# FIRST QUARTERLY REPORT

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

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# ABSTRACT

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Zn(II) was precipitated from tritiated solutions with KOH and NH$_3$. Precipitates formed with KOH contained little activity while those formed with NH$_3$ contained considerable activity. These observations, combined with the results of thermogravimetric experiments, suggest that ZnO is formed by KOH and Zn(OH)$_2$ by NH$_3$.

Thermogravimetric behavior of AgO depends on whether the oxide is formed chemically or electrochemically. There is evidence that AgO decomposes rapidly at 140°C.

## OBJECTIVES

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 and the measurement of the rate of decomposition of $AgO$ and $Ag_2O$ at various temperatures between $110^O$ and $200^OC$.

(3) The deposition of silver cathode material on zinc anodes.

This report deals with parts of the first two objectives and will be divided into: (A) the investigation of the precipitates of $Zn(II)$ when formed by the addition of alkaline solutions and (B) a preliminary thermogravimetric investigation of $AgO$.

## A. PRECIPITATION OF ZINC OXIDE

Introduction.

The reaction occurring at the zinc electrode during the discharge of a Ag-Zn cell is usually expressed in one of two ways:

$$Zn_{(s)} + 2\ OH^- = ZnO_{(s)} + H_2O + 2\ e^- \qquad (1)$$

$$Zn_{(s)} + 2\ OH^- = Zn(OH)_{2(s)} + 2\ e^- \qquad (2)$$
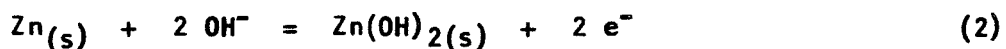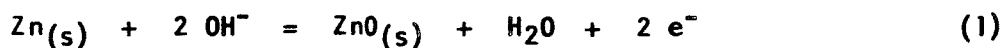
In either case, the pH in the vicinity of the electrode should decrease; however, reaction (1) would produce the greater change since the water formed would dilute the solution. The greater change in pH should produce a greater change in electrode potential.

The physical nature of a metal hydroxide is quite different from that of an oxide, the former being more gelatinous and less easily caused to settle in a fluid. One would expect significant differences in mechanical and electrical behavior of the electrode if the hydroxide rather than the oxide were formed during discharge.

The literature is not consistent in characterizing the zinc precipitate. Papers by Chalyi and co-workers (1, 2) appear to be contradictory. Duval (3) presents thermogravimetric evidence which suggests different types of precipitate depending on the method of preparation, yet he refers to all as being hydroxides. On the other hand, he states that many metals form only hydroxides when precipitated by KOH. Sneed (4) states that the hydroxide can be prepared only under carefully controlled conditions.

If tritiated water is added to an alkaline solution, there should be a rapid exchange of tritium between water and hydroxide. Any metal hydroxide precipitated from such a solution should contain activity proportional to the amount of hydroxide in the solid; an oxide should contain no activity. This technique should provide a means of determining the nature of the zinc precipitate formed in alkaline solution. Thermogravimetry may be used to support the findings made by tracer techniques.

Experimental.

Concentrated $Zn(NO_3)_2$ stock solutions were prepared from J. T. Baker Reagent Grade materials and were standardized iodometrically (5). J. T. Baker Reagent Grade 45% KOH solution was standardized against HCl and stored under nitrogen. Concentrated DuPont Reagent Grade ammonia was used without standardization.

Liquid scintillation solutions contained 7 g/l PPO, 0.3 g/l dimethyl POPOP, and 100 g/l reagent grade naphthalene in J. T. Baker Reagent Grade p-dioxane stabilized with sodium diethyldithiocarbamate. The fluors were obtained from the Packard Instrument Company. The solutions and the stock p-dioxane were stored under nitrogen.

Stock $H_2^3O$ was added to known volumes of supernatant and redissolved precipitate obtained from the system originally containing no activity. From the measured count rate and the known activity, the counting efficiency was calculated in each case, these values being used to calculate the activities in the tagged systems.

Zn(II) was precipitated with $NH_3$ in the same manner except that $NH_3$ was added until the pH of the mixture was approximately 8 as measured with a pH meter. This pH value should be sufficiently high to ensure complete precipitation of the zinc but sufficiently low to prevent re-solution as $Zn(NH_3)_4^{2+}$.

The precipitates from the first two experiments were incompletely washed. Subsequently, washing was continued until the washings showed no indication of nitrate (6). The precipitates were dried by washing with p-dioxane followed by absolute ethanol. The solids were allowed to stand exposed to room air for several days.

Potassium nitrate tended to form supersaturated solutions; therefore, the precipitates from the last experiment were allowed to stand in contact with the supernatant for at least 24 hours before separation.

All scintillation samples were placed in the refrigerator chamber at least 12 hours before counting. Counting time was adjusted to provide at least 10,000 counts per sample. Data were taken manually.

A thermogram of a sample of precipitate formed by each of the two procedures was made. The initial sample weights from the $NH_3$ and KOH precipitations were 15.75 mg and 24.14 mg, respectively. The heating rate was $5^\circ$C/minute.

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## Results and Discussion.

The results of the experiments with KOH are summarized in Table 1. All values reported are averages of three or more precipitations. The precipitates in experiments 1 and 2 contained considerable amounts of $KNO_3$, which accounts for the high weights. The precipitate in experiment 3 was washed thoroughly and dried in air. The mixture in experiment 4 was not separated until the supernatant was no longer supersaturated with $KNO_3$.

The supernatant activity is reported in dpm/$\lambda$ because it is difficult to determine the correct total volume of the supernatant, a quantity necessary in the calculation of total activity. Calculations were made assuming that: (1) all of the $KNO_3$ had precipitated, (2) reaction (1) is applicable, and (3) the volume could be calculated from the changes in densities whose values could be graphically determined. The results showed the total activity in the supernatant to be about 1-2% higher than the total added to the system originally. A small error in the calculated volume could easily account for the discrepancy.

If we assume that all of the Zn(II) is recovered in the precipitate, we can calculate how much activity should be present if the precipitate is $Zn(OH)_2$.

Assume the following densities determined graphically (7):

4.000 <u>VF</u> $Zn(NO_3)_2$ $\rho$ = 1.565 g/ml

10.00 <u>VF</u> KOH $\rho$ = 1.400 g/ml

Then, the weight of water in the system is:

12.50 ml $Zn(NO_3)_2$ contains 10.09 g $H_2O$

10.00 ml KOH contains 8.39 g $H_2O$

Total $H_2O$ = 18.48 g $H_2O$

Since there are 2 moles of H in every mole of $H_2O$ and 0.100 mole of KOH in that solution,

$$H = 2(18.48)/(18.02) + 0.100 = 2.152 \text{ moles H}$$

The total activity in the system is $8.470 \times 10^7$ dpm which can be expressed as $3.936 \times 10^7$ dpm/mole H. The least amount of hydrogen expected in 50 millimoles of $Zn(OH)_2$ is 100 millimoles. Therefore, the expected activity, $A_p$, is

$$A_p = 0.100 \text{ mole H} \times 3.936 \times 10^7 \text{ dpm/mole H} = 3.936 \times 10^6 \text{ dpm}$$

The maximum found was $1.066 \times 10^5$ dpm, about 2.7% of that expected, which suggests that the precipitate formed is ZnO rather than $Zn(OH)_2$.

The possibility that tritium in $Zn(OH)_2$ might exchange rapidly with water and thus be lost during the washing process was considered. Therefore, an experiment which might produce another form of the precipitate was desirable. Duval's thermogravimetric data showed considerable differences in the materials formed, depending on whether they were precipitated by KOH or by $NH_3$, a definite break in the thermogram of the latter suggesting loss of bonded water or hydroxide. The results of the experiment with $NH_3$ are summarized:

| | |
|---|---|
| Quantity of Zn(II) | 50.00 millimoles |
| Total activity | $8.470 \times 10^7$ dpm |
| Supernatant activity | $3.545 \times 10^3$ dpm/$\lambda$ |
| Precipitate weight | 2.838 g |
| Precipitate activity | $1.815 \times 10^6$ dpm |

There is much more activity in this precipitate than appeared in those from KOH precipitations, which suggests that a considerable portion of the precipitate is $Zn(OH)_2$. The weighed material corresponds to 57.1% of the total which should have been collected if one assumes that the

precipitate is $Zn(OH)_2$. On this basis, the activity found is 72% of that expected.

The thermograms for the two types of precipitate are shown in Figure 1. The rate of weight loss with temperature shown in Figure 1a is essentially constant while the curve in Figure 1b shows a distinct break beginning about $100^O$C. The span of the break is about 1.71 mg corresponding to about 60% $Zn(OH)_2$ in the precipitate.

Hüttig (8) reports that $Zn(OH)_2$ is unstable above $39^O$C. The temperature of the mixtures during precipitation rose to maxima of $52-54^O$C. While these temperatures may prevent complete formation of $Zn(OH)_2$, they cannot be the cause of the observed differences in the behaviors of the solids. However, experiments presently are being performed with temperatures being held around $25^O$C.

## Conclusions.

Thermogravimetric and tracer experiments indicate that ZnO is the predominant product when KOH is added to an equivalent amount of $Zn(NO_3)_2$, while $Zn(OH)_2$ is the predominant species when precipitation is accomplished with $NH_3$. Exchange between $Zn(OH)_2$ and water is sufficiently slow that it cannot be completed during a normal washing procedure at room temperature. As yet, there is little to indicate that temperature affects the character of the precipitate.

The data show that the character of the precipitate is strongly dependent on the conditions of formation. Therefore, the experiments reported here can throw no light on the electrochemical reaction even though one might be induced to favor reaction (1).

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## Proposed Work.

Precipitations of ZnO or $Zn(OH)_2$ will be continued at lower temperatures. $Zn(OH)_2$ samples will be stirred in water to try to determine the rate of exchange of hydroxide between the solid and water. ZnO will be mixed with tritiated water to try to determine the rate of hydration of the oxide, if any. Precipitations will be made in concentrated base to determine what species is formed under these conditions. Exchange experiments will be performed in concentrated base.

## B.  THERMAL DECOMPOSITION OF AgO

### Introduction.

Argentic oxide decomposes at high temperatures in a manner which may be described by the equations:

$$2 \, AgO \; = \; Ag_2O \; + \; 1/2 \, O_2 \qquad (3)$$

$$Ag_2O \; = \; 2 \, Ag \; + \; 1/2 \, O_2 \qquad (4)$$
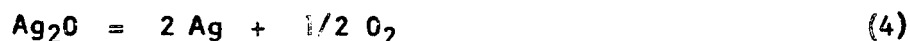
Reaction (3) apparently begins to be significant at about $120^{\circ}C$ and may be quite rapid at $140\text{-}150^{\circ}C$, depending on conditions.

Crude experiments done at JPL showed that both reactions (3) and (4) occur to some extent in the vicinity of $135^{\circ}C$. The rate of reaction (3) seemed dependent on very slight exposure to light or very small variations in oxygen pressure or both. Allen (9) reports several discontinuities in thermograms made in vacuum below $200^{\circ}C$. Evidently, a carefully controlled investigation is required.

The early work at JPL was done by heating samples in a crucible in a drying oven. It was necessary to cool the samples in a desiccator before weighing; thus drastic, periodic temperature changes occurred throughout each experiment and the samples were disturbed during the transfers. Use of a thermobalance will permit control of exposure to light, control of the atmosphere over the solid, and continuous recording of weight changes.

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Experimental.

AgO was prepared by a modification of the method described by Bailar
(10). The washed precipitate was dried over $P_2O_5$ at about 35 torr. The
weighed material was analyzed by heating it to 600°C for 20 minutes,
cooling, and weighing. The precipitate was considered dry if the observed
loss in weight agreed with that calculated.

AgO was prepared electrolytically by a modification of the method
described by Jolly (11). Electrodes were platinum screen instead of
smooth platinum.

Samples of AgO prepared by both methods were investigated on the
thermobalance without temperature control; the temperature probably in-
creased at 40-50°C/minute. One sample of chemically prepared AgO was
investigated at a programmed temperature increase of 5°C/minute.

Results and Discussion.

Argentic oxide samples prepared by the different methods were differ-
ent in appearance; the chemically prepared material was dark gray in
color and consisted of very small crystals (less than $5\mu$ in diameter)
while the electrolytically prepared material was almost black and consist-
ed of crystals as large as $50\mu$ in diameter. However, the electrolytically
prepared AgO slowly turned dark gray on standing for about one month in a
dark container.

Figure 2 shows thermograms for the two different materials. The
curves have been normalized to permit better comparison. The abscissa is
a time scale since the heating rate is unknown, though fairly reproducible.

Both curves show breaks at about 3.5 and 12 minutes. This was ex-
pected in spite of particle-size differences. The portion of the curve
for the electrolytically prepared AgO between the breaks is fairly flat

and corresponds well with the expected 50% loss of available oxygen while that region on the curve for chemically prepared material is much steeper and falls below the point corresponding to a 50% loss of oxygen. In no case was the total weight change such as to suggest significant impurities.

The small break at the beginning of curve (1) is probably caused by a small amount of moisture.

The chemically prepared powder tended to cake so that, during sieving operations, small, hard balls formed. Crystals within the balls were about the same size as those found in the powder. Balling did not affect the rough thermogram significantly; this suggests that particle size, itself, may not be too important.

The trace for the one programmed thermogram is not shown because an equipment malfunction destroyed part of it. The sample lost weight rapidly around $140^{\circ}C$ and decomposition was complete at $440^{\circ}C$. These temperatures are somewhat lower than expected, especially since earlier experiments did not indicate such a rapid decomposition of AgO at such a low temperature. However, it must be emphasized that these experiments were done under conditions considerably different from those in the preliminary study.

## Conclusions.

The method of preparation of AgO affects the physical properties of the material. No proof of chemical differences is available yet.

Rough thermograms suggest that the decomposition of $Ag_2O$ begins at lower temperature if the particle size is small. However, the curves also suggest that decomposition of AgO is retarded under those conditions; this seems improbable.

Rapid decomposition of AgO seemingly occurs near $140^{\circ}C$. This is a serious consideration if charged Ag-Zn batteries are to be heat sterilized. Alteration of experimental conditions may affect this value.
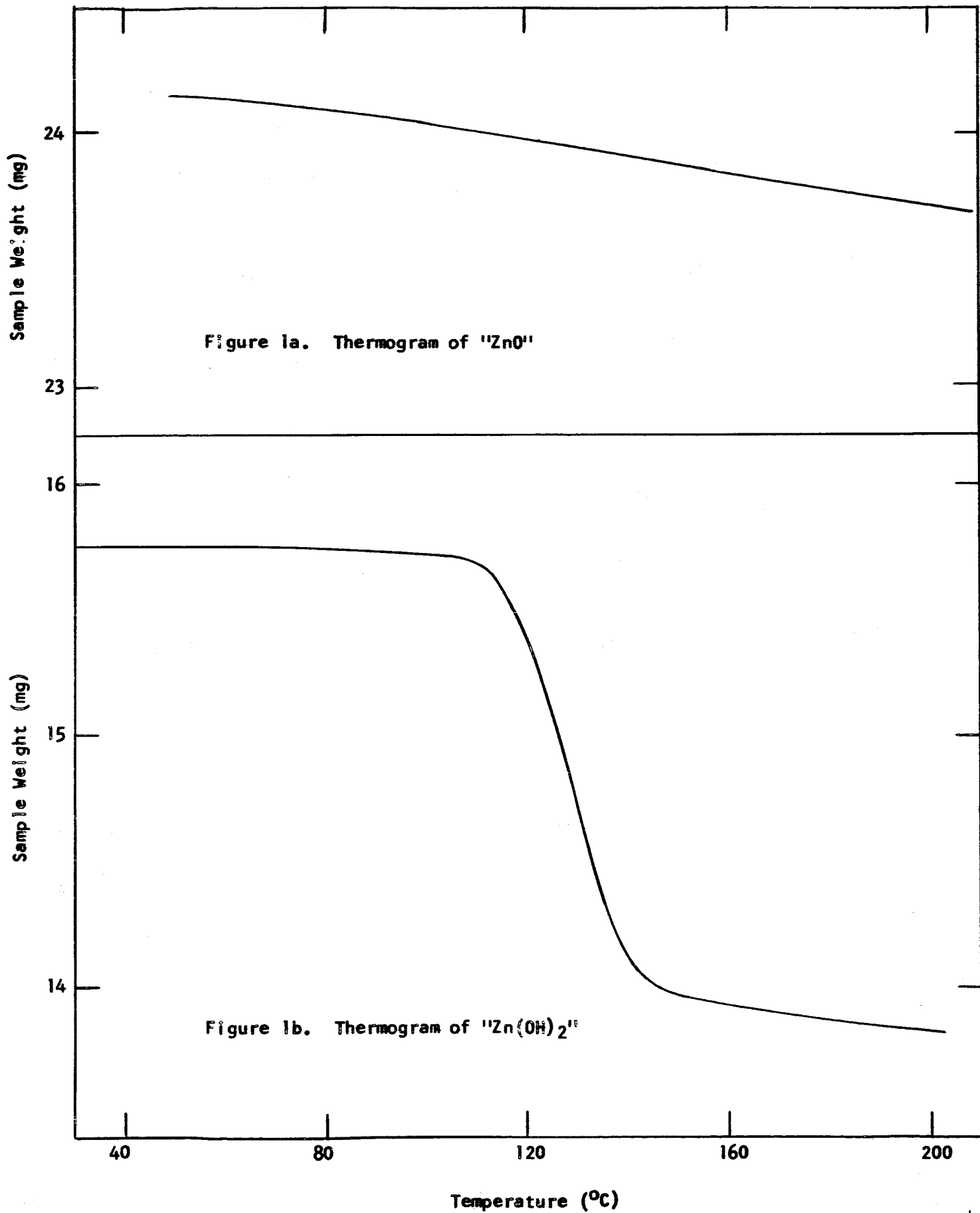
## Proposed Work.

Further programmed thermograms will be made with both types of AgO. Constant-temperature thermograms will be made in room light and with light excluded. Constant temperatures will be adjusted at appropriate values between $100^{\circ}C$ and $200^{\circ}C$, the values depending somewhat on the results of the programmed thermograms. Particle-size distribution will be determined microscopically.

Table 1

Precipitation of ZnO with KOH

| Experiment Number | Stock Concentration (VF) $Zn(NO_3)_2$ | KOH | Volume used (ml) $Zn(NO_3)_2$ | KOH | Supernatant Activity $(dpm/\lambda \times 10^{-3})$ | Precipitate Activity $(dpm \times 10^{-4})$ | Precipitate Weight (g) |
|---|---|---|---|---|---|---|---|
| 1 | 2.000 | 10.00 | 25.00 | 10.00 | 1.181 | 10.66 | 5.72 |
| 2 | 4.000 | 10.00 | 12.50 | 10.00 | 3.592 | 4.652 | 5.26 |
| 3 | 4.000 | 10.00 | 12.50 | 10.00 | 3.982 | 8.25 | 4.34 |
| 4 | 4.000 | 10.00 | 12.50 | 10.00 | 3.899 | 8.65 | 4.35 |

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Figure 1a.   Thermogram of "ZnO"



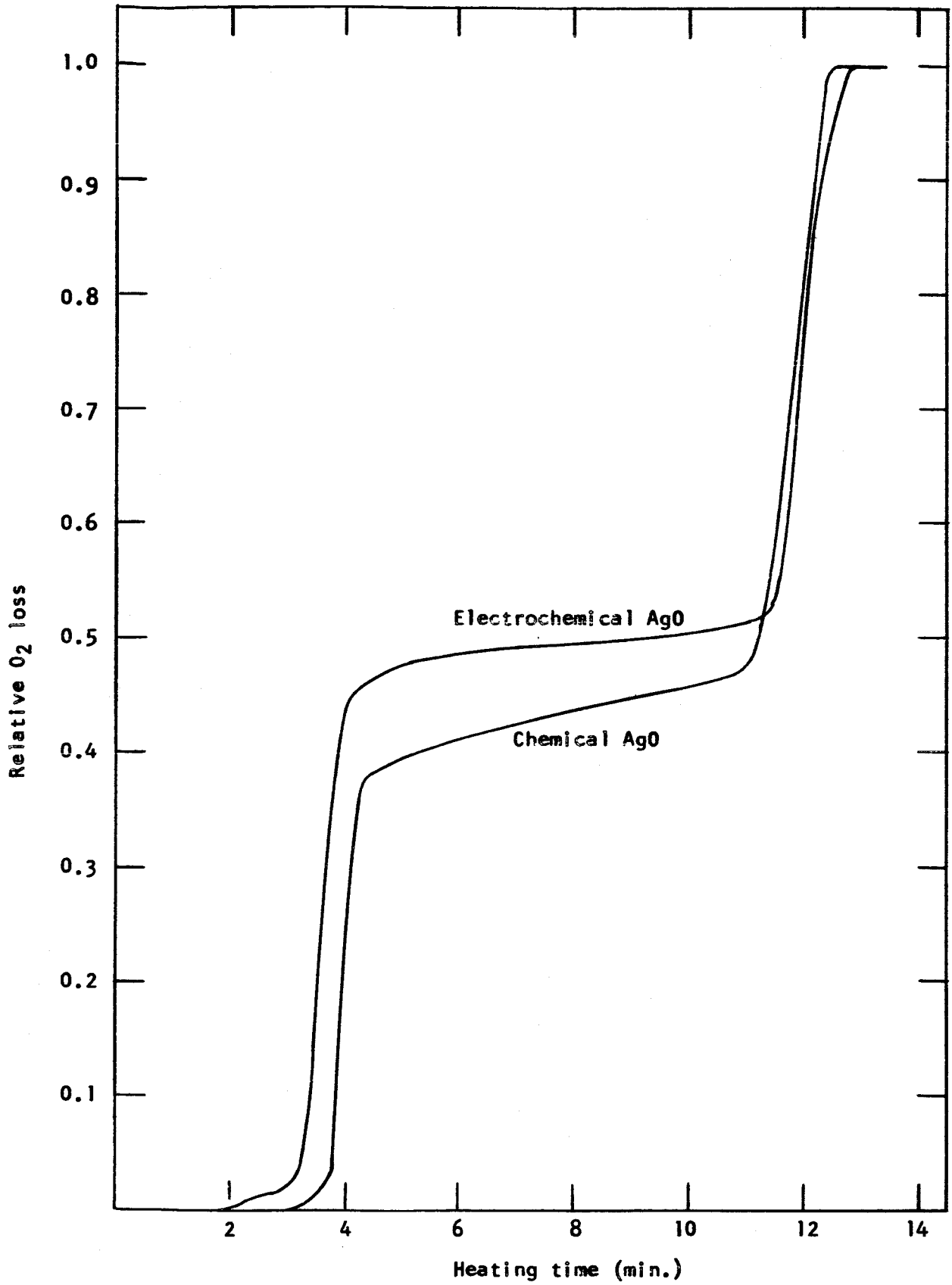Figure 1b.   Thermogram of "Zn(OH)$_2$"

Temperature ($^O$C)

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Figure 2.  Thermograms of AgO

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