

# A STUDY OF THE CONSTANT POTENTIAL OXIDATION OF SILVER IN POTASSIUM HYDROXIDE SOLUTION

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## A STUDY OF THE CONSTANT POTENTIAL OXIDATION OF SILVER IN POTASSIUM HYDROXIDE SOLUTION

By

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#### **ABSTRACT**

The formation of  $Ag_2O$  and AgO was studied by means of the constant aqueous potential exidation of a silver electrode in/potassium hydroxide solutions. The range of concentrations used was from 8 percent to 42 percent and in each solution, voltages spanning the range 0.05 to 0.4 volts above the  $Ag_2O$  reversible potential were used. The constant potential method was utilized in an attempt to clarify the kinetics and mechanisms of the electrolytic formation of the exides of silver.

The efficiencies of the electrode processes under consideration were calculated by determining the weight gained by the electrode and then comparing this to the quantity of current used. It was found that the exide formation processes were approximately 100 percent efficient under all conditions except those at which exygen was evolved. The relation between the hydroxide ion concentration and the potential required for exygen evolution was also noted.

The extent of the conversion of Ag to  $Ag_20$  was studied under a variety of conditions in an attempt to determine the nature of the oxide surface and its effect on the formation of Ag0. The results indicate that it is not possible to realize 100 percent conversion of silver to  $Ag_20$  and that the presence of a film of  $Ag_20$  on an electrode decreases the initial rate of Ag0 formation.

The shape of the current-time curves obtained at each condition of voltage and potassium hydroxide concentration was given special attention. These curves were then compared to the theoretically determined curves for the reactions being considered. The comparisons showed that there was agreement between the theoretical and experimental curves at 0.05 volts only. At all higher potentials the presence of convections currents caused the reaction rate to deviate from the theoretical.

On the basis of the information gained from these studies some suggestions are made as to the nature of the electrode processes involved in the electrolytic formation of  $Ag_2O$  and AgO.

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#### IN TRODUCTION

A General Review of Silver and Its Oxides

Silver is a member of the Group 1-b metals which are characterised by their low chemical activity. The general outer electron configuration is  $(n-1)d^{10}ns^1$  and this permits the removal of more than one electron since the energy differences between the (n-1)d and ns electrons are not very large. The characteristic oxidation state of copper is two; for silver it is one and for gold it is three. However, in addition to the above most stable oxidation states, it has been shown that compounds corresponding to all three exidation states have been characterized for each of the coinage metals. Thus it might be expected that there would be three exides of silver corresponding to the empirical formulas  $Ag_2O$ , AgO and  $Ag_2O_3$ .

A review of the literature indicates that there is definite evidence for the existence of the monovalent and bivalent exides of silver. However, there seems to be some question about the validity of the information used to show the existence of an exide of silver containing trivalent silver. In the paragraphs that follow the characteristics, methods of preparation, and the evidence for the valence state of each of the exides of silver will be indicated.

Ag<sub>2</sub>O is a covalent compound which crystallises in a face-centered cubic lattice. It is characterised by its case of thermal reduction and its low solubility. It exhibits both alkaline and acidic properties; its aqueous suspension absorbs carbon dioxide and its solubility in alkaline solution increases with increasing hydroxyl ion concentration(1).  $Ag_2O$  can be prepared by both chemical and electrolytic methods. The chemical method involves the precipitation of  $Ag_2O$  by treatment of monovalent silver ion with alkali metal hydroxide solutions. It can be prepared electrolytically by anodic treatment of silver in alkaline solutions. The standard oxidation potential value given by Latimer for the Ag-Ag\_O couple in alkaline solution is -0.344 volts.

A great deal of work has been reported on AgO. The classic work on the higher exides of silver was done by Noyes, et al. Their studies of the oxidation of silver nitrate in nitric acid by ozone indicate that the exidation state of silver in the black compound produced is bipositive. In addition, the fact that on electrochemical reduction two Faradays of electricity are obtained per gram atom of silver would seem to be conclusive evidence for the divalent state of silver in this compound. The magnetic data on AgO does not give definite evidence for the valence state of silver. The divalent state of silver would be expected to exhibit paramagnetic properties but Neiding and Kasarnovski(2) report that solid AgO is not paramagnetic. However, in nitric acid solution it is paramagnetic. This paramagnetism has not been observed in alkaline solution. The formula of the oxide indicates a 1:1 stoichionstry but there is evidence that this may not be necessary. Dirkse(3) found that prolonged anodic treatment of silver in potassium hydroxide solution produced oxides whose compositions varied from AgO1 to AgO16. Determination of the exidation potentials of these electrodes showed that they corresponded to the potentials for the divalent oxides of

silver. Latimer's value for the exidation potential of the  $Ag_2O-AgO$ couple in alkaline solution is -0.57 volts. AgO is less stable than  $Ag_2O$  and in the presence of silver it will slowly decompose to form the more stable  $Ag_2O(4)$ . AgO can also be prepared by chemical and electrochemical methods. The chemical methods involve the exidation of Ag er silver nitrate by ozone(5), permanganates(6), and persulfates(7). AgO can be prepared electrolytically by the exidation of silver nitrate between platinum electrodes(8) or by the anodic treatment of silver in alkaline solution(9).

The evidence for the existence of the trivalent oxide of silver is less conclusive. Jirsa and Jelinek(10) reported the formation of  $Ag_2O_3$  by exidizing silver (I) exide with esone. However, the compound was very unstable and decomposed rapidly in water. Hickling and Taylor(11) suggest that the primary product of the exidation of  $Ag_2O$  is  $Ag_2O_3$ , which subsequently decomposes to form AgO. However, it has been suggested that there is no conclusive evidence for the trivalent oxide of silver(12). All available data can be satisfactorily explained by assuming that the highest exidation state of silver in all of these processes is a positive two.

Our work is concerned with the electrochemical preparation of the exides of silver in potassium hydroxide solution. The monovalent and divalent oxidation states of silver are apparent when a silver electrode is treated anodically in alkaline solution. At potentials below 0.35 volts above the  $Ag-Ag_2O$  potential  $Ag_2O$  is formed and at higher potentials the product is AgO. However, there are some problems connected

with the anodic treatment of a silver electrode in potassium hydroxide solution. The nature and mechanism of the electrode processes are still open to question. Also, results have been obtained(3) which indicate that the conversion of silver to silver(1) oxide in potassium hydroxide solution is never complete. The relation between the concentration of hydroxyl ion and the efficiency of the process is somewhat obscure. It is the purpose of our work to attempt a clarification of some of the problems cited above and possibly make suggestions as to the nature and mechanisms of the reactions involved.

Nost of the work on the formation of the oxides of silver has been done using constant current techniques. However, the electrochemical kinetics of reactions are functions of overvoltage rather than current density(13). Therefore, the use of constant potential methods can reveal some aspects of reaction kinetics which cannot be obtained through the use of constant current methods. At constant potential a particular reaction can be chosen for study, whereas at constant current the reaction that is kinetically most favored may take place. This is particularly true where the growth of an oxide film may render the electrode passive.

The rate of an electrochemical reaction carried out at constant potential is dependent on a number of factors, such as, concentration polarisation, the electrical resistance of the system, the overvoltage, and the rates of linear diffusion of the ions involved. However, in most electrochemical reactions this is somewhat simplified, because the limiting factor is either the overvoltage or the rate of diffusion. Before a substance can react at an electrode surface it must overcome

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an energy barrier. This energy barrier in an electrochemical process is the overvoltage. The magnitude of the evervoltage can be evaluated by determining the potential at which the desired reaction will take place and comparing this with the equilibrium potential, calculated from the Nernst equation. As the potential is further increased, the theoretical rate of the reaction will increase very rapidly. But this theoretical rate can be attained only if the rate of transport of ions to the electrode surface is equal to the demand. This is normally not the case and thus at increasing potentials the rates of most electrochemical reactions are limited by the rates of ionic diffusion.

#### **EXPERIMENTAL**

The apparatus shown in Figure 1 (see Appendix) was designed to charge the silver electrodes at constant potential. Resistance A is a precision resistor from which the desired potential can be applied to an electrode. In this way electrode B can be maintained at a constant potential above electrodes C and C<sup>4</sup>. Electrode B is the experimental electrode and was prepared by pressing moist  $Ag_2O$  on a platinum screen and reducing it thermally to silver. Electrodes C and C<sup>4</sup> are comparatively large electrodes prepared by pressing  $Ag_2O$  on a silver screen. The current flow through the cell is measured by tapping from resistance D and feeding into a recording potentiometer. The voltage difference between the experimental electrode and the  $Ag_2O$  electrodes is measured by tapping from resistance E and feeding into a recording potentiemeter.

Although the above described process is actually a process carried out at constant cell potential, it is in effect a constant electrode potential process, for by making the  $Ag_2O$  electrode surface very large in comparison with the gross surface area of the experimental electrode the current density on the reference electrodes will always be very small. Thus the  $Ag_2O$  electrode will be operating very close to its reversible potential. In our work we have assumed that the veltages measured across the plates of the cell represent the potential difference between the experimental electrode and the  $Ag_2O$  reversible potential. The procedure which was employed to study the constant potential exidation of silver can best be divided into two parts.

The first part of our procedure was designed to show the effect of a prior charge on the voltage-current characteristics of  $Ag_2O$  and AgOfermation in various concentrations of potassium hydroxide. To accomplish this the silver electrode was treated anodically at 0.05 volts for forty-eight hours or until the current was zero. The electrode was then seaked in distilled water for at least eight hours to wash out the electrolyte, dried in a stream of purified nitregen, placed in a desiccator for at least eight hours and then weighed. The increase in weight was assumed to be due to oxygen. The electrode, which now contained some  $Ag_2O$ , was placed on charge at 0.35 volts for forty-eight hours and the gain in weight was again noted. This was repeated at  $O_{\rm e}O$  volts above the  $Ag_2O$  potential.

It should be noted that we deviated from the above outlined sequence of voltages in eight percent potassium hydroxide solution because so little silver was converted to Ag<sub>2</sub>O at 0.05 volts.

The second part of our procedure was designed to study the effect of anodically charging a silver electrode at 0.15, 0.30, and 0.35 volts respectively, in various concentrations of potassium hydroxide. The experimental electrode was thermally reduced to silver between each veltage step. The gain of exygen and the efficiency of the process were again noted at each of these voltages.

The composition of the product on the experimental electrode was determined by visual inspection, by obtaining x-ray diffraction patterns

with a Norelco x-ray spectrometer, and by comparing its potential to that of the  $Ag_2O$ -Ag electrodes.

#### RESULTS

#### Efficiency of the Electrode Processes

The efficiency of the process was determined by assuming that the increase in weight experienced by the silver electrode was due to exygen and comparing this to the number of milliampere hours of electricity consumed in the process. It was also assumed that the solubility of the  $Ag_2O$  would not produce a significant loss of exide from the electrode surface. These results are given in Table I (see Appendix).

The data show that at 0.05 and 0.15 volts above the  $Ag_20$  potential the anodic oxidation of silver was approximately 100 percent efficient in concentrations of potassium hydroxide between eight percent and forty percent. This would indicate that under these conditions the reaction by which silver is converted to  $Ag_20$  is the only reaction of any consequence. This reaction is generally considered to proceed according to the following equations

2Ag + 20H ----- Ag\_0 + H\_0 + 2e

In the formation of  $Ag_20$  and Ag0 at 0.30 and 0.35 volts some experimental difficulty was encountered and the results are not as easy to interpret. However, there appears to be a pronounced drop in current efficiency in forty percent potassium hydroxide.

At 0.40 volts the change in current efficiency with hydroxide ion concentration is very pronounced. In these runs, the electrode had been anodized at 0.05 volts and 0.35 volts respectively, for 48 hours prior to the application of the 0.40 volt potential. However, the prior formation of the oxides of silver on the electrode surface is apparently not relevant to the efficiency of the process. Figure 5-b on Table I (see Appendix) shows that treatment of a previously anodized electrode at 0.35 volts resulted in the formation of AgO with 100 percent current efficiency. Figure 2 (see Appendix) contains a plot of current efficiency vs. potassium hydroxide concentration and shows that the current efficiency falls off very rapidly with increasing hydroxide ion concentration. The decrease in current efficiency is due at least in part, to the evolution of oxygen at the anode and our results indicate that at potentials of 0.30 volts and above, the reaction is favored by increasing potassium hydroxide concentration. This indicates that the potential for oxygen evolution at the Ag-Ag<sub>2</sub>O and Ag<sub>2</sub>O-AgO couples decreases with increasing hydroxide ion concentration. Reference to the curves labeled "C" on Figures 4, 5, and 6 (see Appendix) shows that the surrent densities were approximately the same in all concentrations of potassium hydroxide. Thus the current density factor is largely eliminated in the consideration of the differences in the potential for oxygen evolution at the various concentrations of electrolyte.

## Conversion of Ag to Ag<sub>2</sub>O

Results reported previously by Dirkse (3) indicated that at potentials below that at which AgO forms it was impossible to convert all of the silver on the active electrode to  $Ag_2O$ . Inspection of Table I (see Appendix) reveals that our work verifies this contention. The

best conversion (approximately 80%) was obtained in 28 percent potassium hydroxide at potentials of 0.15 and 0.30 volts. Under these conditions the current-milliampere hour curves (Figure 5, d and e; see Appendix) show a high current density at the anode for some time and then a rather abrupt drop to zero current. These curves also show that the total number of milliampere hours of electricity consumed at this high current density is approximately the same at both potentials. This offers further substantiation for the idea that the rapid drop in current density occurs when all of the surface silver atoms have reacted to form  $Ag_2O$ .

The rapid change in current density could be accounted for in two ways. The first suggestion takes into account the high electrical resistance of  $Ag_2O$ . The specific electron conductance of  $Ag_2O$  is reported to be  $10^{-6}$  ohm<sup>-1</sup> (14) and thus the formation of the exide film on the surface of the electrode would increase the electrical resistance of the system and bring about a decrease in current flow. However, the inoreased resistance would only decrease the rate of the reaction and thus complete conversion of Ag to  $Ag_2O$  should be achieved after a sufficiently long anodic treatment. Our results show that this does not occur. The ether possibility is that the  $Ag_2O$  layer presents a barrier to the diffusion of hydroxids ion to the unreacted silver. When the formation of the exide film on the surface is complete the reaction at the site of there are no more hydroxide ions available for reaction at the site of the free silver. It should be noted that, in this mechanism, there is ne electron flow across the  $Ag_2O$  film. The electron transfer takes

place at the silver - hydroxide ion interface and thus the resistance of the system must be due to the difficulty of transporting hydroxide ion through the oxide layer.

The data in Table II give additional evidence on the formation of Ag<sub>2</sub>O. (See Appendix). These data were obtained using the same experimental techniques described earlier, with the exception that the voltage increments were smaller. An electrode was exidized at 0.05 volts for 24 hours and the increase in weight was noted. The pertially exidized electrode was then charged at 0.10 volts for another 24 hours and the weight was again determined. This procedure was repeated at 0.05 volt intervals, up to 0.35 volts. Inspection of Table II (see Appendix) shows the maximum conversion of Ag to Ag<sub>2</sub>O after the 24 hour anodic treatment at 0.10 volts. However, the percent of Ag converted to Ag<sub>2</sub>O varied with the hydrexide ion concentration. Figure 7 (see Appendix) shows a plot of the specific conductivity of petassium hydroxide solutions superimposed on a plot of the percent of silver converted to Ag.O at 0.10 volts vs. the potassium hydrexide concentration. This graph indicated that the extent of Ag<sub>2</sub>O formation is a function of the specific conductivity of the electrolyte. Also, inspection of Table II (see Appendix) reveals that no further exidation of the electrode is accomplished by continued anodic treatment for 24 hour periods at each of the potentials below 0.35 volts. Since the conductivity of the electrolyte, and not the activity of the hydroxide ion, is involved, this would seem to indicate that the resistance of the electrolyte controls the depth of the oxide film on the silver electrode. It does not seem possible to explain this on the basis of the decreased rate of reachion in lower concentrations of KOH, because if it were kinetically possible to exidize the silver this would have occurred, at least to some extent, during the 96 hours of anodic treatment.

A consideration of the voltage distribution across the cell before and after the formation of the exide layer at first suggested a possible explanation for the above results. When the voltage is first applied acress the cell the silver electrode offers little or no resistance and therefore the full potential gradient is applied across the elsctrolyte. Oxidation occurs at the silver electrode and an exide film is produced. Since the oxide film has a high electrical resistance this forces a redistribution of the potential across the cell. A certain fraction of the cell potential then produces a voltage gradient across the exide layer and the significant fact is that the magnitude of this voltage gradient increases as the specific conductivity of the electrolyte increases. If we now assume that the continued oxidation of silver involves the diffusion of hydroxide ions through the oxide layer, under the influence of the voltage gradient, it might be suggested that, in solutions of high electrical resistance, the difference in potential may not be great enough to overcome the resistance of the film to the transport of hydroxide ion to the unreacted silver. This explanation is at least consistent with the observation that the extent of the reaction is a function of the specific conducivity rather than the activity of the hydroxide ion. This explanation, while tempting, is incorrect, however, because an increase in cell potential would increase the voltage gradient across the oxide layer, resulting in the formation of more Ag<sub>2</sub>O. Our results show that this does not occur.

In fact, the electrode resists further oxidation at all potentials up to the potential at which  $Ag_2O$  is oxidized to AgO. It appears then, that the exide film produced at 0.1 volts, regardless of its thickness, prevents the diffusion of hydroxide ion to the surface of the active silver. If this is the case, the only reaction possible is the conversion of  $Ag_2O$  to AgO, at the  $Ag_2O$  - potassium hydroxide interface.

Apparently, the extent of silver-to-silver (I) exide conversion may be dependent on a number of factors, such as, specific conductivity, the voltage at which the initial exide film is formed, and the electrical resistance of  $Ag_2O_2$ .

Inspection of Table I (see Appendix) reveals that, in 8 percent and 20 percent KOH, after the test electrode had been anodically treated to form  $Ag_2O$ , the application of a potential of 0.35 volts resulted in a loss of weight. This occurred despite the fact that exidation was taking place at the electrode as shown by the current flow, Figures 3-c and 4-b (see Appendix). In 28 percent KOH this loss did not occur. In fact ever the voltage span of 0.05 to 0.35 volts the current efficiency was 100 percent.

This apparent loss of oxygen had been observed before and we felt that a systematic study of the oxidation of silver in KOH solution was required to discover the reaction or process responsible. Table II (see Appendix) contains a summary of the results obtained in this study.

The data show that there is a definite loss of weight from the electrode as it is treated at increasingly more positive potentials, up to the point where AgO begins to form. However, reduction of the electrode and comparison of its weight to the weight of the original

electrode showed that some of the silver had been lost. It was found that the amount of silver lost in each series exceeded the loss experienced by the electrode during anodic treatment. A graph of the grams of oxygen gained per gram of silver vs. voltage on Figure 8 (see Appendix) indicates that the loss in weight is independent of the KOH concentration, quantity of oxide on the electrode, and the veltage, Thus it appears rather certain that a competing reaction could not be involved. Evidently there is a certain amount of cracking and flaking off of the oxide material during the processing of the electrode and this accounts for the apparent loss of oxygen. The loss of  $Ag_2O$  could also expose some free silver to the electrolyte and this would account for the fact that some current was observed to flow during the time that the anode appeared to be losing oxygen. It would also follow that the current efficiencies calculated for this process can only be approximate.

## Potential for the Ag20-Ag0 Transformation

Reference to Table I (see Appendix) shows that AgO is not produced in 8 percent potassium hydroxide solution until the electrode was held at 0.40 volts above the Ag<sub>2</sub>O potential. In higher concentrations AgO was fermed at 0.35 volts. Since the standard reversible potential of AgO is about 0.26 volts above the Ag<sub>2</sub>O potential, it is evident that the potential required for the Ag<sub>2</sub>O-AgO transformation is approximately 0.1 volts above the standard potential and that this value decreases with increasing hydroxide ion concentration. This is the expected trend if we assume the following reaction:

 $Ag_20 + 20H^2$  2Ag0 + H<sub>2</sub>0 + 2e<sup>2</sup>, and express E in terms of the Mernst equation.

 $E = -0.57 - \frac{0.059}{2} \log \frac{(A_0 O)^2 H_2 O}{(A_0 O)(OH^2)^2}$ 

Since AgO and Ag<sub>2</sub>O are solids we may consider their activities to be unity and it is then apparent that as the activity of the hydroxide ion increases and the water activity decreases, the value of E will approach  $E^{O}$ .

Justification for the assumption that hydroxide ion and not water is the active species can be obtained from Figures 3-6, e and f (see Appendix). A comparison of the current densities shows that the rate of the reaction increases with increasing hydroxide ion concentration. If water were the active species one would expect the opposite effect. It will be shown later in this paper that the rate controlling factor (in the potential range considered here) is the speed at which the active material is brought to the surface of the electrode. The higher viscosity and lower water activity in the more concentrated potassium hydroxide solutions would lower the rate at which water molecules would diffuse to the electrode surface. Thus it seems unlikely that water could be directly involved in this process.

#### Analysis of the Current VS. Milliampere Hour Curves

When the potential of the working electrode was held at 0.05 volts above the  $Ag_2O$  potential (curve "a" in Fig. 3 to 6, see Appendix) the current slowly decreased with time. However, when the silver electrode was exidized at higher potentials ("d" in Fig. 3 to 6) the current remained constant for several hours and then dropped rapidly to a very low value. This difference in behavior suggests that different rate controlling factors are involved.

It was pointed out in the introduction that two of the rate controlling factors which must be considered in a constant potential process are overvoltage and rate of linear diffusion.

If we assume that the electrolytic oxidation of silver proceeds in accordance with the following equation:

$$Ag + OH^{-} \longrightarrow \frac{1}{2} Ag_{2}O + \frac{1}{2} H_{2}O + 1 e^{-}$$

then following the treatment of Delahay (15) we can indicate the dependence of current en overvoltage by

$$I = KAFC_{OH} - C_{Ag} = \frac{Af}{RT}$$
 where

K is the rate constant, A is the area of the electrode, F is the Faraday,  $-\frac{\Delta f}{RT}$ and e represents the fraction of molecules in the activated state. A, F, and C<sub>OH</sub>- are constant so

$$i = K^{*}C_{Ag} e^{-\frac{Af}{RT}}, \text{ and substituting}$$
$$i = K^{*}C_{Ag} e^{-\frac{nFE}{RT}} \text{ which, at 25^{\circ} becomes}$$

$$\log i = \log C_{Ag} + \frac{E}{.059} + \log K'$$
.

The plot obtained in Figure 9 (see Appendix) was derived by assuming that the electrode surface had a total capacity of 100 milliampere hours and this was considered to be  $C_{Ag}$ . Thus, after 10 milliampere hours of

charge the concentration of Ag was reduced to 0.9, and after 20 milliampere hours  $C_{Ag}$  was 0.8, etc. The plot of i vs. milliampere hours shows that the rate increases with potential and at constant overpotential the rate decreases with time.

The high current rate predicted by the current-overvoltage relationship is seldom achieved at high overvoltage values because a point is soon reached where the rate of diffusion of the electrolyte to the electrode surface limits the rate of the reaction. Under these conditions a concentration gradient is established between the electrode and the body of the solution, the concentration of the reacting species being sure at the electrode surface. Delahay (16) has shown that the limiting current in a constant potential process controlled by the rate of diffusion is expressed by

$$i = nFAD_0^{1/2}C^0 \frac{1}{\frac{1/2}{\pi^{1/2}t^{1/2}}}$$
 where n is the number of electrons,

F is the Faraday, D<sub>0</sub> is the diffusion coefficient, and C<sup>0</sup> is concentration. The quantity  $\frac{nFAD_0^{1/2}}{\pi^{1/2}}$  is a constant in a given potassium

hydroxids solution. Simplifying,

$$i = Kt^{-1/2}$$

A graph of this equation (Figure 10, see Appendix) shows that the current will decrease with time.

The above considerations would lead us to suspect that the reaction is rate controlled by the overvoltage at 0.05 volts and by the rate of diffusion at higher potentials. However, examination of curves 'a' and 'd' in Figures 3 to 6 (see Appendix) indicates that 'a' could be rate controlled by either factor while 'd' resembles neither of the theoretical curves.

At this point it is necessary to note that in the derivation of the equation for current in the diffusion controlled process it was assumed that the concentration gradient remains constant. This would not hold true if the electrode were held at a constant potential for a long period of time, because the difference in density between the electrolyte near the electrode surface and the body of the selution would soon cause convection currents. Laitenen and Kolthoff (17) studied the effect of convection currents on the shape of current vs. voltage curves in a diffusion controlled constant potential process. They found that large deviations from the theoretical were produced by convection currents and that the amount of deviation is dependent on the erientation of the electrode in the solution. If the electrode is positioned so that diffusion can take place only in a vertical direction, and if the solution of lowest density is always at the top, convection is eliminated and the theoretical curve is obtained. However, if diffusion is permitted from the side, convection takes place, the concentration gradient is largely removed, and a greater number of ions are made gvallable for reaction at the electrode surface than would be provided by the process of linear diffusion. This results in a high constant current for a period of time with a rapid drop in current when most of the active material has reacted.

In this work our electrode was mounted vertically in the potassium hydroxide solution and the oxidation was carried out over a period of

24 hours or more. It seems very probable then that the reactions carried out at potentials greater than 0.05 volts were controlled by the rate of transport of hydraxide ion to the electrode surface.

For the reaction at 0.05 volts it is now quite obvious that the limiting current is established by the overvoltage. The fact that the convection currents which are established, have little or no effect on the rate of the reaction, indicates that the rate is independent of the hydroxide ion concentration.

The shape of the current-time curves in 42 percent potassium hydroxide, Figure 6, e and f (see Appendix), differs markedly from those observed in lower concentrations. The initial current density was high but it dropped rapidly to low value in a very short time. Analysis of the experimental electrode revealed that Ag\_O was formed at 0.30 volts and AgO at 0.35 volts, but the extent of oxids formation was very low in each case. Since previous work indicated that the amount of Ag<sub>2</sub>O and AgO produced at high current density was related to the porosity or total surface area of the electrode, we suspected that the high temperature of thermal reduction may have been responsible for a decrease in porosity. To check this, an Ag<sub>2</sub>O electrode was reduced at 500°C. and placed on charge at 0.35 volts. A high current density was maintained for 4.5 hours and the composition of the product was  $AgO_{0.42}$ . The same electrode was then reduced at 900°C. and treated anodically at the same potential. The current density dropped to a low value in 20 minutes and the product composition was AgO<sub>0.1</sub>. The melting point of silver is approximately 900°C. so it is quite evident that at high temperature some of the silver fuses and thus reduces the surface area

of the electrode. The rapid decrease in current density is undoubtedly due to the formation of the film of  $Ag_2O_2$ , which offers high resistance to the flow of hydroxide ions to the surface of the unreacted silver.

## Mechanism of the Conversion of Ag<sub>2</sub>0 to Ag0

It was pointed out earlier that  $Ag_2O$  has a high electrical resistance but this apparently is not involved in the control of the reaction rate in the formation of  $Ag_2O$ , since there is no electron flow through the oxide film during the reaction. However, in the conversion of  $Ag_2O$  to AgO the situation is different. If we assume that the reaction of  $Ag_2O$  with hydroxide ion is represented bys

 $Ag_20 + 20H^- \longrightarrow 2Ag0 + H_20 + 2e^-$ , and if we also assume that hydroxide ions are available only at the surface of the  $Ag_20$ , then it can be seen that electrons will be transported across the  $Ag_20$  layer. The resistance of  $Ag_20$  to electron flow should then limit the rate of the reaction. Evidence for this was observed. When an electrode that contained the maximum amount of  $Ag_20$  on its surface was anodized at 0.35 volts, the conversion to Ag0 occurred (Table II, 22.7% KOH, see Appendix). The current flow, initially, was very low and gradually increased to a maximum over a period of a few hours. This is interpreted as evidence that the resistance of  $Ag_20$  limits the electron flow, but as the formation of Ag0 continues the thickness of the  $Ag_20$  layer decreases and this allows the current flow to increase to a maximum.

It might also be noted that, while our work cannot prove or disprove the existence of  $Ag_2O_3$ , it does indicate that AgO is produced directly from  $Ag_2O$  and Ag without the formation of  $Ag_2O_3$  as an intermediate, as suggested by Hickling and Taylor (11). The standard exidation potential value given by Latimer for the  $AgO-Ag_2O_3$  couple in alkaline solution is -0.74 volts and therefore it is not likely that we could have formed any  $Ag_2O_3$ , even at the highest potentials used.

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#### SUMMARY

While the results are qualitative in nature, it appears that several suggestions can be made concerning the constant potential oxidation of Ag in potassium hydroxide solution.

- 1. The current efficiencies for the reactions which result in the formation of  $Ag_Z^0$  and  $Ag_0$  are 100 percent efficient at potentials below that at which exygen evolution occurs.
- 2. Evidence has been obtained which indicates that the rate controlling reaction in the electrolytic formation of the oxides of silver, in potassium hydroxide solution, involves the reaction of hydroxide ion, and not water, at the electrode surface.
- 3. The conversion of Ag to  $Ag_2O$  is never complete and this is due to the formation of a film of oxide, which hydroxide ion cannot penstrate, on the surface of the silver electrode. It is also apparent that the extent to which Ag is converted to  $Ag_2O$  is a function of the specific conductivity of the potassium hydroxide solution.
- 4. It is obvious that  $Ag_2O_3$  need not be an intermediate in the formation of AgO.

We believe that this work shows that important information on the kinetics and mechanisms of electrode processes can be obtained by a study utilizing constant potential techniques. Also, further work on the constant potential exidation of silver is indicated. This investigation has shown that more reproducible electrodes should be obtained, in order that a more accurate analysis of the surface area factor may be made. It would also be necessary to devise and experimental set-up which would eliminate convection currents in a prolonged electrolysis. APPENDIX

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Figure 1

Diagram of the circuit used for constant potential oxidation.



The relation between current efficiency and hydroxide ion concentration for the anodic treatment of an  $Ag-Ag_2O$  electrode at 0.4 volts above the  $Ag_2O$  potential.

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|----|-----|---|--|
|    |     |   |  |

| <b>K</b> KOH | Figure     | Volts above<br>Ag <sub>2</sub> O<br>potential | % current<br>efficiency | % Ag<br>converted<br>to Aj <sub>2</sub> 0 | Product               | Nature<br>of<br>surface |  |  |
|--------------|------------|---|-------------------------|---|-----------------------|-------------------------|--|--|
| 8.25         | 3-a        | 0.05  | 70                      | 9   | Ag00.04               | Ag <sub>2</sub> O       |  |  |
|              | Ъ          | 0.15  | 90                      | 57  | Ag00.31               | Ag <sub>z</sub> O       |  |  |
|              | C          | 0.35  | 0                       | 53  | Ag0 <b>0-27</b>       | Ag <sub>2</sub> 0       |  |  |
|              | d          | 0.35  | 94                      | <b>59</b> ·                               | Ag0                   | Ag <sub>2</sub> O       |  |  |
|              | •          | 0.40  | 84                      | -   | Agoess                | Ago                     |  |  |
| 20.7         | <b>4-a</b> | 0.05  | 98                      | 62  | Ag0                   | Agg0                    |  |  |
|              | b          | 0.35  | 0                       | 48  | Ag0                   | AgaO                    |  |  |
|              | <u>C</u>   | 0.40  | 80                      | ***<br>***                                | Ago                   | AgO                     |  |  |
|              | ٩          | 0.15  | 100                     | 57  | Ag0                   | AggO                    |  |  |
|              | •          | 0.30  | 86                      | 53  | Ag0                   | AggO                    |  |  |
|              | 1          | 0.35  | 100                     |   | Ag0 <sub>0.46</sub>   | AgO                     |  |  |
| 28.3         | 5-a        | 0.05  | 87                      | 63  | Ag0                   | AgzO                    |  |  |
|              | Ъ          | 0.35  | 100                     |   | Ag00.73               | AgO                     |  |  |
|              | ¢          | 0.40  | 47                      |   | Ag03                  | AgO                     |  |  |
|              | đ          | 0.15  | 94                      | 79  | Ag0 <sub>0,39</sub>   | AggO                    |  |  |
|              | •          | 0.30  | 100                     | 76  | Ag0                   | Ag <sub>2</sub> O       |  |  |
|              | £          | 0.35  | 96                      | ***                                       | Ag00.51               | AgO                     |  |  |
| 42.3         | 6-a        | 0.05  | 100                     | 50  | Ag025                 | AgzO                    |  |  |
|              | b          | 0.35  | 77                      |   | Ag0                   | AgO                     |  |  |
|              | 3          | 0.10  | 8                       | 10-00<br>                                 | Aguo.se               | AgO                     |  |  |
|              | ٩          | 0.15  | 100                     | 56  | Ag00.25               | Ag <sub>2</sub> O       |  |  |
| ,            | •          | 0.30  | 64                      | 8   | Ag00.04               | Ag <sub>2</sub> O       |  |  |
|              | £          | 0.35  | 77                      | -   | Ago <sub>0 • 17</sub> | AgO                     |  |  |

Summary of Results of Constant Potential Oxidation of Silver

#### Figures 3-6

Current vs. milliampere hour graphs for the constant potential oxidation of a silver electrode in 8%, 20%, 28%, and 40% potassium hydroxide. The curves labeled a, b, and c were obtained by anodic treatment at 0.05, 0.35, and 0.40 volts above the Ag<sub>2</sub>O reversible potential. The electrode was not reduced between voltage steps. The curves on the lower half of each page (d, e, and f) were obtained by anodic treatment of the electrode at 0.15, 0.30, and 0.35 volts respectively, with the electrode being reduced to silver between each potential increase.



Figure 3.



**MILLIAMPERES** 

Figure 4.



Figure 5.



Figure 6.

## TABLE II

A summary of the results obtained by charging a silver electrode at each of the potnetials listed, for a period of 24 hours or until the current flow was zero, no reduction between steps.

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| <b>X</b> KOH | Volts above<br>Ag <sub>2</sub> O potent. | % silver<br>to Ag <sub>2</sub> 0 | Total weight of<br>corygen gained | Loss of<br>silver |
|--------------|--|----------------------------------|-----------------------------------|-------------------|
| 8.24         | 0.05                                     | 18                               | 0.0066                            |                   |
| -            | 0.10                                     | 18                               | 0,0068                            |                   |
|              | 0.15                                     | 18                               | 0.0066                            |                   |
|              | 0.20                                     | 15                               | 0.0057                            |                   |
|              | 0.25                                     | ĩ                                | 0,00,8                            |                   |
|              | 0.30                                     | 14                               | 9,0052                            |                   |
|              | 0.35                                     | 26                               | 0.0096                            | 0.0025            |
| 21.4         | 0.05                                     | 25                               | 0.0067                            |                   |
|              | 0.10                                     | 75                               | 0.0201                            |                   |
|              | . 0.15                                   | 73.5                             | 0.0198                            |                   |
|              | 0.20                                     | 71                               | 0.0191                            |                   |
|              | 0.25                                     | 71.5                             | 0.0192                            |                   |
|              | 0.30                                     | 71.5                             | 0.0192                            |                   |
|              | 0.35                                     | 76                               | 0.0204                            | 0.0045            |
| 22.7         | 0.05                                     | 45                               | 0.01                              |                   |
|              | 0.10                                     | 82                               | 0.0262                            |                   |
|              | 0.15                                     | 80                               | 0.0258                            |                   |
|              | 0.20                                     | 77                               | 0.0245                            |                   |
|              | 0.25                                     | 77                               | 0.0244                            |                   |
|              | 0.30                                     | 78.5                             | 0.0250                            |                   |
|              | 0.35                                     | AgO                              | 0.0374                            | 0.0032            |
| 42           | 0.05                                     | 33                               | 0.0103                            |                   |
| •            | 0.10                                     | 64                               | 0.0201                            |                   |
|              | 0.15                                     | 61                               | 0.0193                            |                   |
|              | 0.20                                     | 61                               | 0.0192                            |                   |
|              | 0.25                                     | 60                               | 0.0191                            |                   |
|              | 0.30                                     | 59                               | 0.0187                            |                   |
|              | 0.35                                     | 56                               | 0.0177                            | 0.0026            |



The relation between the percentage of silver converted to  $Ag_2O$  and the specific conductivity of KOH. Specific conductivity is plotted on the right ordinate and % silver converted to  $Ag_2O$  on the left. The upper curve is specific conductivity.



A graph of the data of Table II showing the inertness of the partially oxidized electrode between 0.1 and 0.3 volts above the  $Ag-Ag_2O$  potential.



Theoretical graph of rate dependence from overvoltage theory. The electrode capacity is 100 milliampere hours.



Theoretical graph of rate vs. time for a constant potential process controlled by the rate of linear diffusion.

#### REFERENCES

- (1) H. L. Johnston, F. Cuta, A. B. Garrett, J. Am. Chem. Soc. <u>55</u>, 2311 (1933).
- (2) A. B. Neiding, I. A. Kazarmovski, Doklady Akademii Nauk, U.S.S.R., <u>78</u>, 713 (1951).
- (3) T. P. Dirkse, Third Technical Report on Contract Nonr-1682(01), 31 December 1956.
- (4) T. P. Dirkse, First Technical Report on Contract Nonr-1682(01), 31 December 1955.
- (5) A. A. Noyes, J. L. Hoard, K. S. Pitzer, J. Am. Chem. Soc. <u>57</u>, 1221 (1935).
- (6) F. Jirsa, Z. anorg. allgen. Chem. <u>225</u>, 302 (1935).
- (7) P. L. Carman, Trans. Faraday Soc. 30, 566 (1934).
- (8) S. Tanatar, Z. anorg. aligem. Chem. 28, 331 (1901).
- (9) J. C. White, R. T. Pierce, T. P. Dirkse, Trans. Electrochem. Soc. <u>90</u>, 467 (1946).
- (10) F. Jirsa, J. Jelinek, Z. anorg. allgem. Chem. <u>158</u>, 61 (1926).
- (11) A. Hickling, D. Taylor, Disc. Faraday Soc. No. 1, 277 (1947).
- (12) C. B. H. Bawn, D. Margerison, Trans. Faraday Soc. 51, 925 (1955).
- (13) M. Fleischmann, H. R. Thirsk, Trans. Faraday Soc. <u>51</u>, 71 (1955).
- (14) M. Le Blanc, H. Sackse, Physik. Zeit. <u>32</u>, 887-9 (1931).
- (15) P. Delahay, "New Instrumental Methods in Electrochemistry," p. 34, Interscience Publishers Inc., New York (1954).
- (16) P. Delahay, "New Instrumental Methods in Electrochemistry," p. 51, Interscience Publishers Inc., New York (1954).
- (17) H. A. Luitinen and I. M. Kolthoff, J. Am. Chem. Soc. 61, 3344 (1939).

