COMPONENTS:	EVALUATOR:
(1) Silver(II) oxide; AgO, [1301-96-8] (2) Water; H_2O, [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

As a member of the transition series of metals, silver has oxidation states greater than +1. However, the only oxide in which silver has a higher oxidation state is AgO. Silver has no solid hydroxide for any of its oxidation states.

Although AgO has been known for a long time and is easy to prepare, the nature of the oxidation state of silver in AgO has been the source of some disagreement. At one time AgO was considered to be a peroxide of unipositive silver, and its formula was written as Ag_2O_2. however, Barbieri (1) showed that this was not a tenable assumption because, when acidified, AgO did not produce hydrogen peroxide.

Later, AgO was considered to be a compound of bipositive silver (2). However, further evidence cast some doubt on this assumption. For example, a study of the magnetic properties of AgO showed it to be diamagnetic (3), whereas bipositive silver should be paramagnetic, having at least one unpaired electron.

When more refined x-ray techniques became available and when neutron diffraction techniques had been developed, a further study of AgO indicated that there were two different Ag-O distances in the AgO crystal (4,5). McMillan (6) suggested that this, as well as the diamagnetism of the compound, could be accounted for by assuming that the silver in AgO was present as an equimolar mixture of Ag^+ and Ag^{3+}.

A photoelectron spectroscopy (ESCA) study of AgO (7) yielded only one peak for silver. This peak was a broad one and could have been the net effect of two peaks: one for Ag^+, and one for Ag^{3+}. No resolution of this broad peak was attempted.

Although AgO is formally called silver(II) oxide, the evidence to date indicates that it more likely is silver(I,III) oxide. Some of the apparently conflicting data reported for AgO may be accounted for by this lack of precise understanding of the oxidation state of silver in AgO.

The main interest in the study of AgO has been associated with its presence on the silver electrode in silver-alkaline batteries. The only solubility data reported for AgO are a result of this interest. And because silver-alkaline batteries use aqueous KOH as the electrolyte, all the solubility data reported for AgO are for its solubility in aqueous KOH. There is, however, very little numerical solubility data.

A study of the solubility of AgO in aqueous KOH solutions (8) showed that the concentration of dissolved silver is a function of time and passes through a maximum. Evidence was collected to show that the AgO in aqueous KOH solutions undergoes a decomposition to Ag_2O and to metallic silver. There is no consensus on the mechanism or the rates of these reactions.

A few numerical solubility data are given for room temperature (9). Most of the numerical solubility data are reported for 298 K (10). So far as comparisons can be made, these solubility values are the same as those for Ag_2O (11). This observation was also made in another report (12) although no numerical solubility data are included in that report.

The fact that the solubilities of Ag_2O and AgO in aqueous KOH appear to be the same, has elicited several explanations. A polarographic study of aqueous KOH solutions saturated with Ag_2O and AgO separately (9) showed that essentially the same polarogram was obtained for each of the two oxides. The conclusion drawn from the results is that the same solute species is formed regardless of whether Ag_2O or AgO is used to saturate the aqueous KOH. The common solute species is the one corresponding to unipositive silver, i.e., $Ag(OH)_2^-$ in the more concentrated KOH solutions. The validity of this explanation will depend on further study of the kinetics of the reduction of AgO to Ag_2O in aqueous KOH solutions.

Fleischer (13) has suggested an explanation based on the equilibrium restrictions required by the phase rule. His argument is that AgO always contains Ag_2O and, hence, two solid phases are present. According to the phase rule this dictates that the concentration of the solution phase is invariant, i.e., the solubility value should be the same whether the aqueous KOH is saturated with Ag_2O or with AgO.

The mechanism of the dissolution of AgO was investigated by McMillan (14). He could observe no paramagnetic species in solutions of AgO in aqueous KOH. He concluded that the mechanism of dissolution of AgO is different in acid media than in alkaline media. In the former, AgO dissolves as some form of Ag^{2+} while in alkaline media McMillan suggested that the solute species would be AgOH, $Ag(OH)_2^-$ and $Ag(OH)_4^-$.

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CRITICAL EVALUATION:

In conclusion, there are too few solubility data for AgO to recommend any values. Furthermore, the data that have been reported are to be received with reservations because of uncertainties about the attainment of equilibrium, the nature of the oxidation state of silver in AgO, and the kinetic and mechanistic factors associated with the dissolution process. A further possible complication is that while AgO can be prepared by different methods, there is evidence that these different preparations are not necessarily the same. There are differences, e.g., in the X-ray diffraction patterns of the various products (10, 15).

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