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SEALED PRIMARY
LITHIUM - INORGANIC ELECTROLYTE CELL

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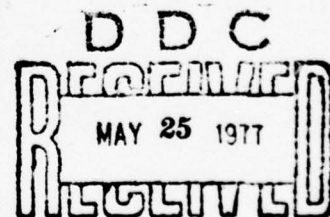
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Li/SOCl ₂ hermetic D cell developed by P.R. Mallory & Co., Inc. met or exceeded all the initial objectives of an E.D of 150 WHr/lbat the thirty-hour rate and a peak power density of 50 watts/lb and the storage and operating temperatures of -40 to 160°F. However, the cells showed severe voltage-delays at -30°C after storage at 72°C, particularly at high rates. We investigated this problem in detail and came up with several methods of → was investigated - deg			

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cont → alleviating this problem. The lowering of the salt concentration in the electrolyte from 1.8(M) to 0.5(M) $\text{LiAlCl}_4\text{-SOCl}_2$ appeared to be an effective way to alleviate the voltage-delay problem. This also resulted in an increase in the intrinsic energy density of the cell.

The cells revealed a serious problem on abuse; they exploded on shorting. We incorporated a low pressure vent in the cells to eliminate the explosions, but a more comprehensive solution is needed to gain an acceptance of the cells for military applications. To this end, we have begun differential thermal analysis of all the known and presumed materials present in fresh and discharged cells. The object is to determine the potentially energetic chemical combinations which could initiate and propagate an explosion as the first step in the development of chemical means to control the explosions. So far, we have identified several potential explosion-causing chemical combinations viz, Li+S , Li+SOCl_2 , Li+glass . We also showed that the temperature at which the ternary composition Li+S+SOCl_2 explodes is higher than that of the Li+S combination. We have also attempted to evaluate the efficacy of a possible quenching agent, such as S_2Cl_2 , on the explosion of the Li+S+SOCl_2 ternary combination. S_2Cl_2 did not inhibit the exothermic reaction of this mixture. We plan to continue the measurements in an effort to increase our understanding of the explosion phenomenon and to develop possible quenching agents.

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I. Introduction

The lithium-thionyl chloride, inorganic electrolyte system comprising a Li anode, a carbon cathode and a $\text{LiAlCl}_4\text{-SOCl}_2$ electrolyte is one of the highest energy density systems known to date (1-4). We realized energy densities in excess of 150 WHr/lb at high rates of discharge. The hermetic D cell (3-7) met and exceeded all the initial program objectives. However, we found that the system suffered from two inherent deficiencies:

(a) Voltage delay, particularly on test at low temperature after storage at high temperatures.

(b) Explosion hazard, particularly on shorting and forced as well as resistive load overdischarge.

We studied the voltage-delay problem in sufficient detail to define its underlying cause (2, 4-12). We established that the voltage-delay of the Li/SOCl_2 cells was due to the Li anode film formed due to the reaction of Li with the inorganic electrolyte. Therefore, we focussed our attention on the study of the Li anode film itself. We mounted Li specimens on stainless steel SEM specimen holders and stored them in the inorganic electrolytes containing various additives and various salt concentrations at 72° , 55° and 25°C for various periods of time. Then we examined the Li anode film using SEM in order to determine the morphology and the thickness of the film. We established that both the morphology and the thickness of the Li anode film affects the voltage delay. We also established that the film is primarily composed of LiCl crystals. The main objective of this part of the investigation was to establish the extent to which electrolyte variables such as salt concentrations and additives could affect either the morphology or the thickness of the Li anode film. The experimental details and the initial results are reported in the 8th, 9th and 10th quarterly reports (10-12). It was possible to reduce the film growth substantially by reducing the LiAlCl_4 concentration in the electrolyte. We presented the SEM photographs of the Li anode film formed at the various temperatures in the various inorganic electrolytes in the previous reports (10-12) in order to demonstrate the morphology of the film. We showed that the addition of SO_2 definitely altered the morphology of the film. We found that the LiCl film displayed a high level of epitaxy in the presence of SO_2 .

We completed the collection of the SEM data and developed a qualitative model to describe the Li film growth phenomenon in the systems studied. This was described in the eleventh quarterly report (13). We also began to evaluate the effect of the electrolyte variables such as LiAlCl_4 concentration, and such as SO_2 electrolyte additives on the voltage-delay characteristics of the Li/SOCl_2 D cells. We found that the LiAlCl_4 concentration affects both the voltage-delay and the intrinsic energy density of the Li/SOCl_2 D cells. The 1.0 and 0.5 (M) LiAlCl_4 - SOCl_2 was found to be the best from both the voltage-delay and the energy density standpoints. We found that 10% (6 wt %) S_2Cl_2 did not affect the voltage-delay significantly. The D cells with SO_2 (11 wt %) in the electrolyte, vented prematurely on storage at 72°C . Three cells which survived the first month of storage at 72°C , did not show any voltage-delay at -30°C on 0.25, 1.0 and 3.0A test. We repeated these tests. Also, we continued the voltage-delay measurements on longer durations of storage. The latest results are reported here.

We investigated the explosion hazard problem in a phenomenological manner (4-7). First we established the conditions under which the hermetic Li/SOCl_2 D cells explode. Then we attempted to develop ways and means to prevent the explosion. We found that the lowering of the rate capability may not prevent cell explosions as long as the cell could get hot enough by other extraneous circumstances such as high temperature storage, heavy insulation of the cell wall and so on. We found that low pressure venting is an effective way of preventing cell explosions on external shorts. However, this approach was ineffective in preventing explosions from forced and/or resistive overdischarge. The fact that some of the cells exploded on resistive load overdischarge was particularly unsettling since it is neither predictable nor easily comprehensible based on the present state of knowledge on the system. A completely discharged battery, while sitting on the shelf at 25°C , may explode quite unexpectedly. This is of concern since it is impossible to prevent resistive load overdischarge and/or storage of partially and/or completely discharged batteries in normal use. We believe that this problem needs to be solved before the field use of the system can be recommended, particularly in regard to D size cells.

In order to address this problem we need to know the chemistry and the thermochemistry of the system in a discharged and partially discharged state. We procured a Differential Thermal Analyzer (DTA)

for carrying out DTA analyses of the chemical compounds and their mixtures that may be present in a partially discharged Li/SOCl₂ cell. The purpose of the DTA approach was to identify the exothermic reactants that might either initiate or propagate any explosive reactions in the system. Once these are identified, one may then attempt either to eliminate the reactants, if possible, or render them inactive by means of suitable inhibitors. We reported our preliminary results in the 10th quarterly report (12), and we have now resumed work in this area. We re-designed the DTA sample ampoules in order to eliminate the interference from the reaction of various chemicals with the thermocouple wires, and we continued the DTA experiments using the improved setup. The latest results are reported here.

II. Differential Thermal Analysis of Li/SOCl₂ Cell Constituents

Our earlier results (12) on the DTA analysis of the cell reaction products indicated that the technique was useful in distinguishing between a pressure burst and a thermal runaway. The former was endothermic, whereas the latter was exothermic. The technique was also found to be useful in determining the temperatures at which the above processes were likely to occur. However, the interpretation of some of the results was complicated because of the reactivity of the thermocouple wire (chromel-alumel) with the chemical to be analyzed. The sample container used, as shown in Figure 1, was a sealed glass ampoule with Pt wire feed-through, the thermocouple wires were welded to the Pt wires inside the ampoule. We chose a sealed sample container as opposed to an open glass tube, as is customary for DTA analysis, because of the reactivity of relatively volatile SOCl₂. The physical contact of the thermocouple wires with the chemicals increased the sensitivity of the measurements, but it also allowed the thermocouple wires to be attacked by reactive substances, particularly, S. We found that the DTA thermograms of S resulted in exothermic peaks corresponding to its reaction with the thermocouple wires which were found to be disintegrated at the end of the run. In order to avoid this problem, we re-designed the sample container so that the thermocouple wires are physically isolated from the chemicals. The details of the design of the sample container and the results of the DTA analysis of the various cell reaction products using the container are discussed below.

We also found that the furnace, provided for the DTA analysis of corrosive chemicals, was too fragile to withstand the minor explosions resulting from the experiments. We designed and fabricated a new furnace using an aluminum body instead of pyrex. The details are described below.

A. Experimental

A cross sectional view of the new sample container is shown in Figure 2. It has a thermocouple well at one end of the container. The thickness of the glass of the thermocouple well was kept at a minimum in order to maintain a reasonable sensitivity. The sample container was filled with the desired chemicals from the end opposite to the thermocouple well and was frozen using liquid nitrogen and then evacuated and sealed with a flame. The absence of any feed-through ensured the hermeticity of the containers. Leaky containers result in spurious endotherms.

The earlier furnace was modified by replacing the pyrex body with a thick-walled aluminum cylinder (Figure 3). Also, the furnace was used in an inverted position in order to ensure that the chemicals in the sample container remain in contact with the thermocouple well.

The sample temperature was increased from room temperature (25°C) to a maximum of 300°C, at an average rate of 10°C/minute. The linearity of the temperature-time profile was found to be adequate for our purpose. Both the sample temperature and the differential temperature were recorded in a dual channel strip chart recorder. The reproducibility of the measurements was checked by replication, and it was found to be satisfactory.

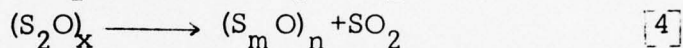
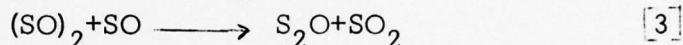
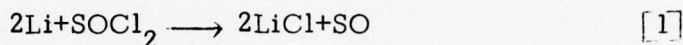
B. Results and Discussion

The chemical species known to be present in the partially discharged Li/SOCl₂ cells are:

1. Li
2. SOCl₂
3. LiAlCl₄
4. Sulfur
5. SO₂
6. LiCl
7. Glass

8. Carbon
9. Teflon
10. Nickel
11. Kovar
12. Trace Impurities (H₂O, etc.)

In addition, transient species may be present that are formed from the primary cell reaction product, SO, (14). In addition to SO they include (SO)₂, S₂O and polymeric (S_mO)_n which may be formed as a result of the chemical reactions [1-4].



Any and all of the above species, along with the other chemical species that may have been formed by chemical interactions between the above listed species, may be responsible for the initiation and the propagation of the thermal runaway encountered in the thionyl cells. For our initial studies, we have restricted ourselves to the stable chemical species. Our first objective is to identify the potential species or combination of species that may cause either a pressure burst and/or a thermal runaway on external heating.

1. Thermograms of Li+S

We carried out DTA analyses of 10 samples of Li+S having various proportions of Li and S. The purpose was to check the reproducibility as well as to ascertain any effect of the sample weights on the nature of DTA thermograms. The results of the 10 DTA runs are summarized in Table 1. Three representative thermograms are shown in Figures 4, 5 and 6. The differential temperature is expressed in millivolts (chromel-alumel thermocouple). When the exothermal peaks went beyond the scale, the sensitivity was reduced by factors of 5, 10, 20 and 50X as shown on the peaks. The reproducibility of the thermograms was found to be excellent. The relative weights of Li and S had no effect on the thermograms

within the limits examined. The thermogram showed two endothermic peaks at approximately 112°C and 122°C, corresponding most likely to the melting points of two types of sulfur, viz, rhombic (113°C) and monoclinic (120°C). There was a very large exothermic peak, occurring in the temperature range of 150° to 184°C, corresponding to a combustion. The heat generated during this exothermal peak was such that the temperature of the sample holder increased by 10°C. Most of the Li was consumed during this combustion, and there was no endothermic peak corresponding to Li melting at higher temperatures.

The data indicated that the exothermic Li+S reaction occurs at a temperature higher than the melting point of S and lower than the melting point of Li when they are present in a dry state. The Li was used as a foil and the S was in a powder form.

2. Thermogram of Li+Ni+S

This DTA run was taken in order to ascertain whether the presence of Ni in the form of foil caused any change to the thermograms of Li+S. Ni is present in the thionyl D cell in the can, the tabs, and in the cathode grid. The thermogram is shown in Figure 7. There is only a very minor difference; the two endothermic peaks corresponding to the melting of sulfur are separated, one occurring at 92°C and the other at 134°C. The large exothermic peak corresponding to Li+S combustion occurred at 182°C as before. There was no change in the intensity of the exothermal combustion of Li and S in the presence of the Ni foil.

3. Thermogram of S+Cathode Mix

In a thionyl cell, the cell reaction product S is expected to precipitate both on the Li anode as well as on the carbon cathode, since S is soluble in SOCl_2 . This DTA run, Figure 8, was taken to determine whether there is any peculiar interaction. The two endothermic peaks corresponding to the transitions of two types of S occurred at 118° and 134°C. There was no exothermic peaks. There was one small endothermic peak at 184°C.

4. Thermogram of S + Cathode Mix + SOCl₂

The effect of SOCl₂ on the thermogram of S+ cathode mix was investigated in these DTA experiments. The experiments were done in duplicate. The thermograms are shown in Figures 9 and 10. The typical two endothermic peaks corresponding to the transitions of two types of sulfur were replaced by one endothermic peak occurring at a lower temperature, 101-102°C. This may indicate the endothermic dissolution of S in SOCl₂. At higher temperature, 197° and 219°C, the sample container burst with a sharp endotherm corresponding to a pressure burst as opposed to an exothermic combustion or thermal runaway as in the case of Li+S. The pressure burst was due to the high vapor pressure of SOCl₂ and SO₂ that might have formed from the decomposition of SOCl₂ at elevated temperatures.

These DTA thermograms, as before (12), appear to be useful in distinguishing between a pressure burst and a thermal runaway.

5. Thermogram of S+SOCl₂

The thermogram is shown in Figure 11. There was one very small endothermic peak at 72° followed by a sharp endothermic peak at 107°C, most likely due to the dissolution of S. The sample container burst as before at 236°C with a large endotherm indicating a pressure burst. The comparison of this thermogram with the previous ones (Figures 9 & 10) indicates that the effect of cathode mix on the thermogram of S+SOCl₂ is insignificant in the temperature range studied.

6. Thermograms of Li+ glass Separator

In a thionyl D cell the Li anode remains in physical contact with the glass separator at all times. We carried out DTA runs using Li and glass separator in duplicate to examine whether this could lead to a hazardous condition. Earlier results (12) showed that Li reacted exothermically with the glass sample container. The thermograms as shown in Figures 12 and 13 indicate a sharp endothermic peak at 187°C corresponding to the melting of Li, followed by a very large

exothermic peak or peaks at 208-214°C corresponding to a reaction of Li and glass. The sample containers were found to be broken after the DTA runs indicating the reaction of Li with not only the glass separator, but also with the sample container. It is important to note that this reaction occurred after the melting of Li, a point that was not clear from our previous experiments (12).

7. Thermograms of Li+SOCl₂

This combination was also run in duplicate; the thermograms are shown in Figures 14 and 15. The first run (Figure 14) showed a small endothermic peak at 187° corresponding to the melting of Li followed immediately by a large exothermic peak at 192°C and an explosion. The latter can be termed as a thermal runaway. This was slightly different from the exothermic combustion observed earlier with the Li+S and the Li+glass mixtures (Figures 4-6, 12, 13) in that there was a loud report and a shattering of the glass container. This was also distinctly different from the pressure bursts observed in the cases of SOCl₂ with S, and cathode mix (Figures 9-11) in that the process was exothermic instead of endothermic.

In the second run (Figure 15) the endothermic peak at 189°C corresponding to Li melting is somewhat sharper. The explosion occurred a bit after the melting of Li at 227°C. It appears that in Li+SOCl₂ mixture, the thermal runaways followed the lithium melting process as was found to be the case with Li+glass mixtures earlier.

8. Thermogram of Li+S+SOCl₂

We examined the Li+S, Li+SOCl₂ and the S+SOCl₂ combinations separately. It is of interest to see whether there is any peculiarity when all three are present together. The thermogram of the ternary combination, Li+S+SOCl₂ is shown in Figure 16. Note that the endothermic transitions related to S are indistinguishable because of the endothermal shifting of the baseline resulted from a difference in the thermal conductivity between the reference and the sample chemicals. The sharp endothermic peak at 194°C corresponding to the melting of Li and the exothermic explosion at 204°C is similar to that observed in the thermogram of Li+SOCl₂ (Figure 15). In general, the

thermogram is similar to the $\text{Li}+\text{SOCl}_2$ thermograms and does not contain any features of the $\text{Li}+\text{S}$ and the $\text{S}+\text{SOCl}_2$ thermograms. In the $\text{Li}+\text{S}$ system, the combustion occurred at a temperature lower than the melting point of Li , whereas, in the $\text{Li}+\text{S}+\text{SOCl}_2$ system, the exothermic explosion occurred at a temperature higher than the melting point of Li .

9. Thermograms of $\text{Li}+\text{S}+\text{SOCl}_2+\text{S}_2\text{Cl}_2$

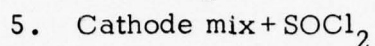
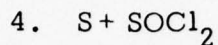
It would appear that the DTA thermograms may be used to evaluate the efficacy of quenching agents added to the cell electrolyte to prevent thermal runaways. S_2Cl_2 [15] has been suggested as a possible quenching agent. We ran DTA thermograms of the $\text{Li}+\text{S}+\text{SOCl}_2+\text{S}_2\text{Cl}_2$, in duplicate, in order to test any quenching action of S_2Cl_2 . The thermograms are shown in Figures 17 and 18. The thermograms looked very similar to the thermogram of $\text{Li}+\text{S}+\text{SOCl}_2$ mixture. The endothermic peaks corresponding to S are absent as before. The endothermic peak at 186°C corresponding to Li melting, followed by an exothermal explosion, occurred as before. These preliminary results do not show any marked quenching effect of S_2Cl_2 on the thermal runaway. We plan to repeat the above experiments with varying quantities of the components as well as at various heating rates in order to establish the efficacy of any potential quenching agents.

C. Conclusions

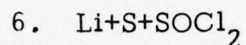
We have examined nine combinations so far, of the many possible combinations of the chemicals present in a discharged Li/SOCl_2 cell, using the improved DTA sample container. The thermograms were found to be better resolved than observed before (12); the endothermic and the exothermic peaks were quite sharp and interpretable based on known endothermic and exothermic transitions of various materials tested. The binary chemical combinations which were found to cause exothermal combustion and/or thermal runaway are:

1. $\text{Li} + \text{S}$
2. $\text{Li} + \text{glass}$
3. $\text{Li} + \text{SOCl}_2$

The exothermal combustion occurs at a lower temperature in the combination (1), than in the combinations (2) and (3). The binary chemical combinations which were found to result in a pressure burst are:



In the case of a ternary combination,



the explosion occurs at a higher temperature than in the binary combination (1).

We also examined the efficacy of S_2Cl_2 as a quenching agent for the explosion in the ternary combination (6), using the DTA method. No quenching effect was observed.

III. Voltage-Delay Measurements of Li/SOCl₂ Hermetic D Cells with Various Electrolytes

We carried out a detailed SEM investigation (9-13) of the Li anode film; the cause of the voltage-delay problem. We found that the lowering of the LiAlCl₄ concentration in SOCl₂ led to a significant decrease in the rate of the LiCl film growth on Li. Also, the addition of SO₂ (saturated at 25°C) in 1 (M) LiAlCl₄-SOCl₂ resulted in the change in the LiCl film morphology. Whereas the addition of S₂Cl₂ (6 wt %) in 1 (M) LiAlCl₄-SOCl₂ did not have any significant effect on the film growth. We constructed (13) hermetic D cells with the above electrolyte variables in order to determine whether the voltage-delays experienced by the cells at -30°C after 72°C storage, are affected similarly, as expected, based on our hypothesis (13) that the voltage-delay is dependent on the nature and the thickness of the Li film. We stored the cells at 72°C and tested them periodically at -30°C at constant currents of 3.0, 1.0 and 0.25A to determine the time taken (voltage-delay) for the cell voltage to reach 2.0 volt after any initial drop below that level. After this test, we put the cells back at 72°C storage and tested again after a certain period. The results of the above type of voltage-delay measurements after the one and two month storage were reported in the 11th quarterly report (13). We continued the voltage-delay measurements. The latest results are reported here.

We found earlier (13) that the D cells with SO₂ additive in the electrolyte vented prematurely due to excessive pressure. We built another group of hermetic D cells with SO₂ (11 wt %) additive in 1 (M) LiAlCl₄-SOCl₂ electrolyte. Unfortunately, these cells showed extensive leakage after 1 month of storage at 72°C. The data obtained from this group of cells are discussed below. The details of the construction of the hermetic D cells are described in the second (4) and the 11th quarterly reports (13).

A. Results and Discussion:

The voltage-delay measurements of Li/SOCl₂ hermetic D cells having 1.8 and 1.0 (M) LiAlCl₄-SOCl₂ electrolytes

were made after a storage of 3 months at 72°C. The results are shown in Table 2. The cells with 0.5 (M) electrolyte were tested after 4 months at 72°C and the cells with 0.25 (M) electrolyte were tested after 3 and 4 months of storage at 72°C. The cells with 6 wt % S_2Cl_2 were tested after 3 months at 72°C; these results are also shown in Table 2. The results indicate a gradual alleviation of the voltage-delays with a decrease in the $LiAlCl_4$ concentration from 1.8 (M) to 0.5 (M). At 0.25 (M), the voltage-delays are somewhat longer. According to our model (13) of the voltage-recovery after the initial depression, the anode dissolution of Li occurs through the pores of the $LiCl$ film. A simple explanation for the observed behavior based on this model is as follows: The thicker film at high salt concentrations (1.8M) results in longer pores and, hence, longer voltage-delays. The thinner film at lower salt concentrations has shorter pores, and, therefore, shorter voltage-delays. However, at even lower salt concentrations, viz, 0.25 (M), the conductivity of the electrolyte is reduced substantially, thus impeding the mass transport necessary for a rapid voltage-recovery. Thus, a minimum in the hypothetical voltage-delay vs salt concentration curve should occur between the 0.25 M and the 1.8 M points on the curve, and this minima is probably near the 0.5 M point.

The voltage-delays of the cells with S_2Cl_2 in the 1(M) $LiAlCl_4$ - $SOCl_2$ electrolyte after 3 months at 72°C, appear to be similar to that of the cells without S_2Cl_2 .

The cells with SO_2 (11 wt %) saturated 1 (M) $LiAlCl_4$ - $SOCl_2$ electrolyte leaked at the end of one month. The weight loss of these cells, as well as the voltage-delays at -30°C test, are shown in Table 3. Note, that the cells showed reasonably good voltage-delay characteristics in spite of the electrolyte loss. Two cells were discharged at 25°C at 1.0 and 0.25A. The capacity recovered was 10.8 and 13.4A.Hr respectively, indicating no significant capacity loss as a result of the storage.

B. Conclusions

The voltage-delays of the hermetic D cells with 0.5(M) $\text{LiAlCl}_4\text{-SOCl}_2$ electrolyte was found to be improved over the cells with the higher and the lower salt concentrations. The control of the salt concentration thus appears to be a viable approach to achieve lower voltage-delays. The effect of SO_2 on the voltage-delays still remained uncertain because of the premature cell leakage. S_2Cl_2 did not have any beneficial effect on the voltage-delay.

IV. Future Work

We plan to continue the DTA measurements with the various chemicals known and presumed to be present in fresh and discharged Li/SOCl_2 cells in order to increase an understanding of the thermal runaway of the cells. We also plan to evaluate the effects of possible quenching agents using the DTA technique. In addition, we plan to continue the voltage-delay measurements of the hermetic D cells with various electrolytes that are stored at 72°C .

V. References

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Table 1.
Summary of DTA Results of Li + S Samples

<u>Sample No.</u>	<u>Wt. of Li (gm)</u>	<u>Wt. of S (gm)</u>	<u>Peak Type</u>	<u>Temp °C</u>	<u>Remarks</u>
41	0.015	0.010	Endo	113°	Excess Li left Tube cracked
			Endo	128°	
			Exo	174 (5X)	
42	0.014	0.015	Endo	113°	Li completely consumed
			Endo	126°	
			Exo	168° (50X)	
43	0.014	0.021	Endo	112°	Tube broke
			Endo	122°	
			Exo	184° (20X)	
44	0.015	0.030	Endo	126°	Excess S left
			Exo	172° (50X)	
45	0.014	0.038	Endo	126°	Excess S left
			Endo	132°	
			Exo	164° (20X)	
46	0.006	0.020	Endo	117°	Excess S left
			Endo	127°	
			Exo	178° (50X)	
47	0.013	0.021	Endo	116°	Tube cracked
			Endo	126°	
			Exo	172° (20X)	
48	0.021	0.019	Endo	120°	Tube broke
			Endo	126°	
			Exo	159° (10X)	

Table 1.
Summary of DTA Results of Li + S Samples (cont.)

<u>Sample No.</u>	<u>Wt. of Li (gm)</u>	<u>Wt. of S (gm)</u>	<u>Peak Type</u>	<u>Temp °C</u>	<u>Remarks</u>
49	0.031	0.021	Endo	118°	Tube broke
			Endo	124°	
			Exo	153°(50X)	
50	0.024	0.020	Endo	118°	Tube broke
			Endo	129°	
			Exo	157° (50X)	

Table 2. Voltage-Delay Characteristics of Li/SOCl₂ D Cells with the Various Electrolytes; Storage at 72°C, Test at -30°C

Voltage-Delay(Seconds) on Storage of

<u>Electrolyte</u>	<u>Test Current</u>				<u>1 Month</u>			<u>2 Months</u>			<u>3 Months</u>		
	<u>(A)</u>												
1.8 (M) LiAlCl ₄ -SOCl ₂	3.0				23			∞			∞		
	3.0				33			∞			∞		
	3.0				31			∞			∞		
	1.0				No-delay			∞			∞		
	1.0				No-delay			∞			∞		
	1.0				No-delay			300			∞		
	0.25				No-delay			No-delay			No-delay		
	0.25				No-delay			No-delay			∞		
	0.25				No-delay			No-delay			No-delay		
1.0 (M) LiAlCl ₄ -SOCl ₂	3.0				162			∞			606		
	3.0				204			-			-		
	3.0				∞			-			-		
	1.0				No-delay			No-delay			220		
	1.0				No-delay			-			-		
	1.0				No-delay			No-delay			No-delay		
	1.0				27			No-delay			1380		
	0.25				No-delay			No-delay			No-delay		
	0.25				No-delay			No-delay			No-delay		
	0.25				No-delay			No-delay			No-delay		

Table 2. Voltage-Delay Characteristics of Li/SOCl_2 D Cells with the Various Electrolytes; Storage at 72°C , Test at -30°C (cont.)

Voltage-Delay (Seconds) on Storage of

Electrolyte	Test Current (A)				
	1 Month	2 Months	3 Months	4 Months	
0.5 (M) $\text{LiAlCl}_4\text{-SOCl}_2$	3.0	290	172	-	900
	3.0	177	665	-	∞
	1.0	No-delay	No-delay	-	No-delay
	1.0	No-delay	No-delay	-	No-delay
	0.25	No-delay	No-delay	-	No-delay
	0.25	No-delay	No-delay	-	No-delay
	3.0	124	No-delay	-	-
	3.0	352	464	300	300
	3.0	No test	300	570	∞
	1.0	110	290	186	∞
0.25 (M) $\text{LiAlCl}_4\text{-SOCl}_2$	1.0	525	261	No-delay	390
	1.0	120	1150	720	1500
	0.25	No-delay	55	No-delay	420
	0.25	No-delay	350	No-delay	300
	0.25	No-delay	No-delay	No-delay	No-delay
			(300 Ω)		
			(1 Ω)		

Table 2. Voltage-Delay Characteristics of Li/SOCl₂ D Cells with the Various Electrolytes; Storage at 72°C, Test at -30°C (cont.)

Electrolyte	Test Current (A)	<u>Voltage-Delay (Seconds) on Storage of</u>		
		<u>1 Month</u>	<u>2 Months</u>	<u>3 Months</u>
1 (M) LiAlCl ₄ -SOCl ₂ + 10% S ₂ Cl ₂	3.0	138	900	∞
	3.0	156	∞	-
	3.0	138	660	∞
	1.0	No-delay	∞	∞
	1.0	No-delay	330	∞
	1.0	No-delay	No-delay	300
	0.25	No-delay	No-delay	∞
	0.25	No-delay	No-delay	No-delay
	0.25	No-delay	No-delay	No-delay
	0.25	No-delay	No-delay	No-delay

Table 3. Voltage-Delay Characteristics of Li/SOCl₂ D Cells with (11 wt %) SO₂ in 1 (M) LiAlCl₄-SOCl₂ Electrolyte; 1 Month Storage at 72°C, Test at -30°C

Wt. Loss (gm)	Voltage-Delay at -30°C		Capacity at 25°C	
	Current (A)	Delay (Sec)	Current (A)	Capacity (A. Hr)
4.8	3.0	240	1	10.8
0	3.0	180		
10.3	3.0	∞		
11.4	3.0	∞		
2.2	1.0	No-delay		
13.6	1.0	∞		
12.1	1.0	∞		
2.8	0.25	No-delay	0.25	13.4
17.8	0.25	No-delay		
9.8	0.25	No-delay		

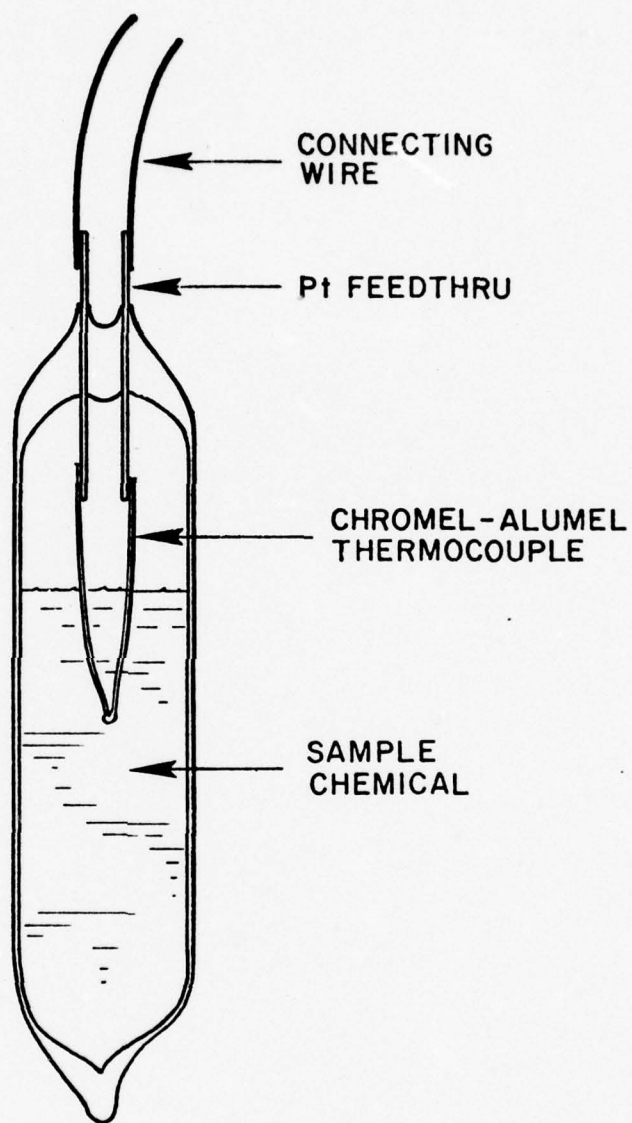


Fig. 1. Cross sectional view of the hermetic sample container

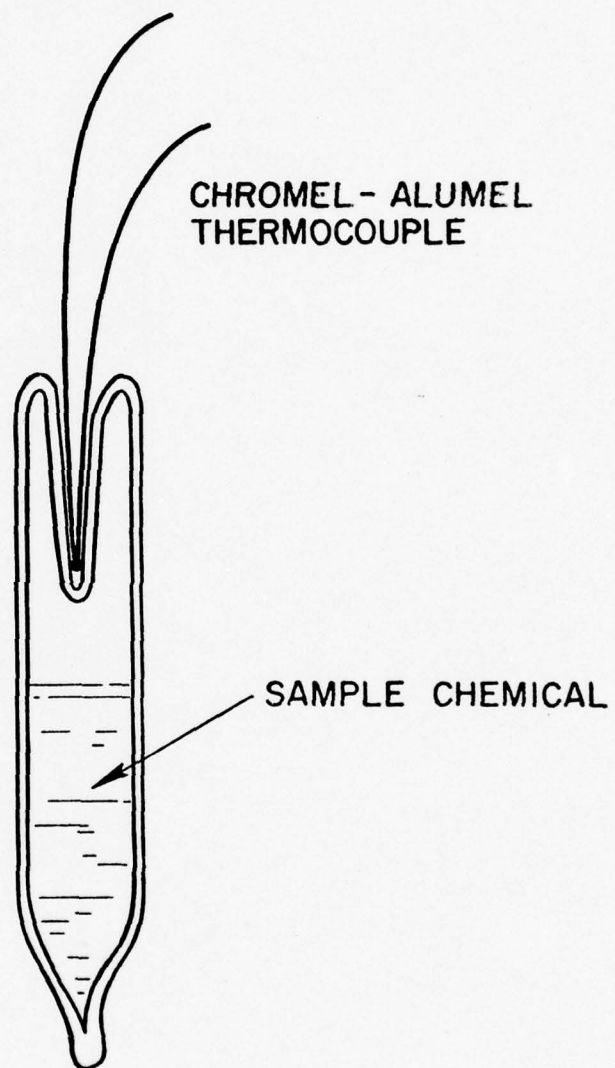


Fig. 2. New sample container with a thermocouple well

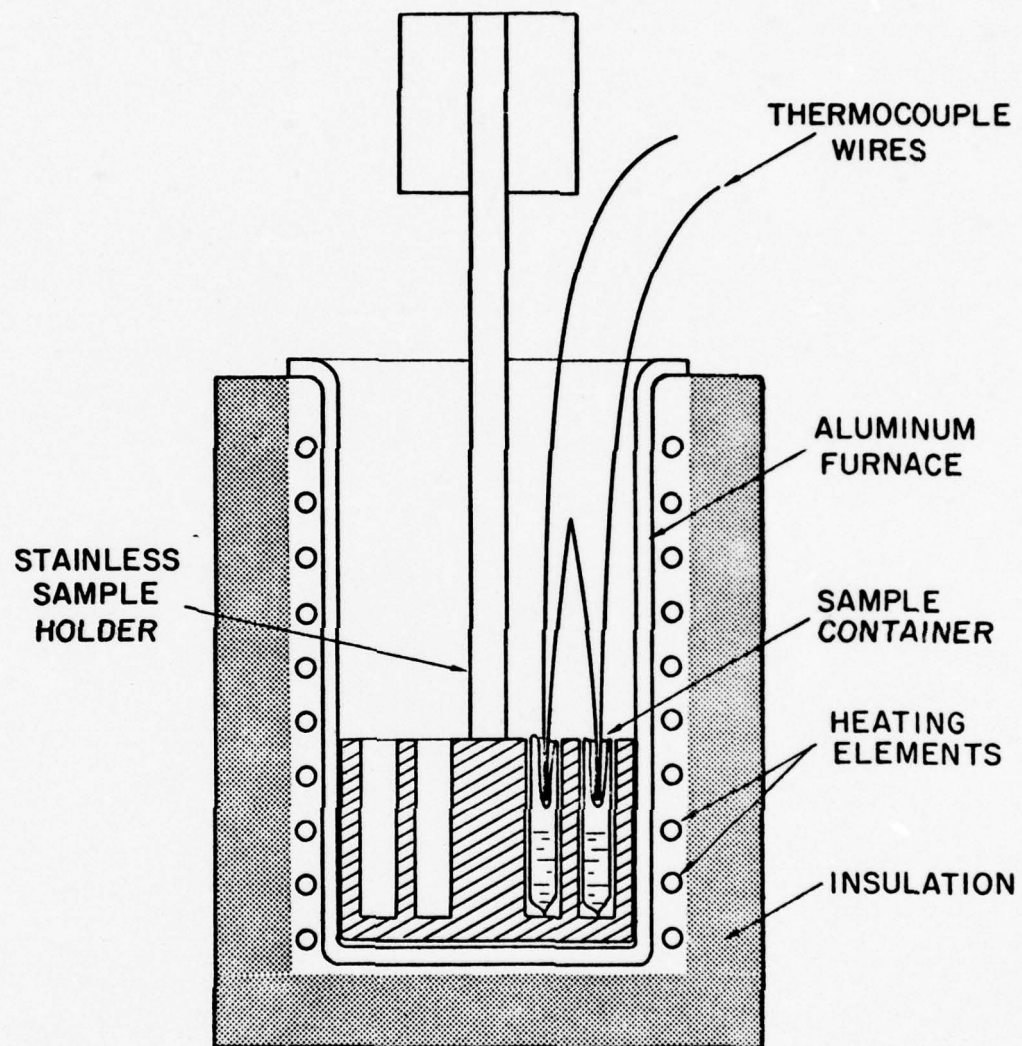


Fig. 3. Cross sectional view of the DTA furnace with the sample holder

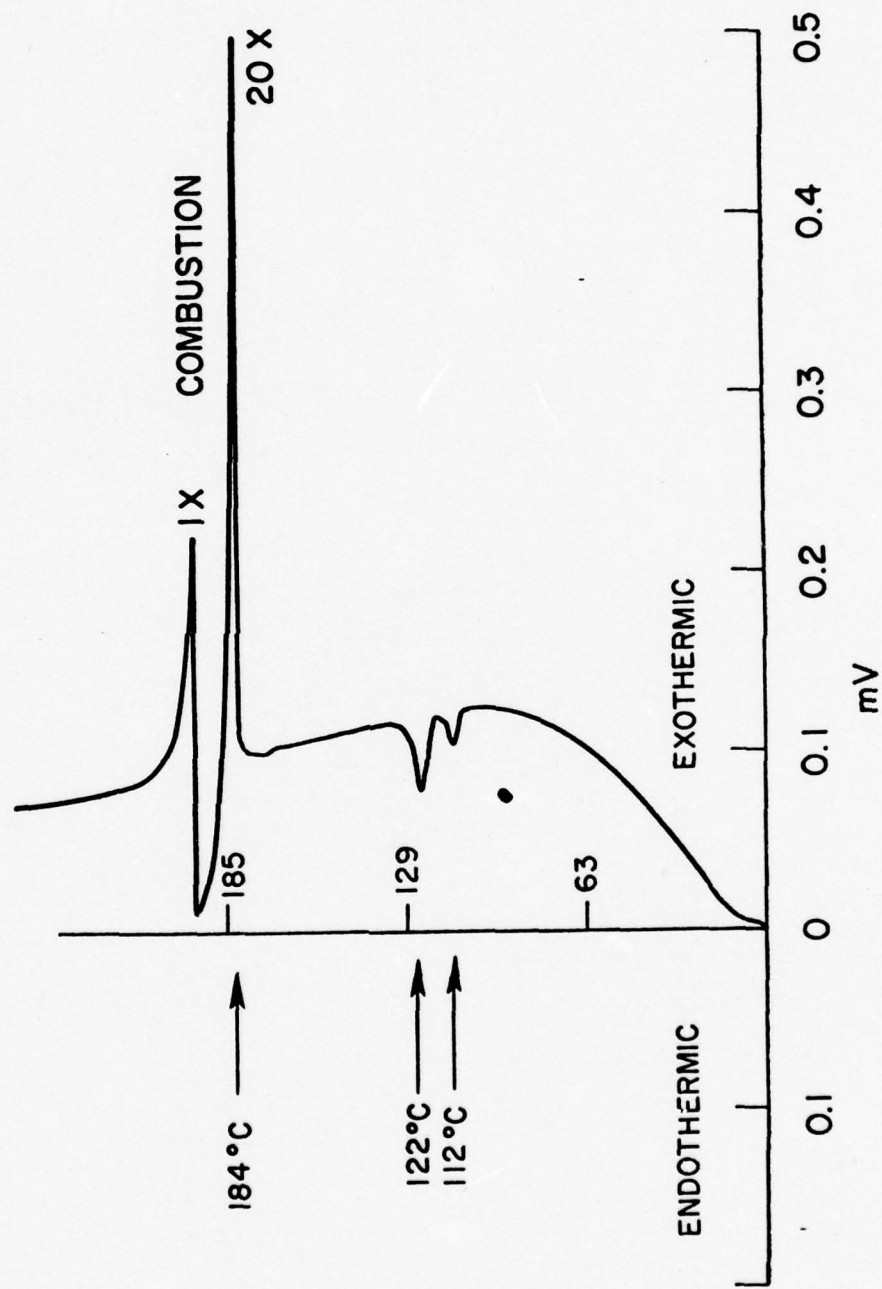


Fig. 4. Thermogram of Li (0.014) + S (0.021), Sample #43

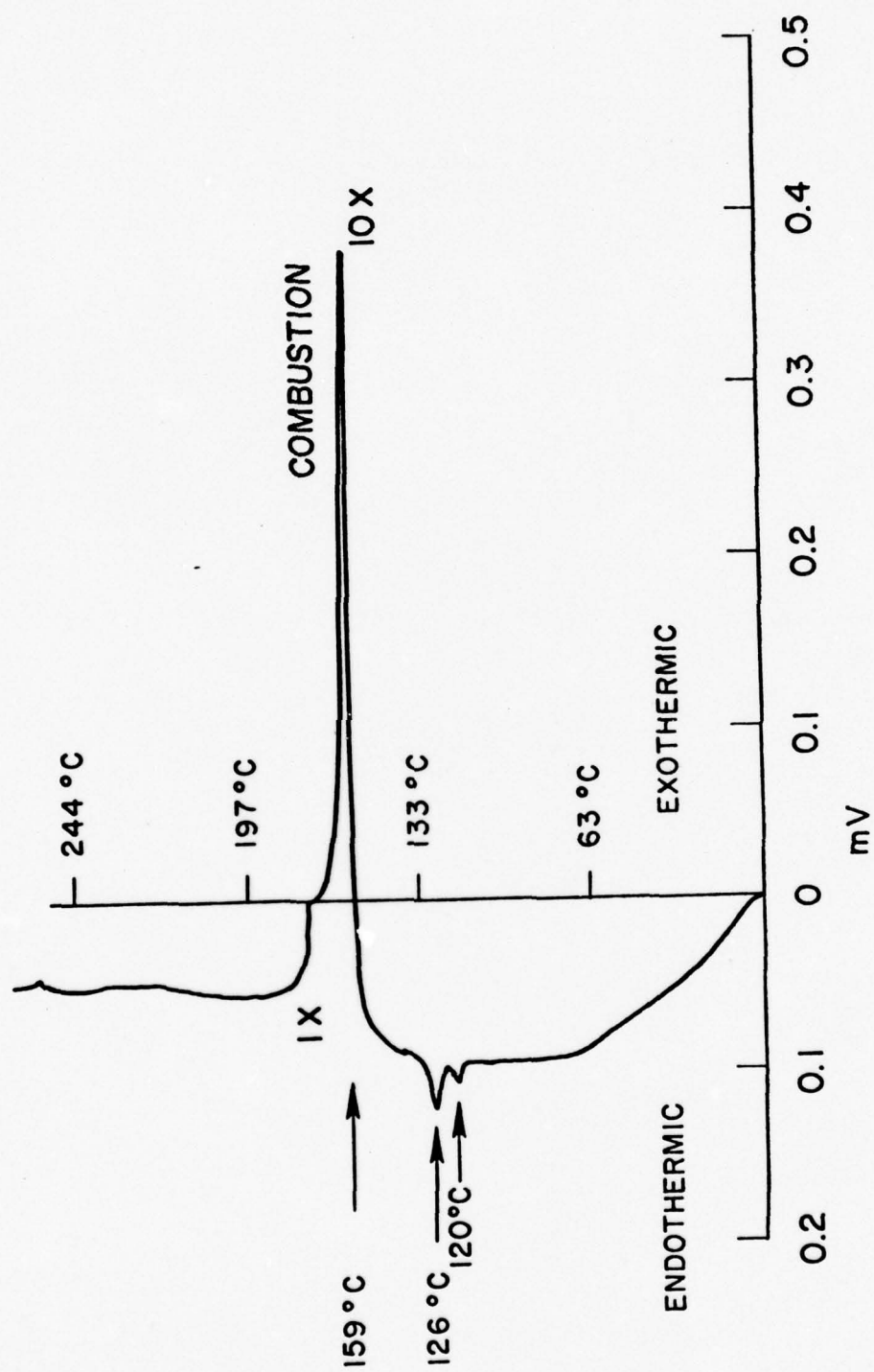


Fig. 5. Thermogram of Li (0.021) + S (0.019), Sample #48

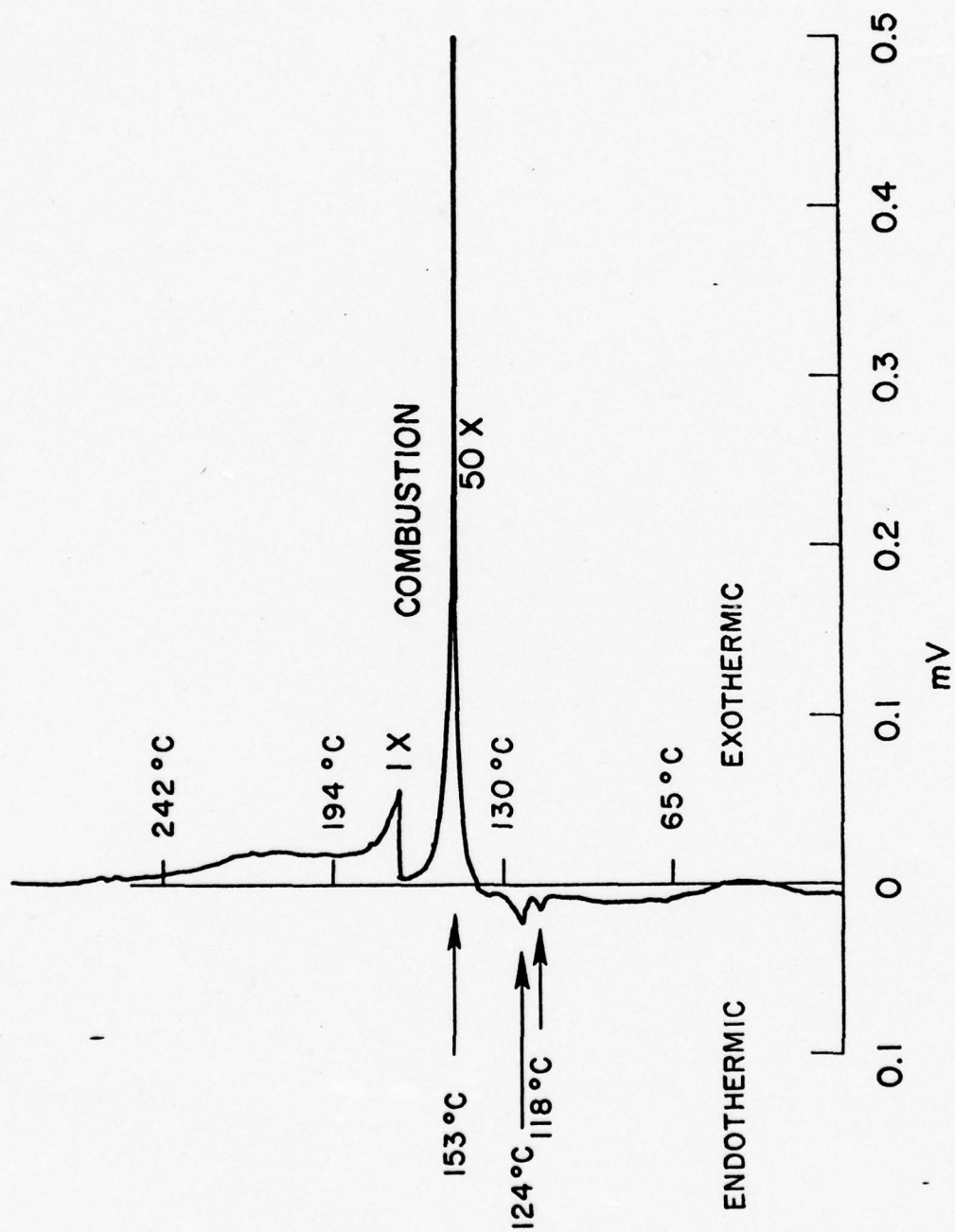


Fig. 6. Thermogram of Li (0.031) + S (0.021), Sample #49

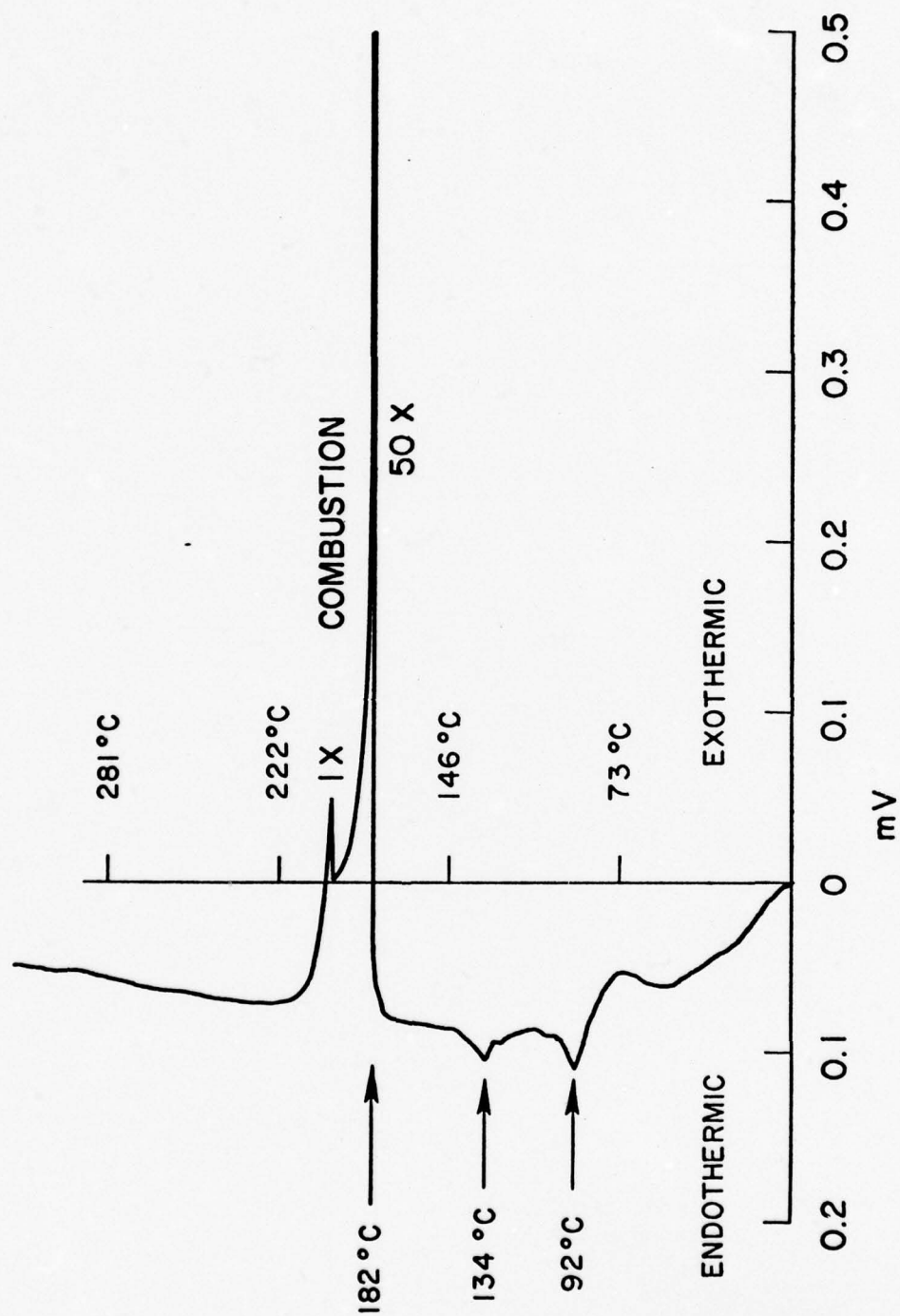


Fig. 7. Thermogram of Li (0.012) + Ni (0.012) + S (0.034) Sample #40

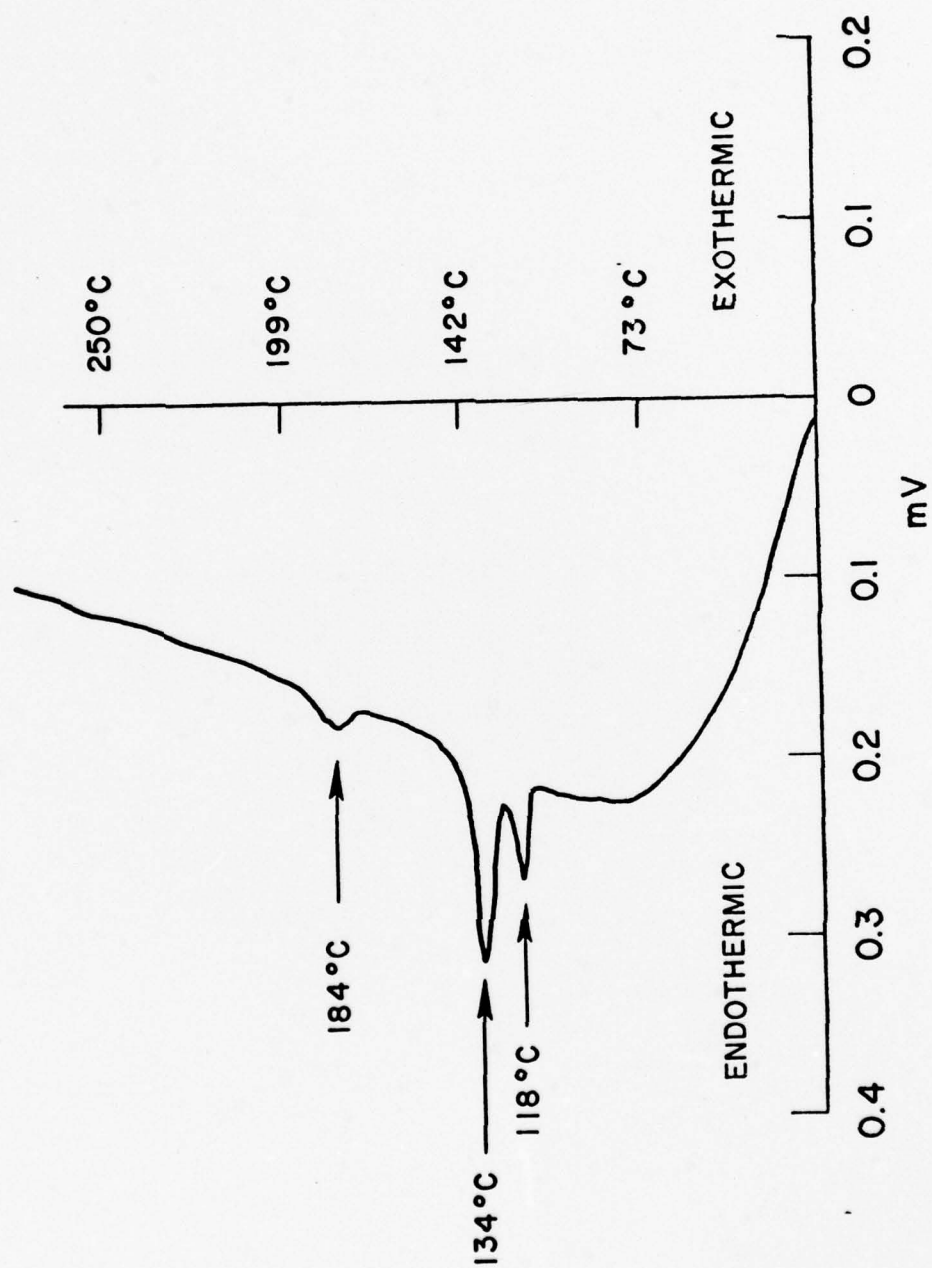


Fig. 8. Thermogram of S (0.060) + Cathode Mix (0.017), Sample #28

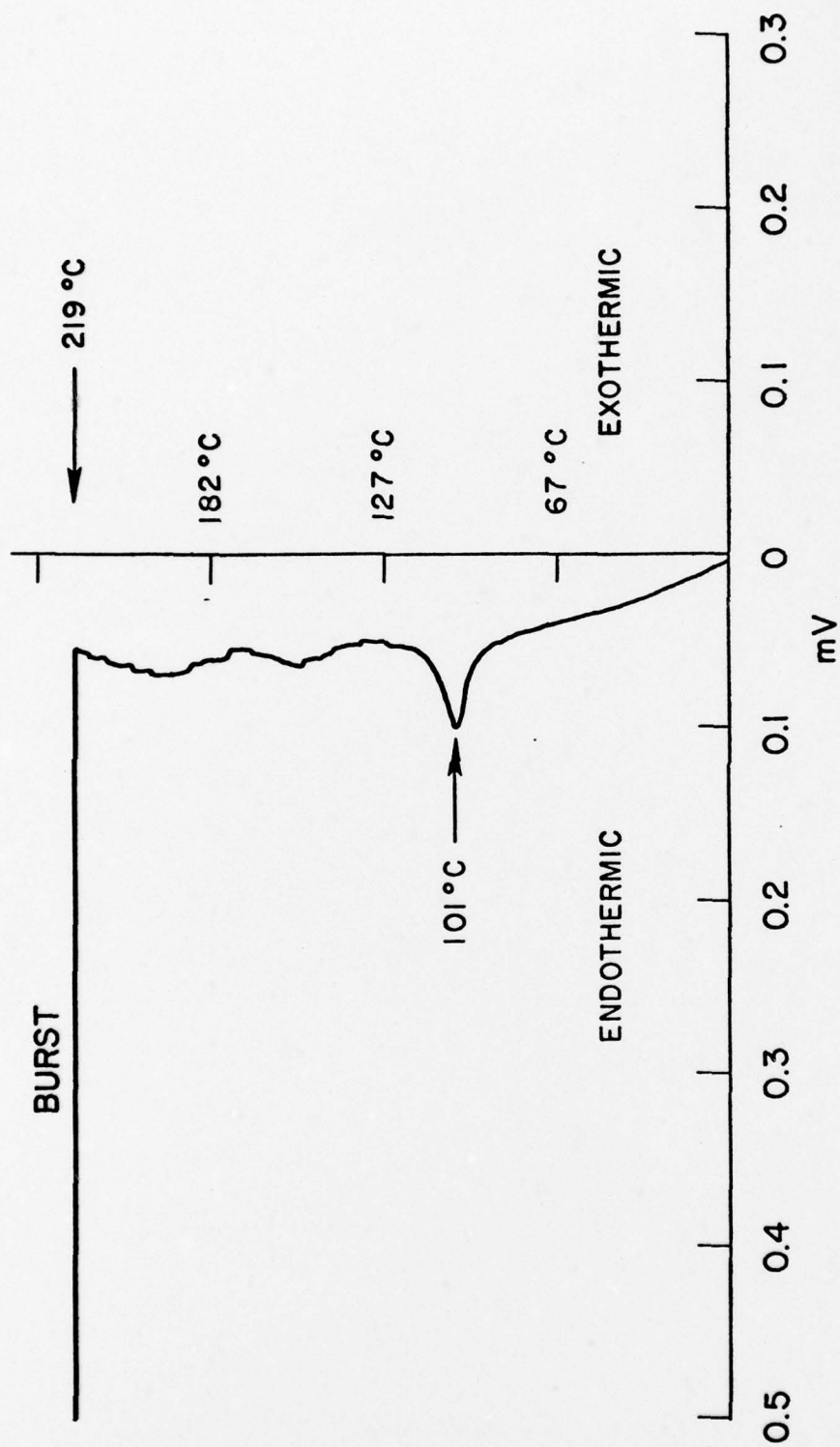


Fig. 9. Thermogram of S (0.050) + Cathode Mix (0.012) + SOCl_2 (0.145), Sample #23

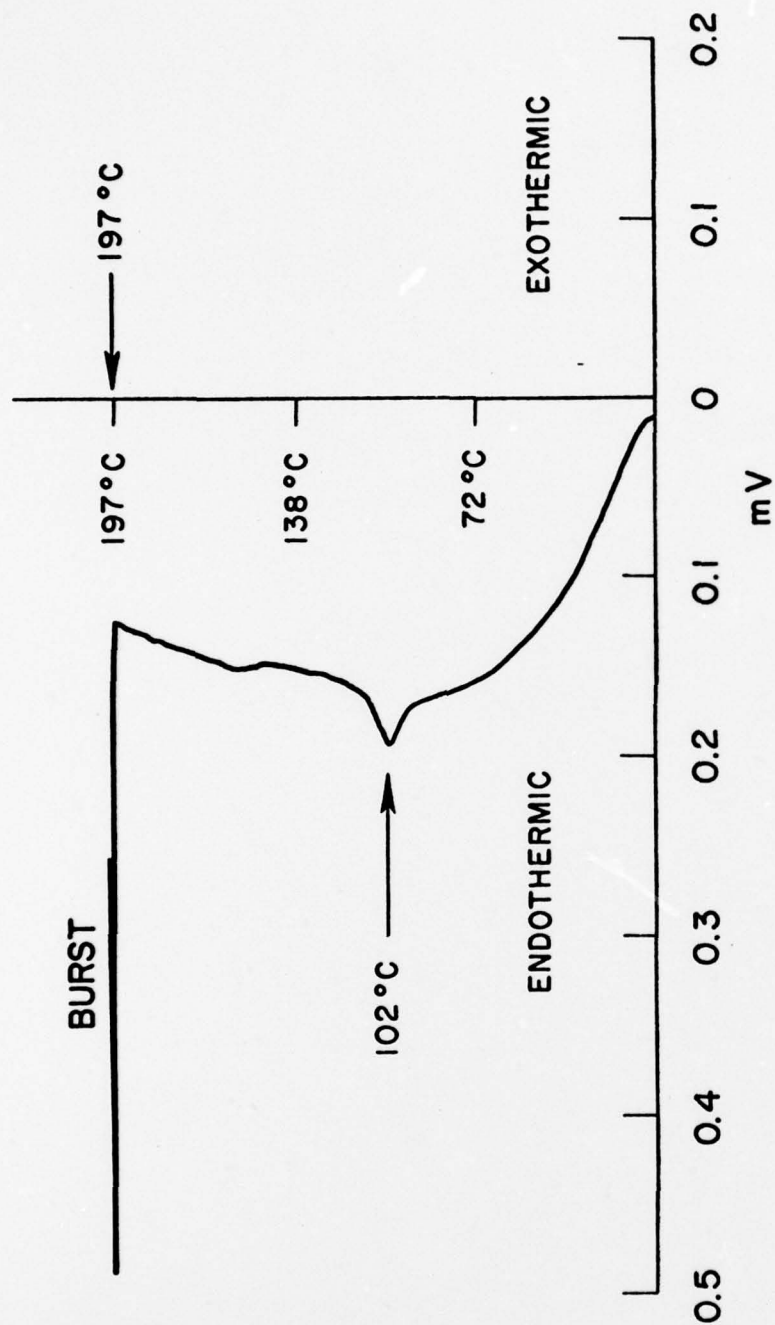


Fig. 10. Thermogram of S (0.050) + Cathode Mix (0.015) + SOCl_2 (0.183), Sample #29

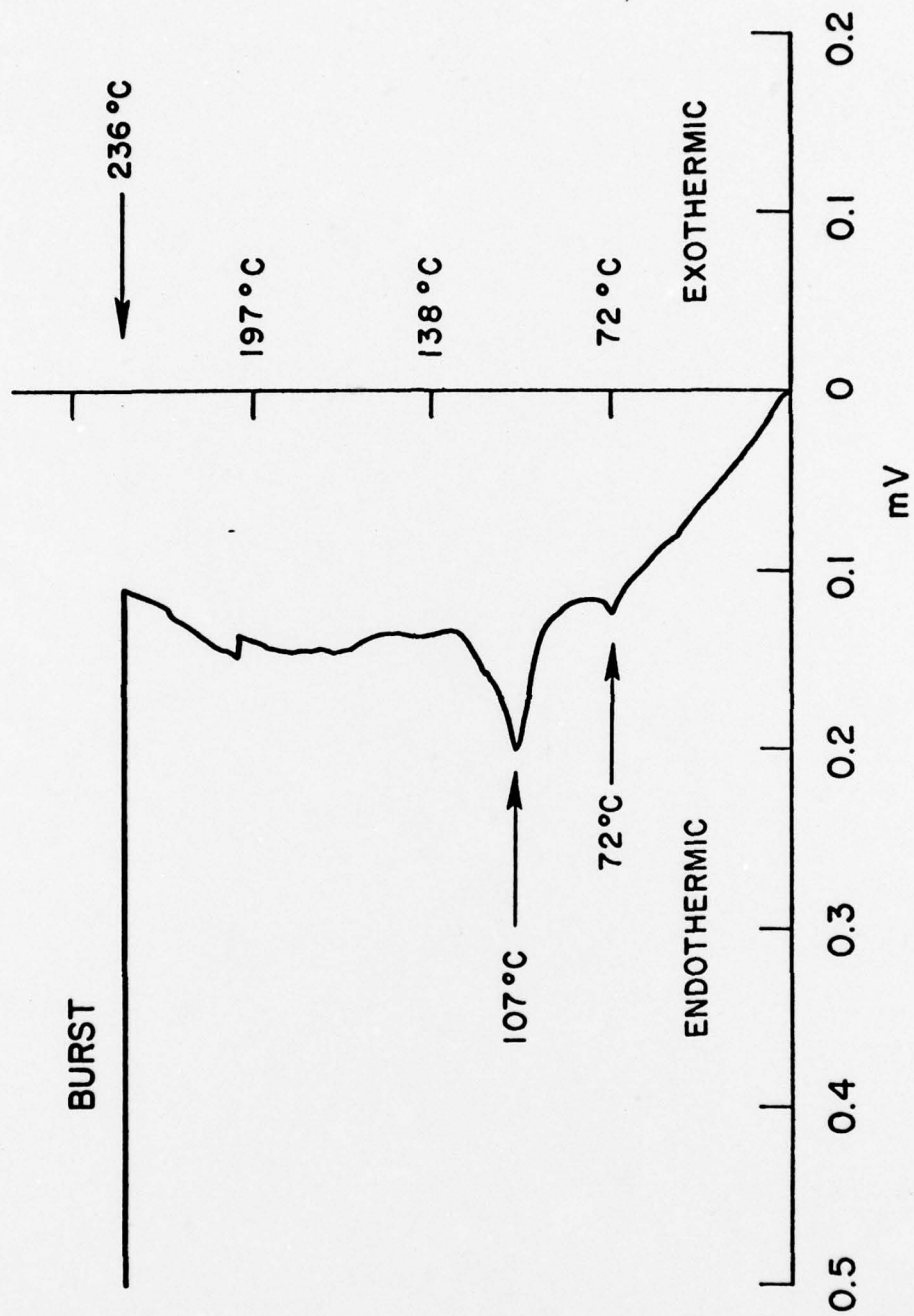


Fig. 11. Thermogram of S (0.087) + SOCl_2 (0.128), Sample #27

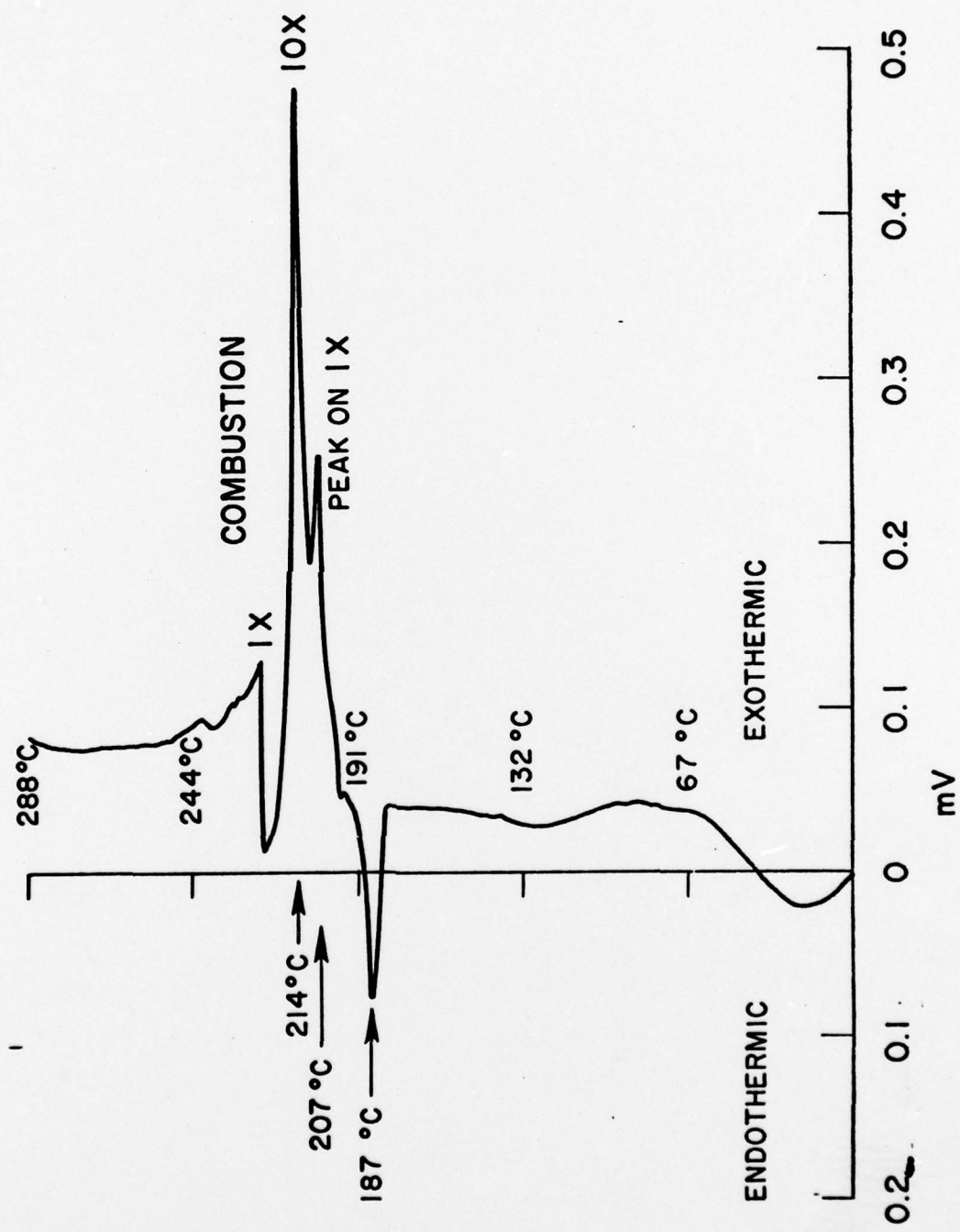


Fig. 12. Thermogram of Li (0.010) + glass separator (0.009), Sample #38

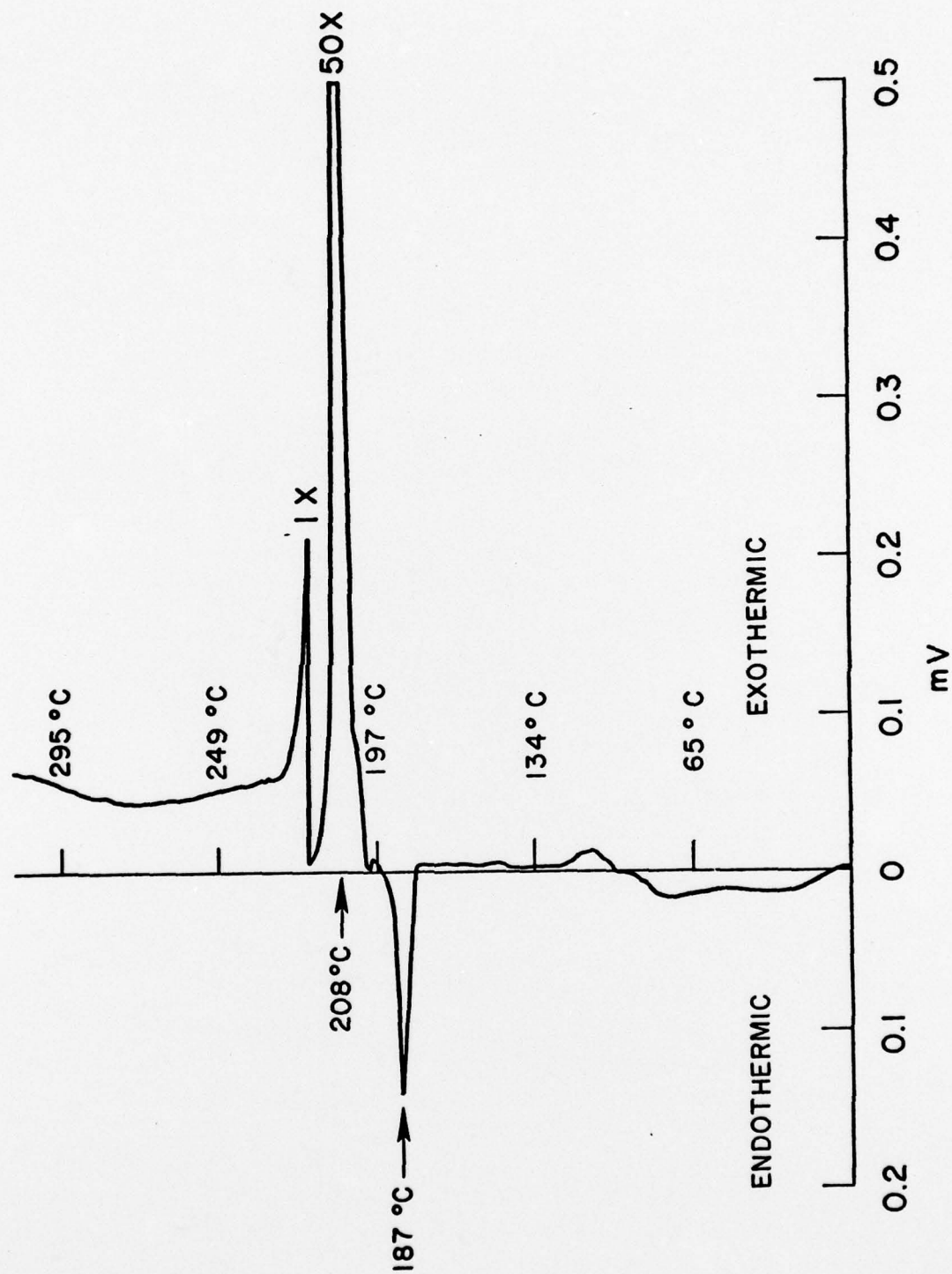


Fig. 13. Thermogram of Li (0.011) + glass separator (0.008), Sample #39

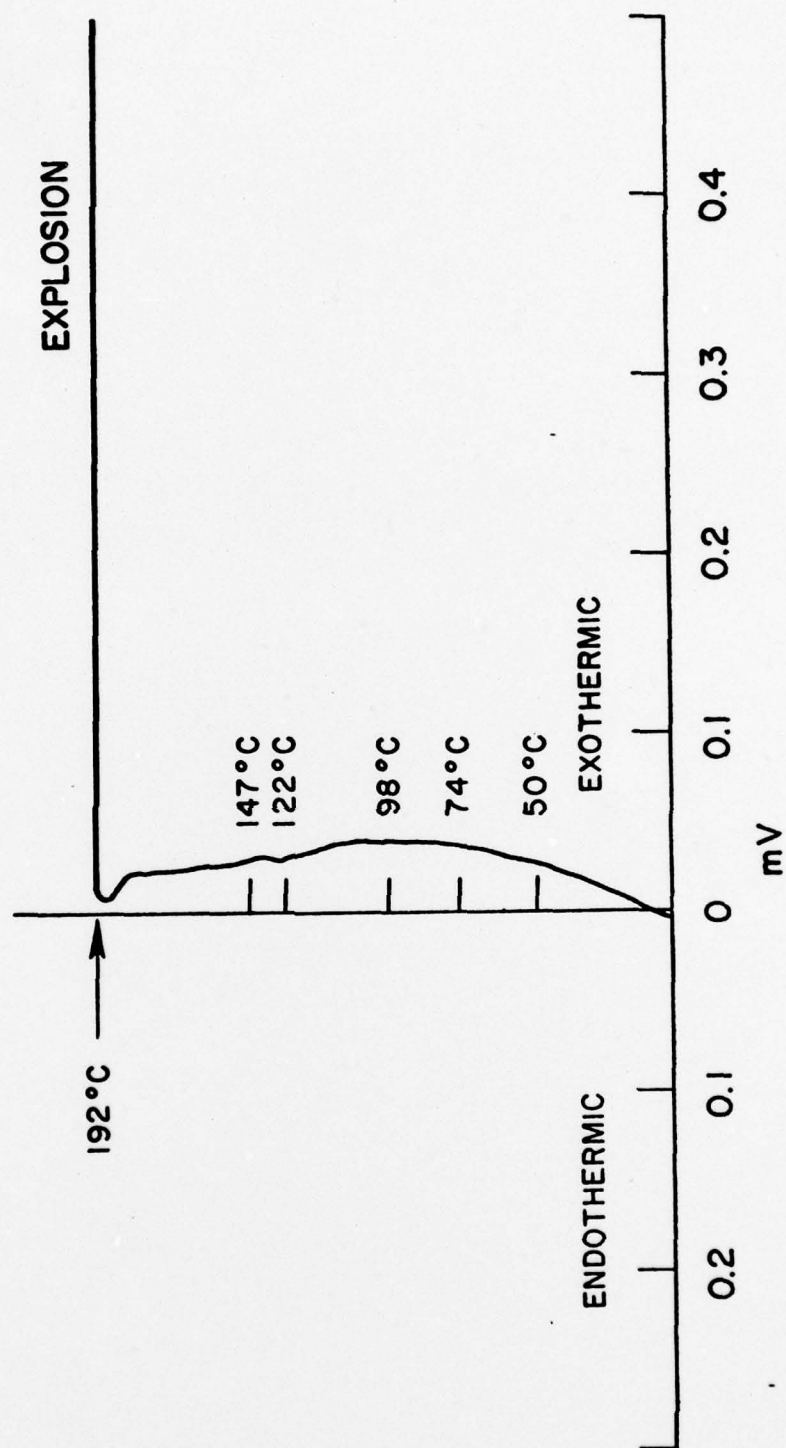


Fig. 14. Thermogram of Li (0.010) + SOCl₂ (0.082), Sample #21

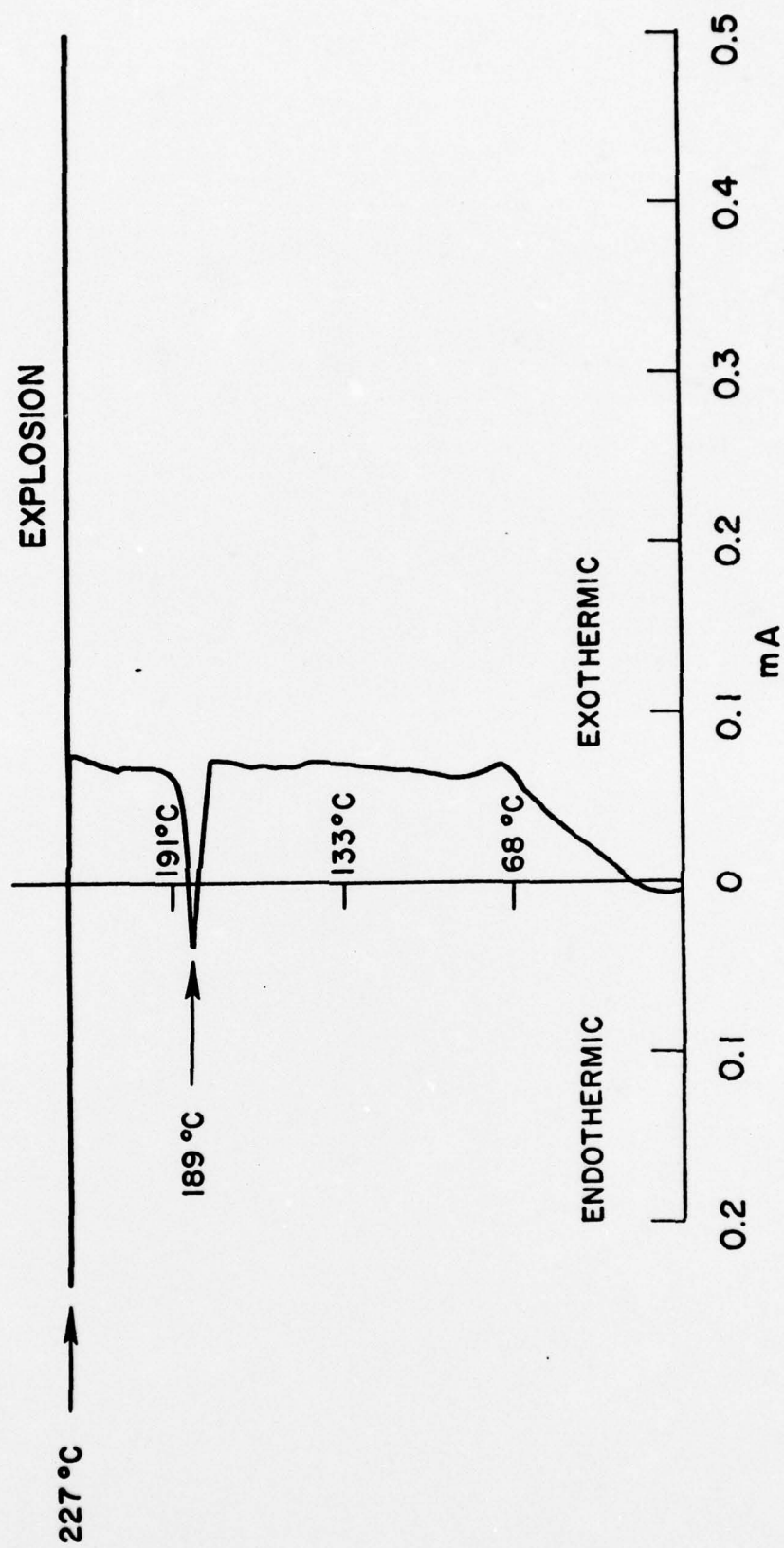


Fig. 15. Thermogram of Li (0.013) + SOCl₂ (0.167), Sample #26

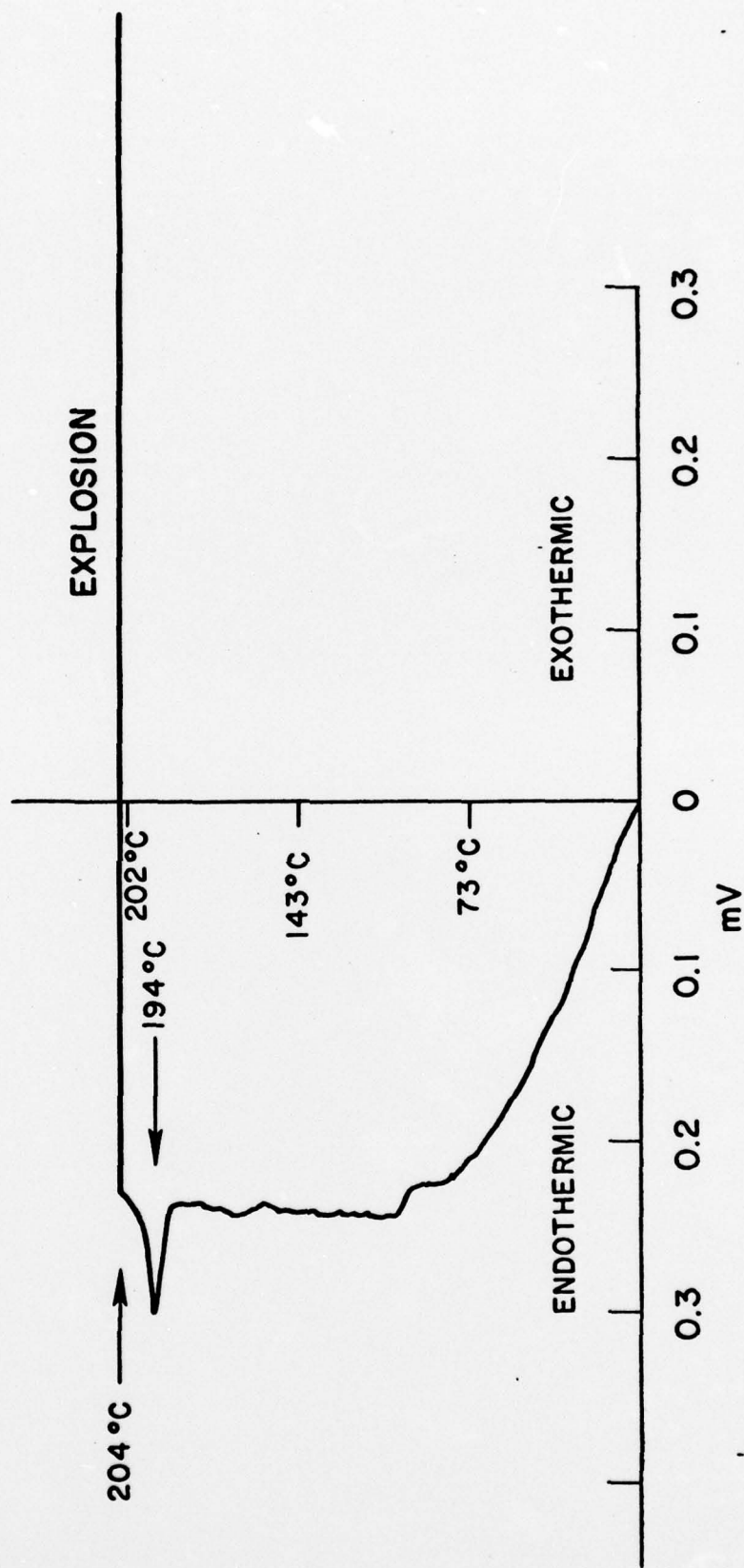


Fig. 16. Thermogram of Li (0.013) + S (0.045) + SOCl_2 (0.161), Sample #25

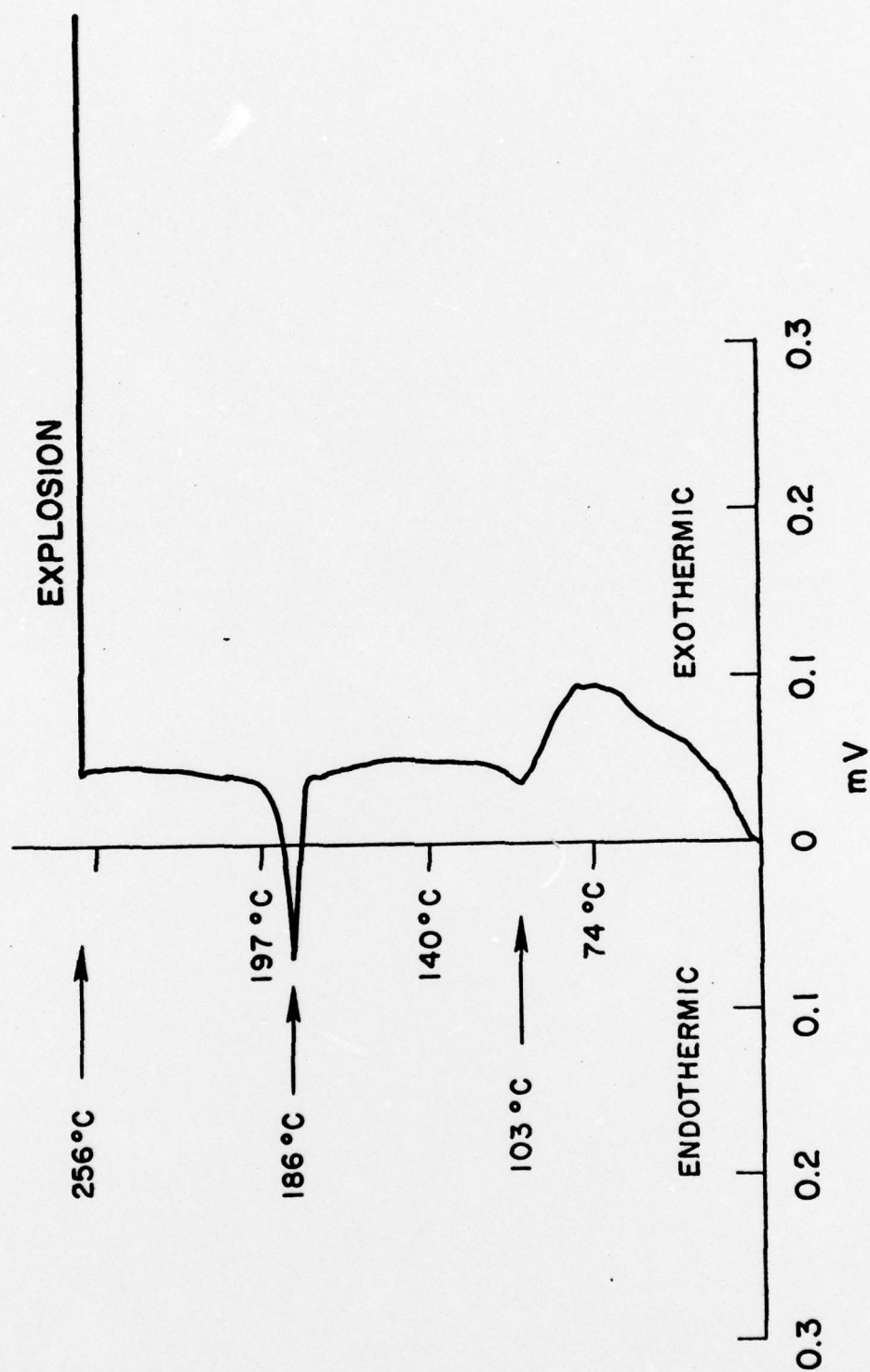


Fig. 17. Thermogram of Li (0.012) + S (0.033) + equal volumes of SOCl_2 + S_2Cl_2 mixture (0.126), Sample #32

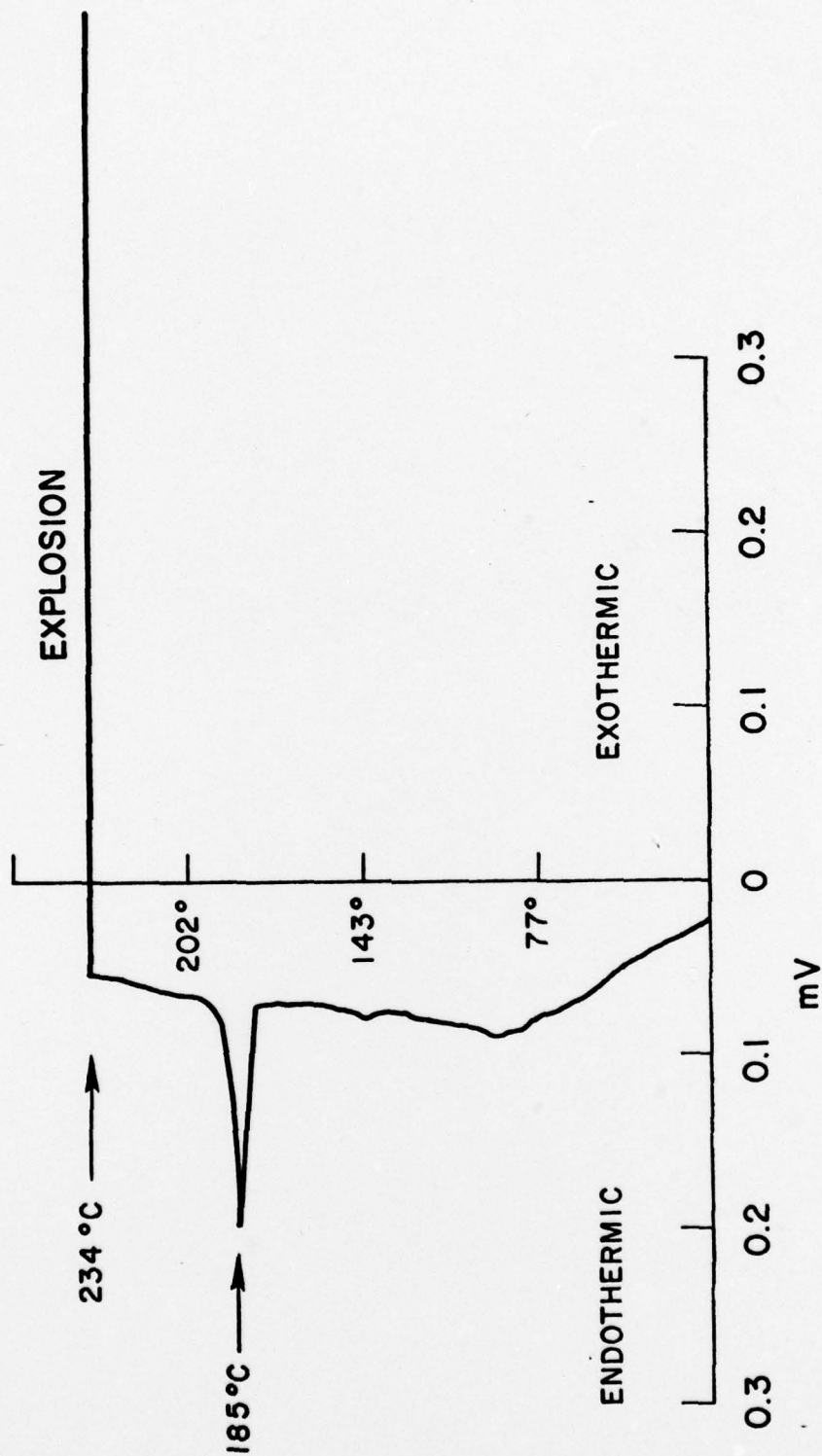


Fig. 18. Thermogram of Li (0.012) + S (0.031) + equal volumes of SOCl_2 + S_2Cl_2 mixture (0.092), Sample #33

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