Copper Dissolution in Concentrated Sulfuric Acid

A. Sulcius*, E. Griskonis, N. Zmuidzinaviiciene

Kaunas University of Technology, Lithuania

*Corresponding author: algirdas.sulcius@ktu.lt

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Abstract When redox reactions are studied in the chemistry course, focus is limited to the use of a series of metal activity, electron or electron-ion balance method, and writing of the reaction equations. Students find the redox reactions that occur during the dissolution of metals in acids difficult. Motivated students should be able to solve four problems while studying redox reactions: 1) indicate oxidizing agent and reducing agent; 2) write correct products forming and balance the redox reaction; 3) calculate the electromotive force $E^0$ of the redox reaction; 4) indicate the thermodynamic possibility of the occurrence of redox reaction by calculating Gibbs energy $\Delta G^\circ$. The proposed improved methodology for studying the reactions of dissolution of metals in acids allows students to systematize and expand knowledge about redox reactions in inorganic chemistry. To improve the assimilation of knowledge about the dissolution of copper in sulfuric acid, mnemonic scheme has been proposed that makes it possible to understand better composition of the products. Copper reacted with concentrated sulfuric acid only when heated and precipitation of black deposit was observed. The amount of black deposit in the acid and on the surface of copper depended on the method and intensity of heating: heating with interruptions or intensive continuous heating. It has been determined, that during copper dissolution in concentrated 96% sulfuric acid two reactions take place (the main and the parallel) and precipitation of black deposit, consisting mainly of Cu$_2$S and a small amount of Cu$_2$O, is observed.

Keywords: high school/introductory chemistry, inorganic chemistry, mnemonics/rote learning, metals, oxidation/reduction, reactions


1. Introduction

Since mineral or inorganic acids (sulfuric H$_2$SO$_4$ and nitric HNO$_3$) are the most frequently used chemicals in research and industry, one of the most important issues is the interaction of metals with solutions of strong acids. Students have serious difficulties when studying different chemistry sections, especially the one related to redox reactions. Students find the redox reactions that occur during the dissolution of metals in sulfuric acid, and especially in nitric acid, difficult.

In the 19th century, Mendeleev wrote, “No equation expresses everything that, in fact, takes place under the action of metals on nitric acid, since always several oxides of nitrogen are formed together or sequentially one after another, depending on the acid strength and temperature.” [1]. It is known, that during dissolution of metals in nitric acid, different gaseous products such as N$_2$O, N$_2$, NO, NO$_2$, NH$_3$ [2], and H$_2$ [3] are formed. It has been also proven that dissolution rate of copper Cu in nitric acid is not controlled entirely by rate of chemical reaction and that it is affected by degree of agitation [4]. Recently, using Fourier transform infrared spectroscopy it has been demonstrated that NO$_2$, N$_2$O$_4$ and NO are the dominant gas phase products of the copper reactions in concentrated and dilute nitric acid, respectively [5].

Many problems involving writing redox reaction equations are solved by memorizing responses or reaction algorithms. However, a person cannot remember everything and does not need to. In order to facilitate and improve learning, different methods such as algorithms [6,7] and mnemonic schemes [8,9] are used. It has been found that visual algorithmic or mnemonic schemes used in studying facilitate the training of teachers and increase the uptake of knowledge and skills of the students.

Chemistry is an experimental science by its nature, therefore in order to consolidate theoretical knowledge students should carry out experimental work in laboratories. Although the use of laboratory works is a rare phenomenon [10], it is known that inquiry based education (IBE) significantly increases the uptake of knowledge and skills [11]. However, Fortus et al. [12] have found that majority of students follow only the instructions for laboratory experiments, what does not encourage students' creativity and critical thinking [13,14].

Copper and its alloys, as well as zinc and it alloys due its protection from corrosion, are the most applicable materials used in industry due to their high electrical conductivity, mechanical workability, relatively noble properties, and good availability. There are many experiments for zinc and copper reactions in dilute sulfuric acid [15-19]. In the textbooks, dissolution of
copper in concentrated sulfuric acid is expressed by a typical reaction equation [20,21]:

\[
Cu(s) + 2H_2SO_4(\text{conc.}) \xrightarrow{\Delta} CuSO_4(aq) + SO_2(g) + 2H_2O(l)
\]  

While reviewing scientific literature, it has been found that besides reaction 1 a number of other parallel reactions take place when copper dissolves in concentrated sulfuric acid. The copper surface becomes passive because Cu$_2$O, CuO, CuS, CuS and CuSO$_4$ deposits form on the copper metal surface:

\[
4Cu(s) + 4H_2SO_4(\text{conc.}) \xrightarrow{\Delta} 3CuSO_4(aq) + CuS(s) + 4H_2O(l)
\]  

\[
5Cu(s) + 4H_2SO_4(\text{conc.}) \xrightarrow{\Delta} 3CuSO_4(aq) + Cu_2S(s) + 4H_2O(l)
\]  

\[
Cu(s) + 2H_2SO_4(\text{conc.}) \rightarrow CuSO_4(s) + SO_2(g) + 2H_2O(l)
\]  

92%  

\[
2Cu(s) + 2H_2SO_4(\text{conc., cold}) \rightarrow CuO(s) + SO_2(g) + H_2O(l)
\]  

\[
2Cu(s) + H_2SO_4(\text{anhydrous, 200 °C}) \rightarrow Cu_2SO_4(s) + SO_2(g) + 2H_2O(l)
\]  

\[
2Cu(s) + H_2SO_4(\text{conc., cold}) \rightarrow Cu_2O(s) + SO_2(g) + H_2O(l)
\]  

It has been noted that along with reaction 1, the formation of black Cu$_2$S deposit (reaction 3) occurs. The rate of this reaction is maximal at 100°C. While increasing temperature, the process rate decreases, and stops above 270 °C [28]. It has been stated that reaction 4 takes place in 92−96% sulfuric acid and the light grey crystals of CuSO$_4$(s) are formed. When concentration of sulfuric acid is higher than 96%, a large amount of black CuO(s) deposit (reaction 5) along with the light grey crystals of CuSO$_4$(s) [28] are formed. The copper ionization mechanism during anodic dissolution in concentrated sulfuric acid is represented in the scheme [29]:

\[
\begin{align*}
\text{Disproportional} & \quad + O_2 \\
Cu + H_2O & \xrightarrow{e, H^+} Cu_2O + H_2O \\
\text{Disproportional (dilute H}_2SO_4) & \quad + H_2SO_4
\end{align*}
\]

The goal of our research is to study thoroughly the copper dissolution reaction in concentrated sulfuric acid and provide students with auxiliary material for a deeper understanding of redox reactions occurring when metals dissolve in strong acids.

**EXPERIMENTAL**

In the experiments, sulphuric acid (H$_2$SO$_4$, Eurochemicals, 96 wt. %, analytic grade), nitric acid (HNO$_3$, Penta, 65 wt. %, analytic grade), Prussian blue (K$_4$[Fe(CN)$_6$], Sigma-Aldrich, 99 wt. % purity), barium chloride (BaCl$_2$, Sigma-Aldrich, 99 wt. % purity) and copper(II) oxide powder (CuO, Reachim, 99 wt. % purity) were used. The morphology and detailed elemental analysis of the surface of deposits were investigated using a scanning electron microscope Hitachi S-3400N (SEM) with an energy dispersive X-ray (EDX) spectral analyzer Bruker Quad 5040 EDS.

**HAZARDS**

Contact of H$_2$SO$_4$ and HNO$_3$ with your skin or your eyes should be avoided! During all experiments with these acids protective equipment (lab coat, rubber gloves, eyeglasses, fume hood) should be used! Students should work under close supervision when handling strong acids. In the case of contact with these acids, the contact area should be rinsed with plenty of water and medical care should be sought. Since barium chloride BaCl$_2$ is highly toxic and harmful, sodium sulphate Na$_2$SO$_4$ could be used as antidotes because it forms barium sulfate BaSO$_4$, which is relatively non-toxic due to its very low solubility.

The chemicals should be disposed of according to state and local environmental regulations. Solutions should be collected in separate waste containers, disposed of according to EPA standards.

**2. Results and Discussion**

![Figure 1](image1.png)

Figure 1. Black deposit on the surface of copper, which was formed during copper dissolution in concentrated sulfuric acid

Copper reacted with concentrated sulfuric acid only when heated and precipitation of black deposit was observed (Figure 1). The amount of black deposit in the acid and on the surface of copper depended on the method and intensity of heating: heating with interruptions or intensive continuous heating. When heating sulfuric acid with interruptions, a large amount of black deposit was formed in the acid and on the surface of copper. After precipitation of black deposit, the acid solution was
colorless and transparent, anhydrous copper sulphate is formed because concentrated sulfuric acid is the dryer [30]. After dilution colourless and transparent solution became blue forming CuSO\textsubscript{4}\textcdot5H\textsubscript{2}O. In the case of intensive continuous heating, black deposit was formed initially in the acid and on the copper surface, the amount of which in the acid and on the surface of copper decreased with further heating, until it disappeared in the acid and only small amount remained on the copper surface. Then solution turned blue. To avoid the influence of ions SO\textsubscript{4}\textsuperscript{2-}, the black deposit on the surface of the copper plate or wire was washed thoroughly with distilled water, kept in distilled water for 6 hours, dried, and analyzed by SEM and XRD methods (Figure 2 and Figure 3).

The results XRD have shown that mainly Cu\textsubscript{2}S prevail in deposit as well as small amount of Cu\textsubscript{2}O (Figure 4). The results of EDX have also confirmed that the amount of sulfur is 3.65 times higher than that of oxygen (20.62 and 5.65 at. %, respectively). Low O concentration in deposit may be due to the fact that most of the resulting Cu\textsubscript{2}O dissolves when the concentrated sulfuric acid is heated:

\[
\text{Cu}_2\text{O}(s) + 3\text{H}_2\text{SO}_4(\ell) \rightarrow \text{2CuSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell) \tag{29}
\]

Based on the experimental data, the copper dissolution reaction in concentrated sulfuric acid could be represented by the scheme:

![Figure 2. EDX spectra (a), elemental composition (b) and SEM image (c) of mechanically scrubbed copper surface](image-url)
**Figure 3.** EDX spectra (a), elemental composition (b), SEM image (c) and elemental mapping (d) of deposits on the surface of copper, exposed in concentrated H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Element</th>
<th>C norm [wt. %]</th>
<th>C atom.[at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>1.68</td>
<td>5.65</td>
</tr>
<tr>
<td>Sulfur</td>
<td>12.27</td>
<td>20.62</td>
</tr>
<tr>
<td>Copper</td>
<td>85.41</td>
<td>72.45</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.64</td>
<td>1.28</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

**Figure 4.** X-ray diffraction patterns of copper and deposit, formed on the surface of copper, exposed in concentrated H$_2$SO$_4$. 
As shown above, when copper dissolves in concentrated 96% sulfuric acid, three reactions could take place: the main one and two side or parallel reactions. Therefore, when students are solving the problem of redox reaction, which takes place during copper dissolution in concentrated sulfuric acid, they could be offered to use Table 1.

Table 1. Unbalanced reactions, which take place during Cu dissolution reaction in concentrated 96% sulfuric acid

<table>
<thead>
<tr>
<th>The main reaction</th>
<th>Side or parallel reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(s) + H2SO4(l) → CuSO4(aq) + SO2(g) + H2O(l)</td>
<td>Cu(s) + H2SO4(l) → CuSO4(aq) + Cu2S(s) + H2O(l)</td>
</tr>
<tr>
<td>Cu(s) + H2SO4(l) → CuSO4(aq) + SO2(g) + H2O(l)</td>
<td>Cu(s) + H2SO4(l) → Cu2O(s) + SO2(g) + H2O(l)</td>
</tr>
</tbody>
</table>

For detection of all possible reaction products (CuS, Cu2S, Cu2O, Cu2+ and SO42- ions, SO2 gas) simple chemical analyses were used, which was described by students in detail (see visual materials of students experiments in Supplementary material).

3. Conclusion

As a long-time experience of the work at the university has shown, students do not always notice various reaction features during chemical experiments. This study aims at teaching to observe the products of copper dissolution reaction in concentrated sulfuric acid. It has been determined, that during copper dissolution in concentrated 96% sulfuric acid two reactions take place (the main and the parallel) and precipitation of black deposit, consisting mainly of Cu2S and a small amount of Cu2O, is observed.

To improve the assimilation of knowledge about the dissolution of copper in sulfuric acid, mnemonic scheme has been proposed that makes it possible to understand better composition of the products.

References


Supplementary Material

Visual materials of students’ experiments

Detection of ions Cu²⁺(aq) in solution

Since solution obtained by dissolving copper in concentrated acid is strongly acidic, a small portion of it is diluted with distilled water until pH = 5-6. Addition of K₄[Fe(CN)₆](aq) to the dilute slightly acidic solution causes precipitation of red-brown sediments:

\[ 2\text{Cu}^{2+}(aq) + [\text{Fe(CN)}_6]^{4-}(aq) \rightarrow \text{Cu}_2[\text{Fe(CN)}_6](s) \text{ brown-red} \]

Detection of SO₂(g)

Into two test tubes aqueous solutions are poured: into first – 1% Ca(OH)₂(aq), into second – KMnO₄(aq).

When white gas of a pungent smell is passed through an aqueous solution of 1% Ca(OH)₂(aq), white sediments precipitate:

\[ \text{SO}_2(g) + \text{Ca(OH)}_2(aq) \rightarrow \text{CaSO}_3(s) + \text{H}_2\text{O(l)} \text{ white} \]

When white gas of a pungent odor is passed through an aqueous solution of KMnO₄(aq), the crimson color of the solution disappears.
Detection composition of black deposits

To avoid the influence of ions $\text{SO}_4^{2-}$, the black deposit on the surface of copper plate or wire is thoroughly washed with distilled water and kept in distilled water for 6 hours. It is hypothesized that the black deposit consists of copper sulfides ($\text{Cu}_2\text{S}$ and $\text{CuS}$) and/or $\text{CuO}$. However, it has been observed that $\text{CuO}$ powder dissolves in dilute sulphuric acid:

\[
\text{CuO(s) + H}_2\text{SO}_4(\text{aq}) \xrightarrow{\Delta} \text{CuSO}_4(\text{aq}) + \text{H}_2\text{O(1)}
\]

Since the black deposit on copper does not dissolve in concentrated sulphuric acid and hydrochloric acid, it is supposed that the black precipitate consists of copper sulphides ($\text{Cu}_2\text{S}$ and $\text{CuS}$). When copper sulphides dissolve in nitric acid, $\text{S}^{2-}$ and $\text{Cu}^{+}$ ions can act as reducing agents:

\[
\begin{align*}
\text{Cu}_2\text{S(s) + 12HNO}_3(l) & \rightarrow \text{CuSO}_4(\text{aq}) + \text{Cu(NO}_3)_2(\text{aq}) + 10\text{NO}_2(g) + 6\text{H}_2\text{O(l)} \\
\text{CuS(s) + 8HNO}_3(l) & \rightarrow \text{CuSO}_4(\text{aq}) + 8\text{NO}_2(g) + 4\text{H}_2\text{O(l)}
\end{align*}
\]

The dissolution of the black deposit and copper in concentrated nitric acid: during the first 20 seconds, black deposit on copper dissolves in nitric acid and $\text{NO}_2$ gas evolution is insignificant. After 20 seconds, intensive $\text{NO}_2$ gas evolution is observed because copper starts to dissolve: $\text{NO}_2$ fills the test-tube with red-brown colour. The colourless liquid becomes green due to formation of complexes of hydrated copper(II) ions with nitrate ions:

\[
\text{Cu(s) + 4H}^+(\text{aq}) + 4\text{NO}_3^-(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow [\text{Cu(H}_2\text{O})_4(\text{NO}_3)_2](\text{aq}) + 2\text{NO}_2(g)
\]

After dissolution of the black precipitate and copper in concentrated nitric acid, the solution is diluted with distilled water. Concentration of nitrate ions becomes much lower after dilution, and green nitrate complexes of copper(II) are converted to blue $[\text{Cu(H}_2\text{O})_6]^{2+}$:

\[
[\text{Cu(H}_2\text{O})_4(\text{NO}_3)_2](\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow [\text{Cu(H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq})
\]

$\text{BaCl}_2(\text{aq})$ is used for detection of sulfate ions $\text{SO}_4^{2-}$:

\[
\text{CuSO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow \text{CuCl}_2(\text{aq}) + \text{BaSO}_4(\text{s})
\]

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