

XArticle ID: 1003 - 6326(1999)03 - 0646 - 05

## Dissolution theory of gold in alkaline thiourea solution( III) —Thermodynamics on dissolution of gold in alkaline thiourea solution containing $\text{Na}_2\text{SO}_3$ ①

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**Abstract:** The oxidants of gold were investigated in an alkaline thiourea solution containing  $\text{Na}_2\text{CO}_3$ , in which  $\text{Na}_2\text{S}_2\text{O}_8$  is a proper oxidant for dissolving gold because of in such homogeneous sulfur system coexisting complex agent, oxidant and stabilizing agent. The thermodynamic analyses were conducted on the dissolving of gold in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  by the oxidants oxygen or  $\text{Na}_2\text{S}_2\text{O}_8$ . The results show that the possibility of gold dissolution reduces with increasing pH value, while oxygen acts as oxidant; and when  $\text{Na}_2\text{S}_2\text{O}_8$  acts as the oxidant of gold in the alkaline thiourea solution of pH 12.5, decomposition potential of thiourea decreases from the standard value 0.42 V to -0.32 V, also the dissolution trend of gold enhances with shifting the mix potential of the solution to the positive direction.

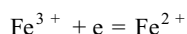
**Key words:** thermodynamic; analysis; gold; dissolution; thiourea leaching

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### 1 INTRODUCTION

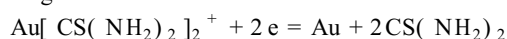
The mechanism and chemical process for dissolving gold in acidic thiourea solution were studied by many researchers<sup>[1-5]</sup>, who generally thought that thiourea as a strong ligand complexes selectively with gold ion to form stable complex ion  $\text{Au}[\text{CS}(\text{NH}_2)_2]_2^+$ , and some oxidants were needed during the dissolution of gold in acidic thiourea solution, e.g.  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$ ,  $\text{MnO}_2$ , by which thiourea itself was oxidized to form formamidine disulfide, even leads sulfur to passivate gold surface<sup>[6-8]</sup>. It was reported<sup>[9]</sup> that the process for dissolving gold by the oxidant  $\text{Fe}^{3+}$  in the acidic thiourea solution belongs to the electrochemical corrosive process, the electrode reactions are as follows.

Positive electrode reaction:



$$\varphi_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V} \quad (1)$$

Negative electrode reaction:



$$\varphi_{\text{Au}[\text{CS}(\text{NH}_2)_2]_2^+/\text{Au}}^{\ominus} = 0.38 \text{ V (vs NHE)} \quad (2)$$

The stronger the oxidizing ability of the oxidant is, the faster the gold dissolves. However, strong oxidant causes easily thiourea, especially in alkaline media, to decompose irreversibly. Thus, the selection of oxidant is of great importance for fast dissolving of gold by thiourea solution. But all these studies were limited only in acidic media. The dissolution of gold was seldom reported in alkaline thiourea solution due to the instability of thiourea in alkaline media.

However, it was found that  $\text{Na}_2\text{SO}_3$  improves greatly the stability of thiourea in alkaline media in our previous work<sup>[10]</sup>. The studies<sup>[11,12]</sup> were mentioned on the polarization behaviors of gold and electrochemical dissolution of Au-Fe mix anode in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  in the previous papers, respectively. The electrochemical dissolution of gold can be carried out easily in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$ . The oxi-

① Received Aug. 18, 1998; accepted Sep. 28, 1998

dants of gold and the thermodynamics on dissolution of gold in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  are further discussed in this paper.

## 2 SELECTION OF OXIDANT FOR DISSOLVING GOLD IN ALKALINE THIOUREA SOLUTION CONTAINING $\text{Na}_2\text{SO}_3$

A part of common oxidants for dissolving gold in the thiourea solution and their standard redox potential can be seen in Table 1.

**Table 1** Standard redox potential of common oxidants for dissolving gold (298 K)<sup>[13]</sup>

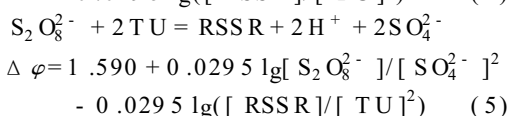
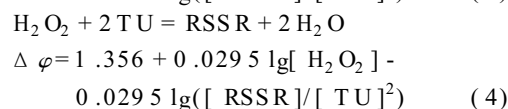
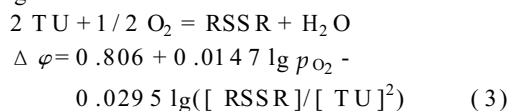
Redox couple	Standard electrode potential $\varphi^\ominus / \text{V}$
$\text{O}_3 / \text{H}_2\text{O}$	2.076
$\text{S}_2\text{O}_8^{2-} / \text{SO}_4^{2-}$	2.010
$\text{H}_2\text{O}_2 / \text{H}_2\text{O}$	1.776
$\text{MnO}_4^{2-} / \text{Mn}^{2+}$	1.507
$\text{ClO}_4^- / \text{Cl}_2$	1.395
$\text{O}_2 / \text{H}_2\text{O}$	1.228
$\text{NO}_3^- / \text{NH}_2\text{OH}$	0.940
$\text{Fe}^{3+} / \text{Fe}^{2+}$	0.770
$\text{RSSR} / \text{TU}^*$	0.420
$\text{SO}_4^{2-} / \text{SO}_3^{2-}, \text{OH}^-$	-0.930

\* RSSR stands for formamidine disulfide, TU stands for thiourea.

The proper oxidants for dissolving gold in acidic thiourea solution are  $\text{Fe}^{3+}$ , formamidine disulfide,  $\text{MnO}_2$  and dissolved oxygen. Air is the cheapest oxidant, but the solubility of  $\text{O}_2$  in the water at room temperature and ambient pressure is very small (to  $0.26 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ). Thus, the mix oxidant of  $\text{O}_2$  and  $\text{Fe}^{3+}$  was utilized in the dissolution of gold in acidic thiourea solution. However, some oxidants listed in Table 1, e.g.  $\text{Fe}^{3+}$ ,  $\text{MnO}_2$  can not be used in alkaline media, in which strong oxidants, e.g.  $\text{O}_3$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}_2$  cause easily thiourea irreversible decomposition. In fact, it was found that  $\text{Na}_2\text{SO}_3$  stabilizes alkaline thiourea in our previous work, the strong oxidant  $\text{Na}_2\text{S}_2\text{O}_8$  at a certain range of concentration in the alkaline thiourea solution con-

taining  $\text{Na}_2\text{SO}_3$  does not cause thiourea to decompose irreversibly<sup>[10]</sup>.

While  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{S}_2\text{O}_8^{2-}$  act as the oxidants in dissolving gold in the alkaline thiourea solution containing a bit of  $\text{Na}_2\text{SO}_3$ , the reactions for oxidizing thiourea are as follows:



It can be seen from equations (3) ~ (5) that, when the concentration of thiourea solution is fixed, the higher the redox potential of oxidant is, the easier the formamidine disulfide forms; only if irreversible decomposition of formamidine disulfide does not occur, the larger the dissolving trend of gold caused by the oxidant in alkaline thiourea solution is.

The effect of oxidants on dissolution rate of gold in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  at pH 12.5 is shown in Fig.1.

**Fig.1** Effect of oxidants on dissolution of gold in  $0.25 \text{ mol} \cdot \text{L}^{-1}$  thiourea solution containing  $0.025 \text{ mol} \cdot \text{L}^{-1}$   $\text{Na}_2\text{SO}_3$  at pH 12.5 and 298 K

From Fig.1, the stronger the oxidizing ar-

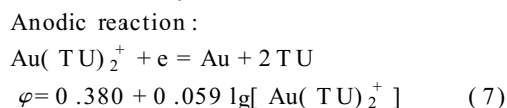
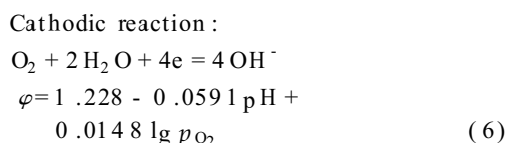
bility of oxidant is , the bigger the dissolution rate of gold will be . The O<sub>2</sub> dissolves difficultly gold in the alkaline thiourea solution containing Na<sub>2</sub>SO<sub>3</sub> because of the limited solubility of O<sub>2</sub> in water . The effect of oxidant S<sub>2</sub>O<sub>8</sub><sup>2-</sup> on the dissolution of gold in the alkaline thiourea solution containing Na<sub>2</sub>SO<sub>3</sub> is the optimum .

Furthermore , the oxidant , stabilizing agent and complex agent coexist in a homogeneous sulfur system , while S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is the oxidant for dissolving gold in the thiourea solution containing Na<sub>2</sub>SO<sub>3</sub> . Also sulfur attends by many kinds of valences , which is advantageous to promoting the dissolution of gold<sup>[14]</sup> .

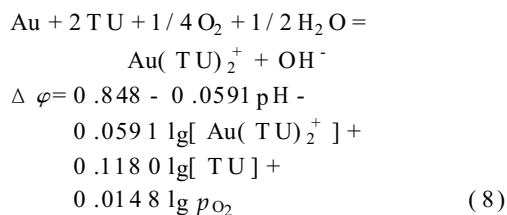
### 3 THERMODYNAMIC ANALYSIS ON DISSOLUTION OF GOLD IN ALKALINE THIOUREA SOLUTION CONTAINING Na<sub>2</sub>SO<sub>3</sub>

#### 3.1 Oxygen as oxidant

In regard to the electrochemical corrosive process for dissolving gold in the thiourea solution containing Na<sub>2</sub>SO<sub>3</sub> , when oxygen is acted as the oxidant , the electrode reactions are as follows .



The total reaction of gold dissolution can be obtained as following from reactions (6) and (7) .



It can be seen from equation (8) that when pH value and the concentration of thiourea are fixed , the dissolution trend of gold increases with increasing the pressure of O<sub>2</sub> .

It is assumed that the total concentration of thiourea is 1.0 mol • L<sup>-1</sup> , also all formamidine disulfide is transferred to both thiourea and Au(TU)<sub>2</sub><sup>+</sup> after gold being dissolved , then equation (9) is obtained .

$$[ TU ] = 1 - [ Au(TU)_2^+ ]$$
 (9)

However , the solubility of O<sub>2</sub> in water is limited ( 0.26 × 10<sup>-3</sup> mol • L<sup>-1</sup> ) , the effect of O<sub>2</sub> on the dissolution of gold is also limited .

Therefore , when dissolution reaction of gold reaches its equilibrium ( i.e. Δφ = 0 ) , the relationship between the dissolution amount of gold and pH value is obtained at the optimum concentration of O<sub>2</sub> dissolved , as seen in equation (10) .

$$\lg \frac{[ Au(TU)_2^+ ]}{1 - [ Au(TU)_2^+ ]} = 13.5 - pH$$
 (10)

The relationship between the concentration of [ Au(TU)<sub>2</sub><sup>+</sup> ] and pH value can be obtained by the equation (10) , shown as Table 2 .

**Table 2** Relationship between c( Au(TU)<sub>2</sub><sup>+</sup> ) and pH

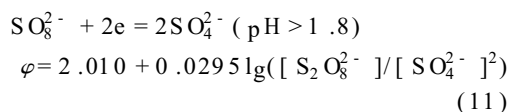
pH	c( Au(TU) <sub>2</sub> <sup>+</sup> ) / ( mol • L <sup>-1</sup> )	pH	c( Au(TU) <sub>2</sub> <sup>+</sup> ) / ( mol • L <sup>-1</sup> )
0	1.0	6.6	0.99
1.4	1.0	9.5	0.98
3.0	1.0	12.5	0.72
4.5	1.0	14.0	0.18

From Table 2 , the dissolution trend of gold in 1.0 mol • L<sup>-1</sup> thiourea solution at the saturated O<sub>2</sub> concentration decreases with increasing pH value . Only based on the thermodynamic analysis , gold is dissolved completely in acidic thiourea solution , and partly in alkaline thiourea solution .

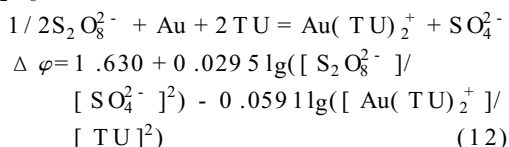
#### 3.2 SO<sub>3</sub><sup>2-</sup> acts as stabilizing agent , S<sub>2</sub>O<sub>8</sub><sup>2-</sup> acts as oxidant

When SO<sub>3</sub><sup>2-</sup> acts as the stabilizing agent of thiourea , S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is as the oxidant of gold , the electrode reactions are represented by the following equations .

Cathodic reaction :



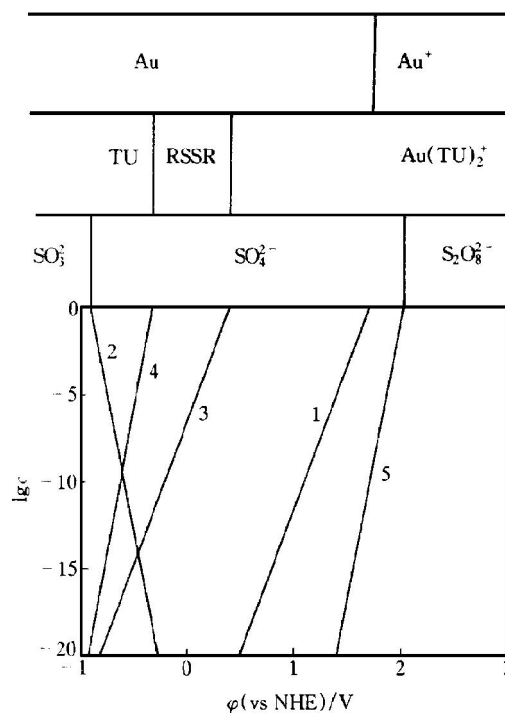
The total dissolution reaction of gold, equation (12), in the thiourea solution by oxidation of  $\text{S}_2\text{O}_8^{2-}$ , is obtained.



When the total concentration of thiourea is equal to  $1 \text{ mol} \cdot \text{L}^{-1}$ , only if thiourea exists steadily, does the concentration of  $\text{Au}(\text{TU})_2^+$  approximate to  $1 \text{ mol} \cdot \text{L}^{-1}$ . That is to say, gold in the thiourea solution can be oxidized completely by  $\text{S}_2\text{O}_8^{2-}$  to form stable complex ion  $\text{Au}(\text{TU})_2^+$ . It is drawn from above that the thermodynamic conditions can be summarized for dissolving gold in the thiourea solution containing  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_8$  at 298 K and pH 12.5, as depicted in Fig. 2. And Table 3 lists the reactions in accordance with Fig. 2.

It can be seen from Fig. 2 that alkaline thiourea is first transferred to formamidine disulfide, and then  $\text{S}_2\text{O}_8^{2-}$  forms stable  $\text{SO}_4^{2-}$ . The major part is the predominant area of  $\text{SO}_4^{2-}$ . The decomposing potential of thiourea decreases from the standard value 0.42 V to -0.32 V. Formamidine disulfide is not easy to decompose irreversibly because of the stabilizing action of  $\text{SO}_3^{2-}$ , which is in equilibrium with thiourea. Thus, gold is oxidized by formamidine disulfide and thiourea complexes with gold ion immediately to form  $\text{Au}(\text{TU})_2^+$ . Therefore, the predominant area of  $\text{Au}(\text{TU})_2^+$  is larger.

Supposing that the total concentration of TU is  $1.0 \text{ mol} \cdot \text{L}^{-1}$ ,  $\lg([\text{Au}(\text{TU})_2^+]/[\text{TU}]^2)$  is equal to -11 at the potential of -0.32 V, thus, the concentration of  $\text{Au}(\text{TU})_2^+$  tends to zero. When the potential is 0 V,  $\lg([\text{Au}(\text{TU})_2^+]/[\text{TU}]^2)$  equals to -6, the concentration of  $\text{Au}(\text{TU})_2^+$  still approximates to zero. Whereas,  $\lg([\text{Au}(\text{TU})_2^+]/[\text{TU}]^2)$  is equal to zero at the potential of 0.38 V, the concentration of  $[\text{Au}(\text{TU})_2^+]$  is  $0.38 \text{ mol} \cdot \text{L}^{-1}$ , the ratio of



**Fig. 2** Thermodynamic analysis of process for dissolving gold in thiourea solution containing  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_8$  at pH 12.5 and 298 K

**Table 3** Reactions corresponded with lines in Fig. 2

Line No.	Reaction	Electrode potential
1	$\text{Au}^+ + e = \text{Au}$	$\varphi = 1.690 + 0.0591 \cdot \lg[\text{Au}^+]$
2	$\text{RSSR} + 2\text{H}^+ + 2e = 2\text{TU}$	$\varphi = -0.320 + 0.059 \cdot \lg([\text{RSSR}]/[\text{TU}]^2)$
3	$\text{Au}(\text{TU})_2^+ + e = \text{Au} + 2\text{TU}$	$\varphi = 0.380 + 0.0591 \cdot \lg([\text{Au}(\text{TU})_2^+]/[\text{TU}]^2)$
4	$\text{SO}_3^{2-} + 2e + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2\text{OH}^-$	$\varphi = -0.840 - 0.0295 \cdot \lg([\text{SO}_3^{2-}]/[\text{SO}_4^{2-}])$
5	$\text{S}_2\text{O}_8^{2-} + 2e = 2\text{SO}_4^{2-}$	$\varphi = 2.010 + 0.0295 \cdot \lg([\text{S}_2\text{O}_8^{2-}]/[\text{SO}_4^{2-}]^2)$

$[\text{Au}(\text{TU})_2^+]/[\text{TU}]$  is 0.38. That is to say, at the potential of -0.32 V the dissolving reaction of gold produces formamidine disulfide, which is not enough to dissolve gold in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_8$ . However, the dissolution of gold is ac-

celerated with shifting the potential to the positive direction, the dissolution trend of gold is obviously accelerated at the potential over 0.38 V.

#### 4 CONCLUSIONS

(1)  $\text{Na}_2\text{S}_2\text{O}_8$  is a proper oxidant for dissolving gold because in such homogeneous sulfur system coexists complex agent, oxidant and stabilizing agent.

(2) With  $\text{O}_2$  being oxidant, the possibility of the dissolution of gold in thiourea solution reduces with increasing pH value, gold is dissolved completely in acidic thiourea solution, and partly in alkaline thiourea solution.

(3) At the potential of -0.32 V the dissolving reaction of gold produces formamide disulfide, which is not enough to dissolve gold in the alkaline thiourea solution containing  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_8$ . However, the dissolution of gold is accelerated with the potential shifting to the positive direction, the dissolution trend of gold enhances obviously at the potential over 0.38 V.

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(Edited by Wu Jiaquan)