

# New data on the stability of gold(I) chloride complexes at 300°C

C.H. Gammons  
A.E. Williams-Jones  
Y. Yu

Dept. of Earth and Planetary Sciences, McGill University,  
Montreal, Quebec H3A 2A7, Canada  
Geochemistry Institute, Academia Sinica, Guiyang, People's  
Republic of China.

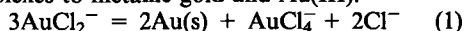
## Introduction

We report results of an ongoing investigation of the solubility of Au-Ag alloys (the mineral electrum) in hydrothermal solutions to 300°C. The results have been used to estimate an equilibrium constant for the dissolution of gold as  $\text{AuCl}_2^-$  at 300°C. This value is in excellent agreement with the theoretical study of Helgeson (1969).

## Methods

Synthetic Au-Ag alloys ( $X_{\text{Au}} = 0.3, 0.5, 0.7$  and  $0.9$ ) were prepared by fusing powders of the pure metals in a graphite crucible at temperatures slightly above the melting point of the binary phase. The products were rolled and cut to obtain small foils which fit inside 9mm x 20cm silica tubes. A fifth tube was loaded with a foil of pure gold. Identical solutions containing 3.0M HCl were added to each tube, along with a pressed pellet of AgCl. The tubes were sealed under a slight vacuum, and placed inside a small pressure vessel. The experiments were reacted at  $300 \pm 1^\circ\text{C}$  for a period of 2 months, using a laboratory oven with forced air convection. At the end of the experiment the pressure vessel was inverted, allowing separation of saturated solution from the solid reactants, which remained lodged at a narrow constriction in the tubes.

Immediately after quenching to room temperature, the solutions were colorless, with a considerable amount of fresh AgCl precipitate in the bottom of the tubes. However, over a period of several days, some of the experimental solutions developed a strong yellow color, with concomitant precipitation of very fine gold crystals. This impressive phenomenon was attributed to the slow disproportionation of Au(I) chloride complexes to metallic gold and Au(III):

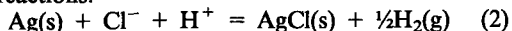


After a period of one week, the tubes were opened, the pellets and foils were dried and weighed, and the solutions were analyzed in the

following sequence: (1) the quenched solutions were removed and filtered; (2) the AgCl precipitate was digested using  $\text{NH}_4\text{OH}$ ; and (3) the gold precipitate was digested using aqua regia. Metal concentrations in each fraction were determined by flame and/or graphite furnace AAS. The total solubility of each metal was obtained by summing the contributions from (1) to (3). Silver solubility was also determined by mass loss of the pellets. In those samples with very high gold solubility, the relative amount of gold in fraction (1) vs. fraction (3) was found to be 1:2, thus confirming the disproportionation hypothesis.

## Redox control

An obvious advantage of using binary alloys as reactants is that the relative and absolute solubility of two metals under identical conditions may be precisely determined. A second advantage is that the compositions of the alloys, in equilibrium with AgCl(s), may be used to calculate the oxidation state of the system, as shown by the following reactions:



$$f_{\text{H}_2} = (a_{\text{Ag}} \cdot a_{\text{Cl}^-} \cdot a_{\text{H}^+} \cdot K_2)^{-2} \quad (3)$$

where  $a_{\text{Ag}}$  is the activity of Ag in the Au-Ag solid solution, and  $K_2$  is the equilibrium constant for reaction (2). The latter was calculated using published thermodynamic data for AgCl(s) and  $\text{Cl}^-$  at 300°C. The quantity  $a_{\text{Ag}}$  was calculated by analyzing the surfaces of the reacted alloys by electron microprobe, and then applying corrections for non-ideality using thermodynamic data for the Au-Ag system (Hultgren *et al.*, 1973). Finally,  $a_{\text{Cl}^-}$  and  $a_{\text{H}^+}$  were calculated using published data on the dissociation of HCl (Mesmer *et al.*, 1988), in conjunction with an extended Debye-Hückle equation for calculating individual ion activity coefficients.

## Results

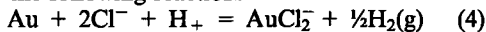
The analytical results of our first set of electrum solubility experiments are summarized in Table 1.

TABLE 1. Analytical data for 300°C, 3m HCl

$X_{Au}^a$	$X_{Au}^b$	$\Sigma Ag^c$	$\Sigma Au^c$	$\log f_{H_2}$	$\log K_4$
0.319	0.500	-0.81	-5.80	-1.92	-5.71
0.525	0.697	-0.79	-5.56	-2.97	-6.35
0.708	0.849	-0.81	-4.17	-4.11	-5.69
0.908	0.981	-0.80	-2.51	-6.42	-5.28
1.000	0.994	-0.81	-2.41	-7.54	-5.74

<sup>a</sup> initial composition of foils; <sup>b</sup> composition of foil surfaces after the run; <sup>c</sup> metal solubility (log molal)

The composition of the alloys changed significantly during the run (in most cases, becoming more Au-rich). As expected, silver solubility was very high for every sample, and was insensitive to alloy composition. In contrast, gold solubility showed a dramatic increase of over 3 orders of magnitude from the experiments using Ag-rich electrum to those with pure gold. Because all five solutions had identical initial HCl concentrations, this variation can only be explained by changes in the activity of Au in the alloy and/or changes in  $f_{H_2}$  between each experiment. The latter quantity is recorded in column 5 of Table 1. Column 6 gives our calculated values of the equilibrium constant for the following reaction:



The average value of  $\log K_4$  obtained in these experiments is  $-5.75 \pm 0.34$  (error represents one standard deviation). The agreement between individual samples is good, especially considering the very wide range in gold solubility and  $f_{H_2}$  of the experiments. However, this value should be considered somewhat provisional, as the stoichiometry of reaction (4) has not been confirmed. Experiments over a range of HCl concentrations are in progress to verify that  $AuCl_2^-$  is indeed the dominant species.

### Discussion

Fig. 1 indicates that our preliminary value for log

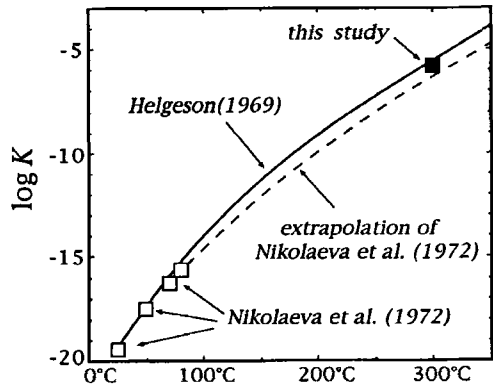


FIG. 1. Comparison of  $\log K_4$  determined in this study with previous estimates.

$K_4$  at 300°C is in superb agreement with the theoretical estimates of Helgeson (1969), and with a simple isocoulombic extrapolation of the low temperature data of Nikolaeva *et al.* (1972). (Our experimental uncertainty lies within the size of the symbol). A lack of published data at 300°C precludes a direct comparison with other experimental studies.

Although more data are needed to confirm our preliminary results, this study illustrates the potential of solubility experiments involving metal alloys. We intend to adapt this method to investigate other alloy systems.

### References

- Helgeson, H. C. (1969) *Amer. J. Sci.*, **63**, 622–35.  
 Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M. and Kelley, K. K. (1973) *Amer. Soc. Metals*.  
 Mesmer, R. E., Marshall, W. L., Palmer, D. A., Simonson, J. M. and Holmes, H. F. (1988) *J. Soln. Chem.*, **17**(8), 699–718.  
 Nikolaeva, N. M., Yerenburg, A. M. and Antinina, V. A. (1972) *Izvest. Sib. Otd. Akad. SSSR, Ser. Khim.* **4**, 126–9.