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Thermodynamic analysis of ammoniacal thiosulfate leaching of gold catalyzed by Co(III)/Co(II) using E_h-pH and speciation diagrams

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Abstract

In this paper, E_h-pH and speciation diagrams are constructed for gold leaching in the Co-NH_3-$S_2O_3^{2-}$-H_2O system from thermodynamic calculations. The diagrams show that thermodynamically stable redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1–6) can be formed and drive the dissolution of gold in ammoniacal thiosulfate solutions. Based on the diagrams, a possible mechanism for the Co(III)/Co(II) electrochemical-catalytic leaching of gold with ammoniacal thiosulfate is proposed. The calculation also reveals the differences in the oxidization potential and structural stability of the $Co(NH_3)_6^{3+}$ and $Cu(NH_3)_4^{2+}$, which explains the much reduced thiosulfate consumption in the Co-NH_3-$S_2O_3^{2-}$-H_2O system compared to that in the Cu-NH_3-$S_2O_3^{2-}$-H_2O system. Results presented in this paper offer a theoretical basis for the optimization of the cobalt-catalyzed thiosulfate leaching of gold.

Keywords: *gold leaching, ammoniacal thiosulfate, cobalt-catalyzed, thermodynamic analysis*

1. INTRODUCTION

Cyanidation has been the dominant method for extracting gold from its ores. However, cyanide is extremely toxic to the ecological environments and biological creatures (Xu et al., 2017; Zhang and Senanayake, 2016). Significant efforts have been devoted to searching for alternative lixiviants to cyanide with thiosulfate being identified as the most promising candidate. This is mainly due to that thiosulfate is nontoxic and cheap, has a good selectivity toward gold with limited interference from foreign cations and high gold recoveries from a wide range of gold ores such as high copper ores, carbonaceous ores, and sulfidic ores (Aylmore and Muir, 2001b; Grosse et al., 2003; Liu et al., 2017a, 2017b; Xu et al., 2017; Zhang and Senanayake, 2016).

A major drawback for thiosulfate is its slow kinetics. A catalyst is required to achieve an acceptable rate of leaching of gold. Cu(II)-NH_3 complexes was the first one to be used as the catalytic oxidant, significantly increasing the rate of gold leaching. However, a high consumption of thiosulfate, likely to be caused by the oxidation of Cu(II), is a significant problem. A number of other transition metals have since been proposed as the potential catalysts, including iron, nickel, and cobalt. Fe(III)-$EDTA^{4-}$ and Fe(III)-oxalate($C_2O_4^{2-}$) complexes were found to be effective oxidants for the aerobic and anaerobic dissolution of gold in thiosulfate solutions, but both were much less reactive toward thiosulfate than Cu(II)-NH_3 complexes (Chandra and Jeffrey, 2004; Heath et al., 2008). However, the required thiourea to catalyze the oxidation of gold during leaching is potentially carcinogenic. Nickel was found to be an effective catalyst for gold leaching from gold ores in ammoniacal thiosulfate solutions (Arima et al., 2004; Xia, 2001; Xu et al., 2016). Compared with Cu(II), it achieved a comparable gold recovery but had a much lower thiosulfate consumption. However, a decreasing leaching kinetic, possibly caused by the formation of Ni_3O_4 on the surface of gold and Ni_3O_4 particles in the form of colloidal sol in the solution, is a critical problem to overcome (Arima et al., 2004; Xu et al., 2017; Xu et al., 2016). Experiments in electrochemical leaching and solution stability showed that Co(III)-NH_3 complexes could effectively oxidize gold in thiosulfate solutions with a noticeably lower consumption of thiosulfate (Breuer and Jeffrey, 2002; Feng and van Deventer, 2002; Dasgupta et al., 1997; Han, 2001; Xia, 2001). No thermodynamic analysis on the Co(III)-NH_3 system has been conducted, leaving the possible mechanisms for the catalytic effects and a reduction in thiosulfate consumption remaining unclear.

This paper uses thermodynamic calculations to construct relevant E_h-pH and speciation diagrams under various solution conditions. The diagrams provide a theoretical basis for the possible catalytic mechanisms for gold leaching and reasons for the reduced thiosulfate decomposition in the cobalt-ammonia-thiosulfate system. They can also serve to guide the optimization of the cobalt-catalyzed thiosulfate leaching of gold.

2. CONSTRUCTION OF E_h-pH AND SPECIATION DIAGRAMS

E_h-pH diagrams for Co-NH_3-$S_2O_3^{2-}$-H_2O, Au-NH_3-$S_2O_3^{2-}$-H_2O and S-H_2O systems were constructed using HSC Chemistry 6.0 for Windows software (Roine, 2006). Under different solution conditions of temperatures, pressures, and element combinations and concentrations, the thermodynamic stability areas of various species can be shown in E_h-pH diagrams on relevant pH and E_h (vs. SHE) scales.

The construction of speciation diagrams for cobalt and gold species was carried out using HYDRA/MEDUSA software (Puigdomenech, 2004). Under specific solution conditions in association with metal concentration, ligand concentration, pH and E_h, the distributions in concentration (M) or fraction (%) for species in solution can be determined from equilibrium constants (log K or log β) derived from minimized Gibbs free energy of the considered equilibria.

The available thermodynamic data are listed in Appendices A and B, which were used to conduct the construction of E_h-pH and speciation diagrams. Note that the rather thermodynamically stable sulfate species (i.e., HSO_4^{-} and SO_4^{2-}) that are the end-products from the oxidation of thiosulfate were omitted to show the stability regions of metastable sulfur species such as $S_2O_3^{2-}$, $S_4O_6^{2-}$ and SO_3^{2-}, Co(II) thiosulfate complex, i.e., $Co(S_2O_3)^0$, and gold species such as $Au(S_2O_3)_2^{3-}$ and $Au(S_2O_3)(NH_3)^{-}$.

3. THERMODYNAMICS OF FORMATION OF Co(III)/Co(II) REDOX COUPLE

3.1. Effect of pH and E_h on the stability of cobalt species

The E_h-pH and speciation diagrams of Co-NH_3-$S_2O_3^{2-}$-H_2O system clearly show the effects of pH and E_h on the predominance areas and species distributions of cobalt species as seen from Figures 1−3. Given the system status of 1×10^{-3} M Co^{3+}, 1.5 M NH_3/NH_4^{+}, 0.5 M $S_2O_3^{2-}$, the E_h-pH diagram (Figure 1) illustrates that the stability areas of various aqueous Co(II) species including Co^{2+}, $Co(S_2O_3)^0$ and $Co(NH_3)_x^{2+}$ (x = 1−6) are generated at pH < 11 within E_h of -0.3−+0.5 V. In terms of Co(III) species, only the stability area of $Co(NH_3)_6^{3+}$ exists at pH of 8.8−9.7 with E_h > 0.20−0.23 V. Particularly, the stability area of a mixed valence cobalt precipitate, i.e., Co_3O_4, can be formed at pH < 8.8 and pH > 9.7. So an appropriate pH range is required to avoid the precipitation of cobalt out from the solution. In the pH range of 8.8−9.7, the stable Co(III)/Co(II) redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 4, 5) are formed with an equilibrium potential E_h of 0.20−0.23 V. It should be noted that the pH range for a particular species could change noticeably with a change in the concentration of either ammonia or cobalt, which will be discussed in Section 3.2. In addition, the equilibrium between Co(III) and Co(II) ions is influenced by E_h. Co(III) ammine complexes exist at high E_h, whereas Co(II) ammine and thiosulfate complexes occur at low E_h. If E_h drops to about -0.18 V at pH 9.5, cobalt will precipitate out as a sulfide of CoS_2.

At a constant E_h of 0.25 V, the effect of pH on the speciation of cobalt species is shown in Figure 2. It can be seen from Figure 2 that when E_h is fixed at 0.25 V the formation of Co_3O_4 can be averted in the pH range of 8.8−9.7. Meanwhile, the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1−6) are formed with relatively high fractions of $Co(NH_3)_6^{3+}$ (70%−90%). The effect of E_h on the speciation of cobalt species at a constant pH of 9.5 is also illustrated in Figure 3. It is shown that within E_h of 0.05 V– 0.35V the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1–6) can be formed without the formation of Co_3O_4.

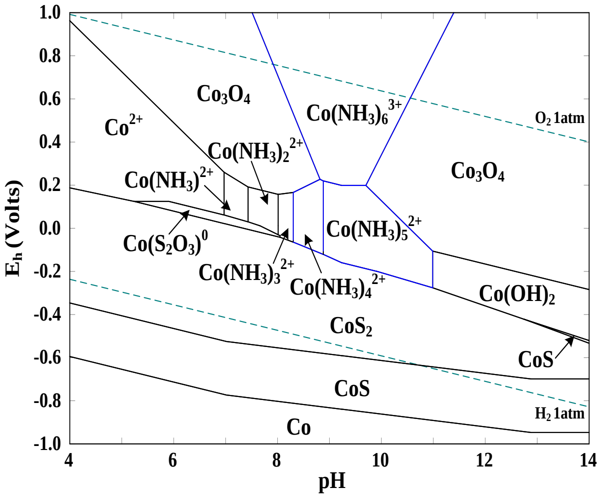

Figure 1. E_h-pH diagram of Co-NH_3-$S_2O_3^{2-}$-H_2O system.
Conditions: 1×10^{-3} M Co^{3+}, 1.5 M NH_3/NH_4^+, 0.5 M $S_2O_3^{2-}$.

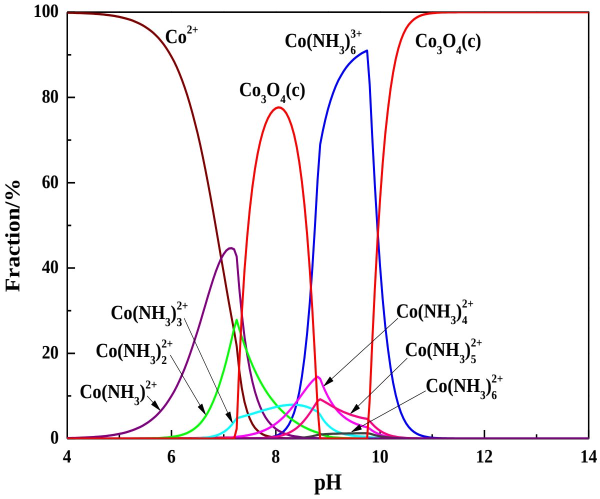

Figure 2. Effect of pH on speciation of cobalt species in Co-NH_3-$S_2O_3^{2-}$-H_2O system.
Conditions: E_h = 0.25 V, 1×10^{-3} M Co^{3+}, 1.5 M NH_3/NH_4^+, 0.5 M $S_2O_3^{2-}$.

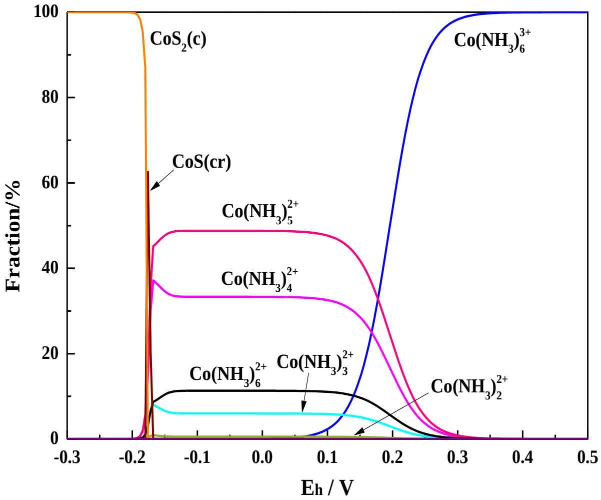

Figure 3. Effect of E_h on speciation of cobalt species in Co-NH_3-$S_2O_3^{2-}$-H_2O system.
Conditions: pH 9.5, 1×10^{-3} M Co^{3+}, 1.5 M NH_3/NH_4^+, 0.5 M $S_2O_3^{2-}$.

The rise of E_h significantly increases the fraction of $Co(NH_3)_6^{3+}$, meaning that a higher fraction of $Co(NH_3)_6^{3+}$ can provide a higher oxidization potential. Therefore, the conditions of E_h and pH for the formation of Co(III)/Co(II) redox couples can be ascertained for a specified cobalt ammoniacal thiosulfate solution.

3.2. Effect of reagent concentrations on the stability of cobalt species

As shown in Figure 1, the predominance area of $Co(S_2O_3)^0$ is narrow likely due to the metastability of $S_2O_3^{2-}$ and the low stability constant of $Co(S_2O_3)^0$ ($\log \beta = 2.05$) as listed in Appendix A. In comparison, the stability constants of $Co(NH_3)_x^{2+}$ (x = 1–6, $\log \beta$ = 2.11–5.73) are obviously higher than that of $Co(S_2O_3)^0$. So it is reasonable to consider that the effect of $S_2O_3^{2-}$ on the thermodynamic stability of $Co(NH_3)_x^{2+}$ (x = 1–6) is negligible under typical range of concentration of 0.1–1.0 M. Instead of thiosulfate, ammonia plays an important role in forming and stabilizing the Co(III)/Co(II) redox couples. Based on the effects of pH and E_h, the effects of the concentration of NH_3/NH_4^+ and Co^{3+} on the stability of cobalt species were further investigated by the speciation diagram of cobalt species for $Co\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system under a range of reagent concentrations as described in Figure 4.

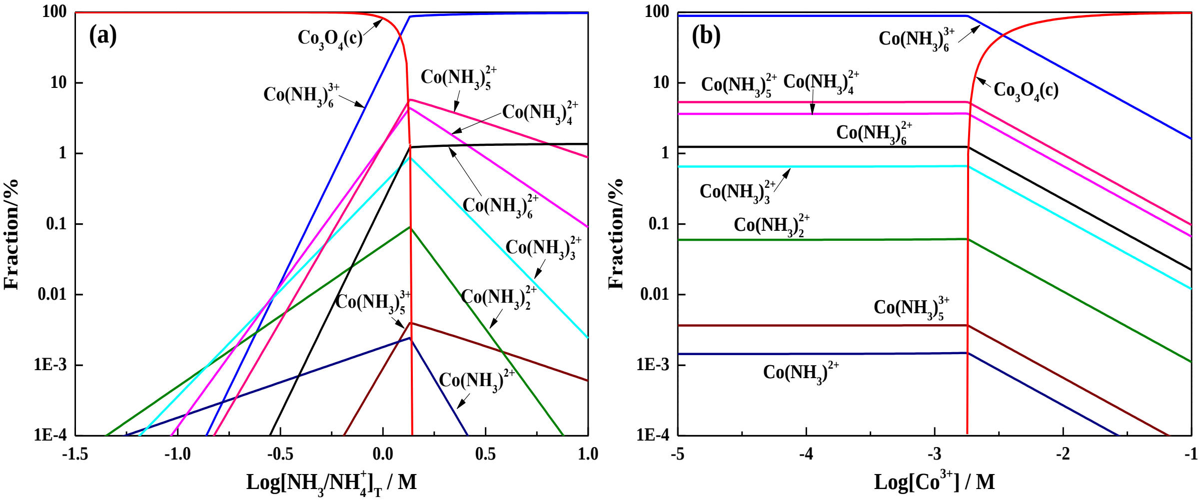

Figure 4. Effect of the concentration of (a) NH_3/NH_4^+ and (b) Co^{3+} on the speciation of cobalt species in $Co\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system. Conditions: (a) 1×10^{-3} M Co^{3+}; (b) 1.5 M NH_3/NH_4^+; 0.5 M $S_2O_3^{2-}$, pH 9.5, E_h 0.25 V in both cases.

Under the condition of 0.5 M $S_2O_3^{2-}$, pH 9.5 and E_h 0.25 V, it is illustrated from Figure 4(a) that the concentration of NH_3/NH_4^+ should be higher than 1.3 M to avert the precipitation of cobalt (1×10^{-3} M Co^{3+}) as Co_3O_4. Likewise, Figures 4(b) shows that the appropriate concentration of Co^{3+} is lower than 1.8×10^{-3} M in the presence of 1.5 M NH_3/NH_4^+. This suggests that a higher concentration of NH_3/NH_4^+ and/or a lower concentration of Co^{3+} can stabilize Co(III/II) ammine complexes, and thereby are beneficial for the formation of Co(III)/Co(II) couples. So the appropriate concentrations of reagents for the formation of Co(III)/Co(II) redox couples can also be determined at constant E_h and pH.

4. THERMODYNAMICS OF GOLD DISSOLUTION CATALYZED BY Co(III)/Co(II) REDOX COUPLE

Based on the thermodynamic analysis of Co(III)/Co(II) redox couples in Section 3, the dissolution of gold in ammoniacal thiosulfate solutions catalyzed by the oxidant of Co(III) ammine complexes were discussed. The reported stability constants ($\log \beta$) for $Au(NH_3)_2^+$ and $Au(S_2O_3)_2^{3-}$ vary within a large range of $\log \beta$ = 13–26 and $\log \beta$ = 24–28, respectively (Aylmore, 2001; Aylmore and Muir, 2001a; Perera and Senanayake, 2004; Senanayake et al., 2003). It has been shown that the most acceptable values are $\log \beta[Au(NH_3)_2^+] = 13$ and $\log \beta[Au(S_2O_3)_2^{3-}] = 24$ by the studies on the basis of linear free energy correlations and half wave potential measurements (Zhang and Senanayake, 2016). In addition, the thermodynamic data for mixed ligand complexes of gold such as $Au(S_2O_3)(NH_3)^-$ and $Au(NH_3)(OH)^0$ have also been confirmed as listed in Appendices A and B (Perera and Senanayake, 2004; Senanayake, 2004b). Based on this, the E_h-pH and speciation diagrams of gold species for $Au\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system were created as depicted in Figures 5 and 6.

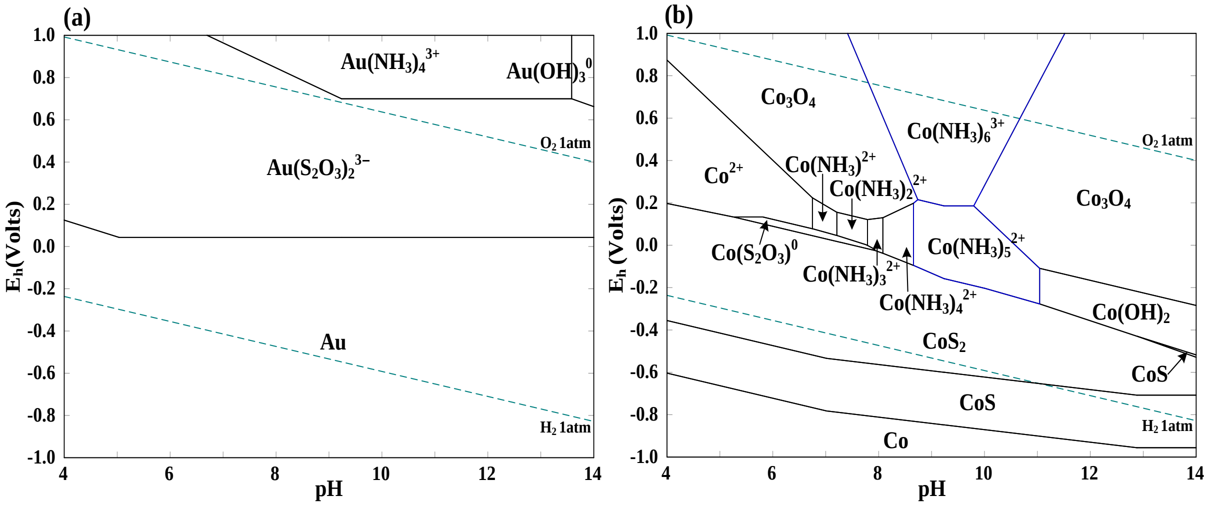

Figure 5. E_h-pH diagrams of (a) $Au\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system and (b) $Co\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system. Conditions: 1×10^{-4} M Au^+, 0.01 M Co^{3+}, 2.5 M NH_3/NH_4^+, 1.0 M $S_2O_3^{2-}$.

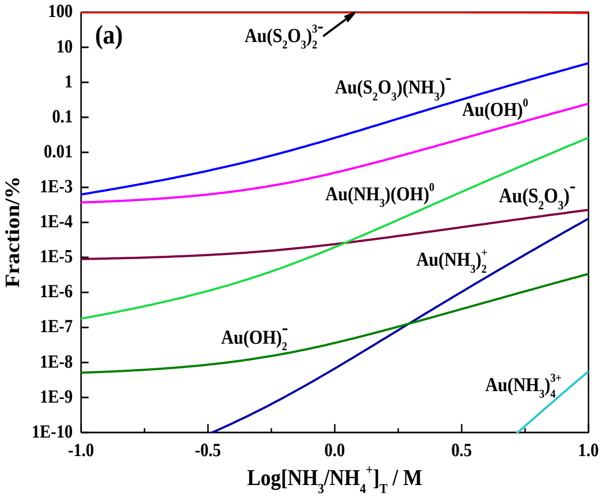

Figure 6. Speciation diagram of gold species in $NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system at varying concentrations of NH_3/NH_4^+. Conditions: 1×10^{-4} M Au^+, 0.5 M $S_2O_3^{2-}$, pH 9.5, E_h 0.250 V.

The E_h-pH diagram of Figure 5(a) shows that the predominant gold species is $Au(S_2O_3)_2^{3-}$ rather than $Au(NH_3)_2^+$, which is further confirmed by the distribution of gold species in Figure 6. Nevertheless, ammonia is considered to catalyze the anodic dissolution of gold via the formation of surface adsorbed species $Au(S_2O_3)(NH_3)^{2-}_{(ads)}$ (Senanayake, 2005a). It can be seen from Figure 6 that a small amount of $Au(S_2O_3)(NH_3)^-$ is formed, which is possibly an intermediate derived from the oxidation of $Au(S_2O_3)(NH_3)^{2-}_{(ads)}$. The possible catalytic role of ammonia in gold dissolution can be shown as Equations (1)–(3).

$$Au + S_2O_3^{2-} + NH_3 = Au(S_2O_3)(NH_3)^{2-}_{(ads)} \quad (1)$$

$$Au(S_2O_3)(NH_3)^{2-}_{(ads)} = Au(S_2O_3)(NH_3)^- + e \quad (2)$$

$$Au(S_2O_3)(NH_3)^- + S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + NH_3 \quad (3)$$

More importantly, according to the E_h-pH diagrams at different reagent concentrations for $Co\text{-}NH_3\text{-}S_2O_3^{2-}\text{-}H_2O$ system as depicted in Figures 1 and 5(b), the redox potentials of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x is mainly 4 and 5) are obviously higher than that of $Au/Au(S_2O_3)_2^{3-}$. Thus,

$Co(NH_3)_6^{3+}$ can act as an oxidant for gold dissolution in ammoniacal thiosulfate solutions, which takes place as Equation (4). The produced $Au(S_2O_3)(NH_3)^-$ will re-equilibrate in solution with $S_2O_3^{2-}$ as more stable $Au(S_2O_3)_2^{3-}$ as shown in Equation (3). Associating Equation (3) with Equation (4), the gold dissolution in cobalt ammoniacal thiosulfate solutions can be represented as Equation (5).

$$Au + S_2O_3^{2-} + Co(NH_3)_6^{3+} = Au(S_2O_3)(NH_3)^- + Co(NH_3)_x^{2+} + (5\text{-}x)\ NH_3 \quad (x = 1-6) \tag{4}$$

$$Au + 2\ S_2O_3^{2-} + Co(NH_3)_6^{3+} = Au(S_2O_3)_2^{3-} + Co(NH_3)_x^{2+} + (6\text{-}x)\ NH_3 \quad (x = 1-6) \tag{5}$$

In the presence of dissolved oxygen, $Co(NH_3)_x^{2+}$ ($x = 1-6$) can be re-oxidized back to $Co(NH_3)_6^{3+}$ as shown in Equation (6) for the continuous oxidation of gold. So the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ ($x = 1-6$) can work as the catalytic oxidant for gold leaching in oxygenated ammoniacal thiosulfate solutions. The overall reaction is expressed as Equation (7).

$$Co(NH_3)_x^{2+} + (6\text{-}x)\ NH_3 + 1/4\ O_2 + 1/2\ H_2O = Co(NH_3)_6^{3+} + OH^- \quad (x = 1-6) \tag{6}$$

$$Au + 2\ S_2O_3^{2-} + 1/4\ O_2 + 1/2\ H_2O = Au(S_2O_3)_2^{3-} + OH^- \tag{7}$$

Based on the above analysis, a possible cobalt-catalyzed mechanism of gold leaching with ammoniacal thiosulfate can be illustrated in an electrochemical model. At the anodic area of gold surface, ammonia catalyzes the oxidation of gold whilst at the cathodic area, the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ ($x = 1-6$) catalyze the reduction of dissolved oxygen, which is shown to be similar with the copper-catalyzed mechanism for leaching of gold in ammoniacal thiosulfate solutions.

5. THERMODYNAMIC STABILITY OF THIOSULFATE IN THE PRESENCE OF Co(III)/Co(II) REDOX COUPLE

A series of stable and metastable sulfur-oxygen species can be formed in solution as shown from the E_h-pH diagram of S-H_2O system (Figure 7). In the absence of sulfate species, thiosulfate ($S_2O_3^{2-}$) occurs in a narrow elongated stability area of pH 5.2–14 and E_h -0.6–+0.02 V. Clearly, $S_2O_3^{2-}$ is metastable and tends to undergo decomposition in aqueous solutions. The reported decomposition products include tetrathionate ($S_4O_6^{2-}$), trithionate ($S_3O_6^{2-}$), pentathionate ($S_5O_6^{2-}$), sulfur (S^0), polysulfide (S_n^{2-}, n = 2–6), sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}), which can influence the kinetics of gold leaching (Zhang and Senanayake, 2016).

Thermodynamically, the reported redox potentials for copper couples are greater than that for the $S_4O_6^{2-}/S_2O_3^{2-}$ couple as listed in Table 1, leading to the oxidation of $S_2O_3^{2-}$ by Cu(II) ammine complexes. The relevant redox potentials for cobalt couples and $S_4O_6^{2-}/S_2O_3^{2-}$ were calculated from stability constants log β (Appendix A) and ΔG (Appendix B), which are also listed in Table 1. Obviously, accompanying with the oxidation of gold, thiosulfate can also be oxidized by Co(III) ammine complexes because most of the redox potentials for $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ ($x = 1-6$) are greater than that for the $S_4O_6^{2-}/S_2O_3^{2-}$ couple. Nevertheless, the redox potentials for Co(III)/Co(II) appear to be lower than those for Cu(II)/Cu(I), which thermodynamically results in a reduced oxidation of thiosulfate.

As previously described for the oxidation mechanism of thiosulfate in copper ammoniacal thiosulfate solutions, Cu^{2+} mainly occurs as $Cu(NH_3)_4^{2+}$ with the remaining two axial coordinate sites occupied by water, and it is believed that the oxidation of thiosulfate by Cu(II) almost certainly occurs via a complexation of thiosulfate firstly substituting water from an axial coordinate site (Breuer and Jeffrey, 2003; Byerley et al., 1973; Liu et al., 2017a). Thus, an intermediate mixed ammonia/thiosulfate complex of $Cu(NH_3)_4S_2O_3^0$ is formed. Moreover, the oxygen molecule can also be axially associated with the Cu(II) center to form a Cu(II)-O_2-$S_2O_3^{2-}$complex, further catalyzing the oxidation of $S_2O_3^{2-}$ by Cu(II) (Byerley et al., 1975). In terms of the cobalt ammoniacal thiosulfate solutions, Co^{3+} primarily occurs in the form of $Co(NH_3)_6^{3+}$ which obeys the 18-electron rule and is considered to be an exchange inert metal complex with an octahedral Co(III) center (Greenwood and Earnshaw, 1997). The NH_3 is so tightly bound to the Co(III) center that NH_3 is difficult to be replaced by $S_2O_3^{2-}$ and O_2. So Co(III) ammine complexes are likely not reactive towards $S_2O_3^{2-}$ compared to Cu(II) ammine complexes, and thereby significantly alleviating the decomposition of thiosulfate. Thermodynamically, the possible reaction between Co(III) and $S_2O_3^{2-}$ is represented in Equation (8). Actually, the decomposition mechanism of

$S_2O_3^{2-}$ is complex, and thus further research is required to confirm the mechanism of thiosulfate oxidation by Co(III) ammine complexes.

$$S_2O_3^{2-} + Co(NH_3)_6^{3+} = 1/2\ S_4O_6^{2-} + Co(NH_3)_x^{2+} + (6\text{-}x)\ NH_3 \qquad (x = 1\text{–}6) \qquad (8)$$

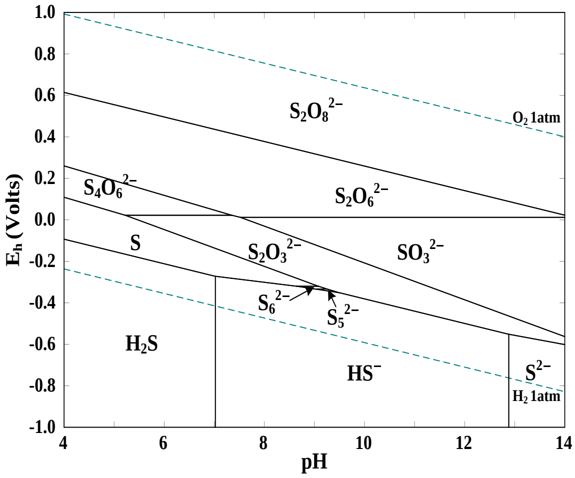

Figure 7. E$_h$-pH diagram of S-H_2O system. Conditions: 1.0 M S, without considering the sulfate species.

Table 1 Redox potentials for ammonia and thiosulfate complexes of cobalt and copper

Redox couple	Redox potential E^0/V [a]	Redox couple	Redox potential E^0/V [b]
$Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$	0.17	$Cu(NH_3)_4^{2+}/Cu(S_2O_3)_3^{5-}$	0.22 (0.24)
$Co(NH_3)_6^{3+}/Co(NH_3)_5^{2+}$	0.21	$Cu(NH_3)_4^{2+}/Cu(S_2O_3)_2^{3-}$	0.14 (0.16)
$Co(NH_3)_6^{3+}/Co(NH_3)_4^{2+}$	0.20	$Cu(NH_3)_3^{2+}/Cu(S_2O_3)_3^{5-}$	0.36 (0.36)
$Co(NH_3)_6^{3+}/Co(NH_3)_3^{2+}$	0.15	$Cu(NH_3)_3^{2+}/Cu(S_2O_3)_2^{3-}$	0.27 (0.26)
$Co(NH_3)_6^{3+}/Co(NH_3)_2^{2+}$	0.09	$S_4O_6^{2-}/S_2O_3^{2-}$	0.12
$Co(NH_3)_6^{3+}/Co(NH_3)^{2+}$	-0.01	$S_4O_6^{2-}/S_2O_3^{2-}$	0.022 [a]

[a] E^0 was calculated using $E^0[Co^{3+}/Co^{2+}] + 0.0591 \log[\beta_{Co(II)}/\beta_{Co(III)}]$ and $\Delta G_f^0 = -nFE^0$, of which the formation constants of relevant Co(III/II) complexes ($\beta_{Co(II)}$ and $\beta_{Co(III)}$) and ΔG_f^0 are listed in Appendices A and B.

[b] E^0 values were reported by Aylmore and Muir (2001b); values in parentheses were reported by Senanayake and Zhang (2012).

6. CONCLUSIONS

The thermodynamics of gold leaching in cobalt(III) ammoniacal thiosulfate solutions are elucidated based on the construction of E$_h$-pH and speciation diagrams under different conditions of pH, E$_h$ and varying concentrations of Co^{3+}, NH_3 and $S_2O_3^{2-}$. The thermodynamic calculations suggest that under appropriate reagent concentrations, the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1–6) with an E$_h$ of 0.05–0.35 V could be formed at pH of 8.5–9.7 without producing cobalt precipitate (Co_3O_4). Thermodynamically, $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1–6) can catalyze the dissolution of gold in ammoniacal thiosulfate solutions. A possible electrochemical-catalytic mechanism that the oxidation of gold is catalyzed by ammonia at the anodic area of gold surface while the reduction of oxygen at the cathodic area is catalyzed by the redox couples of $Co(NH_3)_6^{3+}/Co(NH_3)_x^{2+}$ (x = 1–6) is proposed, which is similar to the catalysis of the Cu(II)/Cu(I) redox couples. Co(III) can also oxidize thiosulfate like Cu(II), but the redox potentials of Co(III)/Co(II) are revealed to be lower than those of Cu(II)/Cu(I). In addition, the reactivity between Co(III) and thiosulfate seems to be less active in comparison with that between Cu(II) and thiosulfate possibly because the structural stability of octahedral $Co(NH_3)_6^{3+}$ is much more stable than that of $Cu(NH_3)_4^{2+}$. So the decomposition of thiosulfate can be significantly reduced using Co(III) ammine complexes as the oxidant for gold dissolution in ammoniacal thiosulfate solutions. The thermodynamic analysis in this paper can also provide a theoretical basis for the optimization of the cobalt-catalyzed leaching of gold with ammoniacal thiosulfate.

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APPENDICES

Appendix A. Equilibrium constants log K (log β) for the complexation of Co(III/II), Au(III/I) with thiosulfate, ammonia and hydroxide, and for the precipitation of the metal ions with hydroxide at 25±5°C

Metal ion	Ligand	Equilibrium	log K(log β) [a]	Reference
Co(III)	NH_3	$Co^{3+} + NH_3 = Co(NH_3)^{3+}$	6.7	
		$Co^{3+} + 2\ NH_3 = Co(NH_3)_2^{3+}$	14	
		$Co^{3+} + 3\ NH_3 = Co(NH_3)_3^{3+}$	20.1	
		$Co^{3+} + 4\ NH_3 = Co(NH_3)_4^{3+}$	25.7	
		$Co^{3+} + 5\ NH_3 = Co(NH_3)_5^{3+}$	30.8	
		$Co^{3+} + 6\ NH_3 = Co(NH_3)_6^{3+}$	35.2	
	OH^-	$Co^{3+} + OH^- = Co(OH)^{2+}$	12.69 [b]	
		$Co^{3+} + 3\ OH^- = Co(OH)_3(c)$	45.3	
Co(II)	$S_2O_3^{2-}$	$Co^{2+} + S_2O_3^{2-} = Co(S_2O_3)^0$	2.05	
	NH_3	$Co^{2+} + NH_3 = Co(NH_3)^{2+}$	2.11	
		$Co^{2+} + 2\ NH_3 = Co(NH_3)_2^{2+}$	3.74	
		$Co^{2+} + 3\ NH_3 = Co(NH_3)_3^{2+}$	4.79	
		$Co^{2+} + 4\ NH_3 = Co(NH_3)_4^{2+}$	5.55	
		$Co^{2+} + 5\ NH_3 = Co(NH_3)_5^{2+}$	5.73	
		$Co^{2+} + 6\ NH_3 = Co(NH_3)_6^{2+}$	5.11	
	OH^-	$Co^{2+} + OH^- = Co(OH)^+$	4.8	
		$Co^{2+} + 2\ OH^- = Co(OH)_2^0$	9.4	
		$Co^{2+} + 3\ OH^- = Co(OH)_3^-$	10.3	
		$Co^{2+} + 4\ OH^- = Co(OH)_4^{2-}$	9.6	

		$2\ Co^{2+} + OH^{-} = Co_2(OH)^{3+}$	4.2	
		$4\ Co^{2+} + 4\ OH^{-} = Co_4(OH)_4^{4+}$	26.1	
		$Co^{2+} + 2\ OH^{-} = Co(OH)_2(c)$	15.8	
		$Co^{2+} + 2\ OH^{-} = CoO(c) + H_2O$	14.22 [b]	
Au(III)	NH_3	$Au^{3+} + 4\ NH_3 = Au(NH_3)_4^{3+}$	46	Skibsted and Bjerrum, 1974
	OH^{-}	$Au^{3+} + OH^{-} = Au(OH)^{2+}$	17.99	
		$Au^{3+} + 2\ OH^{-} = Au(OH)_2^{+}$	31.49	
		$Au^{3+} + 3\ OH^{-} = Au(OH)_3^{0}$	42.94	
		$Au^{3+} + 4\ OH^{-} = Au(OH)_4^{-}$	46.71	
		$Au^{3+} + 5\ OH^{-} = Au(OH)_5^{2-}$	47.35	
		$Au^{3+} + 6\ OH^{-} = Au(OH)_6^{3-}$	45.38	
		$Au^{3+} + 3\ OH^{-} = Au(OH)_3(c)$	44.08 [b]	
		$2\ Au^{3+} + 6\ OH^{-} = Au_2O_3(c) + 3\ H_2O$	97.6 [b]	
Au(I)	$S_2O_3^{2-}$	$Au^{+} + S_2O_3^{2-} = Au(S_2O_3)^{-}$	16.6 [c]	Senanayake, 2004a
		$Au^{+} + 2\ S_2O_3^{2-} = Au(S_2O_3)_2^{3-}$	24 [c]	Senanayake et al., 2003
	NH_3	$Au^{+} + 2\ NH_3 = Au(NH_3)_2^{+}$	13 [c]	Aylmore and Muir, 2001b; Senanayake, 2004b
	OH^{-}	$Au^{+} + OH^{-} = Au(OH)^{0}$	22.36	
		$Au^{+} + 2\ OH^{-} = Au(OH)_2^{-}$	22	Stefánsson and Seward, 2003
		$Au^{+} + OH^{-} = Au(OH)(c)$	-23.99 [b]	
	$S_2O_3^{2-} + NH_3$	$Au^{+} + S_2O_3^{2-} + NH_3 = Au(S_2O_3)(NH_3)^{-}$	20	Perera and Senanayake, 2004
	$NH_3 + OH^{-}$	$Au^{+} + NH_3 + OH^{-} = Au(NH_3)(OH)^{0}$	20.6 [c]	Senanayake, 2004b

[a] Data from NIST Critical Stability Constants database (NIST, 2004) unless stated otherwise.

[b] Calculated using equation of $\Delta G_r° = -RT \ln K = \sum v_i\, \Delta G_f°(i)$, of which $\Delta G_f°$ values are listed in Appendix B.

[c] Based on linear free energy correlations.

Appendix B. Free energies of formation (kcal/mol or kJ/mol) for relevant species [a]

Species	$\Delta G°_{298}$ (kcal/mol)	$\Delta G°_{298}$ (kJ/mol)	Species	$\Delta G°_{298}$ (kcal/mol)	$\Delta G°_{298}$ (kJ/mol)	Species	$\Delta G°_{298}$ (kcal/mol)	$\Delta G°_{298}$ (kJ/mol)
S	0	0	H^{+}(a)	0	0	Co	0	0
H_2S(a)	-6.607	-27.656	OH-(a)	-37.577	-157.29	CoO	-51.194	-214.290
HS^{-}(a)	2.973	12.445	O_2(a)	3.899	16.321	Co_3O_4	-189.986	-795.253
H_2SO_3(a)	-128.552	-538.098	H_2O(a)	-56.678	-237.227	CoO_2	-48.656	-203.668
$H_2S_2O_3$(a)	-128.006	-535.813				$Co(OH)_2$	-109.479	-458.263
$H_2S_2O_4$(a)	-147.385	-616.933	Au	0	0	$Co(OH)_3$	-142.526	-596.593
HSO_3^{-}(a)	-126.103	-527.847	AuO_2	47.971	200.8	CoS	-23.13	-96.819
HSO_4^{-}(a)	-180.524	-755.647	Au_2O_3	18.609	77.894	CoS_2	-34.808	-145.701
$HS_2O_3^{-}$(a)	-127.183	-532.368	$Au(OH)_3$	-75.729	-290.0	Co^{3+}(a)	31.937	133.684
$HS_2O_4^{-}$(a)	-146.862	-614.743	Au(OH)	34.126	142.8	Co^{2+}(a)	-13.021	-54.504
S^{2-}(a)	20.548	86.011	Au^{3+}(a)	103.316	433.5	$Co(NH_3)^{3+}$(a) [b]	16.501	69.071
S_2^{2-}(a)	19.055	79.763	Au^{+}(a)	39.174	163.2	$Co(NH_3)_2^{3+}$(a) [b]	0.171	0.716
S_3^{2-}(a)	17.657	73.910	$Au(S_2O_3)^{-}$(a) [b]	-108.288	-453.3	$Co(NH_3)_3^{3+}$(a) [b]	-14.522	-60.787
S_4^{2-}(a)	16.589	69.439	$Au(S_2O_3)_2^{3-}$(a) [b]	-243.204	-1018.0	$Co(NH_3)_4^{3+}$ (a) [b]	-28.533	-119.435
S_5^{2-}(a)	15.821	66.223	$Au(NH_3)_4^{3+}$(a)	15.385	64.4	$Co(NH_3)_5^{3+}$ (a) [b]	-41.863	-175.232
S_6^{2-}(a)	15.827	66.250	$Au(NH_3)_2^{+}$(a) [b]	8.697	36.4	$Co(NH_3)_6^{3+}$ (a) [b]	-54.238	-227.032
SO_3^{2-}(a)	-116.287	-486.761	Au(OH)(a) [b]	-26.494	-110.9	$Co(OH)^{2+}$ (a) [b]	-23.017	-96.346
SO_4^{2-}(a)	-177.907	-744.691	$Au(OH)_2^{-}$(a) [b]	-65.979	-276.2	$Co(NH_3)^{2+}$(a) [b]	-22.249	-93.131
$S_2O_3^{2-}$(a)	-124.825	-522.5	$Au(OH)^{2+}$(a) [b]	41.455	173.522	$Co(NH_3)_2^{2+}$(a) [b]	-30.846	-129.117
$S_2O_4^{2-}$(a)	-143.539	-600.833	$Au(OH)_2^{+}$(a) [b]	-14.531	-60.826	$Co(NH_3)_3^{2+}$(a) [b]	-38.653	-161.796
$S_2O_6^{2-}$(a)	-231.605	-969.465	$Au(OH)_3$(a) [b]	-75.731	-283.5	$Co(NH_3)_4^{2+}$(a) [b]	-46.064	-192.817
$S_2O_8^{2-}$(a)	-266.460	-1115.362	$Au(OH)_4^{-}$(a) [b]	-110.439	-462.282	$Co(NH_3)_5^{2+}$(a) [b]	-52.685	-220.532
$S_3O_6^{2-}$(a)	-228.814	-957.784	$Au(OH)_5^{2-}$(a) [b]	-148.889	-623.225	$Co(NH_3)_6^{2+}$(a) [b]	-58.214	-243.675
$S_4O_6^{2-}$(a)	-248.626	-1040.714	$Au(OH)_6^{3-}$(a) [b]	-183.779	-769.271	$Co(OH)^{+}$(a)	-56.018	-234.483
$S_5O_6^{2-}$(a)	-228.331	-955.759	$Au(S_2O_3)(NH_3)^{-}$(a) [b]	-119.299	-499.4	$Co(OH)_2$(a)	-101.28	-423.943
			$Au(NH_3)(OH)$(a) [b]	-32.869	-137.6	$Co(OH)_3^{-}$(a)	-139.635	-584.491
NH_3(a)	-6.375	-26.685	AuO_3^{3-}(a)	-5.805	-24.3	$Co(OH)_4^{2-}$(a) [b]	-176.394	-738.359
NH_4^{+}(a)	-18.977	-79.433	$HAuO_3^{2-}$(a)	-27.593	-115.5	$Co_2(OH)^{3+}$(a)	-69.86	-292.424
$NH_4(S_2O_3)^{-}$(a) [b]	-62.662	-262.3	$H_2AuO_3^{-}$(a)	-45.773	-191.6	$Co_4(OH)_4^{4+}$(a)	-239.137	-1000.992
			H_3AuO_3(a)	-61.780	-258.6	CoO(a) [b]	-44.043	-184.357
						CoO_2^{2-}(a) [b]	-63.179	-264.458
						$Co(S_2O_3)$(a)	-140.617	-588.601
						$HCoO_2^{-}$(a) [b]	-83.426	-349.209

[a] Data from HSC database 6.0 (Roine, 2006) and Thermochemical Data of Pure Substances (Barin, 1995).

[b] $\Delta G°_{298}$ values were calculated using equation of $\Delta G_r° = -RT \ln K = \sum[v_i \Delta G_f°(i)]$, of which log K values are listed in Appendix A and log $K[NH_4(S_2O_3)^{-}] = 0.93$ (Senanayake, 2005b).