Ni

951887



GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

FOURTH 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.

G. Myron Arcand

Department of Chemistry

Idaho State University

Pocatello, Idaho

March 15, 1968

ABSTRACT

Tracer studies have demonstrated that electrochemical oxidation of zinc and cadmium in 10 VF KOH solutions produces a zinc product which is less than 5% $Zn(OH)_2$ and a cadmium product which is 50-80% $Cd(OH)_2$. Oxidation of cadmium in a Cd-AgO cell containing a tritiated electrolyte solution results in a decrease in solution activity which cannot be accounted for simply by the formation of $Cd(OH)_2$.

The rates of decomposition of AgO and $Ag_2O$ apparently depend on how the original materials are prepared. These rate differences are very pronounced for $Ag_2O$ at temperatures between 320° and 420° and are real, though smaller, for AgO at 160°.

A procedure has been established for determining silver in KOH solutions by liquid scintillation counting using $^{110m}Ag$ as a tracer.

NOTICE

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

a. Makes warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or

b. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employees or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment with such contractor.

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Washington 25, D.C.

Attention: AFSS-A

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 oxides.

(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 PRODUCTS OF THE ELECTROCHEMICAL OXIDATION OF ZINC AND CADMIUM

### Introduction

The objective of this phase of work was to determine the products formed upon electrochemical oxidation at the zinc and cadmium electrodes in alkaline cells of the silver-cadmium and silver-zinc types. While transient products are certainly produced[1], the stable, solid products should be described by either of the two formulas: MO or $M(OH)_2$.

If a metal hydroxide is precipitated from a solution containing tritium, the precipitate should be active while if the oxide is precipitated from a similar solution, the precipitate should be inactive. Therefore, determination of tritium activity in the solid oxidation products of zinc and cadmium should provide a means of estimating the relative amounts of oxide and hydroxide present.

Literature references[2] have stated that many metals form only oxides when precipitated from solutions of strong bases. Experiments here[3] have shown that zinc is precipitated primarily as the oxide from KOH solution and as the hydroxide from $NH_3$ solutions. Cadmium forms the hydroxide when precipitated from KOH solutions. It remained only to determine the products of electrochemical reaction.

## Experimental

Electrochemical reactions were performed in rectangular cavities in either of two Lucite containers. In one, the cavity dimensions were 4.1 x 4.1 $cm^2$ by 5.0 cm deep; in the other it was 1.5 x 4.0 $cm^2$ by 5.0 cm deep. The anodes were wrapped in polypropylene and sausage casing separators while the AgO cathodes were wrapped in sausage casing. One anode was placed between two cathodes and the unit wedged into the cell cavity with polyethlene spacers. The cells were activated with 10-15 ml of tritiated 10 VF KOH solution. Where zinc anodes were used, the electrolyte solution was saturated with ZnO.

Three types of zinc electrode were used. Commerical electrodes, made by the Electric Storage Battery Co. (ESB), were cut to fit the cell compartment. These electrodes contained some mercury. Zinc sheet electrodes were prepared from 6N grade metal 0.25 mm thick which was manufactured by Electronic Space Products, Inc. The third type was prepared by plating zinc onto sheet platinum of the proper size. The plating solution was 30% $ZnSO_4$, 1.3% NaCl, 2.0% $H_3BO_3$, 2.6% $Al_2(SO_4)_3$, and 1.3% dextrine in water. The solution was stirred vigorously while plating was accomplished at 3 $ma/cm^2$ for about 2 hours. The electrodes were washed with water and mounted in the cell.

Cadimum anodes were cut from Electronic Space Products, Inc. 5N grade sheet metal 0.5 mm thick.

Current through the cell was controlled by a Model C629CMK Electronics Measurements Constant Current power supply. The current was maintained at 50 ma for several hours or until the anode was completely oxidized and the circuit broken. The system was dismantled, the anodic product removed, washed carefully with tritiated water having the same activity as the electrolyte solution, and dried in vacuum over $P_2O_5$ for several days. The precipitate was then dissolved in a minimum amount of dilute $HNO_3$ and made up to a known volume with water in a volumetric flask. 50-$\lambda$ portions of the solution were pipetted into 15 ml of

scintillating fluid and counted with a Nuclear-Chicago Model 703A liquid-scintillation counting system. Counting efficiency was determined by the channels ratio method.[4] Zinc and cadmium in the solution were determined polarographically.[5]

## Results and Discussion

The analysis is based on the assumption that the ratio of tritium to hydrogen will be the same in the hydroxide precipitates as in the electrolyte solution. Since this ratio is known, the amount of hydroxide in a precipitate containing a measured amount of metal ion can be calculated and the relative amounts of hydrogen and oxide estimated. This is reported as the percentage of metal hydroxide.

The precipitates were washed with water containing the same tritium concentration as in the electrolyte solution in order to prevent significant loss of activity through exchange with the wash water. This exchange, although slow, was sufficient to cause severely erratic results in some early experiments.[3]

Table 1 shows the relative amounts of $Zn(OH)_2$ calculated from tracer data. Most values are less than 10%; the high values probably resulted from incomplete drying. The seven low values have an average of 2.8% with a sample standard deviation, $s$, of 1.3% absolute. The next lowest value, 9.1%, is 3.2 $s$ above the average of the low values. The statistical probability of a random deviation of this magnitude is less than 0.2%. Thus, tracer analysis indicates that the product contains less than 5% hydroxide.

Attempts were made to correlate tracer results with thermogravimetric measurements. Two thermograms reported earlier[3] showed double breaks which were difficult to interpret. If the weight decreases were attributed to loss of water or hydroxide, the measured activites should have been much higher. On the other hand, if only the first break were attributed to loss of water, the results agree well with the tracer data. The second break would be assigned to the decomposition of the carbonate, probably

through adsorption of $CO_2$ from the air by the KOH. Duval[2] states that $ZnCO_3$ decomposes over a wide range of temperatures, but probably assumes onset of the decomposition at too high a temperature.

Figure 1 shows the thermogram of a zinc sample prepared electrochemically which is presumed to be 1.8% hydroxide. Loss of weight begins at about $40^{\circ}$ and continues fairly steadily up to $550^{\circ}$ and probably beyond. The plot starts below 1.000 because the sample was subjected to temperatures between 40 and $50^{\circ}$ before the experiment began. No definite breaks can be seen in this plot over the entire range. If one assumes that any hydrogen-containing component was removed below $120^{\circ}$, the results compare favorably with tracer data. The assumption seems valid since similar correlations are found where definite breaks are observed. Beyond $120^{\circ}$, weight loss is attributed to evolution of $CO_2$. This was slight in the electrochemical preparation because the operation was carried out in a glove bag under nitrogen.

The above conclusions were further checked by counting samples of the electrolyte solution before and after oxidation of zinc anodes. No significant activity difference was observed, which supports the argument that little hydroxide is formed.

The results in Table 1 show that the nature of the product is not affected by the form of the anode. This conclusion might be questioned in the case of the zinc-plated electrode since only two experiments were made. However, most spurious results observed previously have been on the high side.

The results of oxidation of cadmium anodes are shown in Table 2. These values range from 50 to 80% hydroxide and are different from the products formed by chemical precipitation which ranged from 80 to 100% hydroxide. The electrochemical product is light yellow to tan in color which indicated significant oxide content, but the color is sufficiently faint to support the conclusion that considerable hydroxide is present.

Tritium activity in the electrolyte solutions was measured before and after oxidation of cadmium. In the first case, about 15 milliequivalents of cadmium was oxidized and the solution activity decreased by 10%. In the second case, 71 milliequivalents of cadmium was oxidized while the solution activity decreased 30%. These results were gratifying in the sense that a method for determining state of charge might be possible.[6] However, the loss cannot be attributed to the formation of $Cd(OH)_2$ in any simple way because it is too great. That the silver electrode and/or the separators might be adsorbing tritium seems unlikely since this phenomenon was not observed during the oxidation of zinc anodes. Furthermore, the preferential adsorption of tritium would be surprising. There is some evidence of hydrogen formation at the cathode during the reaction. However, the total current passed through the system in the second experiment would correspond to, at most, 108 milliequivalents. If only hydrogen were formed at the cathode and only $Cd(OH)_2$ at the anode, the observed activity change would be 100% too high. This does not take into account the facts that water would be used at the cathode causing a concentration of tritium and that electrolysis causes enrichment of the heavier isotopes in the solution. Furthermore, hydrogen would not be formed at the cathode to the exclusion of all reduction of AgO; this is further demonstrated by the very slow gas evolution.

The loss in solution activity is a curious phenomenon. Experiments are underway to determine whether tritium is selectively adsorbed by $Cd(OH)_2$, the separators, or the AgO and whether reduction of $Cd(OH)_2$ formed in a tritiated solution will cause an increase in solution activity.

## Conclusions

Tracer studies on zinc and cadmium anodes indicate that less than 5% of the zinc product is $Zn(OH)_2$ while 50-80% of the cadmium product is $Cd(OH)_2$. These results show that the method of preparation significantly affects the nature of

the product. Considerable tritium activity is lost by the electrolyte solution when cadmium is oxidized. The mechanism by which the loss occurs is not yet known, but may be of considerable importance if a tracer method is used for determining the state of charge in a silver-cadmium cell.

Suggested Future Work

Although the primary objectives of this phase of the contract have been accomplished, much is yet to be learned about the anodic behavior of zinc and probably cadmium. Independent studies[7] have shown that the transient products formed during oxidation are varied and probably complicated. Since the formation of these materials seems to depend on the current density at the electrode, the substances may appear in an operating battery under certain load conditions. The nature of the materials is difficult to determine because they exist only while current is flowing. Nevertheless, information about these coating will be required before optimum operating conditions can be evaluated. It is suggested that a program be initiated to study these transient materials.

## B. THERMAL DECOMPOSITION OF AgO

Experimental

The thermogravimetric procedure has been described previously.[8] The experimental set-up has been modified slightly to make it more versatile. A Cahn Mark II Time Derivative Computer has been installed and calibrated. With this unit, rates of weight-loss can be measured directly making possible better estimates of activation energies. The ice-bath thermocouple reference junction has been replaced with a Model MC11B-3C Mini-Comp Cold Junction Compensator manufactured by West Instrument Corp., Schiller Park, Ill. This unit makes possible long-term temperature monitoring without the inconvenience of constantly checking the ice-bath.

Material was removed from a formed silver oxide electrode and dried over $P_2O_5$ in a vacuum. Thermograms of this material were run at a constant 160° and at a heating rate of 5°/minute. Temperatures were measured with a thermocouple mounted about 2 mm below the sample inside the hangdown tube.

## Results and Discussion

The constant-temperature thermograms of Ames AgO (M. Ames Chemical Works, Inc., Glen Falls, N. Y.), electrochemically-prepared AgO (Jolly[9]), and electrode AgO are shown in Figure 2. The initial decomposition rates for the Ames and the electrode samples are about the same and are considerably greater than that of the electrochemically-prepared material. The relative amount of AgO in the electrode sample is less than in the others which accounts for the smaller total decomposition at 160°.

The behavior of the three types of material at steadily increasing temperature is shown in Figure 3. All materials appear to undergo the first decomposition to $Ag_2O$ at essentially the same temperature; i.e., the temperatures at the midpoints of the first break are not significantly different. However, the midpoints of the second break (decomposition of $Ag_2O$) occur at 355°, 400°, and 430° for electrode, Ames, and electrochemical samples, respectively. Thus, the rates of decomposition of $Ag_2O$ at fixed temperatures between 320° and 420° appear to be very much dependent on how the material is formed. It is difficult to attribute these large differences to simple variations in particle size.

## Proposed Work

Electrode AgO will be studied at 130° and its behavior compared with AgO formed by other methods. Experiments in controlled atmospheres will begin soon. Further attempts will be made to determine the mechanism of decomposition and the energies of activation. The behavior of $Ag_2O$ will be studied at 160° and, if time permits, in the region above 320°.

## C. DEPOSITION OF Ag ON ZINC ELECTRODES

### Experimental

$^{110m}Ag^{+}$ in a dioxame-dimethyl POPOP-PPO-naphthalene mixture can be determined efficiently with a liquid scintillation counter. Errors caused by adsorption of silver on the walls of the polyethylene counting vials can be minimized by soaking them in dilute HCl after each use.

Stock silver nitrate has been prepared which is approximately 0.025 VF and contains about 5 $\mu$curies/ml of $^{110m}Ag$ activity. The stock was standardized against thiocyanate and the activity in counts per minute/milliequivalent of total silver determined. Required amounts of the active stock solution are added to KOH solutions.

There is some evidence that KOH affects the counting efficiency of this system. Therefore, the following procedure will be used to prepare counting samples: To calibrate the stock solution, 10 $\lambda$ of stock and 10 $\lambda$ of KOH solution will be pipetted into the counting vials containing the scintillator fluid. Experiment samples will be prepared by pipetting 10 $\lambda$ of the solution containing KOH and silver and 10 $\lambda$ of water.

When $^{110m}Ag$ stands in the scintillator solution in the counting vials for several hours, the activity is found to decrease. The reason for this is not known although it is probably related to adsorption effects. It will be necessary to reproduce the time between preparation of the sample and counting in each case.

### Proposed Work

The solubility of $Ag_2O$ in KOH will be re-checked by the tracer technique. Corrections will be made for adsorption of silver by the container walls. The rate of deposition on zinc plaques and on zinc electrodes will be determined both by measuring the decrease in solution activity and by measuring the activity on

the zinc surface. Silver electrodes containing $^{110m}$Ag will be prepared and the rate of diffusion from these electrodes will be estimated.

Table 1

Product of Electrochemical Oxidation of Zinc

| % Solid $Zn(OH)_2$ Formed | | |
|---|---|---|
| Zn Sheet Anodes | ESB Porous Anodes | Zn-on-Pt Anodes |
| 9.1 | 20 | 12.0 |
| 16.0 | 2.9 | 1.1* |
| 4.3 | 5.4 | |
| 1.8* | | |
| 1.7* | | |
| 2.2* | | |

*Reaction in $N_2$ atmosphere

Table 2

Product of Electrochemical Oxidation of Cadmium

| % $Cd(OH)_2$ Formed |
|---|
| 52 |
| 76 |
| 69 |

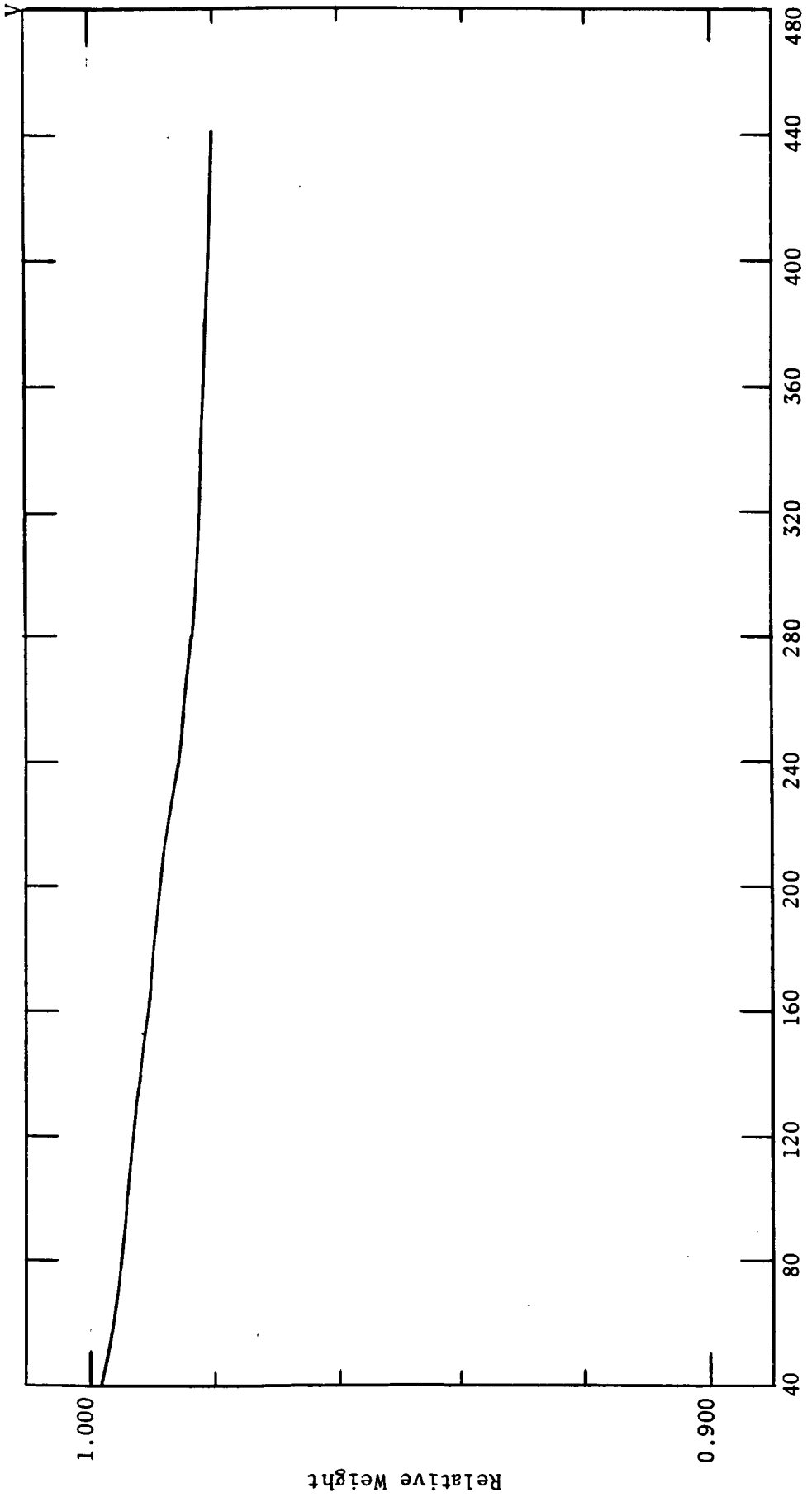


Figure 1. Thermogram of Electrochemical ZnO at $\Delta T = 5^{o}/min.$

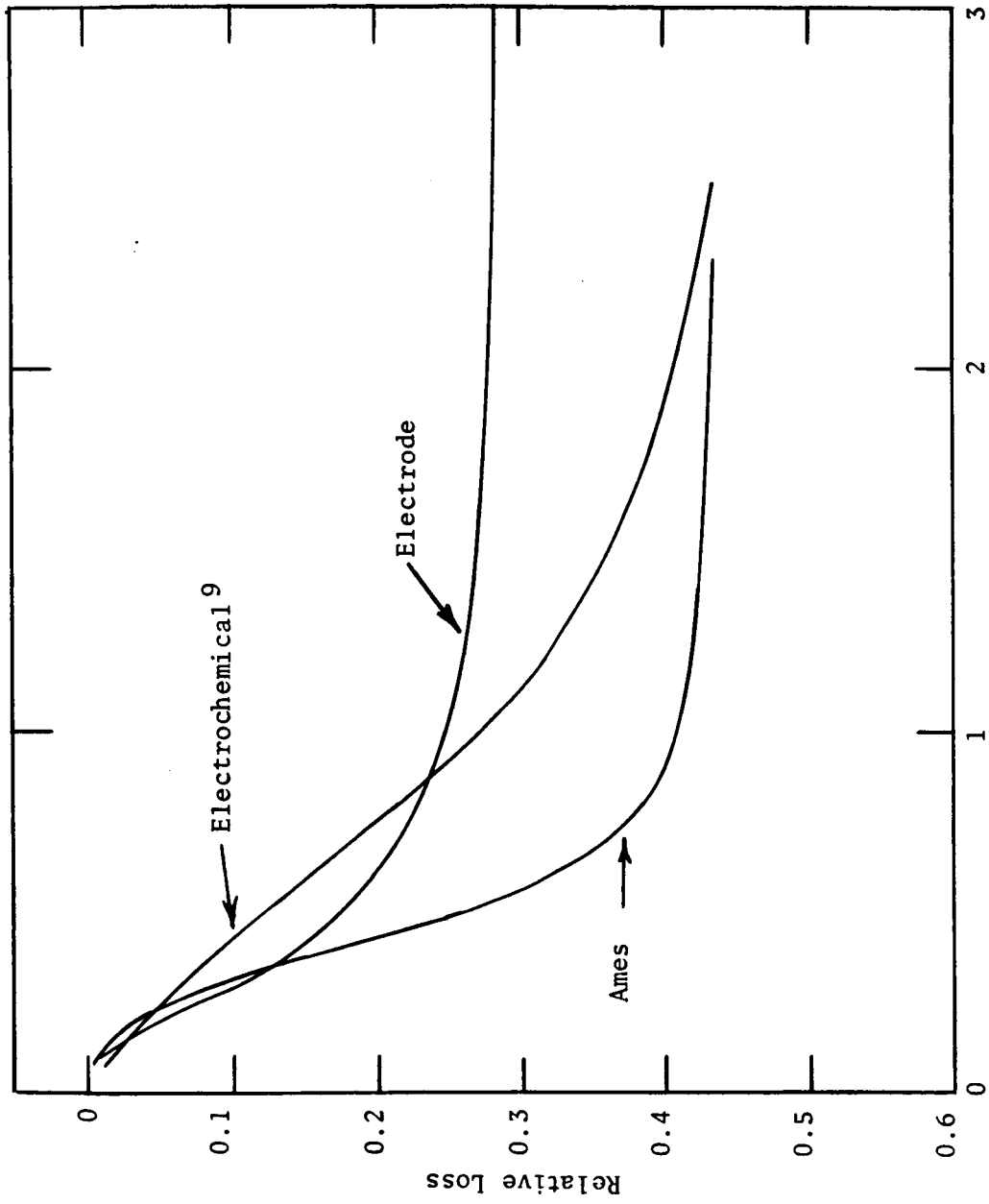


Figure 2. Thermal Decomposition of AgO at 160°

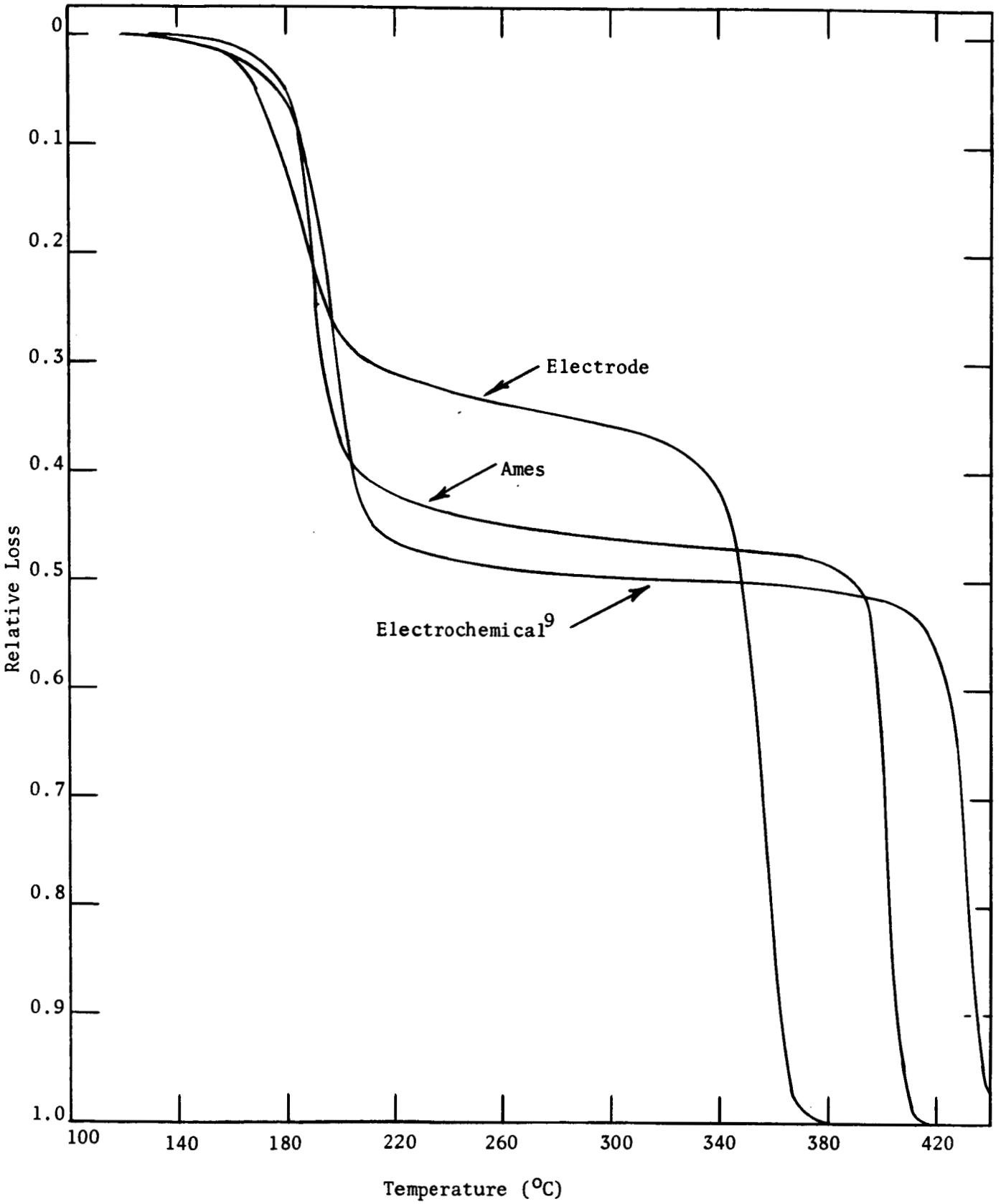


Figure 3. Thermograms of AgO at $\Delta T$ Rate of 5°/min.

## REFERENCES


[1] J. Euler, Electrochim. Acta 11, 701(1966)

[2] C. Duval, "Inorganic Thermogravimetric Analysis", Elsevier Publishing Co., New York, N. Y., 1953, pp. 275-9.

[3] G. M. Arcand, "The Reactions Pertaining to Zinc-Silver and Cadmium-Silver Batteries", April 1, 1967, Final Report on Contract JPL 951458.

[4] E. T. Bush, Anal. Chem, 35, 1024(1963)

[5] I. M. Kolthoff and P. J. Elving, "Treatise of Analytical Chemistry", Part II, vol. 3, Interscience Publishers, New York, N. Y., 1961, pp. 158, 215.

[6] "Method for Determining the State of Charge of Batteries by Use of Tracers", G. M. Arcand (to U. S. National Aeronautics and Space Administration). U. S. 3,317,352 (Cl. 136-182) May 2, 1967. Appl. Feb. 5, 1965, 3 pp.

[7] Unpublished experiments by D. L. Johnson and G. M. Arcand.

[8] G. M. Arcand, "The Reactions Pertaining to Zinc-Silver and Cadmium-Silver Batteries", December 15, 1967, Third Quarterly Report on Contract JPL 951887.

[9] W. L. Jolly, "Synthetic Inorganic Chemistry", Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, pp. 148-9.