# Studies on the Hydrolysis of Metal Ions

## 27. Potentiometric Study of the Argentate(I) Complex in Alkaline Solution

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The composition of the argentate(I) complex formed in alkaline solutions of silver oxide has been studied by emf titrations with constant ionic medium (0.95 and 12.6 M NaOH, 1.15 and 11.5 M KOH) using Ag-AgI electrodes. The data indicate that only mononuclear complexes are formed; from this result, together with the solubility data of other workers, it is concluded that the formula of the complex is $Ag(OH)_2^-$. No evidence has been found for the presence of the polynuclear argentate complexes proposed by some previous workers [5].
The solubility product of $Ag_2O(s)$ in 3 M $Na(ClO_4)$ at 25°C was determined as $\log K_{s_0} = \log [Ag^+][OH^-] = -7.42 \pm 0.02$.

Silver oxide is appreciably more soluble in strongly alkaline solutions than in water, which proves that one or more argentate species are formed. The formula of the argentate species is the problem of the present work.
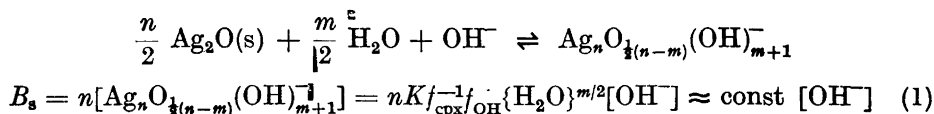
The solubility of $Ag_2O$ in NaOH (0.1 to 5.3 M) was studied by Laue [1] in 1927. The solubility, which we may express as a total concentration of $B_s$ moles Ag/l in a saturated solution, was approximately proportional to $[OH^-]$, more nearly so after an activity correction. Laue concluded that the formula of the complex formed is $AgO^-$. We shall use instead the equivalent formula $Ag(OH)_2^-$; from equilibrium studies in aqueous solutions it is hard to distinguish between formulas that differ only by the content of $H_2O$ and we shall keep to the convention of writing OH complexes if there is no definite evidence for other formulas.

In 1933, Johnston, Čuta and Garrett [2] published their data on the solubility of $Ag_2O$ in NaOH (0.001 to 6.6 M) and KOH (0.0005 to 5.2 M). Like Laue, whose work they do not seem to have seen, they found a solubility minimum at 0.015 M $OH^-$, and a linear course of $B_s$ with higher $[OH^-]$. They explained their data assuming the species AgOH and $AgO^-$; in addition, they found evidence for an unknown species, perhaps $Ag_2OH^+$, besides $Ag^+$, in solutions on the acid side of the solubility minimum.

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Their data [2] have later been discussed by Reynolds and Argersinger [3] and by Beck [4], who used the position of the solubility minimum to calculate the equilibrium constants. Neither quotes the work of Laue [1], in spite of its high quality.

The fact that the solubility, $B_s$, is proportional to [OH⁻] may be explained by assuming the predominant complex to be $Ag(OH)_2^-$ (or $AgO^-$), as was done by the authors quoted [1-4]. However, the same result would be obtained with any argentate complex of the charge −1. For instance, we have, with the general formula:

$$\frac{n}{2} Ag_2O(s) + \frac{m}{2} H_2O + OH^- \rightleftharpoons Ag_nO_{\frac{1}{2}(n-m)}(OH)_{m+1}^-$$

$$B_s = n[Ag_nO_{\frac{1}{2}(n-m)}(OH)_{m+1}^{-1}] = nKf_{cpx}^{-1}f_{OH}\{H_2O\}^{m/2}[OH^-] \approx const\ [OH^-] \quad (1)$$

Here $K$ is the equilibrium constant for (1), $f_{cpx}$ is the activity factor of the argentate complex and $f_{OH}$ that of the OH⁻ ion. The two activity factors may approximately cancel each other out. The "conventional" formula for the complex, $Ag_n(OH)_{n+1}^-$, is obtained by setting $m = n$.

The fact that $B_s/[OH^-]$ must be constant for any value of $n$ in (1) was realized by Pleskov and Kabanov [5], who measured the solubility of $Ag_2O$ in KOH (3 to 15 M). For the logarithm of the ratio, log $(B_s[OH^-]^{-1}) = $ log $nK$, at 25°C, Laue gave −3.76, Johnston et al. −3.71, and Pleskov and Kabanov $\approx$ −3.8. From the variation of the solubility with water activity, Pleskov and Kabanov moreover concluded $m = 1$ in eqn. (1)

Pleskov and Kabanov tried to determine the number of Ag atoms, $n$, in the argentate ion by studying the emf:s of silver concentration cells with various total concentrations, $B$, of Ag. Applying the Nernst equation (eqn. 3 or 6a below), they concluded that $n = 3$. The complex would then be trinuclear, $Ag_3(OH)_4^-$ or rather $Ag_3O(OH)_2^-$.

Recently, Antikainen and Dyrssen [6] studied the distribution equilibria of silver(I) between 3 M $Na(ClO_4,OH)$, and benzene solutions of quinoline. Their data, however, indicate that the predominant complex is the mononuclear $Ag(OH)_2^-$. Because of this apparent contradiction between the distribution [6] and emf [5] data, it was thought necessary to make a new emf investigation as a check of the Russian work.

The cell used in the present investigation had the following composition:

$$-Ag/I\ M\ M^+OH^-,\ with\ B\ M\ Ag/I\ M\ M^+OH^-\ with\ B_0\ M\ Ag/Ag+ \quad (2)$$
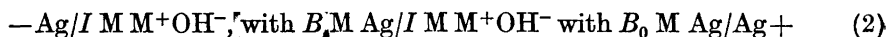
In our experiments, M⁺ was Na⁺ or K⁺, and the concentration, $I$, was about 1 or 12 M. Pleskov and Kabanov used 6 and 16 M KOH.

According to the Nernst equation, the emf of this cell (2) is given by the ratio between the concentrations of free Ag⁺ in the two half-cells. Now, $B$ is always very small as compared with $I$, and so the liquid junction potential in (2) is certainly negligible, and the activity factors may be assumed to be the same on both sides. Thus we have

$$E = 59.15\ log\ ([Ag^+]_+[Ag^+]_-^{-1}) \quad (3)$$

For any dissolved species, $Ag_n(OH)_{n+r}^{r-}$, the law of mass action gives ($\beta =$ equilibrium constant):

$$[Ag_n(OH)_{n+r}^{r-}] = \beta[Ag^+]^n[OH^-]^{n+r} \tag{4}$$

Now let us assume that, in the solutions with $I$ M $OH^-$, one single complex of this type predominates and that the concentrations of all other species, including $Ag^+$, are much smaller. The concentration of the predominating species, $[Ag_n(OH)_{n+r}^{r-}]$, is then equal to $B/n$, and so eqn. (4) becomes

$$B/n = \beta[Ag^+]^n I^{n+r} \tag{5}$$

The activity factors are included in the equilibrium constant, $\beta$ ,in eqns. (4) and (5); this can be done, provided that only experiments at the same $I$ are compared.

In our cell (2) we have on both sides the same values for $\beta$ and $I$ and so it follows from eqns. (3) and (5)

$$E = \frac{59.15}{n} \log B_+/B_- \tag{6}$$

Here, $B_+$ and $B_-$ are the total concentrations of silver at the two electrodes.

In the present work, $B_+$ was kept constant at the value $B_0$, whereas $B_-$ was varied; it is denoted by $B$. In practice the two solutions were prepared by mixing the same stock solution — an almost saturated solution of $Ag_2O$ in $I$ M MOH — with various amounts of pure $I$ M MOH; thus the ratio $B_0/B$ is known with better accuracy than the separate values of $B_0$ and $B$.

We then have

$$E = \frac{59.15}{n} \log (B_0/B) \tag{6a}$$

## EXPERIMENTAL

*Sodium hydroxide* solutions were prepared as usual here (see, *e.g.*, Ref. [7]), starting from a 50 % solution of the commercial *p.a.* reagent, which was kept in a polythene bottle. To prepare the 12.6 M solution, the 50 % solution (which is 18 M) was filtered through a G4 Jena glass filter funnel into a Büchner flask of Jena glass and diluted. In the making of the 0.957 M NaOH solution, recrystallized $Ba(OH)_2$ was added to the 50 % NaOH to remove the last trace of carbonate before the solution was filtered and diluted as before.

*Potassium hydroxide*, 11.5 M, was prepared from commercial *p.a.* reagent, which was dissolved in distilled water, after which $Ba(OH)_2$ was added. The 1.15 M KOH solution was prepared by simple dilution.

*Silver oxide* was prepared from recrystallized $Ba(OH)_2$ and $AgNO_3$. It was first washed carefully with de-aerated water until Ba could not be detected with sulfuric acid. The silver oxide was then washed three times with $I$ M MOH and finally suspended in $I$ M MOH and transferred to a polythene flask. The flask was shaken for 19 — 48 h and the solution so obtained, which may not have been quite saturated ($B_0 \leqq B_s$) was the starting solution of concentration $B_0$.

Some polythene flasks were found to reduce alkaline argentate(I) solutions, forming metallic silver; usually Polva polythene flasks, which do not seem to reduce silver, were used.

The *total silver concentration*, $B_0$, in the argentate solutions was determined as follows: the 12.6 M NaOH was diluted, hydrazinium sulfate was added, the metallic Ag was filtered off, washed, dissolved in $HNO_3$ and titrated with KCNS in the usual way. $B_0 = 0.7 \pm 0.2$

mM was found. To 11.5 M KOH, $HClO_4$ was added, $KClO_4$ was filtered off, and $Ag^+$ in the filtrate was titrated with KCNS. Result: $B_0 = 0.6 \pm 0.1$ mM. From the diagram of Pleskov and Kabanov we may read the solubility $B_s$ between 0.60 and 0.65 mM Ag in 11.5 M KOH, which indicates that our solutions were close to saturation.

With 1 M NaOH, $B_0 = 0.12 \pm 0.01$ mM was found, which is somewhat less than the solubility $\approx 0.18$ mM found from Johnston's, Čůta's and Garrett's data.

For our equation (6a) we do not need an accurate value for $B_0$ but only for $B_0/B$ which is obtained, with all the accuracy necessary, from the volume ratio of dilution. Even the approximate values for $B_0$ show that in our experiments we have used the same range of $B_0$ and $B$ as have Pleskov and Kabanov.

Nitrogen gas was bubbled through 10 % $H_2SO_4$, 10 % NaOH, and finally through the ionic medium, $I$ M MOH.

*Electrodes.* Some preliminary experiments were made with Ag, AgCl-electrodes; however, the emf was found to drift as much as 4 mV in 1.5 h, probably because of the dissolution of AgCl. If the AgCl was first washed away with conc $NH_3$, and then with water, $E$ showed no continous drift but rather small jumps so that the accuracy was not more than $\pm 1$ mV.

For all the following experiments, Ag, AgI-electrodes were used. Pt coils were covered with Ag and then electrolyzed as anodes in 0.1 M NaI (30 min, 0.3 mA). Even with them a drift around 1 mV/h was noticed, in 1 M NaOH (KOH) solution.

In 12.6 M NaOH, $E$ was more constant and the difference between two Ag, AgI-electrodes in the same solution was at most 0.3 mV in one experiment; between different solutions the deviations were sometimes as high as 1 mV. One had to wait $15-60$ min for a stable potential.

In 11.5 M KOH, the emf was somewhat less stable than in 12.6 M NaOH.

The cell (2) consisted of a reference half-cell with $B = B_0$ and the "titration" half-cell with $B$ variable. The reference half-cell, in the final experiments, was always a "Wilhelm" apparatus [9]; for the 1 M MOH experiments it was shortened by leaving out the middle part of the salt bridge. Some attempts were made to use polythene bridges of different constructions, but so great were the difficulties met with — solution was pumped out or in through the flexibility of polythene, silver was reduced — that a glass "Wilhelm" was finally used. Changes within the reference electrode may account for the fact that the line constructed on eqn. (6a) does not always pass through the origin. See especially 0.957 M NaOH, where the reference electrode was Ag, AgCl which had been kept for a day in the "Wilhelm"; in all other experiments the reference electrode was Ag, AgI.

For the titration half cell, a vessel of Jena glass was used with 1 M MOH, and one of polythene with 12 M MOH. To check whether the reduction of Ag made any perceptible difference, a glass vessel was also used in some of the experiments with 12 M MOH. No difference was found.

Table 1 shows, for each titration, the order in which the additions were made. A known amount of $I$ M MOH with $B_0$ M Ag was added through a pipet and the emf measured. The solution was then diluted by addition of several portions of $I$ M MOH without Ag (denoted as "0") and $E$ was measured after each portion. All additions were made by means of pipets, which were filled with nitrogen before the solution was sucked up into them. In the course of the titration, a certain amount of solution was withdrawn with a pipet (denoted by "—" in the table) to keep the total volume within reasonable limits. At the end, a "back-titration" was made by adding again one or several portions of the $B_0$ solution.

Two electrodes were used in the titration cell in all experiments with 12 M MOH. The difference between them was in general less than $0.2-0.3$ mV (see table and figs.).

The whole cell was kept in a thermostat room at $25 \pm 0.2°C$, and the emf was measured with a Cambridge type K potentiometer.


RESULTS


Table 1 gives our data in a short-hand form which we hope will be easily understood. The corresponding graphs, $E$ *versus* log $(B_0/B)$, are given in the four fields of Fig. 1. In each field are also given lines with slopes corresponding to

*Table 1.* Results of emf measurements. For each experiment ("titration"), first the various additions in ml are given; "0" stands for $I$ M MOH without Ag, "$B_0$" for the stock solution, $I$ M MOH with $B_0$ M Ag. The figures given are then $\log(B_0/B)$ and $E$ in mV (sometimes for two different electrodes).

a) 0.957 M NaOH

I. 49.89 ml $B_0$ + 3 · 9.95 ml 0—49.89 ml + 4 · 9.95 ml 0 + 9.95 ml $B_0$.

$\log(B_0/B)$, $E$ : 0.000 −18.7; 0.079 −14.3; 0.146 −10.3; 0.203 −6.4; 0.328 0.3; 0.426 4.8; 0.505 8.9; 0.572 13.4; 0.444 6.8 (9.6 after 5 h).

II. 29.63 ml $B_0$ + 2 · 5.00 ml 0 + 10 ml 0 + 2 · 5.00 ml 0 − 29.63 ml + 3 · 10.00 ml 0 + 20.00 ml $B$.

$\log(B_0/B)$, $E$ : 0.000 −17.1; 0.068 −13.1; 0.126 −9.6: 0.224 −3.2; 0.266 −0.5; ).304 2.2; 0.429 10.1; 0.526 16.1; 0.605 22.3; 0.360 6.0;

b) 12.6 M NaOH

I. 29.25 ml $B_0$ + 2 · 4.91 ml 0 + 2 · 9.75 ml 0−29.63 ml + 4.91 ml 0 + 9.75 ml 0 + 4.91 ml $B_0$ + 19.85 ml $B_0$.

$\log(B_0/B)$, $E$(two electrodes): 0.000 −0.3 0.3; 0.068 3.2 3.5; 0.126 6.2 6.6; 0.223 12.0 12.4; 0.301 16.8 17.0; 0.370 21.1 21.2; 0.479 27.4 27.1; 0.399 23.3 23.3; 0.241 14.2 14.5;

II. 29.25 ml $B_0$ + 2 · 4.91 ml 0 + 2 · 9.75 ml 0−29.63 ml + 2 · 9.75 ml 0 + 3 · 9.75 ml $B_0$.

$\log(B_0/B)$,$E$(two electrodes): 0.000 0.8 1.1; 0.068 4.5 4.7; 0.126 7.8 8.1; 0.223 13.5 13.2; 0.301 18.6 17.7; 0.427 27.1 25.7; 0.524 34.2 32.7; 0.381 24.7 24.3; 0.301 18.9 17.7; 0.250 15.7 14.6;

c) 1.15 M KOH

I. 29.63 ml $B_0$ + 2 · 5.00 ml 0 + 2 · 10.00 ml 0−29.63 ml + 10.00 ml 0 + 2 · 10.00 ml $B_0$ + 9.90 ml 0.

$\log(B_0/B)$ $E$: 0.000−4.1; 0.066 0.4; 0.125 3.9; 0.222 9.5; 0.301 15.6; 0.426 24.4; 0.301 16.2; 0.234 11.6; 0.301 16.2.

II. Same as I except that last point is left out:

0.000 2.1; 0.066 6.3; 0.125 10.6; 0.222 17.1; 0.301 23.2; 0.426 31.4; 0.301 23.8; 0.234 19.3

d) 11.5 M KOH

I. 29.25 ml $B_0$ + 4.91 ml 0 + 2 · 9.75 ml 0 + 4.91 ml 0−29.63 ml + 2 · 9.75 ml 0 + 2 . 9.75 ml $B_0$.

$\log(B_0/B)$, $E$(two electrodes): 0.000 0.8 0.9; 0.067 4.3 4.5; 0.177 9.7 9.7; 0.264 14.0 13.9; 0.302 17.2 17.0; 0.428 23.0 22.6; 0.525 26.3 25.7; 0.428 21.1 20.9; 0.301 17.5 17.3.

II. 29.25 ml $B_0$ + 4.91 ml 0 + 2 · 9.75 ml 0 + 4.91 ml 0−29.63 ml + 9.75 ml 0 + 19.85 ml $B_0$ + 9.75 ml $B_0$.

$\log(B_0/B)$, $E$ (two electrodes): 0.000 0.9 0.5; 0.067 4.6 4.0; 0.177 9.7 9.1; 0.264 14.0 12.8; 0.302 15.2 15.9; 0.428 20.6 21.4; 0.232 12.4 12.6; 0.190 10.4 10.5.

$n$ = 1, 2, and 3, according to eqn. (6a). Obviously, the slope of the present data is not compatible with $n$ = 2 or $n$ = 3 but agrees fairly well with $n$ = 1.

Admittedly, the silver electrodes do not behave very well in these solutions. It is seen, however, from the "back titrations" that the emfs are fairly reproducible; a small drift of the order of 1 or 2 mV would not affect the general conclusions.

The conclusions are the same for ~1 M and ~12 M alkali, as could be expected from the equilibrium condition, eqn. (1): in a saturated solution, the ratios between the species, say, $Ag(OH)_2^-/Ag_3(OH)_4^-/OH^-$ would be practically independent of $[OH^-]$. Thus, if the trinuclear complex predominates at low $I$, it should do so at high $I$ too; if it is insignificant (as it seems to be) at low $I$, one could not increase its importance by increasing $I$.

One may ask why Pleskov and Kabanov got a so much lower slope, that it would correspond to $n$ = 3. We would think that the main cause is in the electrodes. They seem to have used silver wires (instead of electrolytically
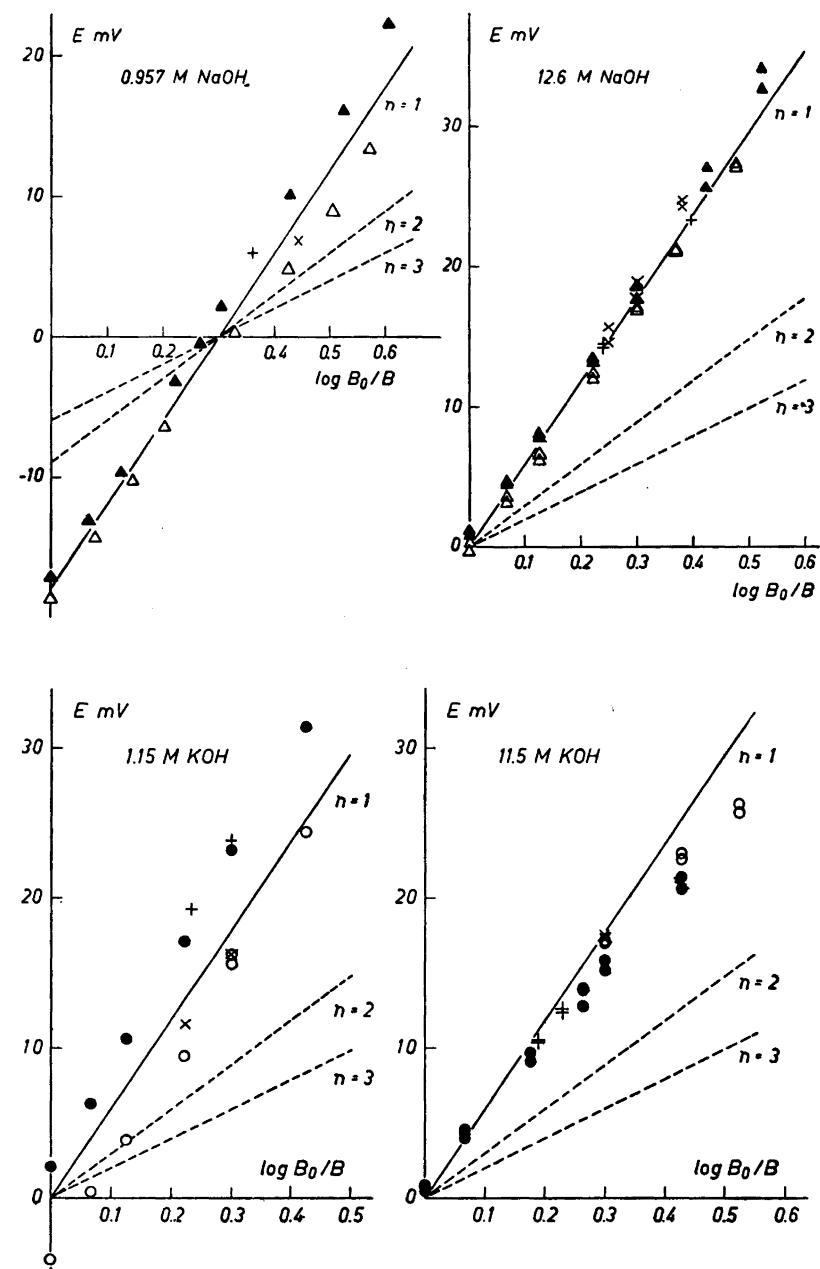
Fig. 1. Experimental results, plotted as $E$ (mV) *versus* $\log(B_0/B)$. Full-drawn line: calculated with eqn. (6a) and $n = 1$; dotted lines calculated with eqn. (6a) and $n = 2$ or 30 Different runs, or electrodes, are denoted by different symbols.

precipitated silver), which, according to our experience, can give rise to emf:s somewhat different from the standard emf:s for pure silver; the deviations are especially great at low $[Ag^+]$. Covering the silver electrolytically with an oxide "$Ag_2O_2$" layer and then reducing it (method not mentioned) [5], might lead to difficulties. If solid $Ag_2O$ is left on the silver surface, it is likely to dissolve in a unsaturated solution and the actual concentration of $Ag^+$ would be higher than calculated from the dilution, the emf measured would be less than expected and so would the slope.

It is apparent from the present work how important is the treatment of the electrodes. It should be mentioned that, in a few of our preliminary experiments, the apparent slope would have corresponded to $n \sim 1.5$.

In conclusion, our present data give no reason to assume any polynuclear species in argentate solutions. In the region where the solubility is proportional to $[OH^-]$, the formula of the predominant species can be simply written as $Ag(OH)_2^-$. At very high alkalinities, $> 5$ M $OH^-$, other species such as $Ag(OH)_3^{2-}$ may perhaps occur; the bend in the solubility curve is however not upward, as would be expected from terms for higher complexes, but downward, presumably because of activity factors.

## SOLUBILITY PRODUCT OF $Ag_2O$

In connection with other work [6], the solubility product of AgOH was determined in the medium 3 M $(Na)ClO_4$. Silver electrodes were used for determining $[Ag^+]$; they were standardized against acid solutions of known $Ag^+$. Three titrations were carried out, starting with acid silver solution and adding alkali. A glass electrode was used as a check, but $[OH^-]$ was taken from the analytical composition of the solution. The average value obtained was

$$\tfrac{1}{2}Ag_2O(s) + \tfrac{1}{2}H_2O \rightleftharpoons Ag^+ \pm OH^-; \log K_{s0} = -7.42 \pm 0.02 \ (25°C, 3 \text{ M } (Na)ClO_4)$$

The measurements could have been made more accurate but the precision sufficed for our needs.

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