# Synthesis of $Au_2S$ and $Au_2S_3$ Using $H_2S$, Short-chain and Ring-Structured Sulfur as Sulfur Sources

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# Abstract

To determine which of the two known gold sulfides (containing either mono- or trivalent gold) are formed by reacting trivalent gold with different allotropes of sulfur, experiments were made using three different sources of sulfur. When trivalent gold in the form of $Au_2(SO_4)_3$ in concentrated acid is reacted with electrolytically formed short-chain sulfur, monovalent gold sulfide is formed. If hydrogen sulfide gas reacts with the same solution, trivalent gold as $Au_2S_3$ is produced. Alternatively, if ordinary α-sulfur (ring structure) is used, a 50/50 mixture of $Au_2S$ and $Au_2S_3$ is formed. A mechanistic set of reaction steps is proposed to explain each reaction. The speculative model supports the short-chain structure of the sulfur produced by electrolysis. The synthesis procedure for the two gold sulfides is substantially simpler than previously reported methods of preparation.

# INTRODUCTION

In the reported methods [1,2 3] to synthesize the monovalent and trivalent gold sulfides, $Au_2S$ and $Au_2S_3$, only $H_2S$ has been used as the source of the $S^{2-}$ion. Examination of the literature reveals no instance where any solid form of sulfur has been used to carry out the synthesis. Solid sulfur exists in many allotropic forms such as multiple-atom rings of sulfur or open chains of sulfur atoms containing an indeterminant number of atoms. The reactivity of an element is affected by its allotropic form, and thus one would expect that trivalent gold will react differently with different allotropic forms of sulfur. In this investigation, $H_2S$, the ordinary eight-atom ring form of sulfur ($\alpha$-sulfur), and chain sulfur ($\omega$- or catenapolysulfur) are compared as sulfur sources in the synthesis of $Au_2S$ and $Au_2S_3$ using trivalent gold.

The known method of preparation of monovalent and trivalent gold sulfide use gold complexes having the appropriate valance state of gold. Hirsch, et al [4] formed $Au_2S$, a brownish-black precipitate, by bubbling $H_2S$ through an acidified solution of $K[Au(CN)_2]$. After drying, the $Au_2S$ is very slightly soluble in water, insoluble in mineral acids, or KOH, but is soluble in aqua regia and sodium cyanide solutions. No diffraction pattern has been indexed by the International Center for Diffraction Data [17].

Early attempts to synthesize the trivalent sulfide, $Au_2S_3$, from aqueous solutions failed primarily because water causes the formation of auric oxide or hydroxide. To circumvent this problem, Antony and Lucchesi [5] passed $H_2S$ over dry lithium tetrachloraurate and then washed with alcohol, $CS_2$, and ether to purify the $Au_2S_3$. Gutbier and Dürrwächter [6] passed $H_2S$ through an acidified solution of $H(AuCl_4)$ in absolute ether and precipitated a copious quantity of $Au_2S_3$ with a small amount of metallic gold. Hoffmann and

Höchtlen [7] used a similar preparation except they used $AuCl_3$. $Au_2S_3$ is a black precipitate that reacts vigorously with nitric acid and is insoluble in the other mineral acids. It is soluble in sodium cyanide and concentrated sodium sulfide solutions. The material appears to be amorphous and has no reported X-ray diffraction pattern.

In this work we use trivalent gold in the form of $Au_2(SO_4)_3$ in concentrated $H_2SO_4$ to synthesize both forms of gold sulfide. The strong acid solution of trivalent gold is reacted with short-chain sulfur, ring sulfur ($\alpha$-sulfur) and $H_2S$, each of which gives a different product. The synthesis of both $Au_2S$ and $Au_2S_3$ is significantly easier than the previously reported methods. A speculative model is proposed to show the possible reaction steps which may lead to the formation of each of the gold sulfides.

## EXPERIMENTAL SECTION

Before discussing the synthesis experiments it is pertinent to explain the source of the trivalent gold and the chain sulfur solutions. Both the $Au_2(SO_4)_3$ and a chain form of sulfur are prepared by electrolyzing concentrated $H_2SO_4$ (97 percent) in a U-tube with gold electrodes [8]. A 1.5 x 3 x 20 mm gold bar of 99.99 percent purity was used as an anode and a 1.5 x 3 x 10 mm gold bar cut from the same stock was used for the cathode. After electrolysis at 5 V and about 100 mA for an hour or two, the anolyte containing $Au_2(SO_4)_3$ is yellow-orange in color and the catholyte has a milky appearance due to finely divided colloidal sulfur (white) formed by the reduction of $H_2SO_4$. The catholyte and anolyte are easily removed from the U-tube for further experiments.

The colloidal electrolytically-formed sulfur, unlike ordinary $\alpha$-sulfur, is white and insoluble in $CS_2$, and in this respect resembles "flowers of sulfur" or $\omega$-sulfur [9,10,11] which are forms of catenapolysulfur with chains of indeterminant length. If the colloidal acid solution is diluted with water, the sulfur coagulates and immediately reverts to the normal yellow $\alpha$-sulfur. As long as the sulfur remains as a colloid in the concentrated acid, it is stable for weeks at room temperature. However, if it is brought down and concentrated by centrifuging, some of the sulfur reverts to the $\alpha$ form of sulfur. Catenapolysulfur has an electron on each of the terminal sulfur atoms and therefore has characteristics of a free radical [12,13]. The relatively high concentration of $H_3SO_4^+$ ions in concentrated sulfuric acid is conducive to a loose association at the terminal sulfur atoms of the chain, and is probably the cause of the chain's stability in the concentrated acid. When the acid is diluted with water the autoprotonation process in $H_2SO_4$ is repressed, leaving the terminal sulfur atoms "exposed". The chain subsequently breaks into the more stable eight atom sections and joins forming $S_8$ rings. Gillespie and Ummat [14] found that at a somewhat higher temperature (70°C), similar colloidal solutions of sulfur in concentrated $H_2SO_4$ were stable for only about 12 hours. These properties are essentially the same as those formed for the fibrous or $\omega$-sulfur formed by cooling and stretching melted sulfur. Sulfur was identified by X-ray fluorescence but X-ray diffraction of the colloidal solutions yielded no pattern indicating extremely short chains of sulfur atoms compared with the usual much longer chains of $\omega$-sulfur. Short chains and the exceedingly fine particle size of the sulfur would account for the absence of a diffraction pattern for the electrolytically formed sulfur. The properties of the electrolytically formed sulfur are generally the same as those described by Donohue and Meyer [9] for $\omega$-sulfur; therefore it is believed that the colloidal solution is composed of a catenapolysulfur allotrope of sulfur ($\omega$-sulfur), but with much shorter chains of sulfur atoms.

The following synthesis experiments were performed by reacting $Au_2(SO_4)_3$ with ω-sulfur, α-sulfur and $H_2S$.

**Gold Sulfide from short-chain ω-sulfur.** In this experiment it was necessary to completely mix the catholyte containing the short-chain sulfur with the anolyte containing $Au_2(SO_4)_3$. Electrolysis of concentrated sulfuric acid was therefore carried out in an open 250 ml beaker at a potential of 5 V, and a current of 110-120 mA over a period of 3 to 5 hours. Throughout the electrolysis the electrolyte was continuously mixed. Within a few minutes after initiation of electrolysis the electrolyte started to darken and eventually became a dense black color as the anolyte and catholyte reacted. No gas other than the gas generated at the electrodes was evolved during the reaction process. Following electrolysis, the electrolyte and reaction product were removed, centrifuged, and the nearly clear supernatant acid was decanted. The black precipitate was washed first with 100 ml of fresh concentrated sulfuric acid to remove any unreacted $Au_2(SO_4)_3$, and then with some 500 ml of distilled water to dilute any residual acid. After centrifuging and decanting the water, the precipitate was finally washed in acetone and air-dried to a brownish-black powder. X-ray diffraction showed the precipitate to be amorphous. It was only very slightly soluble in water, insoluble in mineral acids or KOH, but soluble in aqua regia and NaCN solutions.

To establish the compound formed, gravimetric analyses were made on the dried precipitate. Table 1 shows the gravimetric measurement of the average gold and sulfur concentrations in the specimens. Gold was measured by ashing each of the sample preparations at about 500°C, and sulfur was determined by standard chemical methods. The chain-sulfur produced during the electrolysis process may not have reacted completely with the gold, and as this form of sulfur is insoluble in $CS_2$, it was difficult to wash the precipitate free of all of the residual elemental sulfur. The presence of residual ω-sulfur in the $Au_2S$ is further explained by the model discussed below. As a consequence of the residual sulfur, the experimental values in the table vary slightly from the theoretical values. Both the qualitative properties described above and the gravimetric analysis of the precipitate correspond to $Au_2S$ and, thus the data supports the identification of the product as being primarily $Au_2S$.

**Gold Sulfide from α-Sulfur.** Gold sulfide was also prepared from reagent α-sulfur reacted with a solution of $Au_2(SO_4)_3$ in concentrated sulfuric acid prepared in the U-tube electrolysis cell as described above. The sacrificial gold anode was weighed prior to and again after the electrolysis to determine the amount of gold dissolved in the concentrated acid. After the gold sulfate solution was removed from the U-tube, a small amount of ordinary reagent grade α-sulfur was added to the solution. To ensure a complete reaction of all the gold present, the amount of sulfur added was slightly more than that necessary to completely react with the measured amount of gold present. A black precipitate was formed immediately with the evolution of $SO_2$ gas. After centrifuging, the residue was washed with fresh concentrated sulfuric acid to remove any excess gold sulfate. Care was taken not to wash the precipitate initially with water because it was found that, if water is added to a concentrated acid solution of $Au_2(SO_4)_3$, the gold precipitates as gold oxide and gold hydroxide which would contaminate the gold sulfide precipitate. After washing with concentrated acid, the black precipitate was washed with water to remove all traces of acid, and then with acetone, and air dried. The dried black precipitate was finally extracted with $CS_2$ to remove any excess α-sulfur. Attempts to obtain an X-ray diffraction pattern were unsuccessful due to the amorphous state of the product. The gravimetric data in Table 1 using ring-type α-sulfur as a sulfur source do not correspond to either $Au_2S$ or $Au_2S_3$. However, the average values of gold and sulfur correspond approximately to 86.02, and 13.97 percent, respectively, the values expected for equal mixture of AuS. If the sulfur is in its common valence state of 2-, then one would expect gold to be in the 2+ valence state. Divalent gold is uncommon and according to Remy [18], Bergendahl [19] and Johnson and Davis [3], in almost all cases where gold corresponds to $Au^{2+}$, it is found that double compounds are formed e.g. $Au_2S \cdot Au_2S_3$ or $Au^{II}[Au_2{}^{III}S_4]$. Thus, we conclude that a double sulfide is formed from the oxidation of α-sulfur rather than AuS.

**Gold Sulfide from $H_2S$.** For comparison with the solid forms of sulfur, gold sulfide was also prepared by bubbling $H_2S$ through a concentrated sulfuric acid solution of $Au_2(SO_4)_3$ prepared electrolytically as described above. The black precipitate formed was washed with fresh concentrated sulfuric acid, water and acetone. After drying to a black powder, it was found that the product reacted with nitric acid, but insoluble in other mineral acids. It was soluble in sodium cyanide and concentrated sodium sulfide solutions. The concentration of gold and sulfur was determined gravimetrically as shown in Table 1. The data correspond to $Au_2S_3$ as the product of the reaction.

## RESULTS and DISCUSSION

The reasons for the different compounds formed in the three reactions are not immediately clear and it is unlikely that a definitive explanation can be obtained without extensive research. However, from the experimental results and consideration of charge balance, it is possible to develop a speculative model to account for the products formed. After considering several possible explanations the following proposed set of steps appears to be the most plausible to explain the data in all three experiments. The steps proposed are highly speculative, and, although very hypothetical, the model is considered better than no explanation at all. Because of the complexity, a step by step mechanism is presented.

**Synthesis from $H_2S$.** When $H_2S$ gas is allowed to pass through an acidic solution of $Au_2(SO_4)_3$ there is sufficient ionization of $H_2S$ so that the $S^{2-}$ ions react with the $Au^{3+}$ present according to the reaction

$$Au_2(SO_4)_3 + 3\ H_2S \rightarrow Au_2S_3 + 3\ H_2SO_4 \tag{1}$$

As no chains or rings are involved, the reaction is essentially one of simple ion exchange, which yields only $Au_2S_3$. This reaction also confirms the presence of trivalent gold and $SO_4^{\ 2-}$ ions in the acidic $Au_2(SO_4)_3$ solution.

**Synthesis from short-chain sulfur.** The overall reaction of short-chain ω-sulfur with the acidic solution of $Au_2(SO_4)_3$ is given by

$$Au_2(SO_4)_3 + 2S \rightarrow Au_2S + 4\ SO_3 \tag{2}$$

Because $SO_3$ is not a gas at room temperature and is very soluble in concentrated $H_2SO_4$, the $SO_3$ was totally absorbed by the large volume of acid (250 ml) used compared with the other reactants.

An $Au^{3+}$ ion attacks the terminal sulfur atom of the chain by removing one of the electron pairs (Step 1). The $Au^{3+}$ ion is thus reduced to $Au^+$. Thus,

$$Au^{3+} + 2e^- \rightarrow Au^+ \tag{3}$$

Simultaneously, an electron pair on the second sulfur atom exchanges with the bonding electrons between the terminal and second sulfur to maintain the stability of the terminal sulfur atom (Step 2). The electron pair originally on the second sulfur atom is replaced by electrons donated by a $SO_4^{\ 2-}$ group (Step 3). These first three steps are initiated by each of the two $Au^{3+}$ ions to form 2 $Au^+$ ions. The second $Au^{3+}$ ion similarily removes an electron pair from the terminal sulfur (Step 4), causing the formation of an additional $Au^+$ ion, and the addition of a second $SO_4^{2-}$ to the sulfur chain via an electron pair transfer to the terminal sulfur atom (Step 5 and 6). To complete the octet on the terminal sulfur atom, electrons transfer from the second sulfur atom, and induces the bond between the second and third sulfur atom to break homolytically, and a third $SO_4^{2-}$ ion adds to the second sulfur atom to complete its octet (Step 7). An intermediate trisulfate compound and a shorter sulfur chain with the orginal electron distribution are formed. The two $Au^+$ ions formed in Steps 1 and 4 react with the $S^{2-}$ ion in the intermediate compound to form $Au_2S$ (Step 8). The unstable intermediate compound, $S(SO_4)_3$, decomposes to 4 $SO_3$ molecules (Step 9). The process initiated by the attack of other $Au^{3+}$ ions continues until the chain is consumed. According to this mechanism only $Au_2S$ and $SO_3$ are formed, as is observed experimentally in accordance with equation 2. The reaction utilizes two sulfur atoms and for chains containing an odd number of sulfur atoms, a sulfur atom remains unreacted. The final disposition of these atoms is unknown, but, as they can unite to form chains, i.e. ω-sulfur, they may contribute to the excess ω-sulfur found in $Au_2S$ as mentioned above (see Table 1).

**Synthesis from α-Sulfur.** When α-sulfur is reacted with the $Au_2(SO_4)_3$ solution an equal mixture of the mono- and trivalent gold sulfides is formed. The presence of both sulfides in approximately equal proportions can be accounted for by the reaction

$$2\ Au_2(SO_4)_3 + S_8 \rightarrow Au_2S_3 + Au_2S + 4\ SO_3 + 6\ SO_2 \qquad (4)$$

The α-sulfur forms an eight-sulfur atom ring, $S_8$, in the shape of a "puckered" crown (see, for example, ref. 15). When α-sulfur is introduced into the

$Au_2(SO_4)_3$ solution, the reactions are different from those with short-chain sulfur because there are no terminal sulfur atoms available, and all the sulfur atoms are equivalent. The suggested steps in Figure 2 lead to the formation of a equal mixture of the two sulfides.

We propose that two of the four gold trivalent ions in equation 3 initially react with three consecutive sulfur atoms in the ring forming ionic bonds (Step 1). The two gold and three sulfur atoms form $Au_2S_3$ which then drops out of the ring by severing the weakened bonds as shown by the arrows. Both bonding electrons at each arrow remain with the $Au_2S_3$ to preserve the electron octet about each of the sulfur atoms. Thus,

$$2\ Au^{3+} + 3\ S^{2-} \rightarrow Au_2S_3 \tag{5}$$

The remaining five atoms in the ring open out into a straight chain with a positive charge at each end. As in Figure 1 an $Au^{3+}$ ion removes the two electron pairs on one of the terminal sulfur atoms forming an $Au^+$ ion (Step 2), and following electron transfer (Step 3) the addition of an $SO_4^{2-}$ takes place (Step 3 and 4). The process is repeated with steps 5, 6, and 7. While the process is similar to that in figure 1 up to this point, there is one important difference. The terminal sulfur atom is positively charged. To maintain the octet on the terminal sulfur the second sulfur must supply two electrons causing both bonding electrons between the second and third sulfur to remain with the second sulfur. An $SO_4^{2-}$ ion adds to the second sulfur to maintain its octet (Step 8) forming the trisulfate intermediate compound in addition to a charged three sulfur chain. As in figure 1 the remaining two $Au^+$ ions react with the $S^{2-}$ in the trisulfate compound to form $Au_2S$, and $S(SO_4)_3$ which decomposes to $SO_3$ (Steps 9 and 10). The positively charged sulfur chain reacts with 2 $SO_4^{2-}$ ions and subsequently decomposes to 4 $SO_2$ and an $S^{2+}$ ion molecule (Steps 11 and 12). The remaining $SO_4{}^{2-}$ ion reacts with the $S^{2+}$ ion and forms two additional $SO_2$ molecules (Step 13).

The steps in Figure 2 account for all the products formed by the overall equation 4. It should be kept in mind that Figures 1 and 2 show a hypothetical, dynamic process used to establish a rational explanation of the experimental results. Other mechanisms may be possible but these are the only ones we have found which maintain the proper charge balance and fit the experimental facts.

The model describing the three methods of synthesis, although somewhat speculative, fits the experimental facts. Several alternative explanations were attempted, but in all cases they either did not fit the data or were rejected on theoretical grounds.

## CONCLUSIONS

Relatively simple methods of preparing mono- and trivalent gold sulfide, $Au_2S$ and $Au_2S_3$, from $Au_2(SO_4)_3$ and specific forms of sulfur are shown which do not require the synthesis of complex compounds of gold generally used to form these sulfides. If open chain sulfur (ω-sulfur) is reacted with trivalent gold in the form of $Au_2(SO_4)_3$ in concentrated $H_2SO_4$, the trivalent gold is reduced and monovalent gold sulfide ($Au_2S$) is formed. Bubbling $H_2S$ through a similar solution of $Au_2(SO_4)_3$ yields the trivalent sulfide ($Au_2S_3$). If the ordinary ring form of sulfur (α-sulfur) is used, a mixture of mono- and trivalent gold sulfide is formed. A speculative model proposing steps leading to the sulfides formed in each reaction has been presented and gives a possible explanation of the experimental results. The formation of different gold sulfide compounds from the three forms of sulfur dramatically demonstrate Schmidt and Siebert's [16] insistence that the allotropic forms of sulfur are indeed different compounds of sulfur, and should be considered as such.

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## Figure Captions

Figure 1. Proposed mechanism leading to the formation of $Au_2S$ showing the reaction of $Au^{3+}$ ions with the open sulfur chain of polycatenasulfur.

Figure 2. Proposed mechanism leading to the formation of $Au_2S$ and $Au_2S_3$ showing the reaction of $Au^{3+}$ with an eight atom ring of $\alpha$-sulfur.

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Table 1. Percentage gold and sulfur measured in samples of gold sulfide prepared from three different forms of sulfur.

| SULFUR SOURCES | PERCENT GOLD |  | PERCENT SULFUR |  | TOTAL COMPOSITION |
|---|---|---|---|---|---|
|  | AVERAGE | THEORETICAL | AVERAGE | THEORETICAL |  |
| Short Chain Sulfur | 90.16 ± 1.67% | 92.49%[a] | 8.10 ± 0.22% | 7.51%[a] | 98.27% |
| Ring Type Sulfur | 85.46 ± 1.59% | 86.02%[b] | 13.58 ± 0.22% | 13.97%[b] | 99.04% |
| $H_2S$ Gas | 80.81 ± 1.7% | 80.41%[c] | 19.8% |  19.59%[c] | 100.61% |

[a] - For $Au_2S$

[b] - For a 50:50 mixture of $Au_2S$ and $Au_2S_3$

[c] - For $Au_2S_3$

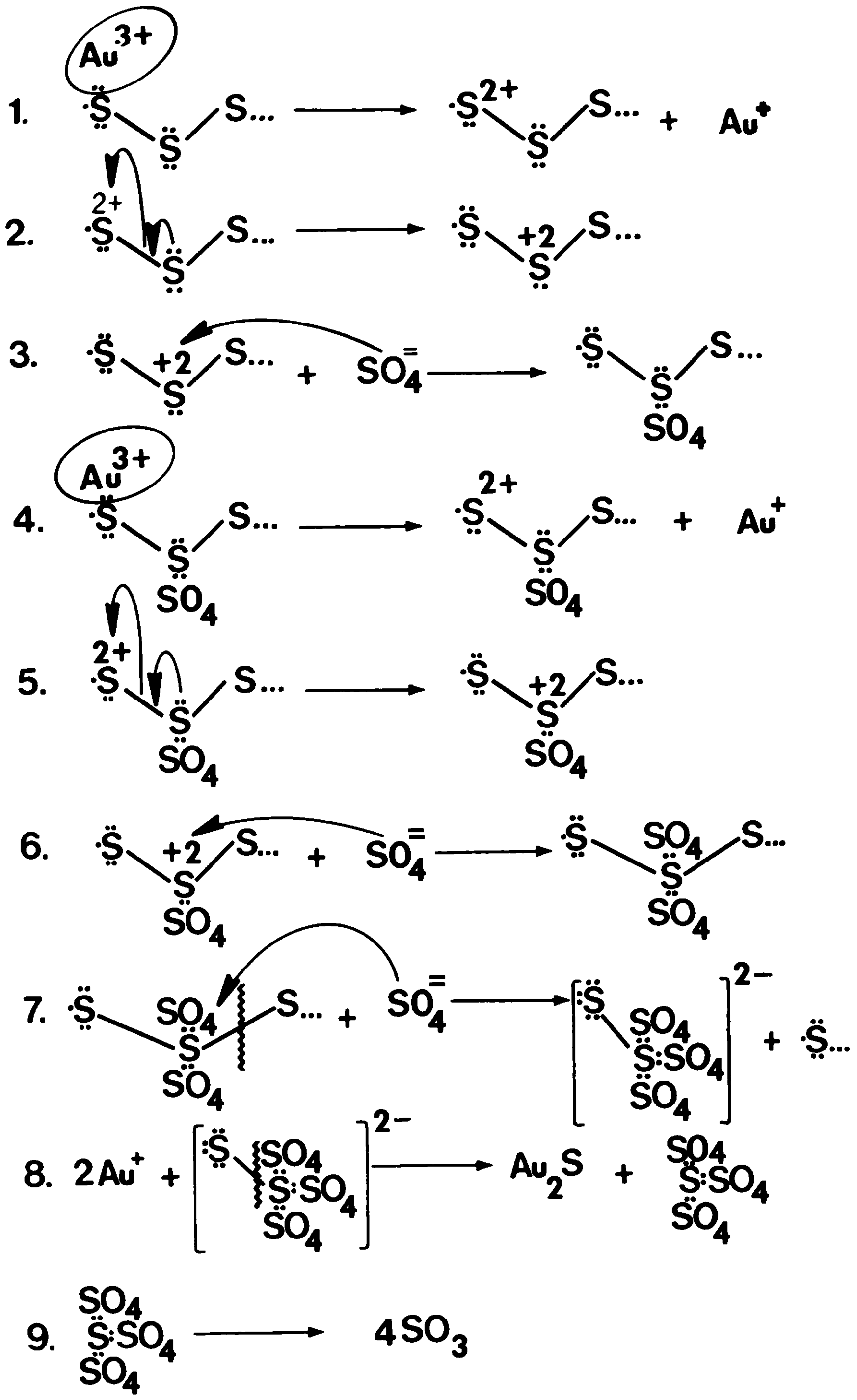

Fig 1

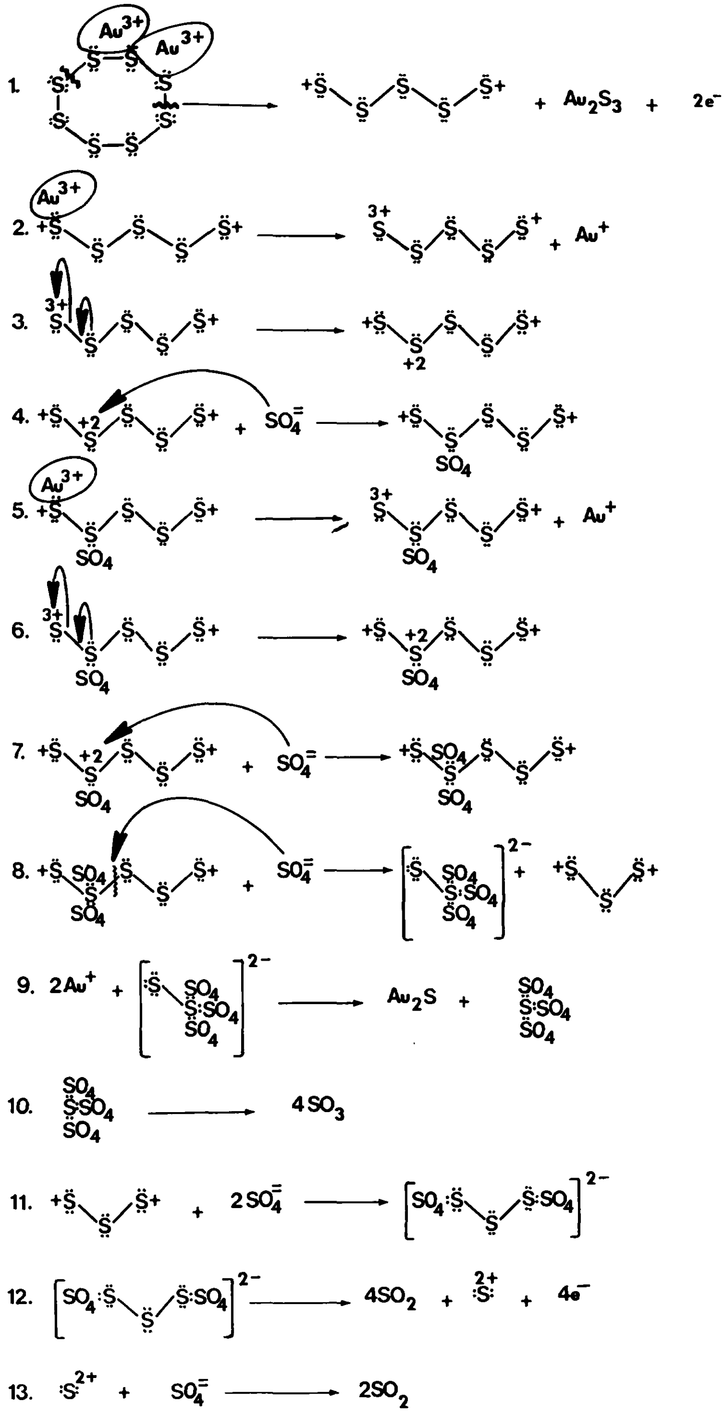
1.
Au3+
Au3+
+ Au2S3 + 2e⁻
2.
Au3+
3+
+ Au+
3.
3+
+2
4.
+2
+ SO4=
SO4
5.
Au3+
SO4
3+
+ Au+
6.
3+
SO4
+2
7.
+2
SO4
+ SO4=
8.
SO4
+ SO4=
2−
9. 2Au+ +
2−
Au2S +
10.
4SO3
11.
+ 2SO4=
2−
12.
2−
4SO2 + S2+ + 4e⁻
13. S2+ + SO4= → 2SO2

Fig. 2