THIRD QUARTERLY REPORT

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

JPL 951887

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ABSTRACT.

Preliminary experiments indicate that electrochemical oxidation of zinc in 10 $\underline{VF}$ KOH produces less than 10% $Zn(OH)_2$ and more than 90% ZnO. The product is blue-gray while in the KOH but changes to white upon being washed with water.

The rate of conversion of AgO to Ag_2O rapidly increases with increasing temperature. Fifty percent conversion occurs in 24 hours at 121°, 11 hours at 131°, 4 hours at 141°, 2 hours at 151°, and 1 hour at 160°. The rate of conversion depends on the method of preparation of the original material.

The solubility concentration of Ag(I) in 10 $\underline{VF}$ KOH saturated with ZnO is about 4×10^{-4} $\underline{VF}$. This concentration is reached in less than a half-hour in a stirred system containing solid AgO and somewhere between 25 and 100 hours in an unstirred system containing a AgO electrode. The concentration of Ag(I) drops to less than 1×10^{-4} $\underline{VF}$ in 24 hours when a zinc plate is placed in the solution, provided no solid AgO is present.

The objectives of the contract are three-fold:

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

(2)   The study of the thermal decomposition of silver oxide.

(3)   The study of the deposition of silver on zinc anodes.

This report is divided into three sections corresponding to the objectives outlined above.

A.   THE PRODUCT OF THE ELECTROCHEMICAL OXIDATION OF ZINC

Experimental

The construction of the two-compartment cell was described in the previous report (1). The working-electrode compartment contained 2 ml of electrolyte solution which was 10 VF in KOH saturated with ZnO and having a tritium activity of 8.20×10^6 dpm/ml. The auxiliary-electrode compartment and the "salt bridge" contained 10 VF KOH. The auxiliary electrode was platinum wire.

A constant, 30-ma current was passed through the system until the zinc was completely oxidized. The cell was then dismantled and the zinc precipitate was dissolved in 1 ml of 5 VF HNO_3 and the solution diluted to 5.00 ml. 50-λ portions of the solution were pipetted into 15 ml of scintillating fluid and counted with a Nuclear-Chicago Model 703A liquid scintillation counting system.

A rectangular Lucite cell was constructed to hold a 20 mm x 20 mm zinc electrode and two AgO electrodes. The zinc electrode, a sheet of 6N Grade metal 0.25 mm thick manufactured by Electronic Space Products, Inc., was wrapped in one layer of polypropylene and three layers of sausage casing. The two AgO electrodes were each about 2 cm^2 and were wrapped in five layers of sausage casing. The zinc plate was placed between the AgO plates and the electrodes were separated by Lucite spacers 1 mm thick. The cell was activated with 4 ml of the tritiated solution described

above. The cell was operated at 50 ma for 4 hours and was then dismantled and the oxidized product recovered and treated as described above.

Results and Discussion

Several experiments were made with the two-compartment cell, but only one has been evaluated. The results of the experiment indicate that only about 1% of the product was $Zn(OH)_2$. However, the data are suspect because some untritiated KOH solution probably drained into the working compartment in spite of the closed stopcock in the bridge. Since the calculation of the relative amount of $Zn(OH)_2$ formed depends on knowledge of the total H in the system, any unknown addition of electrolyte solution would cause an error. However, even if the volume of electrolyte were increased by 50% with inactive solution, the calculated amount of $Zn(OH)_2$ would be only 2%.

The remaining runs made with the two-compartment cell will not be analyzed because of the uncertainty in electrolyte volume. The system is being modified to minimize the drainage problem.

Analysis of the results obtained from the run with the Lucite, single-compartment cell is not complete. Data available so far indicate an even lower activity in this precipitate than was found in the two-compartment system. In any event, it appears that the $Zn(OH)_2$ content in the anodic product is very small.

The physical appearance of the product is interesting. In both cells, the product was contaminated with a grayish or blue-gray material which turned white on washing with water. The product from the Lucite cell was entirely blue-gray with no indication of the white which is characteristic of zinc oxide. Where the electrode was exposed to air, a white residue, possibly KOH or K_2CO_3, was formed. It is difficult to imagine that this material is finely divided zinc metal because there was too much of it present. Furthermore, no gas was evolved when it was washed as would be expected if the metal were oxidized during that process. Still, the prospect of blue ZnO

is not appealing.

Proposed Work

Tracer experiments with zinc anodes will be continued and similar experiments with cadmium anodes will be initiated. An attempt will be made to identify the blue product described above.

B. THERMAL DECOMPOSITION OF AgO

Experimental

Constant-temperature thermograms of electrochemically-prepared AgO (3) were continued as described in the previous report (1). Similar experiments at 160° were performed on commercial AgO supplied by M. Ames Chemical Works, Inc., Glen Falls, N. Y. The Ames material was used both as powder and in pellet form. Pellets were made in a Parr calorimetric press using a 1/4-inch diameter die.

Increasing-temperature thermograms were run on both materials, the temperature being followed with the thermocouple which is mounted inside the hangdown tube near the sample. Ten-degree temperature intervals were recorded on the chart by means of an event marker. The heating rate was about 5°/per minute in all cases.

Results and Discussion

Constant-temperature thermograms of electrochemically-prepared AgO are shown in Figure 1. The curves suggest that the rate of decomposition is approximately doubled for each 10° increase in temperature. The loss in 24 hours is serious at all temperatures investigated.

Figure 2 shows the thermograms of electrochemically-prepared and of Ames AgO at 160°. Obviously, the Ames material decomposes much more rapidly than that prepared in this laboratory. The reason for the difference is not yet known. Possibly the Ames AgO consists of smaller particles. That the state of aggregation

is relatively unimportant is indicated by the similarity of the two Ames curves, one for powder and one for a pellet. Ames is being queried to learn the method of manufacture of this material.

Differences in behavior are seen also in the increasing-temperature thermograms shown in Figure 3. The Ames AgO shows sharper breaks and a "plateau" at a smaller relative loss than does the electrochemically-prepared compound. There is, again, little difference between the two Ames samples. The slight shift toward higher temperatures seen for the pellets is probably caused by a slower <u>mechanical</u> loss of oxygen from the compacted mass. This could account for the difference at the constant 160° for the Ames samples.

The results shown here for the 120° case compare favorably with those presented by Nagy, Moroz, and Casey (4). They report that pellets decompose about twice as fast as powder, but they formed their pellets at 70,000 psi. These authors suggest that the basic crystal size is the important factor in determining the rate of decomposition. This could account for the difference in behavior between the electrochemically-prepared and Ames samples.

Preliminary calculations indicate that the reaction mechanism is quite complex and may involve consecutive and/or concurrent reactions. An analysis by the method of Chatterjee (5) indicates an order of 0.7 for the initial reaction, i.e., near the beginning of the first rapid change in weight. The method of Coats and Redfern (6) yields 33 KCal/mole for the activation energy of this reaction and indicates that another reaction becomes important around 180°.

Proposed Work

Further work will be done on chemically-prepared AgO and on AgO taken from electrodes formed in KOH at 160°. If serious differences are observed, other temperatures will be used. Equipment is on hand to begin controlled-atmosphere experiments and these should start soon. Particle-size distributions will be determined

as soon as sedimentation equipment becomes available.

C. SOLUTION OF AgO AND Ag_2O IN KOH

Experimental

The procedure for solubility determinations was described in the previous report (1). Solutions saturated with both ZnO and AgO but containing none of the solid were allowed to react with sheet zinc, the solution being analyzed for Ag(I) periodically.

Results and Discussion

The results of another determination of the solubility of AgO in 10 VF KOH saturated with ZnO are shown in Table 1. The initial concentrations are comparable, but the slow decrease noted previously (1) does not appear. In fact, the concentration of Ag(I) seems to remain constant over the eight days of the experiment. It is probable that these results are more reliable than those found earlier because considerably greater care was exercised. It is evident from the data accumulated thus far that the maximum concentration of Ag(I) in 10 VF KOH saturated with ZnO is about 4×10^{-4} VF and is reached within one-half hour of mixing the solid AgO with the electrolyte solution.

Figure 4 of the last report (1) showed the change of concentration of Ag(I) with time when a AgO electrode was placed in an unstirred 10 VF KOH solution saturated with ZnO. The concentration rose to about 4×10^{-4} VF in less than 100 hours and stayed essentially constant for the next 60 hours. The experiment was continued for another 200 hours; no change in concentration was observed. The concentration is comparable to those found in the experiments using powdered AgO.

The results of measurements made in the presence of zinc plates have not been satisfactory. Concentrations in the control solutions have been about 4×10^{-4} VF,

as expected, but the determinations in the systems containing solid zinc were not dependable. Rough estimates indicate that the concentration of Ag(I) drops to somewhat less than 1×10^{-4} VF within 24 hours with the most rapid change occurring in the first hour or so. This work will be continued with a new method of analysis.

Proposed Work

The polarographic procedure used to analyze silver did not prove satisfactory for the systems involving reaction with solid zinc. A method using ^{110m}Ag will be tried for subsequent experiments. The rate of reaction of silver oxide with zinc in KOH solutions will be studied and the effects of temperature and KOH concentration will be investigated. The effect of silver deposition on the electrochemical behavior of the zinc electrode will be considered.

Table 1

Solubility of AgO in 10 VF KOH Saturated with ZnO

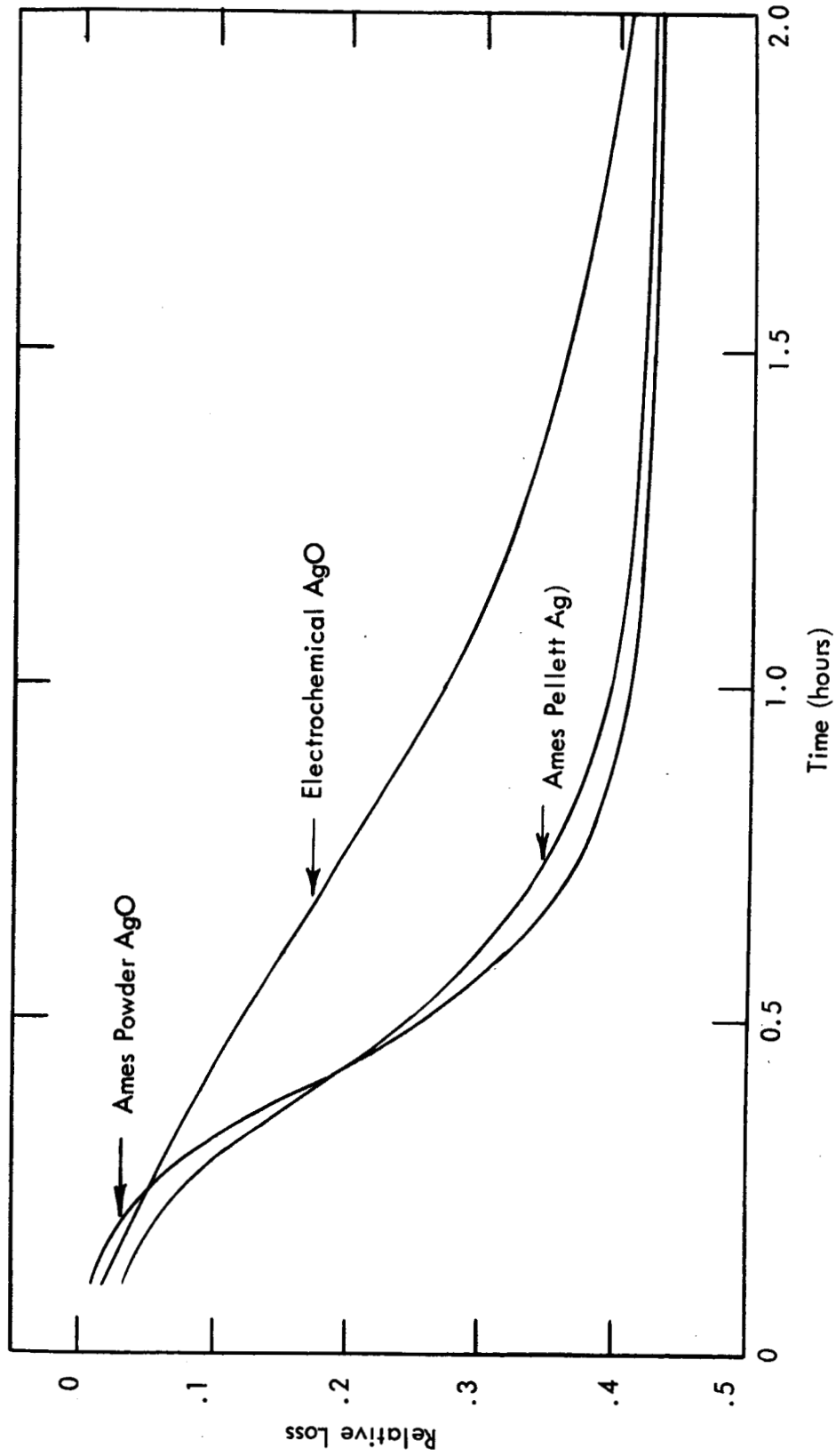| Time (hours)	Concentration of Ag(I) (VF $\times 10^4$)
0.25	3.7
148	3.8
174	3.7
192	3.6
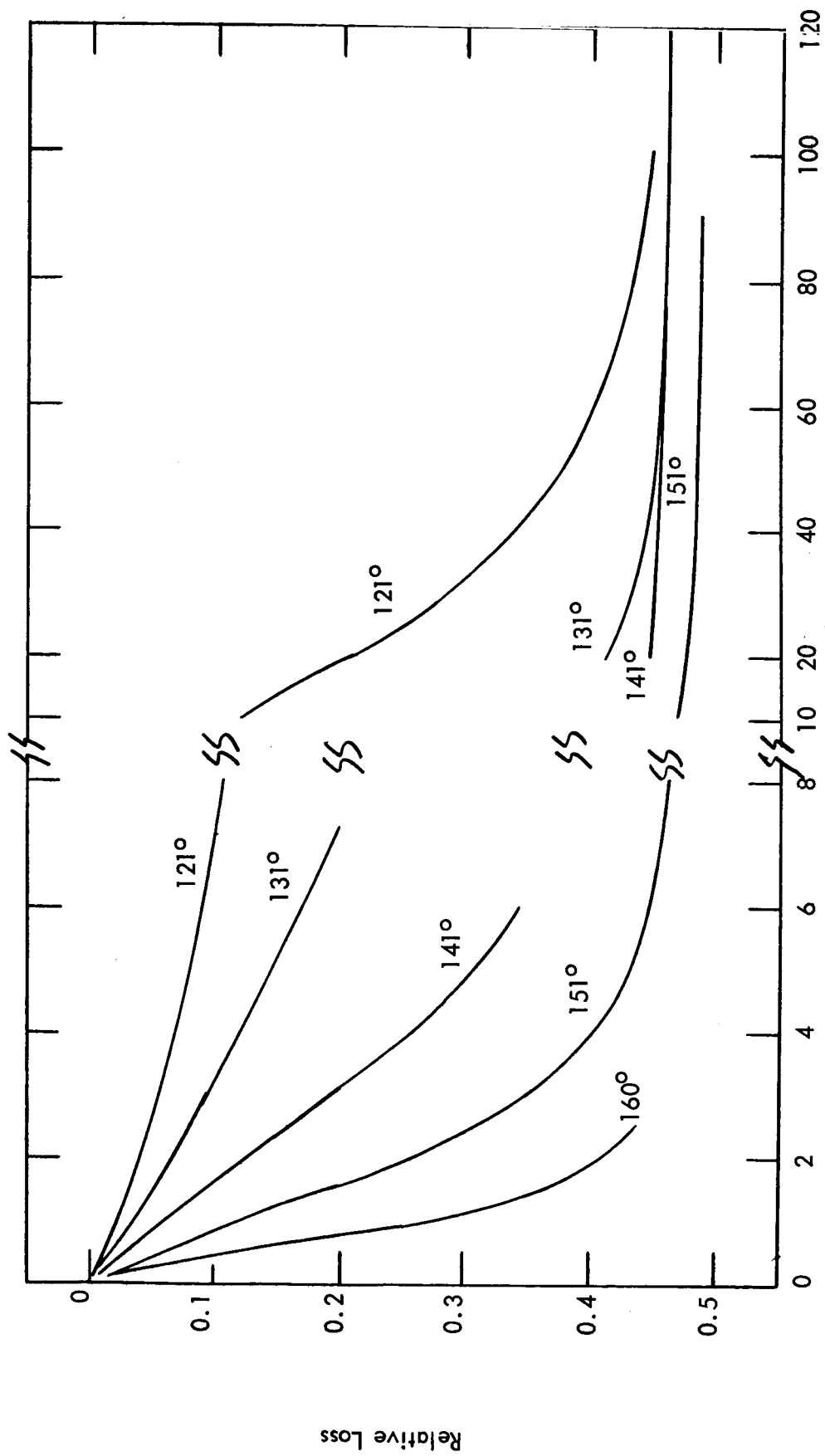
Figure 1. Thermal Decomposition of A_3O
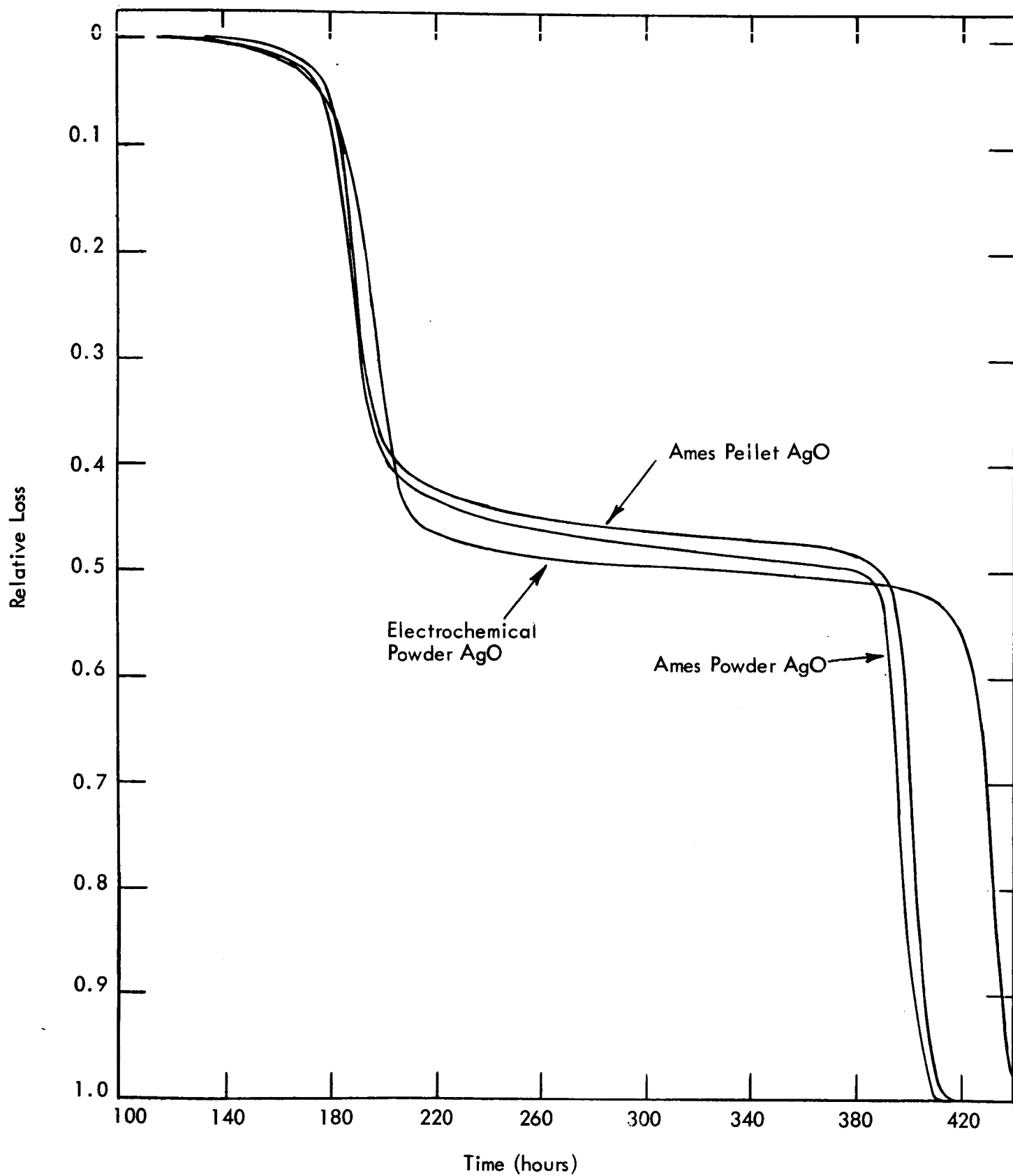
Figure 2. Thermal Decomposition of AgO at 160°

Figure 3. Thermograms of AgO at ΔT Rate of 5°/min.

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