Investigations on the Chlorides of Gold

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1. *Hydrolysis of the $AuCl_4^-$ Ion* (from experiments by N. H. ARNFRED and G. E. HJORT).

Even in acid solution Cl^- ions are only split off from $AuCl_4^-$ ions when HO^- ions are taken up at the same time. In dilute solution (0.01 molar) the hydroxo complexes: $AuCl_3OH^-$, $AuCl_2(OH)_2^-$, $AuCl(OH)_3^-$, $Au(OH)_4^-$ will be formed on addition of NaOH. The equilibrium constants:

$$K_n = \frac{[AuCl_{4-n}(OH)_n][H^+][Cl^-]}{[AuCl_{4-n+1}(OH)_{n-1}]} \cdot f^2$$

(f being a mean ion-activity coefficient) are determined through measurements of pH with a gold electrode in solutions of $HAuCl_4$ (with or without addition of KCl), to which NaOH is added.

$$pK_1 = 6.07; \quad pK_2 = 7.00; \quad pK_3 = 8.04; \quad pK_4 = 8.51.$$

Equilibrium is set up almost immediately except as regards the tetrahydroxo complex for which it takes about 24 hours.

In concentrated solutions complexes with several gold atoms are formed slowly on addition of NaOH, and subsequently a deposition of impure auric hydroxide will occur.

2. *The Redox Potentials of the Gold Chlorides* (from experiments by G. BJØRLING).

If sulphite is added to a dilute solution of auric chloride, aurous chloride is at once formed in the solution. If the course of the redox potential during this addition is followed by means of a platinum electrode, falling potentials will be observed at the beginning. In this initial period the fall of the potential shows that the process determining the potential is $AuCl_4^- + 2e^- \rightleftarrows AuCl_2^- + 2Cl^-$, and for the corresponding standard potential we calculate:

$$_0E_{3,1} = E + 0.029 \log \frac{[AuCl_2^-][Cl^-]^2 f^2}{[AuCl_4^-]} = 0.932 \text{ volts}$$

(E is the measured potential, corrected for diffusion potential and converted to the potential of the standard hydrogen electrode). After the addition of a certain small amount of sulphite the potential begins to *rise*, and at the same time gold deposits on the platinum electrode. The gold does not, however, separate out in the liquid, and even the amount deposited on the electrode is small. When one mole Na_2SO_3 has been added per one mole $HAuCl_4$, and the gold has been completely reduced to aurous chloride, the redox potential passes through a flat maximum simultaneously with decoloration of the solution.

In this 2nd period the process determining the potential is $AuCl_2^- + e^- \rightleftharpoons Au + 2Cl^-$, and for the standard potential corresponding to this process we calculate:

$$_0E_{1.0} = E + 0.058 \log \frac{[Cl^-]_f^2 f}{[AuCl_2^-]} = 1.119 \text{ volts.}$$

If substantially more than one mole Na_2SO_3 is added per one mole $HAuCl_4$, gold also begins to separate out in the solution; but not until somewhat more than $1\frac{1}{2}$ mole Na_2SO_3 per 1 mole $HAuCl_4$ has been added, does the reduction potential decrease to the low value characteristic of sulphite.

3. With a knowledge of the above mentioned four hydrolysis constants and the two redox potentials, it is possible to calculate the composition of a pure auric chloride solution as well as that of a dilute auric chloride solution saturated with gold. The chlorine and oxygen tensions corresponding to equilibrium in such solutions can be calculated, and a quantitative determination of the stability of gold chloride towards bases and reducing substances has been obtained.