COMPONENTS:
(1) Silver(I) oxide; Ag$_2$O; [20667-12-3]
(2) Water; H$_2$O; [7732-18-5]

EVALUATOR:
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June 1984

CRITICAL EVALUATION:

So far as the unipositive oxidation state of silver is concerned, there is no stable solid hydroxide. The only oxide is Ag$_2$O. Rordam (1) made an investigation of the Ag$_2$O/Ag electrode prior to using it as a tool for measuring the acidity of substituted benzoic acid. He came to the conclusion that there were two modifications of Ag$_2$O because he found two different e.m.f. values for the electrode in solutions of alkalies. The different values were assumed to be related to the method of preparation: electrolytically formed Ag$_2$O having a value about 30 mV larger than the value obtained when precipitated Ag$_2$O was used. Later (2) it was shown that this difference in e.m.f. could be explained by a partial reduction of the material as well as by assuming two different modifications of Ag$_2$O. In retrospect, this work was done at a time when the Ag$_2$O/Ag electrode was not very well understood and was considered to be unreliable and irreproducible. Later work (5) established procedures for preparing stable and reproducible Ag$_2$O/Ag electrodes. But the possibility of two forms of Ag$_2$O has again been suggested (3). The two forms are supposedly a black, crystalline and a brown, amorphous (active) form. The suggestion is made that in making solubility measurements, at least ten days should be allowed for equilibration. This length of time is necessary to allow for conversion of the "active" form to the stable crystalline form.

In addition to the above considerations, the possibility of the presence of some colloidal Ag$_2$O must also be taken into account when making and interpreting solubility measurements (4).

Solubility in water

This system has been the subject of many investigations. The solubility has been determined over a wide range of temperatures and several experimental approaches have been used. The results have also been expressed in different ways. Some have expressed the solubility as the concentration of Ag$_2$O, others as the concentration of AgOH, and still others as the concentration of metallic silver.

Three experimental methods have been used: (a) measurement of the e.m.f. of appropriate cells; (b) measurement of the electrical conductance of a saturated solution and the use of this value with accepted values for individual ionic conductances; and (c) a method in which the silver content of the saturated solution is measured by analysis. Of these methods, the analytical method is expected to give the most reliable results. The other two methods are sensitive to the Ag$^+$ ion concentration in solution and these methods are justified only if it is known that all the dissolved silver is in the form of Ag$^+$ ions, or that suitable corrections can be made for other silver-containing solute species. The nature of the dissolved silver-containing species will be discussed later in this Critical Evaluation. The e.m.f. method generally depends on the reliability of the Ag$_2$O/Ag electrode and, until Hamer and Craig (5) described a method for preparing reproducible Ag$_2$O/Ag electrodes, this electrode was known to be erratic in its behavior.

Another factor to be considered in evaluating the solubility data is the length of time allowed for equilibration. In most of the work that has been reported the time allowed for equilibration was a matter of hours, usually about 5 or 6.
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Only one report shows an equilibration time of a matter of two weeks or so (6). In that work the analytical method was used to determine the solubility values. Only one temperature, 298 K, was used. The solubility of Ag₂O in water is given as 2.22 x 10⁻⁴ mol Ag kg⁻¹.

In one other report several days were allowed for equilibration and a solubility value of 1.39 x 10⁻⁴ mol AgOH dm⁻³ was given at 298 K (7). The conductance method was used to obtain this value and that may be the reason it is smaller than the value reported by Johnston, et al. (6). The conductance method, as noted above, may be sensitive to the presence of only some of the dissolved Ag₂O.

Remy and Kuhlmann (8) also used the conductance method and obtained the value 1.1 x 10⁻⁴ mol Ag₂O dm⁻³ (or 2.2 x 10⁻⁴ mol Ag dm⁻³) for the solubility of Ag₂O in water at about 293 K. They allowed less than two hours for equilibration and also introduced corrections for temperature and for the presence of CO₂.

Laue (9) measured the solubility using several experimental methods but allowed only an hour or so for equilibration. He obtained larger values with the analytical method than with the conductance method but then adjusted these values downward to correct for the presence of CO₂.

Other values obtained at 298 K by the analytical method agree fairly well with the results of Johnston, et al. (6) even though only a few hours were allowed for equilibration. These other reported values are: 2.16 x 10⁻⁴ mol AgOH dm⁻³ (10); and 2.26 x 10⁻⁴ mol Ag dm⁻³ (11).

Rebiere (12) reported larger values but he prepared the Ag₂O by different methods and the difference between the largest and smallest values was about half the mean value. Therefore, these results are considered to be unreliable.

In one paper (13) the solubility determinations were made over a temperature range of 303-353 K. All the experimental methods were used. The largest values were obtained by the analytical method. The results are shown on Figure 1. Extrapolation of the values to 298 K gives a lower value than those reported above. This may reflect the relatively short time allowed for equilibration.

The recommended value for the solubility of Ag₂O in water at 298 K is 2.2 x 10⁻⁴ mol Ag kg⁻¹ or 2.2 x 10⁻⁴ mol Ag dm⁻³.

Solubility in aqueous solutions of alkalies.

The measurement of the solubility of Ag₂O in aqueous alkalies is complicated by the fact that the Ag₂O apparently undergoes a reduction to metallic silver. This was first observed by Laue (9) and later studied by others (14). The results show that the decomposition is dependent on the temperature, concentration of alkali, the presence of foreign materials, and photo effects. These facts make it difficult to know when, or whether, equilibrium is attained.
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Figure 1. Solubility of Ag₂O in water.
Aqueous NaOH. There are three reports dealing with this system. Laue (9) attempted to meet the complications caused by the reduction of the Ag$_2$O by limiting the time the mixtures were allowed to stand before measurements were made. For this reason he limited his study to NaOH solutions less concentrated than 5 mol dm$^{-3}$. With more concentrated NaOH solutions the filtration process required too much time. In another report on this system (3) the complication due to decomposition of the Ag$_2$O was obviated by allowing equilibration to take place in an oxygen atmosphere. The third report (6) makes no mention of this complication.

The solubility values for Ag$_2$O in NaOH concentrations up to 7 mol dm$^{-3}$ show a fair amount of scatter. The agreement between the values of two investigations (6, 9) are within experimental uncertainty in NaOH concentrations less than 1 mol dm$^{-3}$. Differences become more pronounced with increasing NaOH concentrations, Figure 2. The scatter in the results is likely due to the instability of the dissolved Ag$_2$O. In the more dilute NaOH solutions the uncertainties are smaller and there is a definite minimum in the solubility curve, Figure 3. This minimum was also observed by Laue (9). The minimum was in about a 0.01 mol dm$^{-3}$ NaOH solution and the solubility was about 9.3 x 10$^{-6}$ mol Ag dm$^{-3}$. The values reported above were obtained in solutions whose total ionic strength was not controlled. In a recent investigation (3) the ionic strength was controlled. Only dilute solutions of NaOH were used and the temperature range was 298-363 K. It appears that the work was carried out with careful attention to experimental details. Yet the results do not add any clarity to the values on Figure 3. Consequently, the solubility of Ag$_2$O in aqueous NaOH solutions must be considered as not being definitively determined. This is due to the experimental difficulties associated with the establishment of solubility equilibria in the system.

Aqueous KOH. Relatively few data have been published for this system. The most extensive work (6) was carried out at 298 K in KOH concentrations up to 5 mol dm$^{-3}$. The solubility values are practically the same as those reported for aqueous NaOH by the same authors. The few numerical data reported by others (15, 16) agree with those of Johnston, et al., (6). In one paper (15) the data are presented in graphical form for the solubility of Ag$_2$O in KOH concentrations up to 13 mol dm$^{-3}$. There is a maximum in the solubility curve at a KOH concentration of about 6 mol dm$^{-3}$.

The solubility of Ag$_2$O in a KOH concentration of 1 mol dm$^{-3}$ was measured at 278 and 300 K (16). In that investigation the solubility was found to go through a maximum about an hour after adding the solid Ag$_2$O to a KOH solution that was stirred at a constant rate. It was also observed that solutions of Ag$_2$O in aqueous KOH decreased in dissolved silver content when allowed to stand out of contact with excess solid Ag$_2$O. During this standing period a small precipitate of black metallic silver was formed. The maximum in the solubility as a function of time has been observed by others (3). The decrease was considered to be due to the conversion of "active" Ag$_2$O to the crystalline Ag$_2$O. At 298 K about 10 days were required to complete the process. The time needed to complete the process was less at higher temperatures. Whitby (17) observed the maximum while studying the solubility of Ag$_2$O in water. (No new solubility data are given in the article.) He detected the maximum after about 5 days, and then the solubility of Ag$_2$O decreased over the next two weeks.
Silver(I) Oxide

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Figure 2. Solubility of Ag₂O in NaOH solutions at 298 K.

Figure 3. Solubility of Ag₂O in dilute NaOH solutions at 298 K.
The solid line is equation (8).
In another investigation, the solubility of AgZO in KOH concentrations up to 10 mol dm\(^{-3}\) was measured at 298, 323 and 351 K \((18)\). The data are presented only in the form of 2 small graphs. The solubility increased with increasing temperatures. At 298 K the data appear to disagree with those reported above \((6, 9)\). In the more concentrated KOH solutions the data show significant experimental uncertainties.

Values for the solubility of AgZO in aqueous KOH at elevated temperatures have been calculated from thermodynamic values \((19)\). The calculations show that at temperatures from 298-573 K the solubility goes through a minimum at about \(pH=12\). No data sheet was prepared for this article because the data were not obtained by solubility measurements.

**Aqueous Ba(OH)\(_2\)**. There is only one article that discusses this system \((6)\). The data at 298 K are said to be the same, within experimental uncertainties, as the solubility of AgZO in aqueous NaOH and KOH reported by these same authors.

In summary, the solubility of AgZO appears to be the same in solutions of each of the alkalies reported above. The experimental uncertainties associated with these values are greater than those ordinarily encountered in making solubility measurements. The uncertainties are the result of the instability of AgZO in these environments. Therefore, the solubility values reported and discussed above can only be considered as tentative. It is possible that true equilibrium values cannot be obtained for the solubility of AgZO in aqueous solutions of alkalies.

However, the solubility data have been used to obtain an estimate of the acidic characteristics of AgZO. The solubility of AgZO in aqueous solutions can be expressed in terms of the solubility product reaction:

\[
\frac{1}{2} \text{AgZO(s)} + \frac{1}{2} \text{H}_2\text{O} = \text{Ag}^+ + \text{OH}^-, \tag{1}
\]

for which

\[
K_1 = K_{pO} = \frac{(a\text{Ag}^+)(a\text{OH}^-)}{(a\text{H}_2\text{O})^{1/2}} \tag{2}
\]

Numerous attempts have been made to evaluate \(K_1\). The most direct way is to measure the e.m.f. of an appropriate cell containing the AgZO/Ag electrode. However, this electrode proved unsatisfactory and not reproducible until the work of Hamer and Craig \((5)\) who developed a method for preparing stable and reproducible AgZO/Ag electrodes. They did not derive a value for \(K_1\) from their work, but a calculation using their results yields a value of \(1.88 \times 10^{-8}\) at 298 K. Others \((20)\) also attempted to evaluate \(K_1\) from e.m.f. measurements and obtained a value of \(3.2 \times 10^{-8}\), presumably at 298 K, but the temperature is not specified. A variation of this method \((21)\) involved the use of a silver electrode whose potential in a saturated solution of AgZO in aqueous NaOH vs a calomel electrode was compared with the potential of a similar silver electrode in a dilute solution of AgNO\(_3\) vs the same calomel electrode. Corrections were made for degree of ionization. No corrections were made for junction potentials, and the reproducibility of the results was not very good. Therefore, of the values reported above, those deduced from the work of Hamer and Craig \((5)\) are to be preferred.
Another experimental approach measures the Cl-/OH" ratio in solutions that are saturated simultaneously with AgCl and Ag2O. The value of this ratio together with an accepted value for the solubility product constant of AgCl can yield a value for $K_1$. One of the earliest attempts to use this method (10) gave a value of $1.90 \times 10^{-8}$ at 298 K. This work was repeated later (22) and a value of $1.98 \times 10^{-8}$ at 298 K was obtained (this value was not included in the original article but was calculated by the Editor from the data presented in the article). The same experimental approach has been used more recently (3). The ratio Cl-/OH" at 298 K appears to have two values which the authors attribute to an "active" and a crystalline form of Ag2O. The value the authors consider to be the more reliable leads to a value of $8.12 \times 10^{-9}$ for $K_1$. The authors did not confirm that both Ag2O and AgCl solid phases were present at the time measurements were made. Where both solid phases were apparently present, the experimentally measured values were not very reproducible but were nearer the values reported above. Kozlov, et al. (3) contend that most investigators, even though the results are consistent with each other, used a metastable form of Ag2O. They also refer to the work of Laue (9) but fail to note that a black precipitate observed by Laue was finely divided metallic silver. Thus, the conclusions in the paper of Kozlov, et al. (3) are considered of doubtful validity.

A third experimental approach which has been used to evaluate $K_1$ involves the measurement of pH in a solution containing AgNO3 and NaOH with, or without, the presence of other, indifferent, electrolytes. The relative concentrations are controlled within such limits that the hydrolysis of the Ag+ ions can be neglected. This method allows the evaluation of $K_{sp}$ as a function of total ionic strength and leads to a value of $1.95 \times 10^{-9}$ at 298 K (23) for $K_1$. Another attempt to use this method (24) leads to a value of $6.7 \times 10^{-9}$ at 298 K. The value was obtained in solutions having a total ionic strength of 1 mol dm$^{-3}$ and therefore should have been larger, not smaller, than the earlier value (23). Part of the reason for the discrepancy may lie in the fact that the concentrations of Ag+ and NaOH were not controlled to limit the hydrolysis of the Ag+ ions. Therefore the result had to be obtained by writing equations involving the possible presence of other species, such as Ag(OH)$_2^-$, and then solving these equations simultaneously. Furthermore, the pH values were in the range 10-14. They were measured with a glass electrode and no indication is given that a correction was made for the effect of the alkali on the glass of the electrode. Therefore, there is a legitimate question about the validity of the basic experimental values obtained in this work.

Another experimental approach uses values obtained by a potentiometric titration of AgNO3 with an alkali such as NaOH. There are several reports based on this experimental method, but in only three was the work carried out at 298 K. Nasanen (25) arrived at a value of $2.57 \times 10^{-8}$ for $K_1$, using this approach. Two comments should be made: (a) the Ag2O/Ag electrode was used as an indicator electrode and at that time it was an unreliable one; (b) the assumption apparently was made that all the silver in solution was present as Ag+ ions. In the light of these comments, the result reported here is not to be preferred to those mentioned above. Similar work was carried out later (26) in which NH4OH was used as the titrant. This complicates the interpretation of the results because of the formation of Ag-NH$_3$ complex ions. The author interprets his results to give a value of $2.37 \times 10^{-8}$. There is no evidence as to what, if any, solid phase was present during the titration.
Silver(I) Oxide

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Oka (27) also used the titration method and reported a value of 1.32 \times 10^{-8} for \( K_1 \) at 298 K. This result is rejected because of lack of experimental details. Then too, the method of treating the experimental data is not described. Another value reported for \( K_1 \) at 298 K is 3.8 \times 10^{-8} (28) but the authors admit that this is an approximate value.

Laue (9) used several methods to evaluate \( K_1 \) at 298 K. He concluded that, on the basis of his work, the value is 1.85 \times 10^{-8}.

The recommended value for \( K_1 \) at 298 K is 1.9 \times 10^{-8}. This value has been obtained in several different investigations using different experimental approaches. This is the same value recommended in an earlier review (29).

Solubility product determinations reported since then (3, 24) have not been sufficiently persuasive to alter this judgment.

Solubility product values have also been reported for other temperatures. Two values at 293 K were obtained by using measurements made during a potentiometric titration. A value of 1.51 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6} (2) is a concentration product and based on assumptions about the degree of ionization of AgNO₃ solutions. Another assumption was that all the silver in solution was present as Ag⁺ ions. Later (30) a value of 1.4 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6} was derived for \( K_{s0} \) at 293 K. In this work the concentration of Ag⁺ was calculated rather than measured experimentally. Furthermore, attempts by the Editor to recalculate the data given in this paper led to different conclusions than those reported by the authors. Therefore, though the two values reported for 293 K are in fair agreement with each other, they cannot be accepted as definitive.

The experimental approach described in the previous paragraph was also used at 289 K and gave a value of 1.15 \times 10^{-8} for \( K_1 \) (31). This value is subject to the same reservations as those expressed in the preceding paragraph.

Other values that have been reported as concentration products, but are rejected for lack of information about experimental details or for failure to include numerical data are: 5.2 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6} (32); 1.87 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6} (33); 10^{-8} \text{ mol}^2 \text{ dm}^{-6} (34); and 5.63 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6} (35).

The acidic character of Ag₂O may be represented by reactions (3) and (4).

\[
\frac{1}{2} \text{Ag}_2\text{O}(s) + \frac{1}{2} \text{H}_2\text{O} = \text{AgOH}(s\text{ln})
\]  

(3)

\[
\frac{1}{2} \text{Ag}_2\text{O}(s) + \frac{1}{2} \text{H}_2\text{O} + \text{OH}^- = \text{Ag(OH)}_2^-
\]  

(4)

which have the following equilibrium constants:

\[
K_3 = \left(\frac{a_{\text{AgOH}}}{a_{\text{H}_2\text{O}}}\right)^{0.5}
\]  

(5)

\[
K_4 = \left(\frac{a_{\text{Ag(OH)}_2^-}}{a_{\text{OH}^-}}\right) \cdot \left(\frac{a_{\text{H}_2\text{O}}}{a_{\text{H}_2\text{O}}}\right)^{0.5}
\]  

(6)
The value of $K_3$ is generally considered to be the value of the minimum solubility. The minimum solubility, as determined by solubility measurements (6), is $5 \times 10^{-6} \text{ mol dm}^{-3}$ at 298 K. A value of $1.6 \times 10^{-6} \text{ mol dm}^{-3}$ was obtained by a curve-fitting approach and extrapolation to zero ionic strength (3). Laue (9) reported a value of about $9 \times 10^{-6} \text{ mol dm}^{-3}$. A recalculation of the data in the literature prior to 1960 yields a value of $1.8 \times 10^{-6} \text{ mol dm}^{-3}$ at 298 K (29). Because of the small values involved and the experimental uncertainties, the recommended value for $K_3$ at 298 K is $2 \times 10^{-6}$.

The value of $K_4$ has been determined from solubility data (6) in very dilute NaOH solutions. The assumptions made were that the activity of water was unity, and that the activity coefficients of all univalent ions had the same value. On the basis of these assumptions, a value of $1.95 \times 10^{-4}$ at 298 K was obtained. Others (36) derived a value of $1.5 \times 10^{-4}$ at constant ionic strength of $3 \text{ mol dm}^{-3}$. In arriving at this value it was assumed that in NaOH solutions more concentrated than $0.1 \text{ mol dm}^{-3}$, Ag(OH)$_2$ is the main solute species. Furthermore, values of pH in the vicinity of 13 were measured with a glass electrode. A recalculation of the results using a curve-fitting technique (29) gave a value of $1.9 \times 10^{-4}$ at 298 K. A more recent attempt to evaluate $K_4$ on the basis of solubility measurements (3) yielded values about a tenth of those reported above. The reason for this may be that in the latter work (3) measurements were made with a rather ill-defined Ag$_2$O. No other work reports values for $K_4$.

One way to check these values is to write an equation for the total solubility of Ag$_2$O in alkaline solutions.

$$C_{\text{Ag}} = C_{\text{Ag}^+} + C_{\text{AgOH}} + C_{\text{Ag(OH)}_2^-}$$

Substituting recommended or tentative values, this becomes

$$C_{\text{Ag}} = 1.9 \times 10^{-8}/C_{\text{OH}^-} + 2 \times 10^{-6} + 1.9 \times 10^{-4}C_{\text{OH}^-}$$

Concentration values (mol dm$^{-3}$) rather than activities are used in equation (8) in order to check this expression against the experimentally reported solubility results. Equation (8) fits the data reasonably well in NaOH concentrations less than $0.8 \text{ mol dm}^{-3}$, Figure 3. At larger concentrations of NaOH the substitution of concentration for activity becomes an increasing approximation.

Equation (8) assumes that in aqueous alkali solutions the silver-containing solute species are: Ag$^+$, AgOH, and Ag(OH)$_2$$. There is a fairly good consensus on this matter. However, other solute species have been suggested. Pleskov and Kabanov (37) measured the e.m.f. of a Ag$_2$O/Ag electrode in KOH solutions as a function of the silver concentration and the OH$^-$ ion concentration. The slopes of the e.m.f. vs concentration lines suggested the presence of a polynuclear solute species. All the data are presented only in graphical form. On the basis of the data collected in KOH concentrations of 3-15 mol dm$^{-3}$ the authors concluded that the solute species is Ag$_2$(OH)$_3$ or Ag$_3$(OH)$_4$. Attempts to repeat this work in KOH concentrations of 1 and 12 mol dm$^{-3}$ (28) failed to substantiate the conclusions of Pleskov and Kabanov (37). Antikainen, et al. (28) believed the cause of the difference was in the silver

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Electrodes that were used. The determination of distribution equilibria of silver(I) between an alkaline solution of NaClO₄ and a benzene solution of quinoline (36) led to the conclusion that the main silver-containing solute species in alkaline solutions is mononuclear, i.e., Ag(OH)₂.

In an attempt to reconcile the fact that the solubility of Ag₂O in water as determined by analysis gives a larger value than the results of conductance measurements, Johnston, et al., (6) suggested the possibility of Ag₂OH⁺ as a solute species. A study of the hydrolysis of the Ag⁺ ion (38) yielded no evidence for the presence of Ag₂O²⁻. Biedermann and Hietanen (38) suggest that a better explanation of the difference is the presence of impurities, such as CO₂. In larger NaOH or KOH concentrations, e.g., 15 mol dm⁻³, there may be some ions of the type Ag(OH)₃²⁻. However, there is no experimental evidence for this and the solubility measurements at such large concentrations of alkali are too few and, perhaps, too uncertain, to verify the presence of such a solute species.

**Solubility in aqueous solutions of acidic oxides**

**Arsenic oxides.** One report (39) deals with arsenic(III) oxide and another (40) with arsenic(V) oxide. The first report (39) contains no solubility data. No analysis for silver was made of the solutions. The object of the work was to determine how much of the arsenic (III) oxide would be removed from solution by a fixed amount of Ag₂O.

The second report (40) presents solubility data only in the form of a phase diagram at 293 K. The main objective of the work was to ascertain which silver arsenates could be formed at this temperature.

**Boron(III) oxide.** The only solubility report on this system is that of Sadeghi (41). The solubility of Ag₂O was determined over the temperature range 273-373 K. The data for temperatures below 303 K are given only in graphical form because of the imprecision of the values obtained. Rather extensive numerical solubility data are listed for the higher temperatures. The objective of this work was to determine the existence of a variety of silver(I) borates. The data are classified as tentative. The work appears to have been done carefully but only meager experimental details are given.

**Chromium(VI) oxide.** There has been a fair amount of interest in determining the number of silver chromates that can be prepared. But only one paper (42) presents solubility data for this system, and these data were obtained only at 303 K. There is no reason to reject these results, but because they are the only values available they are classed as tentative values.

**Iodine(VII) oxide.** One study of this system at 273 K has been reported (43). Solubility data are given but no compilation sheet has been prepared for this article. The data are rejected because of lack of experimental details. The article refers to other work for some of these details but does not indicate where these references are located.

**Phosphorus(V) oxide.** One article (44) appears to present solubility data for this system but the work really is a study of the solubility of silver.
**Silver(I) Oxide**

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**PHASE DIAGRAMS:**

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**CRITICAL EVALUATION:**

phosphates. The analysis for silver was expressed as mass % Ag\textsubscript{2}O, but no solubility of Ag\textsubscript{2}O was studied or measured.

**Selenium(IV) oxide.** A study of this system was a companion piece to a study of the solubility of CuO in aqueous SeO\textsubscript{2} (45). The solubility data in this article are the only ones reported for the Ag\textsubscript{2}O-SeO\textsubscript{2}-H\textsubscript{2}O system and the solubilities were measured only at 373 K. The values reported on the compilation sheet for this article are regarded as tentative until more work is reported on this system.

**Solubility in aqueous NH\textsubscript{3} and its derivatives**

**Aqueous ammonia.** There is very little information available on the solubility of Ag\textsubscript{2}O in this system. Olmer (46) measured solubilities in NH\textsubscript{3} concentrations up to 6 mol dm\textsuperscript{-3}. The determinations were made at room temperature, ~290 K. More concentrated solutions of NH\textsubscript{3} produced explosive mixtures. Later Randall and Halford (47) made solubility measurements in solutions of NH\textsubscript{3} at concentrations up to 1.5 mol kg\textsuperscript{-1} at 298 K. No valid comparison can be made between the two sets of data (46, 47). The reported solubilities are larger at the lower temperature. Both these sets of data must be regarded as tentative.

Nasanen (26) also studied this system at 298 K but obtained no solubility data. He found that in sufficiently dilute solutions having a molar ratio \([\text{NH}_3]/[\text{Ag}] = 2\) no precipitate was formed. He studied this homogeneous equilibrium and found evidence for the presence of Ag(NH\textsubscript{3})\textsuperscript{+} and Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}.

**Aqueous solutions of methylene.** Only Olmer (46) has reported solubility data for Ag\textsubscript{2}O in this system. The work was carried out at about 290 K. The author expresses his doubts about the accuracy of the results and it is best to concur with his judgment.

**Aqueous solutions of the ethanolamines.** Alner and Smeeth (30) measured the solubility of Ag\textsubscript{2}O at 293 K in solutions of each of the three ethanolamines. Just a few data are given for each system. The interest of the authors was to determine the stability constant of each of the complexes that were formed, but they assumed in their calculations that only one complex, in which the ratio of ethanolamine to Ag\textsuperscript{+} is 2:1, is formed in each system. The solubility results must be regarded as tentative.

**Aqueous solutions of the ethanoalones.** Alner and Smeeth (30) measured the solubility of Ag\textsubscript{2}O at 293 K in solutions of each of the three ethanolamines. Just a few data are given for each system. The interest of the authors was to determine the stability constant of each of the complexes that were formed, but they assumed in their calculations that only one complex, in which the ratio of ethanoaline to Ag\textsuperscript{+} is 2:1, is formed in each system. The solubility results must be regarded as tentative.

**Solubility in aqueous salt solutions.**

This type of solubility measurement is usually made in order to measure the effect of change in total ionic strength on the solubility value. Lame (9) used KNO\textsubscript{3} as the source of ions and found that the solubility of Ag\textsubscript{2}O in water did increase significantly with increasing concentrations of KNO\textsubscript{3}. There are too few data to check whether this change in solubility follows the Debye-Hückel limiting law.

A study of the effect of the addition of inert salts to alkaline solutions (6) led the authors to conclude that there was no appreciable influence on the solubility of Ag\textsubscript{2}O in the solutions of alkalies.
Silver(I) Oxide

COMPONENTS:
(1) Silver(I) oxide; $\text{Ag}_2\text{O}$; [20667-12-3]
(2) Water; $\text{H}_2\text{O}$; [7732-18-5]

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June 1984

CRITICAL EVALUATION:

Solubility in aqueous solutions of alcohols.

**Methanol.** In the only report on this system (48) the work was carried out at 298 K. Only one concentration of methanol was used. The concentration was chosen to give a sufficiently large value of the dielectric constant so that the electrolytes could be considered to act as strong electrolytes. The objective was to determine the change of solubility of Ag$_2$O with changes in pH, and to note the effect of a lower dielectric constant (lower than that of water) on the stability of the complex ions that were formed. As in aqueous solutions, the solubility of Ag$_2$O passes through a minimum with increasing pH. However, the solubility of Ag$_2$O is less in the methanol solutions and the minimum on the pH curve is broader, indicating a larger range of stability for AgOH. The solubility data are classed as tentative. There is no other work with which they can be compared.

**Ethanol.** There is also only one paper reporting on this system (11) but in this work, carried out at 298 K, the concentration of ethanol was varied and not held constant. Increasing concentrations of ethanol result in a decreased solubility of Ag$_2$O. There is no reason to have doubts about the data, but they must be classified as tentative until more work on this system is reported.

Solubility under hydrothermal conditions.

Only a few reports present information about the solubility of Ag$_2$O under these conditions. The reports are not very complete. In no papers are any values of the pressure recorded. In one paper (49) the solubility of Ag$_2$O in water is measured but hardly any experimental details are given. Another paper (50) presents solubility data but does not indicate in what concentration units the solubility values are expressed. The solubilities were measured in aqueous solutions of K$_2$SO$_4$ and KN$_3$. The reason given for this procedure is that the "direct determination of Ag$_2$O solubility in water at elevated temperatures is difficult due to the tendency to form colloidal solutions." The solubilities measured in these salt solutions were then converted to water solubilities by means of an extended Debye-Hückel equation. Because no concentration units are specified, the values have been rejected. The same authors also measured the solubility of Ag$_2$O at elevated temperatures in solutions of KN$_3$, with and without the addition of NH$_3$OH (51). The purpose was to evaluate the formation constant of Ag(NH$_3$)$_2^+$ at these temperatures. The data show that the solubility of Ag$_2$O in such solutions increases with increasing NH$_3$ concentration, but decreases with increasing temperature.

There is a considerable difference in solubility values reported for Ag$_2$O in water (13, 49). Therefore, the values must be considered as doubtful. The solubility of Ag$_2$O in water reaches a maximum at about 430 K. This maximum in the solubility curve has attracted some attention. Even though the values in one paper (50) have been rejected because of the failure to specify concentration units, still the numbers calculated for water solubility do show a maximum at about 440 K. It should be noted, however, that the solubility measurements from which the water solubility values were calculated show a steady increase with increasing temperature in the range 323-453 K. An attempt has been made to relate this maximum in solubility to a certain
Silver(I) Oxide

COMPONENTS:
(1) Silver(I) oxide; Ag₂O; [20667-12-3]
(2) Water; H₂O; [7732-18-5]

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dielectric constant of the solvent (52). Solubility measurements of Ag₂O in dioxane-water mixtures (the data are not given) show a maximum in a solvent that has a dielectric constant (relative permittivity) of 40-45. The dielectric constant of water at about 430 K is also said to have the same value (52). However, solubility studies in water-ethanol mixtures (11) show no maximum in a dielectric constant range of 20-78.

In view of the small amount of data available, the incompleteness of the reports, and the fact that none of the work has been duplicated by others, all the solubility measurements of Ag₂O under hydrothermal conditions are to be classified as doubtful.

Table I. Constants for the Ag₂O-H₂O system at 298 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Value</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 Ag₂O(s) + 1/2 H₂O = AgOH(aq)</td>
<td>K₃ = 2 x 10⁻⁶</td>
<td>r</td>
</tr>
<tr>
<td>1/2 Ag₂O(s) + 1/2 H₂O = Ag⁺ + OH⁻</td>
<td>K₅₀ = 1.9 x 10⁻⁸</td>
<td>r</td>
</tr>
<tr>
<td>1/2 Ag₂O(s) + 1/2 H₂O + OH⁻ = Ag(OH)₂⁻</td>
<td>K₄₀ = 1.9 x 10⁻⁴</td>
<td>t</td>
</tr>
<tr>
<td>solubility of Ag₂O in water</td>
<td>2.2 x 10⁻⁴ mol Ag kg⁻¹</td>
<td>r</td>
</tr>
</tbody>
</table>

a r = recommended; t = tentative
**COMPONENTS:**

1. Silver(I) oxide; \( \text{Ag}_2\text{O} \); [20667-12-3]
2. Water; \( \text{H}_2\text{O} \); [7732-18-5]

**CRITICAL EVALUATION:**

**EVALUATOR:**

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**References**

COMPONENTS:

(1) Silver(I) oxide; Ag₂O; [20667-12-3]
(2) Water; H₂O; [7732-18-5]

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