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SECOND QUARTERLY REPORT

THE REACTIONS PERTAINING TO ZINC-SILVER AND CADMIUM-SILVER BATTERIES

JPL 951887

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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NOTICE

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ABSTRACT

A cell for the electrochemical preparation of tagged precipitates of Zn(II) and Cd(II) has been fabricated.

Electrochemically-prepared AgO is 50% converted to Ag_2O in 24 hours when heated at a constant 130^{o}. Conversion is 84% and 90% complete at 140^{o} and 150^{o}, respectively, in the same time.

The maximum solubility concentration of Ag(I) is 4-5 x 10^{-4} VF in 10 VF KOH for both AgO and Ag_2O. The concentration in the AgO system decreases slowly with time. The solubility of Ag_2O depends on the KOH concentration and shows a maximum at about 5 VF KOH.

The objectives of the contract are three-fold:

(1) The characterization of cadmium and zinc anodic reaction products.

(2) The thermal decomposition of silver oxide.

(3) The deposition of silver on zinc anodes.

This report will be divided into: (A) The investigation of the insoluble products of the electrochemical oxidation of zinc, (B) The thermogravimetric investigation of AgO, and (C) The rate of solution of AgO and Ag_2O in KOH solutions.

A. ELECTROCHEMICAL OXIDATION OF ZINC

Introduction

Several problems arose during the initial attempts to obtain insoluble Zn(II) products by electrochemical oxidation. In all cases where the cell was constructed of a zinc sheet anode and a AgO cathode in a polyethylene container, the Zn(II) product tended to supersaturate the solution to the extent that no solid could be recovered. At the same time, the current which could be produced by the cell in the galvanic mode was uselessly small. When current was forced through the system by an external power supply, zinc was found to plate on the cathode thus reducing the Zn(II) almost as rapidly as it was formed. Flat, small-volume cells produced similar problems while permitting only the difficult recovery of small quantities of Zn(II) solid. In order to eliminate these problems, a new cell was designed and tested.

Experimental

A simple two-compartment cell was used. The auxiliary electrode was a platinum wire immersed in 10 <u>VF</u> KOH. An ungreased, closed stopcock was mounted in the center of the electrolyte bridge to minimize material transfer while providing electrical contact. The bridge contact with the electrolyte solution in the working electrode compartment was made through a small hole in the side of the tube, the end being sealed. In this way, gas formed at the anode was prevented from entering the bridge. The bridge electrolyte solution was 10 VF KOH free of zinc.

The working electrode was Electronic Space Product Grade 6N zinc, 0.25 mm thick, cut in a circle of 1.0 cm radius, attached to a rectangular, platinum-sheet contact with Epoxy cement, and placed horizontally on the bottom of a glass weighing bottle (See Figure 1). The electrolyte solution was 2 ml of 10 VF KOH saturated with ZnO.

Constant current at 30 ma was supplied by an Electronics Measurements Model C629 power supply to the cell for about 24 hours until the electrode was completely consumed. Because the cell resistance was high, the applied voltage was about 35 v. The bridge temperature rose significantly in the vicinity of the stopcock but not sufficiently to cause damage.

Operated in the above fashion, the anode produced what appeared to be quite clean ZnO or $Zn(OH)_2$. A very faint gray tinge remained in the residue, but the color probably represents an insignificant quantity of metal. The quantity of product greatly exceeded any previously obtained and should be adequate for analysis.

The surface of the zinc electrode darkened after about one hour of electrolysis and remained dark as long as any metallic zinc was present. Microscopic examination showed that the surface becomes pitted during the reaction. This does not explain the reduced chemical activity which has been observed (1). Similar layers have been reported by Dirkse (2) and by James, Straumanis, and Johnson (3). The latter state that the black material, finely divided zinc, rapidly turns to white in the presence of moisture. Samples prepared in this laboratory were washed and left moist in contact with air but did not turn white over a period of several days. Very likely the method of preparation affects the reactivity of the material.

Proposed Work

Tracer experiments with zinc anodes will be performed with the new cell. Pure sheet cadmium has been ordered and similar experiments will be performed.

B. THERMAL DECOMPOSITION OF AgO

Experimental

A modification of the thermogravimetric weighing system previously described (4) was found to be necessary for constant-temperature experiments. The temperature at the position of the sample is quite different from that at the surface of the heater--the position of the controlling thermocouple. The current procedure is to place the control thermocouple against the hangdown tube and at the surface of the heater directly opposite the sample pan. A second, sensing thermocouple is placed inside the tube about 1 mm below the sample. This thermocouple is connected to a Leeds and Northrup K-3 potentiometer and the temperature (emf) is measured *vs* that of a similar thermocouple immersed in an ice-water bath. Temperature control has not been as good as desired, but the temperature measured on the sensing thermocouple can be held within 1^{0} of that desired.

AgO samples were taken from a single batch prepared electrochemically on a platinum-grid electrode as previously described (4). All samples weighed about 30 mg initially. Runs were made for about one week at controlled temperatures of 130°, 140°, and 150°. Weight changes were measured with a Cahn Model RG electrobalance and recorded either with a Neff Model 401 PA 10-mv recorder or with a Texas Instruments Servo/Riter II 1-mv recorder. Temperature was controlled with an F & M Model 240 M controller. Temperatures were measured periodically and the controller re-set as required.

Results and Discussion

The constant-temperature thermograms run thus far are shown in Figure 2. Each curve is the average of at least two sets of measurements.

The rate of reaction is seen to increase with increasing temperature as is expected. Furthermore, the rate in the first few hours is approximately doubled with each 10° increase in temperature. A rough comparison of half-lives suggests the reaction to be first order with respect to AgO.

From a practical standpoint, the important observation is that AgO is approximately 50% converted to Ag_2O with 24 hours at 130° while conversion is 84% and 90% at 140° and 150°, respectively, in the same time period. One could reasonably extend these observations to predict 25% and 12% conversion at 120° and 110°, respectively, in 24 hours.

A curious characteristic may be observed in the 130° and 150° curves of Figure 2. The slope of each curve gradually decreases as would be expected, but then begins to increase, passes through a maximum, and decreases again. The point of maximum does not occur after some particular heating time, but at a relative loss value of 0.2. The phenomenon was not observed at 140^0, possibly because no data were taken in the proper region. However, the 140^0 line is almost straight from 4.5 to 7 hours of heating as the curve approaches the region of 0.2 relative loss.

Allen (5) observed a similarly shaped curve in the decomposition of AgO in vacuum and attributed the effects to changes in the reaction geometry of the solid with time. Work done here showed the maximum to occur at a much higher degree of decomposition: 40% compared with his 9%. The difference could be caused by the difference in atmosphere and the difference in preparation of the solid.

All of the curves shown here seem to approach asymptotically a relative loss value of about 0.46. This corresponds to a conversion to Ag_2O of 92%. The result is surprising since earlier experiments produced relative losses in excess of 0.50. Those experiments used samples of AgO prepared chemically and the temperatures are uncertain; thus the earlier results may be in error or not comparable.

Proposed Work

Powdered samples of chemically and commercially prepared AgO as well as pressed pellets of all types will be investigated at constant temperatures. Equipment for controlled-atmosphere studies will be available shortly. The effects of sample illumination will be investigated.

C. RATE OF SOLUTION OF AgO and Ag_2O IN KOH SOLUTIONS

Experimental

Chemically-prepared AgO, commercial Ag_2O, or AgO electrodes were used in these experiments. Most of the 10 VF KOH solutions were saturated with ZnO. Solutions other than 10 VF KOH contained no zinc.

Mixtures of solid and electrolyte solution were stirred magnetically in closed polyethylene containers. The temperature was maintained at 25^o ± 0.1^o in a thermostated water bath.

Portions of the solution were withdrawn periodically, filtered, and measured volumes added to an amount of H_2SO_4 necessary to approximately neutralize the base present. These samples were then analyzed for Ag(I) by a modification of the polarographic procedure of Israel and Vroman (6). It was necessary to calibrate the system daily in order to obtain reasonable precision. Calibration consisted of measuring diffusion currents of known concentrations of Ag(I) on either side of the unknown concentration and calculating the latter by interpolation. Precisions in the order of 5% were obtained.

Results and Discussion

Table 1 shows the results of several experiments in which AgO was dissolved in 10 VF KOH saturated with ZnO. Figure 3 shows an averaged plot of the measured concentration of Ag(I) with time. The solubility of AgO in this electrolyte system is between 2×10^{-4} and 5×10^{-4} VF over the period of measurement. Solubilities are expressed in terms of the concentration of Ag(I) in solution. The concentration of Ag(I) reaches a maximum after a few hours, then decreases. The results of Experiment 1 may not be accurate since they were taken while the procedure was still being modified. However, they fit the observed trend roughly.

Figure 4 shows the results of experiments in which AgO electrodes were placed in 10 VF KOH saturated with ZnO. The mixture was stirred only just prior to removal of a sample for analysis. As would be expected, the rate of solution is lower; however, the solubility ultimately reaches that attained by the powdered AgO. The concentration decrease seems to be less and may not be a real decrease. However, the lack of stirring, while slowing the initial increase in concentration, may also slow the later decrease.

Table 2 shows the solubility with time of AgO in 10 VF KOH which is half-saturated with ZnO; i.e., 10 VF KOH saturated with ZnO was diluted with an equal volume of 10 VF KOH containing no zinc. Only one experiment was performed. The data show that this decrease in Zn(II) concentration does not significantly affect the solubility of AgO in 10 VF KOH even though one would expect some difference in the hydroxide activity. This experiment must be repeated.

Table 3 shows the solubility of Ag_2O in 10 VF KOH containing no zinc. Experiments were performed as described above with total time spans as long as three weeks. The values shown here did not vary significantly after one day. No data were taken at shorter periods. Evidently, the concentration of KOH has a significant effect on the solubility of Ag_2O. The difference between 4.2×10^{-4} and 4.6×10^{-4} VF at 10 VF KOH and 5 VF KOH, respectively, amounts to more than three times the sample standard deviation and should indicate a real difference. At 2 VF KOH, the solubility has decreased very significantly. Biedermann and Sillen (7) have suggested the soluble species in KOH solution to be Ag^+, AgOH, and $Ag(OH)_2^-$. It is not possible to correlate the data here with the equilibrium constants of Biedermann and Sillen without knowing the activity coefficients for the pertinent species in the high concentrations of base used. The overall trend is consistent with those constants, but the maximum at 5 VF KOH is not explained.

Dirkse, Vander Lugt, and Schnyders (8) have reported some solubility measurements of both AgO and Ag_2O in 1 VF KOH. The values found were somewhat lower than those shown here as would be expected, although the differences at 2 VF and 1 VF seem very high. They noticed a maximum concentration after a few hours followed by a fairly steady decrease in all cases. Data acquired here show no decrease for the case of Ag_2O. It must be recognized that the conditions of the experiments are drastically different and that hydroxide activities are probably very much higher at 10 VF than at 1 VF. Differences in water activity and solution viscosity would also have an effect.

Proposed Work

Solutions saturated with AgO and ZnO which are 10 VF in KOH will be allowed to react with sheet zinc, with powdered zinc, and with zinc electrodes. The Ag(I) concentration will be monitored as described above and will be compared with similar solutions in which no solid zinc is present. Similar experiments will be performed in the presence of solid AgO and the deposition of Ag on the zinc will be measured.

Table 1

Rate of Solution of AgO in 10 VF KOH Saturated with ZnO

Experiment	Time (hours)	Concentration of Ag(I)(VF x 10^4)
1	0.5	4.1
	4.5	4.7
2	24	4.0
	48	3.5
	96	3.2
	168	3.0
3	24	3.8
	48	3.8
	120	2.3
	168	2.6
4	24	3.7

Table 2

Solubility of AgO in 10 <u>VF</u> KOH Half-saturated with ZnO

Time (hours)	Concentration of Ag(I)(VF x 10^4)
24	3.8
96	4.0
168	3.4

Table 3

Solubility of Ag_2O in KOH Solutions at 25^o

Concentration of KOH (VF)	Concentration of Ag(I)(VF x 10^4)	Standard Deviation
10	4.2	0.11
5	4.6	0.07
2	3.3	0.07

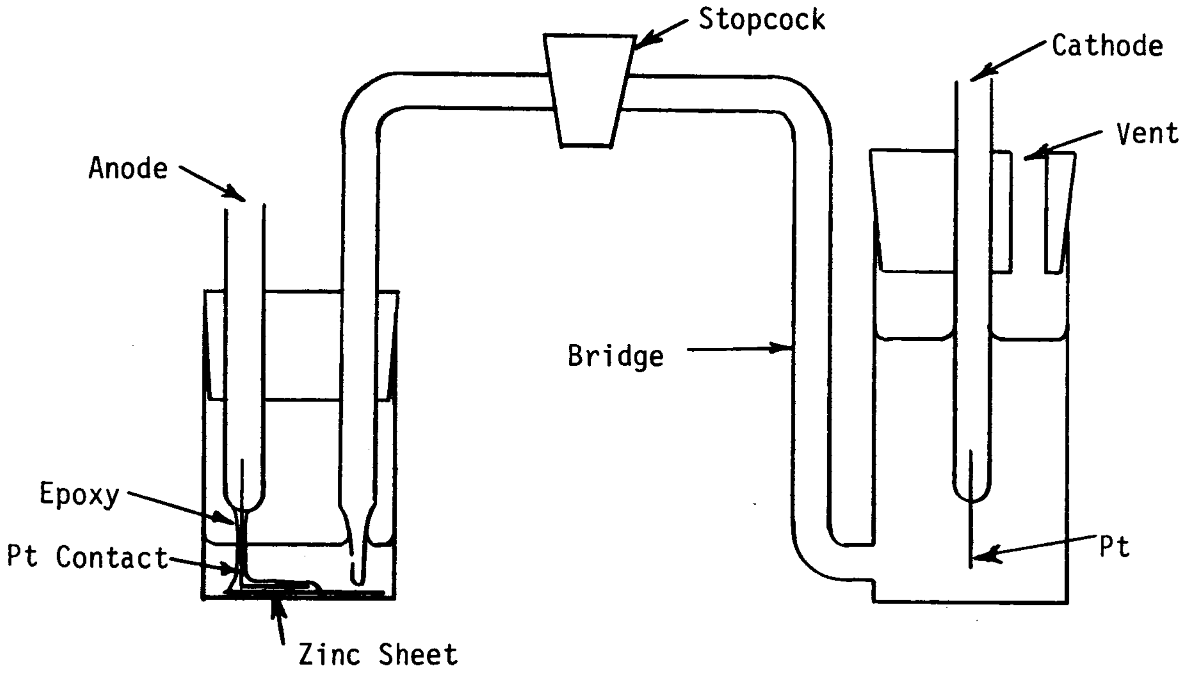

Figure 1. Electrolysis Cell

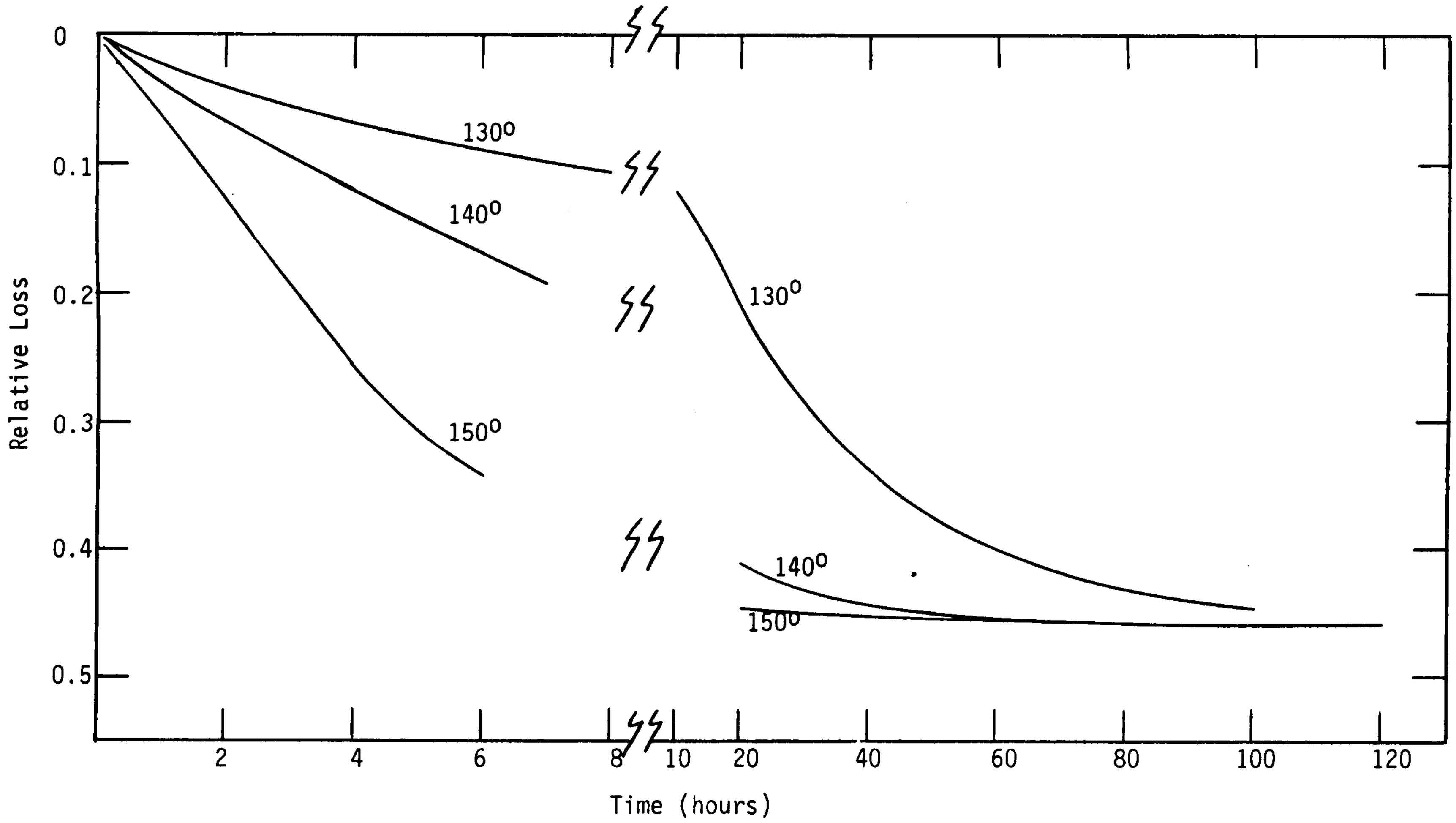

Figure 2. Thermal Decomposition of AgO

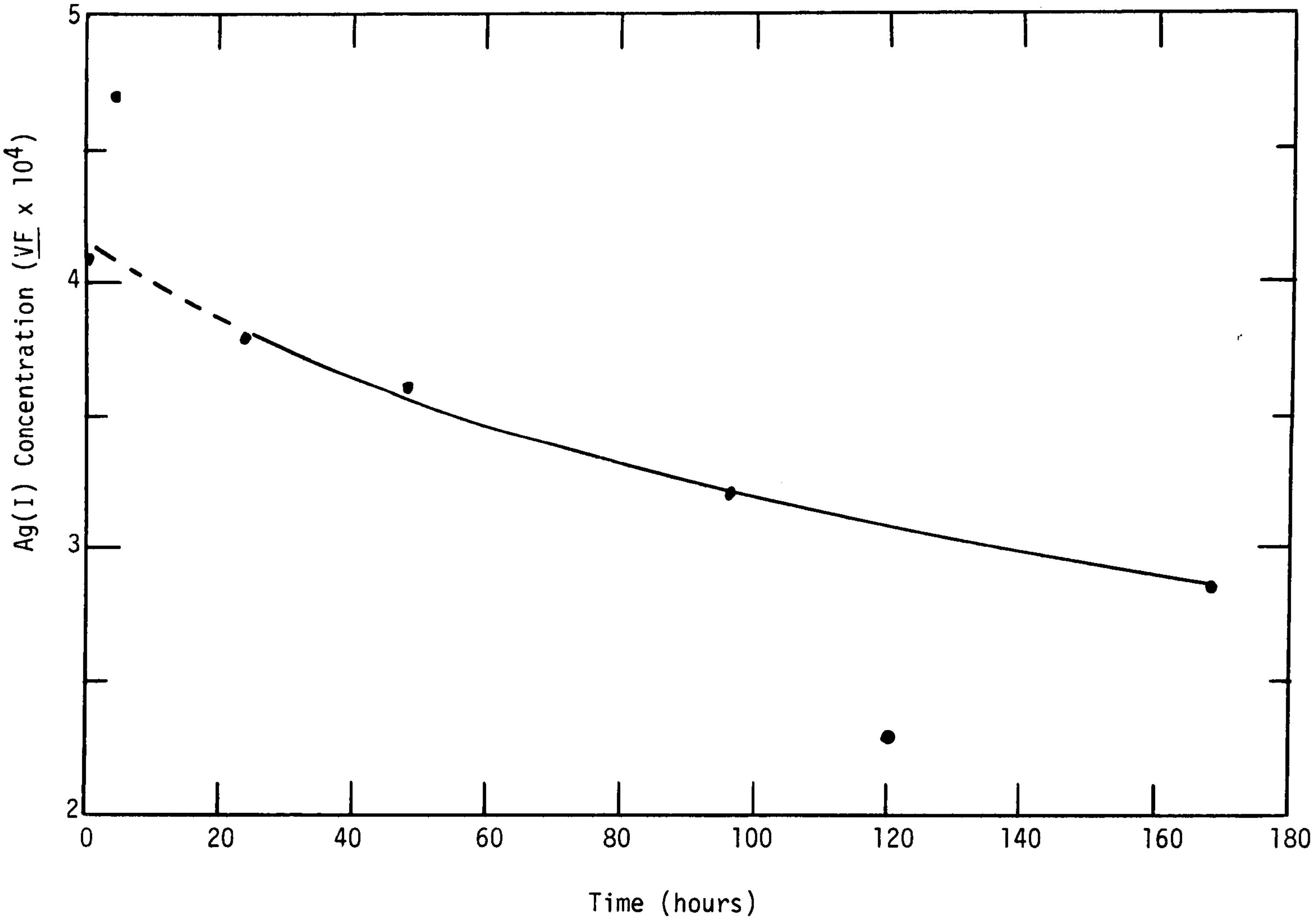

Figure 3. Solubility of AgO in 10VF KOH Saturated with ZnO

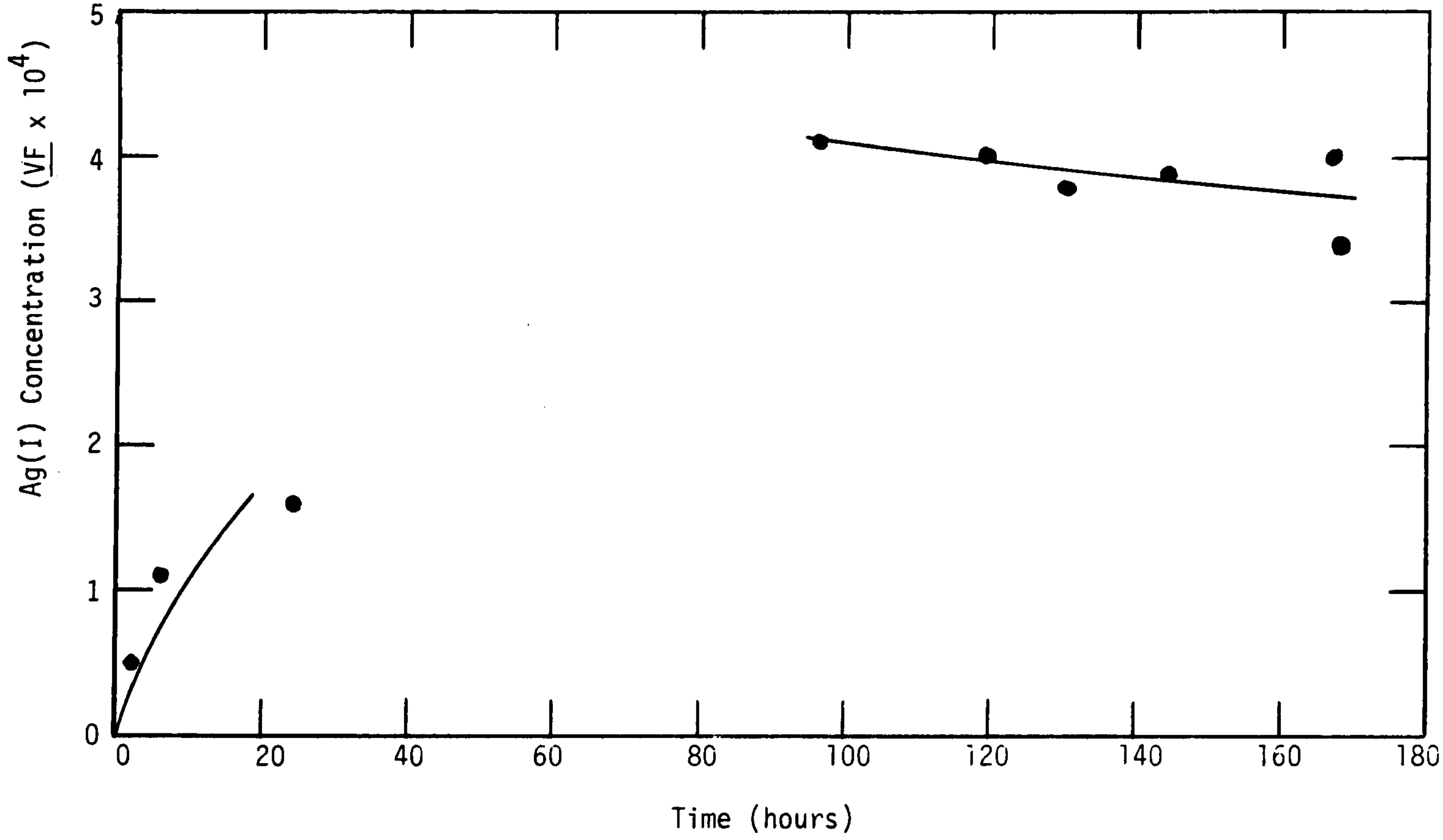

Figure 4. Solubility of Electrode AgO in 10VF KOH Saturated with ZnO

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