

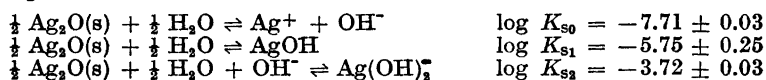
Studies on the Hydrolysis of Metal Ions

Part 30. A Critical Survey of the Solubility Equilibria of Ag₂O

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On the basis of recalculation of the data available in the literature (Table 1) the most probable values of the constants of the following equilibria have been estimated at 25°C:



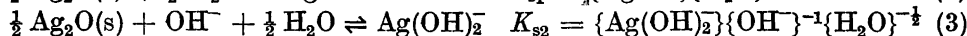
For the complex formation OH⁻-Ag⁺ these data give

$$\begin{array}{l} \log K_1 = \log \frac{[\text{AgOH}][\text{Ag}^+]}{[\text{Ag}^+][\text{OH}^-]} = 2.0 \pm 0.3; \\ \log \beta_2 = \log \frac{[\text{Ag}(\text{OH})_2^-]}{[\text{Ag}^+][\text{OH}^-]^2} = 3.99 \pm 0.05 \end{array}$$

The different experimental methods which were employed to study these equilibria have been discussed in some detail.

In three preceding papers the hydrolysis equilibria of the Ag⁺ ion were studied in acid¹, moderately alkaline² and highly alkaline³ solutions by a group of workers in this laboratory. The data obtained by these investigators could be explained by assuming the formation of the species AgOH and Ag(OH)₂⁻, and no evidence was found for the presence of appreciable amounts of polynuclear products which were claimed by several previous authors^{4,5}.

As a consequence of these results the solubility equilibria of Ag₂O may be written

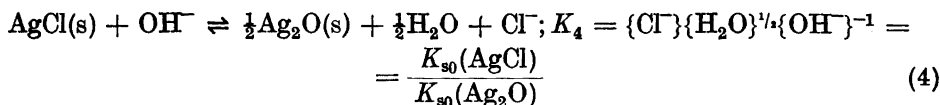


where the symbol {} denotes activity. The present paper is devoted to a discussion of the available data concerning equilibria (1), (2) and (3). On the basis of the discussion an attempt has been made to estimate the most probable values at 25°C of K_{s0}, K_{s1} and K_{s2}, which are collected in the Synopsis.

It is believed that the conclusions reached in this work might find a general interest for the study of equilibria involving slightly soluble metal oxides and hydroxides.

ON THE SOLUBILITY PRODUCT OF Ag_2O , K_{s0}

Four methods have been applied to determine K_{s0} : (A) emf measurements (B) study of the equilibrium



(C) conductance measurements and (D) chemical analysis of the saturated solution.

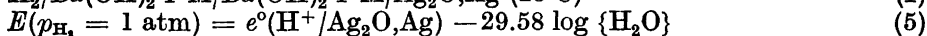
As will be clear from the following discussion K_{s0} may be determined in a straightforward manner by methods (A) and (B), when the measurements are made in solutions of $[\text{OH}^-] \geq 0.01$ M which have an appreciable buffer capacity. Methods (C) and (D) require on the other hand the study of a saturated solution of Ag_2O containing no added electrolyte. Since the solubility product of Ag_2O is rather low ($\log K_{s0}$ is about -7.7) the composition of the saturated solution is influenced considerably by the presence of slight amounts of protolyzing impurities, *e.g.* CO_2 or substances dissolved from glass.

Using methods (C) and (D) therefore the nature and concentration of the impurities must be known and their effect on the data must be taken into account. By a correct treatment of the conductance and the analytical data the uncertainty caused by the presence of impurities may become unappreciable, as it is shown by the fact that the results derived from the experiments of the most careful workers are in agreement with those found by the methods (A) and (B), (see Table 1).

(A) Emf measurements with the half-cell $\text{OH}^-/\text{Ag}_2\text{O(s),Ag}$

Previous workers⁶⁻⁸ had difficulty in obtaining constant and reproducible emf values with $\text{Ag}_2\text{O,Ag}$ electrodes. More recently, however, Makolkin⁹ and Hamer and Craig¹⁰ were able to find the experimental conditions in which the $\text{Ag}_2\text{O,Ag}$ electrodes function reversibly.

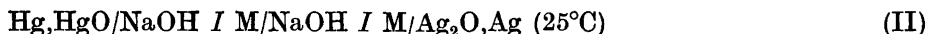
The cell studied by Makolkin had the composition



and he found

$$E = 1171.9 \pm 0.8 \text{ mV}_{\text{int}} = 1172.3 \pm 0.8 \text{ mV}_{\text{abs}}^*$$

The cell of Hamer and Craig was



and they obtained

$$E = 244.0 \pm 0.5 \text{ mV}_{\text{abs}}$$

* The conversion to mV_{abs} was made by the present authors.

Here e° denotes the standard potential referred to the hydrogen scale.

Cells I and II may be expected to yield highly accurate values for K_{s_0} . The solubilities of Ag_2O and HgO are so low that the liquid junction potential is quite negligible for $I \geq 0.01$ M. Both these investigators used solutions of $I \geq 0.1$ M, therefore small amounts of CO_2 and substances dissolved from glass, which can hardly be avoided, do not influence appreciably the composition of the solutions. Moreover since the $[\text{OH}^-]$ is practically the same in both half-cells the effect of the impurities on the emf will be cancelled out.

The correctness of the assumed cell reaction may be tested, *e.g.* by changing I . Hamer and Craig have found that the emf of cell II remains constant within ± 0.5 mV as $[\text{OH}^-]$ is varied from 1.3 to 10 M.

Since

$$e^\circ(\text{H}^+/\text{Ag}_2\text{O}, \text{Ag}) = e^\circ(\text{Ag}^+/\text{Ag}) + 59.15 \log \frac{K_{s_0}}{K_w} \quad (7)$$

where K_w is the ionic product of water, we need in order to calculate K_{s_0} the values of the constants K_w , $e^\circ(\text{Ag}^+/\text{Ag})$ and with cell II also $e^\circ(\text{H}^+/\text{HgO}, \text{Hg})$. We shall use $\text{p}K_w = 13.997$; the most probable values for the standard potentials will be taken from a critical survey¹¹ made in this laboratory: $e^\circ(\text{Ag}^+/\text{Ag}) = 799.4 \pm 0.2$ mV_{abs} and $e^\circ(\text{H}^+/\text{HgO}, \text{Hg}) = 926.1 \pm 0.3$ mV_{abs}. The term containing $\{\text{H}_2\text{O}\}$ in (5) has been neglected, since Harned and Mason¹² have shown that in 0.1 M $\text{Ba}(\text{OH})_2$ (the concentration presumably used by Makolkin) it is less than 0.05 mV.

With the constants selected Makolkin's data give $-\log K_{s_0} = 7.70 \pm 0.02$ and those of Hamer and Craig 7.73 ± 0.02 ; the difference does not exceed significantly the experimental uncertainty.

$$(B) \text{ Determination of } K_4 = \frac{K_{s_0}(\text{AgCl})}{K_{s_0}(\text{Ag}_2\text{O})}$$

Since at 25°C the solubility product of AgCl , $K_{s_0}(\text{AgCl})$, is about $0.01 \times K_{s_0}(\text{Ag}_2\text{O})$ the analytical determination of the ratio $[\text{Cl}^-][\text{OH}^-]^{-1}$ in a solution which is in equilibrium with solid Ag_2O and AgCl may be carried out with a fair degree of accuracy. Two sets of data are available — the measurements of Noyes and Kohr¹³ and those of Newton¹⁴, which are in a satisfactory agreement. These investigators have found that equilibrium is established at 25°C within a few hours, so that the attack of OH^- on the glass surface may not introduce an appreciable error.

No systematic trend can be detected in the $[\text{Cl}^-][\text{OH}^-]^{-1}$ values as $[\text{OH}^-]$ varies from 0.05 to 0.35 M. This fact indicates that in these solutions $f(\text{Cl}^-)f^{-1}(\text{OH}^-)$ is equal to unity within the narrow limits of experimental uncertainty. The deviation of $\{\text{H}_2\text{O}\}$ from unity is certainly negligible. We can thus set $K_4 = [\text{Cl}^-][\text{OH}^-]^{-1}$.

From the data of Newton¹⁴ the average value of $\text{p}K_4$ is calculated to be 2.045 ± 0.015 and from those of Noyes and Kohr¹³ 2.02 ± 0.02 . On the basis of a critical examination of the available data Sillén¹⁵ gave as the most probable value of $\text{p}K_s(\text{AgCl})$ 9.752 ± 0.005 . Introducing this value into (4) we find $\text{p}K_{s_0} = 7.71 \pm 0.03$ from Newton's results, and 7.73 ± 0.05 from those of Noyes and Kohr; the agreement with the figures deduced from the emf measurements is satisfactory.

(C) Conductance measurements

The conductance of a saturated solution of Ag_2O was determined at 25°C with a high accuracy by Böttger¹⁶ and Laue¹⁷. Both these investigators employed a Ag_2O preparation of high purity and used as solvent "conductivity water" which denotes pure water kept in contact with air. Böttger evaluated K_{s0} by the classical method; he set $10^3(\kappa - \kappa_w) = \sqrt{K_{s0}} (\lambda_{\text{Ag}^+} + \lambda_{\text{OH}^-})$ where κ is the conductance of the saturated solution, κ_w is that of the conductance water and λ denotes ionic conductance.

Laue¹⁷ realized that the chief impurity in conductance water is carbon dioxide at such a high concentration (about 10^{-5} M) that a considerable error is made when in the saturated solution $[\text{Ag}^+]$ is set equal to $[\text{OH}^-]$. Laue has given a correct treatment of his data and obtained $\text{p}K_{s0} = 7.71$. The general principles used by this author form the basis of our approach which is somewhat more simple.

The computation of K_{s0} consists of two steps. First α) the total carbon dioxide content, $[\text{CO}_2]_{\text{tot}}$, of the conductance water is calculated from κ_w , then β) the composition of the saturated solution is obtained from $[\text{CO}_2]_{\text{tot}}$ and κ .

Since the ionic strength of a saturated solution is about 10^{-4} M we have assumed the activity factors of all species present to be unity and we have neglected the variation of the ionic conductances with concentration.

α) $[\text{CO}_2]_{\text{tot}}$ was calculated from κ_w by combining

$$10^3\kappa_w = h\lambda_{\text{H}^+} + [\text{HCO}_3^-]\lambda_{\text{HCO}_3^-} = h(\lambda_{\text{H}^+} + \lambda_{\text{HCO}_3^-}) \quad (8)$$

with

$$K_{a1} = \frac{h[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3 + \text{CO}_2]} \quad (9)$$

$$\text{and } [\text{CO}_2]_{\text{tot}} = [\text{H}_2\text{CO}_3 + \text{CO}_2] + [\text{HCO}_3^-] \quad (10)$$

Kolthoff and Elmquist¹⁸ have found that κ_w is decreased by no more than about 90 % if CO_2 is removed by purified air from a conductance water. These experiments indicate that it can be regarded only as a rough approximation if we ascribe κ_w entirely to $[\text{CO}_2]_{\text{tot}}$ because conductance water contains also non-volatile impurities. However the error introduced by calculating $[\text{CO}_2]_{\text{tot}}$ with (8) does not exceed the uncertainty of the κ measurement.

β) In a saturated solution of Ag_2O the concentrations of the ionic species present are related by the equation

$$[\text{Ag}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}], \quad (11)$$

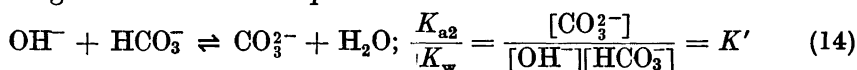
the specific conductance is given by

$$10^3\kappa = [\text{Ag}^+]\lambda_{\text{Ag}^+} + [\text{OH}^-]\lambda_{\text{OH}^-} + [\text{HCO}_3^-]\lambda_{\text{HCO}_3^-} + 2[\text{CO}_3^{2-}]\lambda_{\text{CO}_3^{2-}} \quad (12)$$

and since $\log h$ is about -10

$$[\text{CO}_2]_{\text{tot}} \cong [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (13)$$

By taking into account the equilibrium



insertion of (11) and (13) into (12) yields

$$10^3 \kappa = x(\lambda_{\text{OH}^-} + \lambda_{\text{Ag}^+}) + \frac{[\text{CO}_2]_{\text{tot}}}{1 + K'x} [\lambda_{\text{Ag}^+} + \lambda_{\text{HCO}_3^-} + 2K'x(\lambda_{\text{CO}_3^{2-}} + \lambda_{\text{Ag}^+})] \quad (15)$$

where $[\text{OH}^-]$ is denoted by x for convenience. The unknown $[\text{OH}^-]$ is obtained by a short series of successive approximations from (15) and the known, $[\text{CO}_2]_{\text{tot}}$, K' and the λ 's, then $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ are calculated using (14) and (13). $[\text{Ag}^+]$ is found from (11).

The following numerical values were used: $\text{p}K_{a1} = 6.352^{19}$, $\text{p}K_{a2} = 10.329^{20}$; $\lambda_{\text{H}^+} = 349.8$, $\lambda_{\text{Ag}^+} = 61.92$, $\lambda_{\text{OH}^-} = 197.6$, $\lambda_{\text{HCO}_3^-} = 44.5^{21}$ and $\lambda_{\text{CO}_3^{2-}} = 74.0^{22}$.

Application of this calculation to the κ_w and κ data of Böttger has given $\text{p}K_{s0} = 7.69 \pm 0.02$ while Laue's figures give 7.71 ± 0.02 .

The agreement with the $\text{p}K_{s0}$ values found in sections (A) and (B) shows that conductance measurement is also capable of giving accurate results in such an unfavorable system as that discussed.

(D) Chemical analysis

The attempts of workers prior to Laue to determine $[\text{Ag(I)}]_{\text{tot}}$ in a saturated solution of Ag_2O had the purpose of getting only approximate values. Laue¹⁷ and Johnston *et al.*⁴ were able to work out electroanalytical and potentiometric methods suitable for determining a silver concentration of about 10^{-4} M with an accuracy of a few percent. The results of these very careful workers differ considerably. Laue found that in paraffinized flasks the solubility equilibrium is established at 25°C within an hour and he obtained $[\text{Ag(I)}]_{\text{tot}} = (1.51 \pm 0.10) \times 10^{-4}$ M. According to Johnston *et al.* at least ten days were required to attain equilibrium and they found $[\text{Ag(I)}]_{\text{tot}} = (2.22 \pm 0.04) \times 10^{-4}$ M.

We have reason to assume that Johnston's value for $[\text{Ag(I)}]_{\text{tot}}$ was high, because some OH^- reacted with small amounts of carbon dioxide in the conductance water ($\kappa_w \sim 1.2 - 2 \times 10^{-5}$) and with the surface of the pyrex flask (which was in contact with an alkaline solution for many days) forming silicates, aluminates and borates.

Assuming that $[\text{Ag(I)}]_{\text{tot}} = [\text{Ag}^+]$ we may give a rough estimate of the amount of OH^- ions which by reacting with glass might have caused the high results of Johnston *et al.* These authors used a water of $\kappa_w = 1.2 \times 10^{-6}$ corresponding to $[\text{CO}_2]_{\text{tot}} = 2.4 \times 10^{-5}$ M. With this value and with $\text{p}K_{s0} = 7.70$ we estimate that their solution with $[\text{Ag}^+] = 2.22 \times 10^{-4}$ M contained also $[\text{OH}^-] = 9 \times 10^{-5}$, $[\text{HCO}_3^-] = 1.7 \times 10^{-5}$, $[\text{CO}_3^{2-}] = 7 \times 10^{-6}$ and $[\text{SiO(OH)}_3^-] + [\text{Al(OH)}_4^-] + [\text{B(OH)}_4^-] = 1 \times 10^{-4}$ M. According to experiences in this laboratory such a value for $[\text{SiO(OH)}_3^-] + [\text{Al(OH)}_4^-] + [\text{B(OH)}_4^-]$ does not seem to be unreasonable.

The apparently slow attainment of the solubility equilibrium may also be explained by reaction of OH^- with glass. As the $[\text{OH}^-]$ is decreased more Ag_2O

Table 1. Survey of the calculated pK_{s0} values.

Author	Method	Auxiliary data	pK_{s0}
1. Makolkin ⁹	emf of the cell $H_2/Ba(OH)_2$ I M/ Ag_2O , Ag	$e^0(Ag^+/Ag) = 799.4 \pm 0.2$ mV _{abs}	7.70 ± 0.02
2. Hamer and Craig ¹⁰	emf of the cell Hg, HgO/NaOH I M/ Ag_2O , Ag	$e^0(Ag^+/Ag) = 799.4 \pm 0.2$ mV _{abs} $e^0(H^+/HgO, Hg) = 926.1 \pm 0.3$ mV _{abs}	7.73 ± 0.02
3. Noyes and Kohr ¹³	K for $\frac{1}{2}Ag_2O + \frac{1}{2}H_2O + Cl^- \rightleftharpoons AgCl + OH^-$	$pK_s(AgCl) = 9.75_2 \pm 0.005$	7.73 ± 0.06
4. Newton ¹⁴	as 3.	as 3.	7.71 ± 0.03
5. Böttger ¹⁶	conductance	$\kappa_{H_2O} = 1.15 \times 10^{-6}$	7.69 ± 0.02
6. Laue ¹⁷	conductance	$\kappa_{H_2O} = (1.35 \text{ and } 1.53) \times 10^{-6}$	7.71 ± 0.02
7. Laue ¹⁷	chemical analysis	$\kappa_{H_2O} = 1.2 \times 10^{-6}$	7.75 ± 0.05

will dissolve until $[Ag^+][OH^-]$ becomes again equal to K_{s0} . Dissolution of glass in alkaline solutions is known to be rapid at first, but after prolonged contact the reaction becomes very slow. Thus after a period the increase of the $[Ag^+]$ is expected to be unappreciable.

Recent experimental results on the hydrolysis of the Ag^+ ion ¹ have given no support to the hypothesis of Johnston *et al.* that the high solubility is to be explained by the formation of the species Ag_2OH^+ .

Laue's data may be used to get an approximate value of K_{s0} . We have assumed $[Ag(I)]_{tot}$ to be equal to $[Ag^+]$. The discussion presented in the next section indicates that the error so made is less than the experimental uncertainty. First $[CO_2]_{tot}$ was calculated from (8) using $\kappa_w = 1.2 \times 10^{-5}$ as given by Laue, then $[OH^-]$ was obtained from (14) and (11) by successive approximation. This treatment gave $pK_{s0} = 7.75 \pm 0.05$.

The results of our calculations are summarized in Table 1; this indicates a substantial agreement between the pK_{s0} values based on different assumptions and experimental procedures. As the most probable value we would propose the weighted average $\log K_{s0} = -7.71 \pm 0.03$.

ON THE SOLUBILITY OF Ag_2O IN ALKALINE SOLUTIONS

Johnston *et al.* ⁴ made an extensive and highly accurate study on the solubility of Ag_2O in NaOH, KOH and $Ba(OH)_2$ solutions at 25°C. A few data in NaOH solutions have also been obtained by Laue ¹⁷. It should be pointed out that as $[OH^-]$ exceeds about 0.01 M the solutions attain such a high buffer

capacity that the carbon dioxide content of the conductance water and the dissolution of oxides from the glass surface have a negligible influence on the solubility equilibrium.

Both authors explained their data by equilibrium (3); Laue obtained $\log K_{s2} = -3.70$ and Johnston *et al.* found $\log K_{s2} = -3.71$. The latter authors gave moreover $\log K_{s1} = -5.60$. The validity of the assumption that exclusively mononuclear hydrolysis products are formed was verified only recently by distribution² and emf³ studies carried out in this laboratory.

We have recalculated both sets of data by a more exact method than was done previously, and we have employed the curve fitting technique²³ which may yield a more reliable estimate of the uncertainties of the computed constants. No attention was paid to the results found in solutions of $[\text{OH}^-] \leq 0.01 \text{ M}$ because these may be expected to be not quite reliable.

The water activity and the ratio of the activity factors of OH^- and $\text{Ag}(\text{OH})_2^-$ were assumed to be unity; the error made seems to be negligible compared with the experimental uncertainty. We calculated from the vapor pressure measurements of Robinson and Stokes²⁴ $\frac{1}{2} \log \{ \text{H}_2\text{O} \}$ to be -0.0075 at $[\text{NaOH}] = 1 \text{ M}$; this was the highest $[\text{OH}^-]$ considered.

We have also assumed in the following calculation that $f(\text{Ag}^+) f(\text{OH}^-) = f_{\pm}^2 = 1$; this seems to be permissible because, at the $[\text{OH}^-]$ values where f_{\pm} is expected to deviate appreciably from unity, $[\text{Ag}^+] = \frac{K_{s0}}{f_{\pm}^2 [\text{OH}^-]}$ becomes much less than the uncertainty in the $[\text{Ag(I)}]_{\text{tot}}$ determination.

We started from the equation

$$[\text{Ag}]_{\text{tot}} = [\text{Ag}^+] + [\text{AgOH}] + [\text{Ag}(\text{OH})_2] = \frac{10^{-7.71}}{[\text{OH}^-]} + K_{s1} + K_{s2}[\text{OH}^-] \quad (16)$$

(16) can be rearranged to

$$\log \left([\text{Ag}]_{\text{tot}} - \frac{10^{-7.71}}{[\text{OH}^-]} \right) = \log K_{s1} + \log \left(1 + \frac{K_{s2}}{K_{s1}} [\text{OH}^-] \right) \quad (17)$$

If the data $\log \left([\text{Ag}]_{\text{tot}} - \frac{10^{-7.71}}{[\text{OH}^-]} \right) = f(\log [\text{OH}^-])$ are superimposed on the calculated curve $\log(1 + X) = f(\log X)$ the vertical displacement required to make them coincide yields $\log K_{s1}$ and the horizontal one $\log \frac{K_{s2}}{K_{s1}}$. We have found in this way

$$\log K_{s1} = -5.75 \pm 0.25$$

and

$$\log K_{s2} = -3.72 \pm 0.03,$$

which agree well with the previously determined values.

The solubility equilibria of Ag_2O are visualized in Fig. 1; the curve was calculated with the constants given in the Synopsis. The deviations of the data at $\log [\text{OH}^-] < -2$ illustrate the great difficulties encountered when poorly buffered solutions are studied.

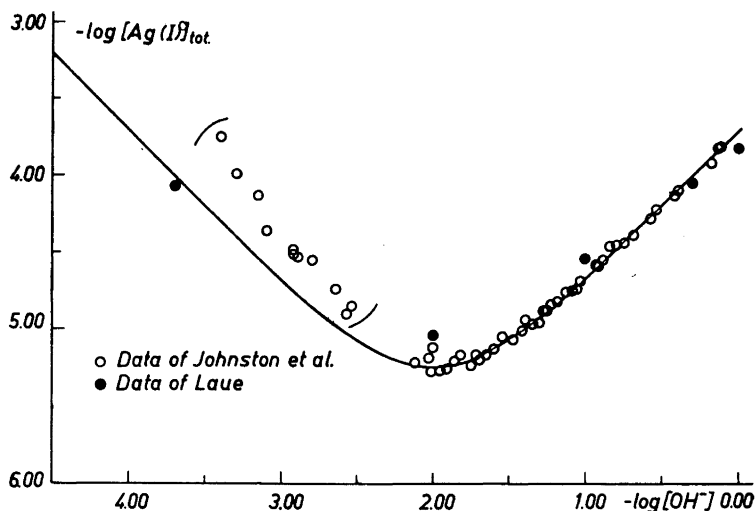


Fig. 1. The solubility equilibria of Ag_2O . $\log [\text{Ag(I)}]_{\text{tot}}$ as a function of $\log [\text{OH}^-]$. \circ measurements of Johnston *et al.*⁴, \bullet : measurements of Laue¹⁷. The curve represents the equation $\log [\text{Ag(I)}]_{\text{tot}} = \log ([\text{Ag}^+] + [\text{AgOH}] + [\text{Ag}(\text{OH})_2^-]) = \log \left(\frac{1.95 \times 10^{-8}}{[\text{OH}^-]} + 1.8 \times 10^{-6} + 1.90 \times 10^{-4}[\text{OH}^-] \right)$

For the complex formation $\text{OH}^- - \text{Ag}^+$ these data give $\log K_1 = \log \{[\text{AgOH}] [\text{Ag}^+]^{-1} [\text{OH}^-]^{-1}\} = 2.0 \pm 0.3$ and $\log \beta_2 = \log \{[\text{Ag}(\text{OH})_2^-] [\text{Ag}^+]^{-1} [\text{OH}^-]^{-2}\} = 3.99 \pm 0.05$, which means that $K_1 \sim K_2$.

The corresponding acidity constants of Ag^+ are then both around $10^{-12.0}$ (since $\log K_w = 14.00$ at 25°C), thus Ag^+ is another of the aquo ions with first and second acidity constant of the same order of magnitude.²⁵

Note added in proof. After this work was submitted to publication Professor Reino Näsänen has kindly informed us on an investigation recently carried out in his laboratory. Näsänen and Meriläinen has determined K_{s0} at 25°C by emf measurements using a glass electrode, and they obtained $\text{p}K_{s0} = 7.74$. This value is in excellent agreement with those calculated by the present authors.

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