COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. 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_2O. Rordam (1) made an investigation of the Ag_2O/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_2O 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_2O having a value about 30 mV larger than the value obtained when precipitated Ag_2O 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_2O. In retrospect, this work was done at a time when the Ag_2O/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_2O/Ag electrodes. But the possibility of two forms of Ag_2O 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_2O 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_2O, 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_2O/Ag electrode and, until Hamer and Craig (5) described a method for preparing reproducible Ag_2O/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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CRITICAL EVALUATION:

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 Ag_2O in water is given as 2.22×10^{-4} mol Ag kg^{-1}.

In one other report several days were allowed for equilibration and a solubility value of 1.39×10^{-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 Ag_2O.

Remy and Kuhlmann (8) also used the conductance method and obtained the value 1.1×10^{-4} mol Ag_2O dm^{-3} (or 2.2×10^{-4} mol Ag dm^{-3}) for the solubility of Ag_2O 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 CO_2.

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 CO_2.

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: 2.16×10^{-4} mol AgOH dm^{-3} (10); and 2.26×10^{-4} mol Ag dm^{-3} (11).

Rebiere (12) reported larger values but he prepared the Ag_2O by different methods and the difference between the largest and smallest values was about half the mean value. Therefore, those 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 Ag_2O in water at 298 K is 2.2×10^{-4} mol Ag kg^{-1} or 2.2×10^{-4} mol Ag dm^{-3}.

Solubility in aqueous solutions of alkalies.

The measurement of the solubility of Ag_2O in aqueous alkalies is complicated by the fact that the Ag_2O 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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CRITICAL EVALUATION:

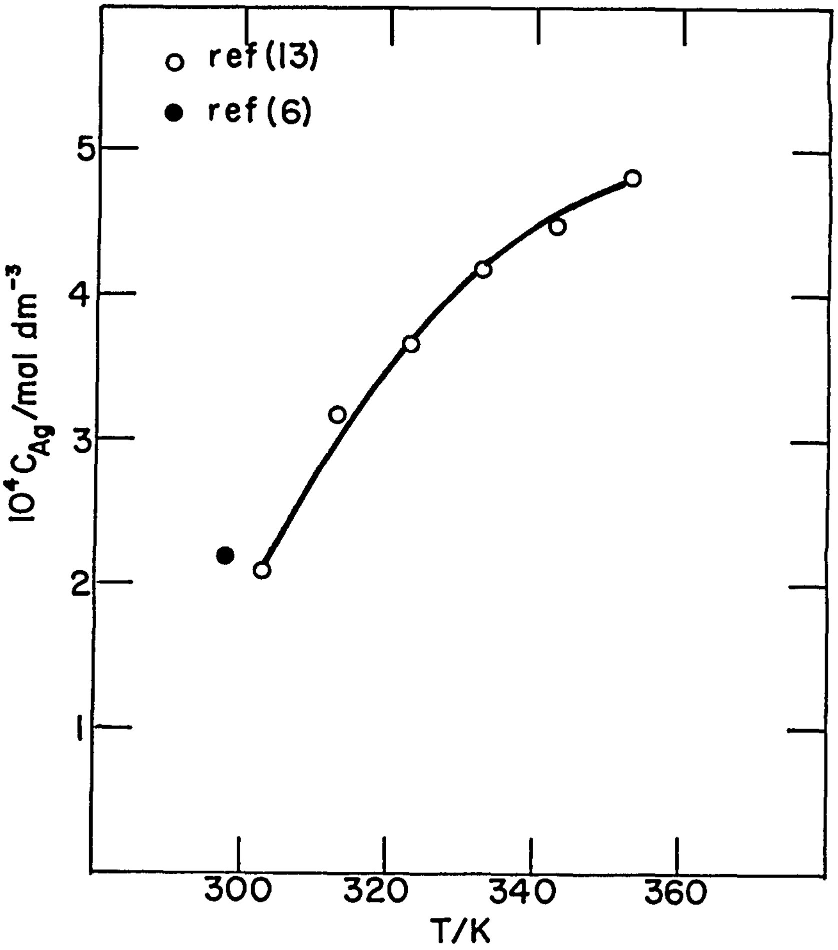

Figure 1. Solubility of Ag_2O in water.

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CRITICAL EVALUATION:

Aqueous NaOH. There are three reports dealing with this system. Laue (9) attempted to meet the complications caused by the reduction of the Ag_2O 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_2O 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_2O 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_2O. 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 9.3×10^{-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_2O 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_2O 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_2O 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_2O to a KOH solution that was stirred at a constant rate. It was also observed that solutions of Ag_2O in aqueous KOH decreased in dissolved silver content when allowed to stand out of contact with excess solid Ag_2O. 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_2O to the crystalline Ag_2O. 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_2O 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_2O decreased over the next two weeks.

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(2) Water; H_2O; [7732-18-5]

EVALUATOR:

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Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U. S. A.
June 1984

CRITICAL EVALUATION:

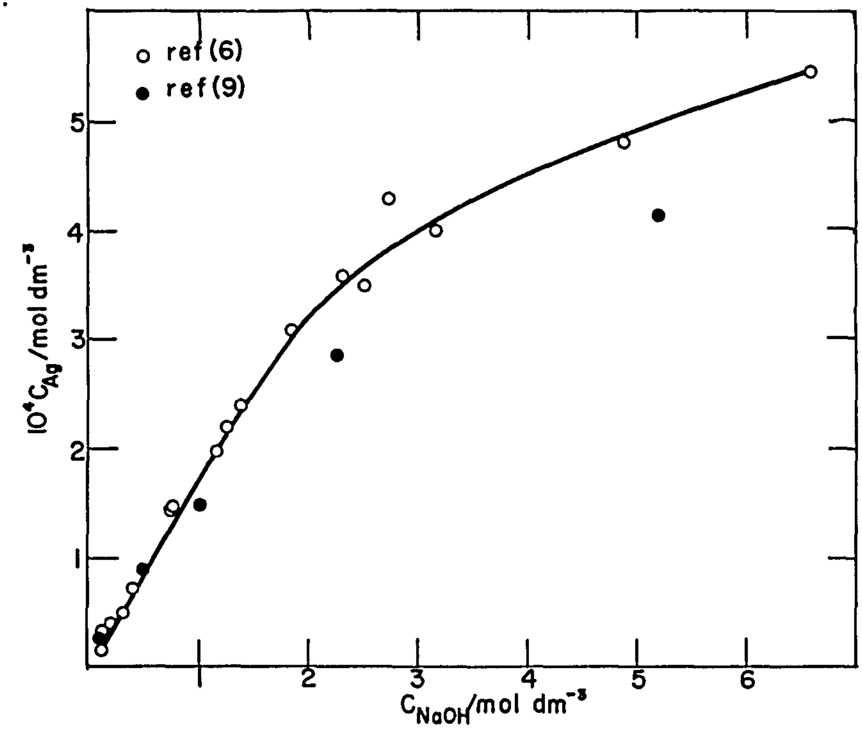

Figure 2. Solubility of Ag_2O in NaOH solutions at 298 K.

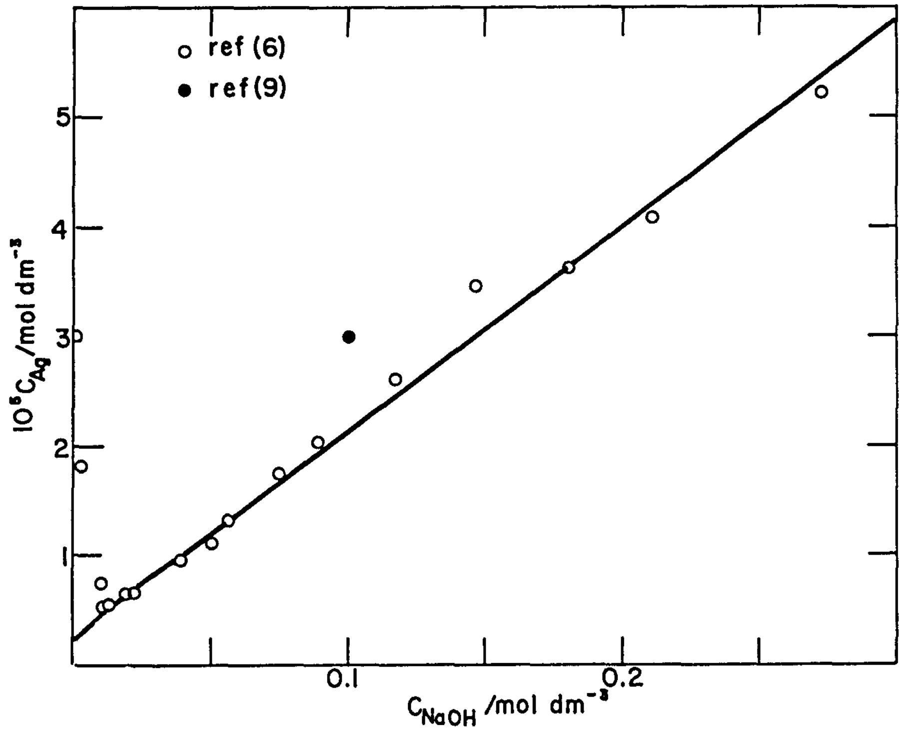

Figure 3. Solubility of Ag_2O in dilute NaOH solutions at 298 K. The solid line is equation (8).

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In another investigation, the solubility of Ag_2O 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 Ag_2O 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 Ag_2O in aqueous NaOH and KOH reported by these same authors.

In summary, the solubility of Ag_2O 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 Ag_2O 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 Ag_2O in aqueous solutions of alkalies.

However, the solubility data have been used to obtain an estimate of the acidic characteristics of Ag_2O. The solubility of Ag_2O in aqueous solutions can be expressed in terms of the solubility product reaction:

$$1/2\ Ag_2O(s) + 1/2\ H_2O = Ag^+ + OH^-, \qquad (1)$$

for which

$$K_1 = K_{so}^{o} = (a_{Ag^+}) \cdot (a_{OH^-})/(a_{H_2O})^{1/2} \qquad (2)$$

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 Ag_2O/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 Ag_2O/Ag electrodes. They did not derive a value for K_1 from their work, but a calculation using their results yields a value of 1.88×10^{-8} at 298 K. Others (20) also attempted to evaluate K_1 from e.m.f. measurements and obtained a value of 3.2×10^{-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 Ag_2O 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.

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CRITICAL EVALUATION:

Another experimental approach measures the Cl^-/OH^- ratio in solutions that are saturated simultaneously with AgCl and Ag_2O. 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 1.90×10^{-8} at 298 K. This work was repeated later (22) and a value of 1.98×10^{-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 Ag_2O. The value the authors consider to be the more reliable leads to a value of 8.12×10^{-9} for K_1. The authors did not confirm that both Ag_2O 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 Ag_2O. 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 $AgNO_3$ 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_{s0} as a function of total ionic strength and leads to a value of 1.95×10^{-8} at 298 K (23) for K_1. Another attempt to use this method (24) leads to a value of 6.7×10^{-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 $AgNO_3$ 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 2.57×10^{-8} for K_1, using this approach. Two comments should be made: (a) the Ag_2O/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 NH_4OH was used as the titrant. This complicates the interpretation of the results because of the formation of $Ag\text{-}NH_3$ complex ions. The author interprets his results to give a value of 2.37×10^{-8}. There is no evidence as to what, if any, solid phase was present during the titration.

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CRITICAL EVALUATION:

Oka (27) also used the titration method and reported a value of 1.32×10^{-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 3.8×10^{-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 1.85×10^{-8}.

The recommended value for K_1 at 298 K is 1.9×10^{-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 1.51×10^{-8} mol^2 dm^{-6} (2) is a concentration product and based on assumptions about the degree of ionization of $AgNO_3$ solutions. Another assumption was that all the silver in solution was present as Ag^+ ions. Later (30) a value of 1.4×10^{-8} mol^2 dm^{-6} was derived for K_{so} 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 1.15×10^{-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: 5.2×10^{-9} mol^2 dm^{-6} (32); 1.87×10^{-8} mol^2 dm^{-6} (33); 10^{-8} mol^2 dm^{-6} (34); and 5.63×10^{-8} mol^2 dm^{-6} (35).

The acidic character of Ag_2O may be represented by reactions (3) and (4).

$$1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH(sln) \qquad (3)$$

$$1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^- \qquad (4)$$

which have the following equilibrium constants:

$$K_3^o = (a_{AgOH})/(a_{H_2O})^{0.5} \qquad (5)$$

$$K_4^o = (a_{Ag(OH)_2^-})/(a_{OH^-}) \cdot (a_{H_2O})^{0.5} \qquad (6)$$

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CRITICAL EVALUATION:

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 5×10^{-6} mol dm^{-3} at 298 K. A value of 1.6×10^{-6} mol dm^{-3} was obtained by a curve-fitting approach and extrapolation to zero ionic strength (3). Laue (9) reported a value of about 9×10^{-6} mol dm^{-3}. A recalculation of the data in the literature prior to 1960 yields a value of 1.8×10^{-6} 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 2×10^{-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 1.95×10^{-4} at 298 K was obtained. Others (36) derived a value of 1.5×10^{-4} at constant ionic strength of 3 mol dm^{-3}. In arriving at this value it was assumed that in NaOH solutions more concentrated than 0.1 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 1.9×10^{-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_2O. No other work reports values for K_4°. Therefore, 1.9×10^{-4} is tentatively accepted as the value for K_4° at 298 K.

One way to check these values is to write an equation for the total solubility of Ag_2O in alkaline solutions.

$$C_{Ag} = C_{Ag^+} + C_{AgOH} + C_{Ag(OH)_2^-} \qquad (7)$$

Substituting recommended or tentative values, this becomes

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

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 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_2O/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 $Ag_3O(OH)_2^-$ 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 $NaClO_4$ 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 Ag_2O in water as determined by analysis gives a larger value than the results of conductance measurements, Johnston, et al., (6) suggested the possibility of Ag_2OH^+ as a solute species. A study of the hydrolysis of the Ag^+ ion (38) yielded no evidence for the presence of Ag_2OH^+. Biedermann and Hietanen (38) suggest that a better explanation of the difference is the presence of impurities, such as CO_2. In larger NaOH or KOH concentrations, e.g., 15 mol dm^{-3}, there may be some ions of the type $Ag(OH)_3^{2-}$. 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 Ag_2O.

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 Ag_2O 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

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phosphates. The analysis for silver was expressed as mass % Ag_2O, but no solubility of Ag_2O 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_2 (45). The solubility data in this article are the only ones reported for the Ag_2O-SeO_2-H_2O 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_3 and its derivatives

Aqueous ammonia. There is very little information available on the solubility of Ag_2O in this system. Olmer (46) measured solubilities in NH_3 concentrations up to 6 mol dm^{-3}. The determinations were made at room temperature, ~290 K. More concentrated solutions of NH_3 produced explosive mixtures. Later Randall and Halford (47) made solubility measurements in solutions of NH_3 at concentrations up to 1.5 mol kg^{-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 $[NH_3]/[Ag] = 2$ no precipitate was formed. He studied this homogeneous equilibrium and found evidence for the presence of $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$.

Aqueous solutions of methylamine. Only Olmer (46) has reported solubility data for Ag_2O 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_2O 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^+ 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. Laue (9) used KNO_3 as the source of ions and found that the solubility of Ag_2O in water did increase significantly with increasing concentrations of KNO_3. There are too few data to check whether this change in solubility follows the Debye-Huckel 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_2O in the solutions of alkalies.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

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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_2O 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_2O passes through a minimum with increasing pH. However, the solubility of Ag_2O 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_2O. 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_2O 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_2O 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_2SO_4 and KNO_3. The reason given for this procedure is that the "direct determination of Ag_2O 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-Huckel equation. Because no concentration units are specified, the values have been rejected. The same authors also measured the solubility of Ag_2O at elevated temperatures in solutions of KNO_3, with and without the addition of NH_4OH (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_2O 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_2O in water (13, 49). Therefore, the values must be considered as doubtful. The solubility of Ag_2O 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

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dielectric constant of the solvent (52). Solubility measurements of Ag_2O 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 Ag_2O under hydrothermal conditions are to be classified as doubtful.

Table I. Constants for the Ag_2O-H_2O system at 298 K.

Reaction	Value	Evaluation
$1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH(sln)$	$K_3^{\circ} = 2 \times 10^{-6}$	r
$1/2\ Ag_2O(s) + 1/2\ H_2O = Ag^+ + OH^-$	$K_{so}^{\circ} = 1.9 \times 10^{-8}$	r
$1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^-$	$K_4^{\circ} = 1.9 \times 10^{-4}$	t
solubility of Ag_2O in water	2.2×10^{-4} mol Ag kg^{-1}	r

[a] r = recommended; t = tentative

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