elemental copper could be formed via an alternate pathway. Recrystallization was used for color removal on the precipitates, while characterization was done through powder X-ray diffraction (XRD) and ultraviolet-visible (UV-Vis) spectroscopy. Solvents that included water, CH₃CH₂OH, and CH₃COCH₃ were tested with the precipitates to see if they would be good recrystallization solvents.
3.5.1 Purification and Recrystallization

Purification is the physical separation of a particular chemical substance from contaminating substances. Recrystallization is a separation process that is used for purifying compounds. The most common situation is where a required compound is mixed with, and thus contaminated by, a small amount of an impurity. This compound and impurity are placed into a hot solvent to fully dissolve the mixture, then as the solution cools, the solubility of compounds in the solution drops. The chosen compound can be removed from the impurity via suction filtration. Figure 3.1 displays a basic suction filtration setup with all of the needed materials and the purposes that they serve.

![Diagram of a filtration setup using the Büchner funnel.](image)

**Figure 3.1.** Diagram of a filtration setup using the Büchner funnel.

3.5.2 Ultraviolet-Visible Spectroscopy

In absorption spectroscopy, ultraviolet spectroscopy is that which occurs in the ultraviolet-visible spectral region. In an electromagnetic spectrum, the visible region is detectable by the human eye between the wavelengths of 390 and 700 nm. Figure 3.2 shows a general UV-Vis spectrum within this wavelength range.
As a quantitative method, UV-Vis spectroscopy is frequently used to verify concentrations of an absorbing species in relatively dilute solution. This is achieved by using the Beer-Lambert law:\(^2\text{3}\)

\[
A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot L \quad (3.2)
\]

where \(A\) is the calculated absorbance, \(I_0\) is the intensity of the incident light at a particular wavelength, and \(I\) is the transmitted intensity. \(\varepsilon\) is the molar absorptivity, which is a measurement of how strongly any chemical species absorbs light at a certain wavelength. \(c\) is the concentration of the measured species, while \(L\) is the pathlength.

![Figure 3.2. Diagram of a UV-Vis spectrum.\(^2\text{4}\)](image)

### 3.5.3 X-ray Powder Diffraction

X-ray crystallography is a method used to establish the assembly of atoms within a crystal. The oldest and most accurate method is X-ray (powder) diffraction, in which a beam of X-rays makes contact with a single crystal, resulting in numerous dispersed beams.\(^2\text{5}\) Chmielová et al.\(^2\text{6}\) state that the X-ray diffraction powder method identifies crystalline phases in corrosion products. It is also useful for the quantitative phase analysis based on the intensity measurement
for a single diffraction. Figure 3.3 shows a photograph of an X-ray diffractometer that is
designed to work with the use of a desktop computer.

For a given crystal structure, Bragg’s Law is used to relate the angle between the incident
ray and scattering planes (θ), the wavelength of the incident X-ray beam (λ), and the interplanar
distance between the atomic layers (d). If the equation is satisfied, it is equal to an integer (n)
multiple of the wavelength, which is when the X-rays diffracting through the crystal will
combine constructively (constructive interference):

\[ n\lambda = 2d\sin\theta \quad (3.3) \]

In a crystal structure, planes are labeled by the Miller indices, which are a group of numbers that
function in quantifying the intercepts and identifying an individual plane or surface. The planes
are represented by the Miller indices as three integers, h, k, and ℓ, which are reciprocals of
fractional intercepts of the axial lengths, a, b, and c, respectively.

![Photograph of a desktop X-ray diffractometer](image-url)

**Figure 3.3.** Photograph of a desktop X-ray diffractometer.
CHAPTER 4
RESULTS

4.1 Analysis of Reactions

4.1.1 Color Change Observations

As the reactions occurred, any physical changes were recorded. These included color changes to the solution and precipitate, along with the appearance of bubbles and anything else that might be unusual or unexpected. Because two of the three reactions contained a different chloride source in aqueous solution reacting with the main metal, the outcomes of each reaction were not expected to be identical.

4.1.1.1 Reaction of Magnesium and CuCl$_2$ (with HCl)

As the magnesium was added to the CuCl$_2$, small bubbles appeared immediately and the solution’s color changed from blue to dark blue green. The bubbles soon grew bigger and emerged more quickly. Smoke rose to the surface of the solution as the color changed to dark green. Bubbling and smoke formation continued as the solution changed to light mint green. Once the HCl was added, the solution immediately turned dark olive green. An extra serving of magnesium caused more bubbles to form rapidly (some magnesium floated to the surface). When the bubbling slowed, the color had turned misty brown, then gradually to a mixture of light brown and orange. Addition of both magnesium (total of 0.750 g, or 0.0309 mol) and excess HCl caused more bubbles and steam to appear. By the end of the reaction, the solution had turned colorless and the precipitate was dark red. The solution was centrifuged in order to collect all of the precipitate. By the next day, the precipitate had air-dried and was a reddish-purple color.
mixed with blue and light brown. After two additional days, it had changed color to a mixture of bright green and aqua with some remaining reddish-purple.

This reaction did not strictly follow the single displacement reaction model; limited literature references on this reaction do not permit an easy explanation as to why elemental copper is not initially formed. It is possible that a single displacement reaction takes place, but competing side reactions occur and potential intermediates form before elemental copper forms.

**4.1.1.2 Reaction of Magnesium and CuCl\(_2\) (without HCl)**

In the absence of HCl, a reaction took place between magnesium and CuCl\(_2\). Almost immediately after the magnesium was added to a beaker containing aqueous CuCl\(_2\), small bubbles began to appear. They grew bigger and formed faster as the solution changed color from blue to dark blue green. As the bubbling continued, some magnesium rose to the surface. The solution’s color turned light green, gradually becoming lighter, almost mint cream. With additional magnesium (up to 0.750 g, or 0.0309 mol), the solution turned deep mustard yellow. By the time the reaction was finished, the major color of the precipitate was light brown with some orange (similar to the color of rusty water). As in the previous reaction, the precipitate was collected by centrifugation and air-dried for a few days. The dry precipitate was light aqua with a hint of brown.

**4.1.1.3 Reaction of Magnesium and CuCl\(_2\) (with NaCl)**

When magnesium was added to the aqueous CuCl\(_2\) solution, small bubbles formed, which appeared faster and in larger quantity as the color changed from blue to dark blue green. Smoke formed on the surface as the bubbles continued to form and the solution’s color turned light mint
green. With the addition of NaCl, a yellow color appeared briefly before the solution turned light yellow green. Additional NaCl (up to 0.320 g, or 0.00548 mol) and magnesium (up to 0.600 g, or 0.0247 mol) were added to the beaker. Bubbling and steam formation decreased and additional color changes occurred. The yellow green color turned dark olive green, then brown (similar to chocolate). The precipitate was light brown, similar to that of the previous reaction. The dry precipitate was aqua, brown, and a hint of blue.

4.2 Purification of Reaction Precipitates

4.2.1 Solvent Test Observations

Six different solvents were tested with each of the three reaction precipitates for color removal, as color removal would indicate that the solvent might be useful for recrystallization. After a few pieces of the precipitates were dissolved in distilled water, the color was removed. The water turned a lighter shade of the green color of the precipitates. CH$_3$CH$_2$OH showed very similar results, and CH$_3$COCH$_3$ extracted the color, although not as strongly as water and CH$_3$CH$_2$OH. CH$_2$Cl$_2$, C$_6$H$_{14}$, and C$_6$H$_6$ did not show any color removal from the precipitates.

Differences in color removal of the precipitates might be partially attributed to the types of the solvents that were used. Of the six different solvents used for testing, water and CH$_3$CH$_2$OH are polar protic, CH$_3$COCH$_3$ and CH$_2$Cl$_2$ are polar aprotic, and C$_6$H$_{14}$ and C$_6$H$_6$ are nonpolar. Water, CH$_3$CH$_2$OH, and CH$_3$COCH$_3$ extracted the color, while CH$_2$Cl$_2$, C$_6$H$_{14}$, and C$_6$H$_6$ did not.
4.2.2 Recrystallization of Precipitates

Since CH$_3$CH$_2$OH had proven to be more useful in color removal for the initial reaction, it was chosen as the recrystallization solvent. The solvent was heated on a hot plate, then poured into a flask with the precipitate from the initial reaction. When mixed with hot CH$_3$CH$_2$OH, the precipitate turned the solvent a light orange and brown color. After the mixture cooled to room temperature, suction filtration was performed to remove the soluble impurities from the precipitate and to collect the pure crystals. The filtrate turned lighter brown and orange, then light lime green after sitting for three hours. The filtrate was subsequently heated to evaporate the CH$_3$CH$_2$OH and put into an ice bath. The crystals turned a combination of light olive and lime green. These crystals had a mass of 0.440 g.

In the case of the precipitate of the reaction without HCl, CH$_3$CH$_2$OH was used again to recrystallize any potential product. The aqua crystals were isolated and had a mass of 0.420 g.

For the precipitate of the reaction with NaCl, CH$_3$CH$_2$OH was once again used to recrystallize the potential product. The dark olive green crystals had a mass of 0.435 g.

4.3 Characterization of Recrystallized Precipitates

4.3.1 Ultraviolet-Visible Spectroscopy Data

Using an Ocean Optics spectrophotometer, UV-Vis spectroscopy was used to characterize the solutions of the precipitates from the reactions to find the wavelength of maximum absorbance ($\lambda_{\text{max}}$). However, isolation of any intermediates as pure compounds proved challenging due to the competing side reactions and varying solubilities. The intermediates were dissolved in CH$_3$CH$_2$OH in order to collect the spectra, but did not completely dissolve. Because of these problems, the UV-Vis spectra for all three reactions do not exhibit conclusive results.
The spectrum for the reaction with HCl (Figure 4.1) gave the most inconclusive results, as it has no clear $\lambda_{\text{max}}$ value.

![Figure 4.1. UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (with HCl, recrystallized).](image1)

The spectrum of the reaction without HCl (Figure 4.2) was noisy in the absorbance at the beginning, but it displayed a reasonable $\lambda_{\text{max}}$ value of 455 nm (absorbance was 0.574).

![Figure 4.2. UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (without HCl, recrystallized).](image2)
The spectrum of the reaction with NaCl (Figure 4.3) showed a $\lambda_{\text{max}}$ value of 452 nm (1.228), which was approximately the same wavelength value for $\lambda_{\text{max}}$ in Figure 4.2.

![UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (with NaCl, recrystallized).](image)

**Figure 4.3.** UV-Vis spectrum of the magnesium and CuCl$_2$ reaction (with NaCl, recrystallized).

### 4.3.2 X-Ray Diffraction Data

Because the UV-Vis spectra did not show very conclusive results, X-ray diffraction was relied on extensively to determine the compounds present in the precipitates. The precipitates of each reaction were crushed to powders with a pestle in a mortar. These powders were leveled out in sample holders, then placed into the diffractometer for the appropriate lengths of time until the scanning processes were finished. The data were analyzed as RAW files using the computer software program MDI Jade. The diffractograms for the precipitates had a 2$\theta$ degree range from 5° to 90°. However, the diffractograms had to be offset in order for the chosen compounds to correspond directly with the peaks.

The identities of the products from the reaction of magnesium and CuCl$_2$ with HCl were unknown because it did not simply follow a single displacement reaction to form the expected products of elemental copper and MgCl$_2$. The addition of HCl and the competing side reactions
that occurred at the same time resulted in a mixture of products. The potential equation of this reaction is

\[
2\text{Mg}(s) + 2\text{Cu}((\text{H}_2\text{O})_6)^{2+} (\text{aq}) + 4\text{Cl}^- (\text{aq}) + 2\text{HCl}(\text{aq}) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Cu(OH)Cl(s)} + 2\text{MgCl}_2\cdot6\text{H}_2\text{O(s)} + 2\text{H}_2(\text{g})
\]

(belloite) (bischofite)

The oxidation state of magnesium changes from 0 to +2, while that of hydrogen changes from +1 to 0. However, the oxidation state of copper remains +2 as it converts from the formula of \(\text{Cu}((\text{H}_2\text{O})_6)^{2+}\) to \(\text{Cu(OH)Cl}\). The acidity of the reaction is due to the HCl and \(\text{Cu}((\text{H}_2\text{O})_6)^{2+}\), but occurs primarily from the HCl. This causes more competing side reactions to occur, including the direct reaction of magnesium with HCl to form \(\text{MgCl}_2\cdot6\text{H}_2\text{O}\). At the same time, the waters of hydration of \(\text{Cu}((\text{H}_2\text{O})_6)^{2+}\) can donate a proton to form hydrogen gas. As the water ligand loses the hydrogen, hydroxides form. Different copper hydroxide chlorides can form depending on how many hydrogen ions are lost.

The precipitate was scanned in the diffractometer for a time that was slightly under one hour with a count time of one second and a step width of 0.025°. The resulting XRD diffractogram (Figure 4.4) was offset by a 2θ value of 0.11°. As predicted, \(\text{MgCl}_2\cdot6\text{H}_2\text{O}\) accounted for every major peak up to 62°. \(\text{Cu(OH)Cl}\) accounted for a few of the same peaks as \(\text{MgCl}_2\cdot6\text{H}_2\text{O}\), but more so after 44°, with smaller peaks coupled with those that were obscured by noise. \(\text{MgCl}_2\cdot6\text{H}_2\text{O}\) belongs to the monoclinic system with a space group of C2/m and a density value of 1.59 g/cm³. Its unit-cell edge length values are 9.871 Å (a), 7.113 Å (b), and 6.079 Å (c), its unit cell volume is 426.82 Å³, and its Z value is 2.²⁹ \(\text{Cu(OH)Cl}\) belongs to the monoclinic system with a space group of P2₁/a and a density value of 3.75 g/cm³. Its unit-cell edge length values are 5.555 Å (a), 6.671 Å (b), and 6.127 Å (c), its unit cell volume is 227.05 Å³, and its Z value is 4.²⁹
As in the initial reaction, the identities of the products of the reaction between magnesium and CuCl$_2$ were complicated by the simultaneous competing side reactions. The potential equation for this reaction is

$$2\text{Mg}(s) + 3\text{Cu(H}_2\text{O)}_6^{2+}(aq) + 6\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{Cu}_2\text{(OH)}_3\text{Cl}(s) + \text{Cu(OH)Cl\cdot16H}_2\text{O}(s) + 2\text{MgCl}_2(aq) + 2\text{H}_2(g) \quad (4.2)$$

In this redox reaction, the oxidation state of magnesium changes from 0 to +2. Without the inclusion of an acid, the acidity of the reaction is due to Cu(H$_2$O)$_6^{2+}$. The waters of hydration help the reaction to occur and form hydrogen gas. As this happens, the oxidation state of hydrogen changes from +1 to 0.

The precipitate was scanned in the diffractometer for over nine hours with a count time of eight seconds and a step width of 0.020°. The resulting XRD diffractogram (Figure 4.5) was offset by a 2θ value of -0.07°. While Cu$_2$(OH)$_3$Cl accounted for all of the major peaks, a
different copper hydrate, Cu$_{11}$(OH)$_{14}$Cl$_8$•6H$_2$O, accounted for the same peaks and a few others.

Cu$_2$(OH)$_3$Cl belongs to the trigonal system with a space group of R$\bar{3}$ and a density value of 3.77 g/cm$^3$. Its unit-cell edge length values are 13.654 Å (a) and 14.041 Å (c), its unit cell volume is 2,266.98 Å$^3$, and its Z value is 24.$^{29}$

![Figure 4.5. XRD diffractogram of the magnesium and CuCl$_2$ reaction (without HCl, recrystallized).](image)

The identities of the solids of the reaction between magnesium and CuCl$_2$ with NaCl were also challenging to determine, due to the side reactions. As in the second reaction, this reaction included Cu(H$_2$O)$_6^{2+}$, but no addition of HCl. This meant that Cu(OH)Cl or Cu$_2$(OH)$_3$Cl could have been produced in the reaction since it included a chloride source. The precipitate was scanned in the diffractometer for over nine hours with a count time of eight seconds and a step width of 0.020°. The resulting XRD diffractogram (Figure 4.6) was offset by a 2θ value of -0.08°. However, the only compound that accounted for all of the major peaks, and many of the smaller peaks, in the diffractogram was NaCl in its mineral form of halite. This most likely
happened due to a presence of excess NaCl that was added to the reaction mixture. NaCl belongs to the cubic system with a space group of Fm\(^{3}\)m and a density value of 2.16 g/cm\(^3\). All of its unit-cell edge lengths are 5.640 Å, its unit volume is 179.41 Å\(^3\), and its Z value is 4.\(^{29}\)

![Figure 4.6. XRD diffractogram of the magnesium and CuCl\(_2\) reaction (with NaCl, recrystallized).](image)

### 4.4 General Summary of Results

Despite the inclusion of HCl, the initial reaction was a redox reaction based on the oxidation state changes that occurred as Cu(OH)Cl and MgCl\(_2\)•6H\(_2\)O formed. The same step occurred for the second reaction as Cu\(_2\)(OH)\(_3\)Cl and Cu\(_{11}\)(OH)\(_{14}\)Cl\(_8\)•6H\(_2\)O formed. For the third reaction, excess NaCl interfered and only it remained in the precipitate, so no redox reaction took place. The product revelations of the first two reactions suggest that copper hydroxide chloride compounds are intermediates that form after the CuCl\(_2\) solution within different reactions. Since Cu\(_2\)(OH)\(_3\)Cl formed without the inclusion of HCl, Cu(OH)Cl is a potential intermediate between CuCl\(_2\) and Cu\(_2\)(OH)\(_3\)Cl. Of these two compounds, a literature procedure\(^{30}\) for the synthesis of
Cu₂(OH)₃Cl was available. Cu₂(OH)₃Cl was independently synthesized, qualitative tests were performed, then it was characterized by UV-Vis and XRD. The synthesized Cu₂(OH)₃Cl was subsequently reacted with magnesium in order to determine what intermediate copper compound formed. It was originally believed that Cu₂O formed in the reaction without HCl. Cu₂O was then hypothesized to form when magnesium and Cu₂(OH)₃Cl combined. Additionally, CuCl₂ and reagent grade Cu₂O were characterized by UV-Vis to see if the three copper compounds (CuCl₂, Cu₂(OH)₃Cl, and Cu₂O) formed a similar pattern. The Cu₂O was also characterized by XRD for the same purpose. The new precipitate of the magnesium and Cu₂(OH)₃Cl reaction was then characterized by UV-Vis and XRD. However, instead of Cu₂O, elemental copper was a product from this reaction.

4.5 Characterization of CuCl₂ and Cu₂O

4.5.1 UV-Vis Spectrum of CuCl₂ Solution

The original aqueous solution of CuCl₂ had a concentration of 1.0 M, which was too concentrated to exhibit a clear $\lambda_{\text{max}}$ value in a UV-Vis spectrum. The solution was diluted with distilled water, then its resulting UV-Vis spectrum (Figure 4.7) showed a distinct $\lambda_{\text{max}}$ value of 814 nm (1.129). Because this was a pure compound in solution, the spectrum contained no noise in its appearance, especially in contrast to Figures 4.1 through 4.3.
4.5.2 UV-Vis Spectrum of Cu$_2$O

The UV-Vis spectrum of powdered Cu$_2$O (Figure 4.8) was collected by dissolving it in CH$_3$CH$_2$OH. The spectrum was fairly inconclusive since it did not display a distinct $\lambda_{\text{max}}$ value. This may have happened due to a solubility problem of the Cu$_2$O in the CH$_3$CH$_2$OH.

Figure 4.7. UV-Vis spectrum of the diluted CuCl$_2$ solution.

Figure 4.8. UV-Vis spectrum of the diluted, powdered Cu$_2$O.
4.5.3 XRD Diffractogram of Cu₂O

The powdered Cu₂O was scanned in the diffractometer for less than one hour with a count time of one second and a step width of 0.025°. The resulting XRD diffractogram (Figure 4.9) was offset by a 2θ value of 0.715°. Seven visible peaks were revealed with positions that were easily identified; Cu₂O accounted for all of these peaks. Cu₂O belongs to the cubic system with a space group of Pn̅3m and a density value of 6.11 g/cm³. All of its unit-cell edge lengths are 4.270 Å, its unit cell volume is 77.85 Å³, and its Z value is 2.

![Figure 4.9. XRD diffractogram of the powdered Cu₂O.](image-url)
4.6 Paratacamite

4.6.1 Synthesis of \( \text{Cu}_2(\text{OH})_3\text{Cl} \)

Following the instructions of Brigandi et al.,\(^\text{30}\) a 0.50 \( M \) solution of \( \text{CuCl}_2\cdot2\text{H}_2\text{O} \) was prepared from 4.37 g (0.0256 mol) dissolved in distilled water. This solution was then diluted to 50.0 mL in a graduated cylinder. Afterwards, the solution was transferred to a beaker. Next, a 0.50 \( M \) \( \text{NaOH} \) solution was prepared from 2.06 g (0.0515 mol) dissolved in distilled water, which was then diluted to 100.0 mL in a second graduated cylinder. This solution was also transferred from the cylinder to a second beaker. In 5-mL aliquots by pipette, the NaOH was added to the \( \text{CuCl}_2\cdot2\text{H}_2\text{O} \), which was now cerulean blue. Adding NaOH briefly and stirring the mixture turned it lighter blue with a hint of green. By the time the pH reached 9, the solution was medium and navy blue; it had also thickened. It was heated on a hot plate for half an hour. After cooling for one hour, the precipitate was collected via suction filtration. This precipitate air-dried for an hour before being heated at 120°C for another hour, after which it was a mixture of dark blue and dark green. When the precipitate was completely dried to a solid state, it had a mass of 2.21 g and was dark bluish-green.

4.6.2 Qualitative Tests on \( \text{Cu}_2(\text{OH})_3\text{Cl} \)

Qualitative tests were performed on \( \text{Cu}_2(\text{OH})_3\text{Cl} \) to confirm its synthesis. The first of these was identifying copper by the complex ion that it forms with \( \text{NH}_3 \), as shown in the equation

\[
\text{Cu}^{2+}_{(aq)} + 4\text{NH}_3_{(l)} \rightarrow \text{Cu(NH}_3)_4^{2+}_{(aq)} \quad (4.3)
\]

The presence of the copper ion was shown by an addition of 6.0 \( M \) \( \text{NH}_3 \) to a small sample of \( \text{Cu}_2(\text{OH})_3\text{Cl} \), resulting in a dark blue solution.\(^\text{30}\)
The second qualitative test identified the hydroxide ion by infrared (IR) spectroscopy, in which the spectrum displayed a broad OH peak located between 3444.64 and 3329.65 cm\(^{-1}\). The literature range for the ion is between 3100 and 3300 cm\(^{-1}\).\(^{30}\)

The third and final qualitative test was the confirmation of the chloride ion by precipitation of silver chloride (AgCl) with AgNO\(_3\):

\[
\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \rightarrow \text{AgCl}_{(s)} \quad (4.4)
\]

A small sample of Cu\(_2\)(OH)\(_3\)Cl was dissolved in HNO\(_3\). The AgNO\(_3\) solution was added to this mixture afterwards. The presence of the chloride ion was recognized by the observation of a white precipitate.\(^{30}\)

Quantitative analyses of the Cu\(_2\)(OH)\(_3\)Cl, specifically finding the percent by masses of the copper and chloride ions, were performed by different procedures. The dark blue color of the copper ammonia complex was analyzed by spectrophotometry. The experimentally determined percent by mass of copper was 75.3\% (theoretical is 59.51\%). Gravimetric analysis determined the percent by mass of the chloride ion as 18.1\% (theoretical is 16.60\%). The calculations for the copper ion are located in Appendix 1, while those for the chloride ion are found in Appendix 2.

### 4.6.2.1 Presence of Copper

#### 4.6.2.1.1 Solutions of CuSO\(_4\)•5H\(_2\)O

The first part of this test involved the creation of a standard curve. First, 0.708 g (0.00284 mol) of CuSO\(_4\)•5H\(_2\)O was dissolved in distilled water and diluted to 100.00 mL in a volumetric flask.\(^{30}\) This resulted in the solution with a concentration of 0.0284 \(M\). Using a graduated cylinder, 60.0 mL of this solution were measured out and diluted to 100.00 mL in a second volumetric flask. This dilution process was repeated to make three additional solutions;
the concentrations of the subsequent four solutions were 0.0170 M, 0.0102 M, 0.00612 M, and 0.00367 M. A small sample of each solution was mixed with an excess amount of 6.0 M NH₃, then placed into a cuvette and spectrophotometer to determine their absorbance values at 650 nm ($\lambda_{\text{max}}$). The addition of NH₃ produced a dark blue color as expected; it appeared in all of the solution samples and gradually lightened with each dilution. The absorbance values of the five solutions at this wavelength (from the first to the last solution) were found to be 0.670, 0.340, 0.183, 0.0492, and 0.0113. After the five absorbance values were collected, a Beer’s Law plot (absorbance vs. concentration) was created (Figure 4.10). The line of best fit was determined including the origin (0, 0). The line of best fit, $y = (m)x + b$, corresponds to the Beer-Lambert Law (as shown in equation 3.2), where the slope, m, is equal to $\varepsilon l$. The line of best fit equation was $y = 24.831x - 0.0617$, so the value of $\varepsilon l$ was 24.831 L mol⁻¹ cm⁻¹.

![Absorbance vs. Concentration of CuSO₄•5H₂O Solutions](image)

**Figure 4.10.** Absorbance vs. concentration calibration curve of five standard solutions of CuSO₄•5H₂O with (0, 0) point.

### 4.6.2.1.2 Solution of Cu₂(OH)₃Cl

A 0.108 g sample of Cu₂(OH)₃Cl was dissolved in 6.0 M NH₃.³⁰ The addition of NH₃ produced a dark blue color, indicating that copper was present. The solution was subsequently
diluted to 100.00 mL with distilled water in a volumetric flask. When some of the solution was placed into a cuvette and into the spectrophotometer, the resulting UV-Vis spectrum (Figure 4.11) showed an absorbance of 0.255 at 650 nm. Using the equation of best fit from the Beer’s Law plot, the concentration of copper for the Cu₂(OH)₃Cl solution was found to be 0.0128 M. This molarity is equivalent to 0.0813 g of copper, resulting in 75.3% copper ion by mass, which is much larger than the theoretical percent copper in Cu₂(OH)₃Cl (59.51%). The percent error value between these two values was 26.5%. The spectrum for the Cu₂(OH)₃Cl solution was cleaner than those Figures 4.1 through 4.3 since the Cu₂(OH)₃Cl was synthesized by Brigandi et al. However, the calculated values may have been larger than expected because the Cu₂(OH)₃Cl may not have been pure and contained some of the other expected product of NaCl (Equation 4.5).

![Figure 4.11. UV-Vis spectrum of the solution of Cu₂(OH)₃Cl.](image)

A defect with the cuvettes used for the blanks could account for the absorbance spectra that appeared to be truncated (Figures 4.7 and 4.11). In this study, general-purpose, inexpensive, plastic cuvettes were used rather than research quality, quartz cuvettes. If the blank cuvette
resulted in a higher absorbance reading (e.g., due to a cloudy surface) than the one used for the test solution, the entire absorbance spectrum would be shifted down. Since one minor goal of the study is to determine if this type of redox experiment could be used in an undergraduate inorganic laboratory, the student cuvettes were used. This also applied for all of the standard test solutions of CuSO₄•5H₂O. As a result, the calibration curve of these five solutions did not result in a line of best fit that went straight through the origin, so the (0, 0) point was included.

4.6.2.2 Presence of Hydroxide Ion

A very small amount, approximately ¼, of Cu₂(OH)₃Cl was placed in the center of the spectrophotometer’s stage, covering its crystal. The piston head was then swiveled so that the pin was located over the crystal and Cu₂(OH)₃Cl, then the knob was tightened. In the resulting IR spectrum (Figure 4.12), the most distinct peaks were located at 3444.64 and 3329.65 cm⁻¹ and had intensities of 84.25% and 78.44%, respectively. Although there was not a single, very broad peak between 3100 and 3300 cm⁻¹ as predicted, the given wavenumbers in the spectrum were still close enough to literature values to indicate the presence of the hydroxide ion.

![IR spectrum of the synthesized Cu₂(OH)₃Cl.](image-url)
4.6.2.3 Presence of Chloride

Approximately 20.0 mL of 6.0 \( M \) HNO\(_3\) were measured out in a graduated cylinder before being transferred to a beaker. While in the beaker, the HNO\(_3\) dissolved 0.103 g of Cu\(_2\)(OH)\(_3\)Cl and turned pale blue. When 6 mL of 0.10 \( M \) AgNO\(_3\) were added by pipette, the solution turned smoky blue. The beaker was subsequently covered with a watch glass as it was heated on a hot plate for half an hour. It was then covered and placed in a dark, closed hood for one hour. The precipitate in the beaker was a mixture of light blue and light purple. One drop of AgNO\(_3\) did not show any immediate formation of any additional precipitate. Additional drops of AgNO\(_3\) were added, then the solution was briefly reheated to ensure complete precipitation. The precipitate was collected via suction filtration and put into a pre-weighed crucible. The crucible and contents were heated at 120°C for two hours. The precipitate, which was now light purple, had a mass of 0.0750 g, resulting in 18.1% chloride by mass. This is close to the theoretical percent chloride in Cu\(_2\)(OH)\(_3\)Cl, which is 16.60% (percent error was 9.04%).

4.7 Characterization of Cu\(_2\)(OH)\(_3\)Cl

4.7.1 UV-Vis Spectrum of Cu\(_2\)(OH)\(_3\)Cl

The UV-Vis spectrum of Cu\(_2\)(OH)\(_3\)Cl (Figure 4.13) was measured in CH\(_3\)CH\(_2\)OH solution. Though the spectrum was noisy in the beginning, it presented a \( \lambda_{\text{max}} \) value of 620 nm (0.123). The spectrum also had a much cleaner appearance than those of Figures 4.1 through 4.3, due to the specific synthesis of Cu\(_2\)(OH)\(_3\)Cl from its literature procedure.
4.7.2 XRD Diffractogram of Cu$_2$(OH)$_3$Cl

Differing from the three main reactions, Cu$_2$(OH)$_3$Cl was synthesized from specific masses of CuCl$_2$•2H$_2$O and NaOH and other detailed instructions from its literature procedure. It was expected to be the major product in the overall equation for its reaction:

\[
2\text{CuCl}_2\cdot2\text{H}_2\text{O}_{(aq)} + 3\text{NaOH}_{(aq)} \rightarrow \text{Cu}_2(\text{OH})_3\text{Cl}_{(s)} + 3\text{NaCl}_{(s)} + 4\text{H}_2\text{O}_{(l)}
\]

(paratacamite) (halite) (4.5)

Unlike the first three reactions, the synthesis of Cu$_2$(OH)$_3$Cl is not a redox reaction because all oxidation states in the reactants remain the same as they convert to the products. For example, the oxidation state of copper remains +2 as it converts from CuCl$_2$•2H$_2$O to Cu$_2$(OH)$_3$Cl.

The Cu$_2$(OH)$_3$Cl was scanned in the diffractometer for over nine hours with a count time of eight seconds and a step width of 0.020°. The resulting XRD diffractogram (Figure 4.14) was offset by a 2θ value of -0.06°. The presence of Cu$_2$(OH)$_3$Cl accounted for many of the strong peaks. NaCl accounted for a few of the other strong peaks, along with many of the smaller ones.
4.8 Reaction of Magnesium and Cu$_2$(OH)$_3$Cl

4.8.1 Observations of Reaction

Magnesium was reacted with Cu$_2$(OH)$_3$Cl to what copper compound would form. First, a 0.50 M solution of Cu$_2$(OH)$_3$Cl was made by dissolving 1.61 g (0.00750 mol) in 15.0 mL (0.0150 L) of HCl. Cu$_2$(OH)$_3$Cl is insoluble in water and organic solvents, but soluble in most acids. When the Cu$_2$(OH)$_3$Cl was placed into the HCl, the solution turned dark olive green mixed with dark yellow green. Almost immediately after adding the magnesium (1.02 g, or 0.0418 mol), the solution had a great deal of bubbles and steam that rose up and appeared very quickly. This was due to the acidity of the solution reacting with the magnesium. An additional amount of magnesium (0.543 g, or 0.0223 mol) was added to the beaker, but the bubbling had greatly diminished since the start of the reaction. When no additional reaction was evident, the dark red precipitate (with some leftover magnesium) was collected and air-dried. The following day, the precipitate was dark red with hints of white. Gradually, the precipitate turned green, as
with the synthesized Cu$_2$(OH)$_3$Cl, but it still had some red. The initial red color of this precipitate was a first possible suggestion that Cu$_2$O was present; it compared fairly well in color with the reagent grade Cu$_2$O.

4.9 Characterization of Reaction Precipitate

4.9.1 UV-Vis Spectrum of Precipitate

The UV-Vis spectrum of the precipitate (Figure 4.15) was measured in CH$_3$CH$_2$OH and displayed a $\lambda_{\text{max}}$ value of 466 nm (0.454). Like Figures 4.1 through 4.3 (for the first three reactions), the appearance of the spectrum was slightly noisy since the precipitate was not a pure sample.

![Figure 4.15. UV-Vis spectrum of the magnesium and Cu$_2$(OH)$_3$Cl reaction.](image)

4.9.2 XRD Diffractogram of Precipitate

The identities of the compounds in the precipitate from the magnesium and Cu$_2$(OH)$_3$Cl reaction were unknown, as in the first three reactions. The solid was scanned in the diffractometer for over nine hours with a count time of eight seconds and a step width of 0.020°.
The resulting XRD diffractogram (Figure 4.16), which was offset by a 2θ value of -0.08°, showed some unexpected results. Elemental copper accounted for the three tallest peaks, while Mg₂(OH)₃Cl•4H₂O accounted for all of the smaller peaks. To explain these products, the equation for this reaction is

\[
2\text{Mg}(s) + \text{Cu}_2(\text{OH})_3\text{Cl}(_{\text{aq}}) + 4\text{H}_2\text{O}(l) \rightarrow \text{Mg}_2(\text{OH})_3\text{Cl}•4\text{H}_2\text{O}(s) + 2\text{Cu}(s)
\] (4.6)

Like the first and second reactions, this is a redox reaction because the oxidation state of magnesium changes from 0 to +2. Unlike the other reactions, though, the oxidation state of copper finally changes, from +2 to 0, as it converts from Cu₂(OH)₃Cl to Cu. Copper belongs to the cubic system with a space group of Fm\text{3}m and a density value of 8.93 g/cm³. All of its unit-cell edge lengths are 3.615 Å, its unit cell volume is 47.24 Å³, and its Z value is 4.²⁹

**Figure 4.16.** XRD diffractogram of the magnesium and Cu₂(OH)₃Cl reaction.
CHAPTER 5

CONCLUSIONS AND DISCUSSIONS

5.1 Summary and Conclusions

The reaction of magnesium and CuCl₂ was expected to be a single displacement redox reaction. The copper in CuCl₂ would be replaced with magnesium; the predicted products would be MgCl₂ and elemental copper. However, the reaction was discovered to be more complicated as it proceeds through a series of steps. While the reaction did exhibit redox, the Cu(H₂O)₆²⁺ present in the solution, along with the addition of HCl, prevented the predicted single displacement reaction, in which elemental copper is a product, from happening. The reduction potential value of Cu²⁺ is smaller than that of Cu⁺, so Cu⁺ is the stronger oxidizing agent. The natures of these ions are different in comparison to those of most other transition metals. This difference of Cu²⁺ may be another explanation as to why CuCl₂ does not undergo the single displacement reaction when it reacts with magnesium metal.

The intermediates of all three different versions of this reaction were different colors; the one from the initial reaction (with HCl) was bright green and reddish purple, while the ones from the second (no HCl) and third reactions (with NaCl) were light aqua with some brown. The intermediates were recrystallized using CH₃CH₂OH, after which the crystals were olive or lime green. Only Figures 4.2 and 4.3 showed distinct λ_max values. Figure 4.4 shows MgCl₂•6H₂O and Cu(OH)Cl, which are the results of a redox reaction. Similarly, Figure 4.5 shows Cu₂(OH)₃Cl and Cu₁₁(OH)₁₄Cl₈•6H₂O, which are also results from a redox reaction. The third reaction used excess NaCl, the presence of which overshadowed any potential reactions, as shown in Figure 4.6.
The copper hydroxide chloride compounds, Cu(OH)Cl and Cu$_2$(OH)$_3$Cl, were hypothesized to be intermediates in the reaction after the CuCl$_2$ solution. Figure 2.2 shows the different oxidation states of copper compounds in a chloride solution. One of these compounds is Cu$_2$(OH)$_3$Cl, which has a pH of 7 and an $E^0_{\text{red}}$ value of +0.70 V. Cu$_2$(OH)$_3$Cl was synthesized by literature methods$^{30}$ and was qualitatively and quantitatively characterized. The Cu$_2$(OH)$_3$Cl was also made into a solution, reacted with magnesium, and characterized by UV-Vis and XRD to see if it resulted in any Cu$_2$O, which was suspected to be the next copper intermediate. The CuCl$_2$ solution and authentic Cu$_2$O were both characterized by UV-Vis, and the Cu$_2$O by XRD, to see if they formed a similar pattern between each other and Cu$_2$(OH)$_3$Cl. Figure 4.16 showed that elemental copper formed from the magnesium and Cu$_2$(OH)$_3$Cl reaction, rather than Cu$_2$O.

5.2 Future Research Directions

The reaction of magnesium and CuCl$_2$ is not a single displacement reaction. However, as presented above, it does exhibit redox behavior when it forms Cu(OH)Cl from the inclusion of HCl, as well as when it forms Cu$_2$(OH)$_3$Cl in absence of HCl. Cu$_2$(OH)$_3$Cl has been shown to be an intermediate between the solution of CuCl$_2$ and elemental copper. A logical next step in future research for this project would be finding a literature procedure for Cu(OH)Cl, followed by its synthesis, purification, and complete characterization. The Cu(OH)Cl would be further tested by reacting it with magnesium to see if it could be a true intermediate between CuCl$_2$ and Cu$_2$(OH)$_3$Cl. Another important step could include isolating and purifying the intermediate of the main reaction. Doing this could make the intermediate more available to react with magnesium in order to determine what other copper intermediates might form.
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APPENDICES

Appendix 1 Calculation of % Copper by Mass in \( \text{Cu}_2(\text{OH})_3\text{Cl} \)

\[
0.708 \text{gCuSO}_4 \cdot 5\text{H}_2\text{O} \left( \frac{1\text{molCuSO}_4 \cdot 5\text{H}_2\text{O}}{249.71\text{gCuSO}_4 \cdot 5\text{H}_2\text{O}} \right) = \frac{0.00284\text{mol}}{0.100\text{L}} = 0.0284M \text{ (Solution #1)}
\]

\[
(0.0284M)(60.0\text{mL}) = M_2(100.00\text{mL})
\]

\[
M_2 = 0.0170M \text{ (Solution #2)}
\]

\[
(0.0170M)(60.0\text{mL}) = M_2(100.00\text{mL})
\]

\[
M_2 = 0.0102M \text{ (Solution #3)}
\]

\[
(0.0102M)(60.0\text{mL}) = M_2(100.00\text{mL})
\]

\[
M_2 = 0.00612M \text{ (Solution #4)}
\]

\[
(0.00612M)(60.0\text{mL}) = M_2(100.00\text{mL})
\]

\[
M_2 = 0.00367M \text{ (Solution #5)}
\]

Absorbance of Paratacamite at 650 nm: 0.255

\[
0.255 = 24.831x - 0.0617
\]

\[
0.317 = 24.831x
\]

\[
x = 0.0128M
\]

\[
0.0128M(0.100\text{L}) = 0.00128\text{ mol Cu}
\]

\[
0.00128\text{molCu} \left( \frac{63.55\text{gCu}}{1\text{molCu}} \right) = 0.0813\text{gCu}
\]

\[
\% Cu = \left( \frac{0.0813\text{gCu}}{0.108\text{gCu}_2(\text{OH})_3\text{Cl}} \right) \times 100\% = 75.3\%
\]

\[
\% Cu = \left( \frac{127.1\text{gCu}}{213.58\text{gCu}_2(\text{OH})_3\text{Cl}} \right) \times 100\% = 59.51\%
\]

\[
\% error = \left| \frac{75.3\% - 59.51\%}{59.51\%} \right| \times 100\% = 26.5\%
\]
Appendix 2 Calculation of % Chloride by Mass in Cu₂(OH)₃Cl

\[
0.0750 \text{g AgCl} \left( \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \right) \left( \frac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} \right) \left( \frac{35.45 \text{ g Cl}}{1 \text{ mol Cl}} \right) = 0.0186 \text{ g Cl}
\]

\[
\% \text{ Cl} = \left( \frac{0.0186 \text{ g Cu}}{0.103 \text{ g Cu}_2(\text{OH})_3\text{Cl}} \right) \times 100\% = 18.1\%
\]

\[
\% \text{ Cu} = \left( \frac{35.45 \text{ g Cl}}{213.58 \text{ g Cu}_2(\text{OH})_3\text{Cl}} \right) \times 100\% = 16.60\%
\]

\[
\% \text{ error} = \left( \left| \frac{18.1\% - 16.60\%}{16.60\%} \right| \times 100\% \right) = 9.04\%
\]