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Author

Lohr, Harold Russell

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Heats of Formation of Some Aqueous Ions of Americium

by

Harold Russell Lohr
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DISSERTATION

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HEATS OF FORMATION OF SOME AQUEOUS IONS OF AMERICIUM

Harold Russell Lohr
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

ABSTRACT

The heats of formation of Pr^{+3} (aq.) and La^{+3} (aq.) have been measured in 1.5M HCl at 25°C. to be -165.9 ± 0.9 kcal/mol and -167.0 ± 0.7 kcal/mol, respectively. The heat of formation of Am^{+3} (aq.) under the same conditions was found to be -161.3 ± 1.4 kcal/mol. The latter value made it possible to calculate the heat of formation of Am^{+4} (aq.) as -112.2 kcal/mol. It was impossible at this time to determine the heats of formation of AmO_2^{+} (aq.) and AmO_2^{++} (aq.).

TABLE OF CONTENTS

I. INTRODUCTION

A knowledge of the free energies of formation of the aqueous ions of an element may be regarded as basic for the understanding of its chemistry in aqueous solution. In particular, such knowledge concerning those ions which represent the stable oxidation states of the element in aqueous solution is of fundamental practical importance.

Americium is known to exist in at least four oxidation states-- the +3 state investigated by Seaborg, James, and Morgan[1] who discovered the element; the +4 state discovered by Cunningham;[2] the +5 state discovered by Werner and Perlman;[3] and the +6 state discovered by Asprey, Stephanou, and Penneman.[4] Of these states, at least three, the +3, +5, and +6, possess sufficient stability in aqueous solution to be of practical interest.

The most accurate and satisfactory method of investigating the equilibria between different oxidation states is by means of a series of potential measurements in which the various couples behave in a reproducible and reversible manner in a chemical cell.

In the case of americium, however, such an approach was not expected to yield satisfactory results, except possibly in the case of the +3 - +4 couple and the +5 - +6 couple. By analogy with other elements of the actinide series the +5 and +6 aqueous ions were expected to be of the type AmO_2^+ and AmO_2^{++}, with covalently bonded oxygens. It is generally accepted that reactions involving the breaking or formation of bonds of this type do not yield readily reproducible potentials.

Attempts to measure the +3 - +4 potential have not thus far been successful, and this potential was estimated by Eyring[5] from measurements of the reaction of AmO_2 with 6M nitric acid and an estimate of ΔS for the reaction. These data indicate that the potential is approximately -2.6 volts.

The +5 - +6 couple is readily reversible, and potential measurements at Los Alamos by Asprey, Stephanou, and Penneman[6] give a value of -1.63 v. in 0.1M $HClO_4$.

Similar measurements at Berkeley by Jones and Cunningham[7] give -1.60 v. in 0.1M $HClO_4$, ca. 0.05M $SO_4^=$.

The present investigation was undertaken for the purpose of securing thermal data, which, together with estimates of entropies of formation based on analogy with similar ions of other actinide elements, could be used to calculate values for the free energies of formation of the americium ions of major interest--notably the uncomplexed ions of the +3, +4, +5, and +6 oxidation states which are the stable ones in acid solution.

This method of arriving at values for the free energies of formation of these ions is admittedly subject to some uncertainty. In no case can it be proved rigorously that the ion concerned is strictly analogous to the reference ion on which the entropy estimate is based.

In all cases, however, there is strong supporting evidence that this is the case, and the general chemical resemblance of the ions of the same oxidation state for the known elements of atomic number 92 and higher is such as to lend confidence to this type of extrapolation.

The quantities of americium available for these measurements were severely limited. It was necessary, therefore, to accept considerable loss in the precision of the calorimetric measurements, since the available apparatus was designed for the measurement of considerably larger heat effects than could be obtained with the small samples that had to be used.

II. HEAT OF FORMATION OF Am^{+3} (Aq.)

In order to determine the heat of formation of Am^{+3} (aq.), it was necessary to measure the heat of solution of americium metal in acid solution:

$$Am + 3H^+ = Am^{+3} + 3/2\ H_2.$$

Because of the limited amount of americium available for this study, it was decided first to measure the heat of solution of praseodymium metal under the same conditions.

Praseodymium was chosen for the initial experiments because its preparation would be similar to that of americium. Also, there was some question as to the correct value for its heat of solution in acid solution.

Preparation of Praseodymium Metal

The source of the praseodymium used in all the metal preparations was the Johnson, Matthey and Co., Ltd. of London. This material, in the form of PrO_2, was further purified in the Radiation Laboratory, University of California, by D. C. Stewart and R. C. Lilly, using a cation-exchange column separation procedure. Spectrographic analysis of the material thus prepared showed it to be free from impurities within the limits of detection. The praseodymium separated in this manner was precipitated as the oxalate, and the latter was ignited in air to form black Pr_6O_{11}. This Pr_6O_{11} was the material used as a source of praseodymium for all metal preparations.

A method similar to that used in this study for the preparation of praseodymium metal has been previously described by Westrum and Robinson[8] and also by Eyring.[5] However, the metal produced earlier in this laboratory failed to give an unambiguous value for the heat of solution, probably because of barium and beryllium impurities introduced during the metal production. Several modifications were made in this investigation, therefore, to insure that the final product was pure metal.

The Pr_6O_{11} stock material was converted to Pr_2O_3 by reduction at 500°C. in a hydrogen reduction apparatus (Fig. 1). A tube of uranium hydride was used as a source of hydrogen and the partial pressure of hydrogen was maintained at 1/3 atmosphere during the reduction. The use of uranium hydride as a hydrogen source has been described by Newton.[9] It is a very convenient method of obtaining a desired pressure of hydrogen, because it obeys the following equation over most of the composition range between uranium hydride and uranium:

$$\text{Log } P_{mm} = -4500/T + 9.28.$$

The praseodymium oxide sample was heated by the use of a molybdenum radiation shield. Molybdenum was found to be resistant to action by hydrogen at the temperatures used for reduction. Temperature was measured by the use of a chromel-alumel thermocouple welded to the bottom of the platinum sample holder. Prior to reduction, the entire system was evacuated to remove all traces of adsorbed moisture.

As reported by Eyring,[5] reduction at 1/3 atmosphere of hydrogen at a temperature of 500°C. for 1-1/2 hours gives the yellow-green oxide, Pr_2O_3.

$$Pr_6O_{11} + 2H_2 = 3Pr_2O_3 + 2H_2O.$$

The Pr_2O_3 prepared in this manner was then transferred to a platinum fluorination line (Fig. 2) for conversion to PrF_3. A mixture of approximately equal parts of HF and H_2 was passed over the sample for one hour at 600°C.

$$Pr_2O_3 + 6HF = 2PrF_3 + 3H_2O.$$

The PrF_3 thus prepared was then pelleted in a pellet press (Fig. 3) to form compact samples for metal production. The crucible assembly used is illustrated in Fig. 4. A PrF_3 pellet was placed in the TaC inner crucible and the latter was capped with the TaC disk. This crucible and cap were then placed in the Ta outer crucible. A piece of freshly cut Li metal was added and the entire assembly was enclosed by inserting the Ta screw cap. During the reduction period, the assembly rested in an Al_2O_3 insulating shell which fit in a tungsten coil furnace in a vacuum system (Fig. 5).

The entire system was evacuated to a pressure of 10^{-7} mm. of Hg before the reduction was begun. The tungsten coil furnace had been calibrated previously by applying an alternating potential to the circuit and determining the temperature of an equivalent crucible system with an optical pyrometer. All reductions were carried out at a temperature of 925°C., the temperature being maintained at this value for from two to two and one-half minutes after the appearance of a Li mirror on the inner surface of the outer glass bulb.

This method of reduction was found to produce spectrographically pure pellets of praseodymium metal, the element being quite malleable and having a gray metallic luster.

These pellets were carefully cleaned under xylene in a dry box to remove any oxide coating that may have been present. Weighings were made by difference into clean glass calorimeter bulbs with a mass of less than twenty milligrams. The Kirk-Craig-Gullberg quartz fiber torsion microbalance[10] was used for these weighings. It has a sensitivity of 10^{-8} gm. and a reproducibility of several hundredths of one percent on a mass of several hundred micrograms. Each weighed sample was enclosed by placing a glass bead in the neck of the microcalorimeter bulb and sealing the bead in place with Apiezon "W" wax.

Description of Microcalorimeter Used For Heat of Solution Measurements

A microcalorimeter was available in this laboratory for obtaining heat of solution data on the small quantities of americium that were available for this investigation. Although the instrument has been described previously in a paper by Westrum,[11] a circuit diagram and several figures are included in this thesis for general information (Figs. 6-9).

As previously noted, the calorimeter was originally designed for measurement of considerably larger heat effects than were possible in the experiments with americium and its compounds. It was found that fluctuations in the thermostat temperature of the order of 10^{-3} degree sometimes occurred during the critical portion of the run when solution was taking place. Determination of the thermal leakage modulus* of the calorimeter gave a value of about 2.5×10^{-2} degree per degree minute. These two factors introduced appreciable errors in the calculation of the actual heat liberated in any particular measurement.

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*The leakage modulus is defined by the equation $d = k\phi$, where d is the drift rate, k is the leakage modulus, and ϕ is the thermal head.

The calorimeter itself is wound with AWG No. 40 copper wire so that the unit serves both as a means for input of electrical energy and as a resistance thermometer. It forms one branch of a simple resistance bridge circuit (Fig. 8) and resistance changes in it can be balanced in another branch of the bridge by manual manipulation of a Leeds and Northrup decade resistance box on the control panel of the instrument.

A Leeds and Northrup high sensitivity galvanometer of the moving coil reflecting type, equipped with a telescope and centimeter scale, is connected across the bridge. Thus, a small resistance change in the resistance thermometer is detected by a corresponding deflection on the centimeter scale. The bridge sensitivity (cms. deflection on scale per 100 ohm change on decade box) is determined several times during the run to facilitate the necessary conversion of scale readings in centimeters to actual resistance corrections in ohms.

The energy equivalent of the calorimeter can be determined during the run by electrical energy inputs of known time duration. During these energy inputs, one measures the potentials across the resistance thermometer and across the bridge with a Rubicon precision potentiometer. Four or five energy inputs are usually made in each experiment. It is then possible to calculate the power factor in calories per minute for the instrument. This power factor is constant over the period of several runs, although it is calculated separately for each run.

When a run is to be made, the glass bulb containing the sample is sealed to the end of the stirring shaft with Apiezon "W" wax and the unit is assembled as shown in Fig. 9. Initially, for exoergic reactions, the calorimeter temperature is slightly below the thermostat temperature so there will be a heat transfer from the thermostat to the calorimeter. The scale is read at minute or half-minute intervals and, during this first portion of the run, bridge sensitivities are determined and two or three energy inputs are made.

In order to minimize drift corrections, it is desirable that the thermal head just before breaking the sample be as nearly as possible the same, with opposite sign, as the thermal head after solution has occurred.

Scale readings are recorded for several minutes before and after the sample bulb is broken. After solution is complete, it is customary to make two or more energy inputs and additional bridge sensitivity determinations.

By use of the various measured bridge sensitivities, it is possible to convert galvanometer deflections on the centimeter scale to decade resistance box readings in ohms, corresponding to balance of the resistance bridge for each scale reading taken during the solution period. These decade resistance box readings are then plotted against time to give a curve for the heat of solution of the sample. A representative curve is shown in Fig. 10.

Sample Calculations for Magnesium Metal Run Number One

It was also desirable to calibrate the instrument chemically before proceeding with the experiments on praseodymium or americium. To do this, it was decided to measure the heat of solution of magnesium metal, both because pure magnesium metal was available in this laboratory and because the value for its heat of solution is known accurately. Shomate and Huffman,[12] operating under similar conditions, obtained a value of -111.322 ± 0.041 kcal/mol for the heat of solution of magnesium in 1.0M HCl at 25°C.

Before discussing the chemical calibration and the work which followed, it may be well to illustrate as briefly as possible the method involved in the calculation of a heat of solution value with this instrument.

Table I contains a portion of the data taken in Run No. 1, a determination of the heat of solution of magnesium metal in 1.0M HCl at 25°C. These data, with the accompanying tables and figures, will serve to demonstrate the method of calculation employed in the experiments which follow.

Table I

Data Taken in Run No. 1, Mg Metal
1.0M HCl at 25°C.

1	2	3	4	5	6	7
29.8	1490		14.43			4.730
30.0			14.52			
31.0		(13.15)	14.92			
32.0			15.34			
33.0			15.75			
34.0	1590		11.65			
35.0		(13.13)	12.04			
36.0			12.41			
37.0			12.79			
37.8			13.08			
38.0	Broke Sample					
38.2	1790		13.13			
38.73	2060		13.13			
38.9			13.60			
39.15			13.73			
39.47			13.63			
40.0			13.50			
40.5			13.42			4.725
41.0			13.33			
42.0			13.11			
43.0			12.91			
44.0			12.67			
45.0			12.44			
46.0			12.27			
47.1			12.09			
48.0		(13.12)	11.90			
49.0	2010		13.82			
50.0			13.60			
51.0			13.40			
51.3		(13.13)	13.35			
51.5	Electrical energy on for 1.0 minute			0.90957	1.42012	4.727
53.2	2470		12.18			
54.0			11.63			
55.0		(13.13)	10.98			
56.0			10.37			4.727
57.0	2350		14.93			
58.0			14.36			

Column

1 Time in minutes from beginning of run
2 Setting in ohms on decade resistance box
3 "Check Point" (Scale reading in cms.)
4 Galvanometer reading (Scale reading in cms.)
5 Divider potential across resistance thermometer in volts
6 Divider potential across resistance bridge in volts
7 Temperature of thermostat in degrees on Beckmann thermometer

After the experimental data have been taken, it is first customary to calculate the bridge sensitivities (cms. deflection on scale per 100 ohm change on decade resistance box). Referring to Table I, it is noted that the scale reading is 15.75 cms. (1490 ohms on decade resistance box) at a time 33.0 minutes after the beginning of the run. After an interval of one minute, during which period the decade box was reset at 1590 ohms, the scale reading is 11.65 cms. Observing the drift on the centimeter scale prior to this latter reading, it is seen that during the one-minute interval, there would have been a drift upwards of 0.40 cm. had the decade box not been reset. Using this information, one calculates for the bridge sensitivity:

$$\text{Sensitivity} = \frac{15.75 + 0.40 - 11.65}{100} = 0.0450 \text{ cms/ohm or } 4.50 \text{ cms/100 ohms.}$$

This sensitivity is then plotted as the ordinate against the average value of the two decade box settings, 1540 ohms. Fig. 11 gives the complete curve for this particular run.

As has been noted previously, several electrical energy inputs of known time duration are made during the course of the run to determine the energy equivalent of the calorimeter. Referring again to Table I, it is seen that an electrical energy input of one-minute duration was made at a time 51.5 minutes after the beginning of the run. The resistance decade box settings, before and after the input, were 2010 ohms and 2470 ohms, respectively.

Table I includes several values enclosed in parentheses; these values represent the so-called "check point," or the centimeter scale reading corresponding to no current flow, i.e., the balance point of the resistance bridge. This value is important in that it serves as a reference point for all corrections of the actual decade resistance box settings to settings which would correspond to balance of the bridge. In this connection, it is important to make an electrical energy input during the run at such a time that the scale reading on the centimeter scale,

extrapolated to the time corresponding to the middle of the energy input, will be as near the "check point" as possible. In the same fashion, after completion of the energy input, the new decade box setting should be such that extrapolation of the afterdrift back to the midpoint of the input will give a scale reading close to the "check point." This practice minimizes the corrections which have to be made in the final calculations.

In Fig. 12, centimeter scale readings prior to and following the energy input at 51.5 minutes are plotted against the time at which the readings were observed. It will be noted that both sets of points are extrapolated to the time corresponding to the midpoint of the input. The extrapolated foredrift and afterdrift are 13.22 cms. and 12.99 cms. respectively, whereas the "check point" was observed to be 13.13 cms.

With this information, it is a simple procedure to calculate the two decade resistance box readings which would correspond to balance of the resistance bridge before and after the energy input, these resistance settings being calculated at the midpoint of the input. It can be shown that the resistance difference, calculated at the midpoint of the energy input, is the total resistance change equivalent to the electrical energy introduced at a constant rate during the interval. Table II lists the values calculated for the electrical energy input at 51.5 minutes after the beginning of Run No. 1. An explanation of the values is included in the table.

Each energy input made during the course of the run is calculated in this manner. The values of $\Delta\theta/t$ (column 13) are then plotted against the corresponding values of $\bar{\theta}$ (column 12), giving a straight line relationship (Fig. 13). The fact that $\Delta\theta/t$ is almost a linear function of $\bar{\theta}$ is demonstrated in Appendix A.

During the interval in which energy is being introduced into the calorimeter, measurements are made of the potentials across the resistance bridge and across

Table II

Calculation of Data for Electrical Energy Input at 51.5 Minutes After Beginning of Mg Metal Run No. 1 in 1.0M HCl at 25°C.

1	2	3	4	5	6	7	8
1.0	IV	4.37	13.13	13.22	2010	+2.1	2012.1
		4.25	13.13	12.99	2470	-3.3	2466.7

9	10	11	12	13
35312.1	283189.	3599.	281390	3599.
35766.7	279590.			

Column

1 Time interval in minutes of electrical energy input
2 Chronological order of energy input
3 Bridge sensitivity (cms. deflection on scale per 100 ohm change on decade resistance box--interpolated from Fig. 11)
4 "Check point" (scale reading in cms.)
5 Scale reading in cms. extrapolated to midpoint of energy input (Fig. 12)
6 R" = Decade resistance box settings in ohms
7 Correction in ohms to convert decade box settings to settings corresponding to balance of resistance bridge = (column 5 - column 4)(100)/(column 3)
8 R' = Corrected decade box settings in ohms corresponding to balance of resistance bridge
9 R = (R' + 33,300) ohms
10 $\theta = 1/R \text{ ohm}^{-1} \times 10^{10}$
11 $\Delta\theta = (\theta_1 - \theta_2) \text{ ohm}^{-1} \times 10^{10}$ (θ_1 = value before energy input; θ_2 = value after energy input)
12 $\bar{\theta} = 1/2\ (\theta_1 + \theta_2) \text{ ohm}^{-1} \times 10^{10}$
13 $\Delta\theta/t$ = (column 12)/(column 1) ohm^{-1}/minute $\times 10^{10}$

the resistance thermometer (calorimeter). These measurements enable one to calculate the power factor, or energy equivalent, of the calorimeter. A sample calculation of this factor is given in Appendix B.

With the values obtained above, it is now possible to consider the data taken during the actual solution period. These data are tabulated in Table III. The values listed in column 7 are plotted against the corresponding times in column 1 to give the solution curve in Fig. 10. The resistance change between the time of

breaking the sample and the time at which solution is complete is taken to represent the heat evolved during reaction. The determination of this resistance change is complicated, of course, by the fact that the drift rate is changing as the thermal head varies. The procedure adopted in these determinations, where solution time was relatively short, was to make extrapolations of the foredrift and afterdrift to the time of breaking of the sample bulb. The difference in resistance at this point, with the slopes of the lines for the foredrift and afterdrift, was used to

Table III

Calculation of Data Taken During Solution Period For Mg Metal
Run No. 1 in 1.0M HCl at 25°C.

1	2	3	4	5	6	7
35.0	4.40	13.13	12.04	1590	-24.8	1565.2
36.0			12.41		-16.4	1573.6
37.0			12.79		- 7.7	1582.3
37.8			13.08		- 1.1	1588.9
38.0	Broke Sample					
38.2	4.43	13.13	13.13	1790	0.0	1790.0
38.73	4.36		13.13	2060	0.0	2060.0
38.9			13.60		+ 7.8	2067.8
39.15			13.73		+13.8	2073.8
39.47			13.63		+11.5	2071.5
40.0			13.50		+ 8.7	2068.7
40.5			13.42		+ 6.9	2066.9
41.0			13.33		+ 4.8	2064.8
42.0			13.11		- 0.2	2059.8
43.0			12.91		- 4.8	2055.2
44.0			12.67		-10.3	2049.7
45.0			12.44		-15.6	2044.4
46.0			12.27		-19.5	2040.5
47.0			12.09		-23.9	2036.1
48.0			11.90		-28.2	2031.8

Column

1 Time in minutes from beginning of run
2 Bridge sensitivity (cms. deflection on scale per 100 ohm change on decade resistance box--interpolated from Fig. 11)
3 "Check point" (Scale reading in cms.)
4 Scale reading in cms. at time given in column 1
5 R" = Decade resistance box setting in ohms
6 Correction in ohms to convert decade box settings to settings corresponding to balance of resistance bridge = (column 4-column 3)(100)/(column 2)
7 R' = Corrected decade box settings in ohms corresponding to balance of resistance bridge.

calculate a value for the thermal leakage modulus. For example, in Fig. 10, the extrapolated resistances at 38.0 minutes, the time of breaking of the sample, are 1590.6 ohms and 2078.4 ohms. The difference is 487.8 ohms. The slopes of the lines for foredrift and afterdrift are respectively +8.5 ohms/minute and -4.7 ohms/minute. Therefore, if $d = k\phi$ (d = drift rate, k = leakage modulus, ϕ = thermal head) and if the subscripts 1 and 2 refer respectively to the time before breaking the sample bulb and the time at which solution is complete

$$d_1 = k\phi_1 \text{ and } d_2 = k\phi_2 \text{ where } \phi_1 - \phi_2 = 487.8 \text{ ohms}$$

$$+8.5 = k\phi_1 \text{ and } -4.7 = k\,(\phi_1 - 487.8)$$

$$13.2 = 487.8\,k$$

$$k = 0.027 \text{ ohms/ohm minute}$$

$$\phi_1 = 314.8 \text{ ohms.}$$

This gives a value of 314.8 + 1590.6 = 1905.4 ohms as the decade resistance box setting corresponding to zero drift.

The period between the time at which the bulb was broken and the time at which solution was complete (latter time chosen as the first point to fall on the straight line representing the afterdrift) was divided into tenth-minute intervals. The difference between the resistance at zero drift (1905.4 ohms in this case) and the resistance at the midpoint of each tenth-minute interval was taken to represent the thermal head during this interval (each midpoint resistance interpolated on the straight lines connecting the experimental points). Since k was also known, it was possible to calculate the drift contributions to the heat rise during each interval for the entire period during which solution was taking place. The algebraic sum of all these drift contributions was then subtracted algebraicly from the resistance value at the time where solution was complete. In the example under consideration, the sum of the drift contributions was -2.4 ohms, which gives a corrected value of the resistance reading at the time of complete solution of

2071.5 - (-2.4) = 2073.9 ohms. Table IV shows how these resistance values are employed to complete the calculation of the heat of solution of magnesium metal in 1.0M HCl at 25°C.

Table IV

Calculation of Data for Determination of Heat of Solution of Mg Metal
For Mg Metal Run No. 1 in 1.0M HCl at 25°C.

1	2	3	4	5	6
1590.6	34890.6	286610.	3916.	284652.	3595.
2073.9	35373.9	282694.			

Column

1 R' = Decade resistance box values from Fig. 10 (Resistance difference corresponds to heat rise accompanying solution of magnesium metal)

2 $R = (R' + 33{,}300)$ ohms

3 $\theta = 1/R$ ohm^{-1} x 10^{10}

4 $\Delta\theta = (\theta_1 - \theta_2)$ ohm^{-1} x 10^{10} (θ_1 = value before breaking sample; θ_2 = value after solution complete)

5 $\bar{\theta} = 1/2\ (\theta_1 + \theta_2)$ ohm^{-1} x 10^{10}

6 $\Delta\theta/t$ ohm^{-1} x 10^{10}/min. (interpolated from Fig. 13)

Calculation of Heat of Solution of Mg Metal

$(\Delta\theta/t)/\Delta\theta = t$ = calculated solution time

q = energy equivalent of calorimeter = 0.8557 cal./min. (Appendix B)

qt = heat evolved in calories

m = weight of sample = 203.22 x 10^{-6} gm.

M = gram atomic weight of Mg = 24.32 gms.

ΔH = heat absorbed in kcal/mol

$$\Delta H = -10^{-3}\ qt\ \frac{M}{m} = -\frac{0.8557}{10^3} \times \frac{3916}{3595} \times \frac{24.32}{203.22 \times 10^{-6}} = -111.6 \text{ kcal/mol}$$

- 111.6 - 0.3 = -111.9 kcal/mol (0.3 kcal/mol is correction for vaporization of water by H_2 evolution)

The result which is calculated in this manner must be corrected for the water vaporized by evolved hydrogen. Before beginning a run, the 1.0M HCl used as the calorimeter solution was always saturated with hydrogen. Using 22.9 mm. of Hg[13] as the vapor pressure of water over the solution at 25°C., 10.5 kcal/mol as[14] the heat of vaporization of water, and assuming that the evolved hydrogen is saturated with water vapor, one calculates a correction of -0.3 kcal/mol of evolved hydrogen. This correction must be added to the value calculated from the experimental data. When pertinent, all values listed in this paper have been corrected for vaporization of water by hydrogen evolution. Similar corrections have been made where necessary for the vaporization of water by the air contained in the glass calorimeter bulbs, assuming a volume of 0.02 milliliter for each bulb.

Several measurements were made of the heat of solution of magnesium metal in 1.0M HCl at 25°C. The corrected values obtained are listed in Table V.

Table V

Chemical Calibration with Magnesium Metal
1.0M HCl at 25°C.

Run No.	Weight-Mg.	Heat Evolved-Calories	-ΔH (kcal/mol)
1	0.2032	0.932	111.9
2	0.1583	0.734	113.0
3	0.5280	2.410	111.3
4	0.2706	1.210	109.0
5	0.5866	2.673	111.1
6	0.2861	1.309	111.6
			111.3 ± 0.8

Heat of Solution of Praseodymium Metal

Table VI gives the corrected values which were obtained for the heat of solution of praseodymium metal

$$Pr + 3H^{+} = Pr^{+3} + 3/2\ H_2$$

Table VI

Heat of Solution of Praseodymium Metal in 1.50M HCl at 25°C.

Run No.	Weight-Mg.	Heat Evolved-Calories	-ΔH (kcal/mol)
1	0.2252	0.2634	165.4
2	0.1933	0.2285	167.3
3	0.1809	0.2044	159.9
4	0.6174	0.7210	165.1
			164.4 ± 2.3
		Omitting Pr-3	165.9 ± 0.9

The literature value which is generally accepted as most likely for the heat of solution of praseodymium metal is that measured by Bommer and Hohmann.[15] By an indirect method they obtained a value of -172.9 kcal/mol. In their investigation of the heats of solution of a number of the rare earth metals, they prepared the metals by reduction of the corresponding rare earth chlorides with potassium. It is possible that small amounts of potassium still remained which would have given a high value. They also note that their metal was prepared in powder form which also may have led to a higher value by the order of a kilocalorie.

Heat of Solution of Lanthanum Metal

In order to check the method used in this laboratory, it was decided to measure the heat of solution of lanthanum metal--both in the microcalorimeter and in a Dewar flask with a Beckmann thermometer. Lanthanum was chosen because samples were available from several different sources. This would indicate whether the metal prepared in this laboratory was different in some respect from metal prepared elsewhere. Metal samples investigated were from the Atomic Research Institute, Iowa State College, Ames, Iowa; Johnson, Matthey and Co., Ltd., London; and from this laboratory. The metal produced in this laboratory was made in the same manner as was the praseodymium already described.

Two determinations were made dissolving milligram amounts of lanthanum metal in 1.50M HCl in a Dewar flask, observing the temperature rise with a Beckmann thermometer. The heat capacity of the system had been determined previously by measuring the heat evolved from samples of magnesium.

Table VII

Approximate Heat of Solution of Lanthanum Metal
1.50M HCl in Dewar Flask

Sple No.	Weight-Mg.	Source of Metal	Purity of Metal	-ΔH (kcal/mol)
1	130.3	Johnson, Matthey	>99.0%	165.5
2	142.8	Iowa State	>95.0%	164.2

Four more measurements were made in the microcalorimeter at 25°C.

Table VIII

Heat of Solution of Lanthanum Metal in Microcalorimeter
1.50M HCl at 25°C.

Sple No.	Weight-Mg.	Source of Metal	Purity of Metal	-ΔH (kcal/mol)
1	0.2428	Iowa State	>99.0%	163.5
2	0.8658	Iowa State	>99.0%	165.9
3	0.5486	Berkeley	>99.5%	167.8
4	0.6396	Berkeley	>99.5%	167.3
				166.1 ± 1.4
			Omitting La-1	167.0 ± 0.7

Bommer and Hohmann[15] report a value of -176.5 kcal/mol for the heat of solution of lanthanum metal, which is also considerably higher than the value measured in this laboratory.

An additional experiment was performed by Broido[16] to check the hydrogen evolution from a sample of the metal obtained from Iowa State College. The observed volume of gas was the same as the theoretical volume well within the limits of experimental error. From these data, it was assumed that the heat of solution values

obtained in these measurements were more nearly correct than the higher ones obtained by Bommer and Hohmann.[15]

Preparation of Americium Metal

Americium trifluoride was precipitated from acid solution with aqueous HF. This product was transferred to the platinum fluorination line (Fig. 2) and treated with a 50-50 mixture of HF and H_2 for approximately one-half hour at 550°C. After pelleting the resulting AmF_3 (Fig. 3), the reduction to the metal was carried out in the same way, with a few exceptions, as already described for praseodymium metal production.

It was found that the use of TaC crucibles failed to give single pellets of metal; therefore, the beryllia system shown in Fig. 14 was used. Barium metal was employed as a reducing agent instead of lithium. The initial temperature at which reduction occurred was 1300°C. When a Ba mirror began to form on the inner surface of the glass bulb (Fig. 5), the temperature was reduced to 1125°C. and maintained at that level for one and one-half minutes.

This method produced single pellets of americium metal which were quite malleable and which possessed a gray luster. X-ray investigation of the samples produced failed to give good patterns, because the metal was not annealed sufficiently. Spectrographic analyses were not made on the original metal samples prepared because the pellets were generally very small and it was desirable to use them in their entireties for the calorimeter runs. Therefore, the procedure adopted was to evaporate down a portion of each calorimeter solution after the completion of each run, and this solution was submitted for spectrographic analysis. An equal portion of the 1.50M HCl used as calorimeter solution, also evaporated down, was submitted as a blank. Naturally, this method resulted in a concentration of impurities present. At best, spectrographic analysis is not accurate to more than a factor of two or three, so there was some question as to the exact percentages

of impurities present. The initial samples contained at least 99.0 percent or more americium, with barium and beryllium present as impurities. Other elements were not detected.

Heat of Solution of Americium Metal

The values obtained for the heat of solution of americium metal are given in Table IX.

Table IX

Heat of Solution of Americium Metal in 1.50M HCl at 25°C.

Sple No.	Weight-Mg.	Heat Evolved-Calories	-ΔH (kcal/mol)
1	0.0557	0.0345	146.7*
2	0.3531	0.2347	160.9
3	0.2952	0.1691	138.0**
4	0.1449	0.0961	160.7
5	0.3425	0.2245	158.7
6	0.7806	0.5248	162.6
7	0.4028	0.2721	163.4
8	0.3604	0.2492	167.4
			162.3 ± 2.2
		Omitting Am-8	161.3 ± 1.4

*Sample too small; insufficient heat liberated for reliable calculation

**Sample did not dissolve immediately; apparently trapped in air bubble

Treatment of Data

The value for the heat of solution of americium metal has not been corrected to zero hydrochloric acid concentration. It is to be pointed out, however, that the corrections for Am^{+3} and for H^+ ions are of opposite sign and of nearly equal magnitude; therefore, the correction would be less than the uncertainty in the experimental value.

$$Am + 3H^+ = Am^{+3} + 3/2\ H_2 \quad \Delta H = -161.3 \pm 1.4$$

This value for the heat of reaction, with an estimate of the entropy change for the reaction, makes it possible to calculate the free energy change. It is

assumed that the entropy change for the given reaction is the same as that for the analogous reaction with plutonium

$$Pu + 3H^+ = Pu^{+3} + 3/2\ H_2 \quad \Delta S = 3.8\ \text{e.u.}^{17}$$

Using these data, one calculates

$$\Delta F = \Delta H - T\,\Delta S$$

$$= -161.3 \pm 1.4 - 298.16(3.8)$$

$$= -161.3 \pm 1.4 - 1.1 = -162.4 \pm 1.4\ \text{kcal/mol}$$

$$\text{and } E = -\frac{\Delta F}{nF} = \frac{162.4 \pm 1.4}{3 \times 23.07} = 2.35 \pm 0.02\ \text{v.}$$

III. HEAT OF FORMATION OF Am^{+4} (Aq.)

Eyring[5] has measured the heat of solution of AmO_2 in 6.0M HNO_3 and 0.1M HBF_4 at 25°C. Using the experimental value for this heat, with the value of the heat of formation of Am^{+3}, one can calculate the heat of formation of Am^{+4}. Consider the following reactions:

$$(1)\quad AmO_2 + 4H^+ = Am^{+4} + 2H_2O \qquad \Delta H_1$$

$$(2)\quad Am^{+4} + 1/2\ H_2O = Am^{+3} + 1/4\ O_2 + H^+ \qquad \Delta H_2$$

$$(3)\quad AmO_2 + 3H^+ = Am^{+3} + 1/4\ O_2 + 3/2\ H_2O \qquad \Delta H_3$$

Reaction (1) represents the solution of AmO_2 in acid to give Am^{+4}, whereas reaction (2) shows the reduction of Am^{+4} to Am^{+3}. The sum of the reactions, reaction (3), indicates the overall reaction which is physically observed when AmO_2 dissolves in acid solution; therefore, ΔH_3 is the heat calculated from the experimental data reported by Eyring.[5]

Because Am^{+4} does not exist in aqueous solutions, making it impossible to actually measure ΔH_1, it was decided to obtain this value by considering reactions analogous to those listed above for U, Np, and Pu. The heats of formation for the pertinent compounds and ions of these elements are available.[18,19,20,21] Using these data, one can calculate the heats of reaction for reactions of the type

$$MO_2 + 4H^+ = M^{+4} + 2H_2O$$

where M represents U, Np, or Pu. If one plots these heats of reaction against the corresponding ionic radii for the plus four ions, a short extrapolation gives a value for ΔH_1 above. These heats are also small, being of the order of twelve to fourteen kilocalories, so a small error in extrapolation would not be too significant.

An extrapolation of these values to americium gave a value of $\Delta H_1 = -15.5$ kcal per mol of AmO_2. ΔH_3 had been measured as -30.4 kcal/mol by Eyring.[5] Therefore,

$$\Delta H_2 = \Delta H_3 - \Delta H_1$$
$$= -30.4 + 15.5 = -14.9 \text{ kcal/mol.}$$

The heat of formation of Am^{+3} has been found to be -161.3 kcal/mol in the present investigation. The heat of formation of 1/2 H_2O is -34.16 kcal/mol.[22] From reaction (2) above

$$\Delta H_2 = -161.3 - \Delta H_f(Am^{+4}) + 34.16 = -14.9$$
$$\Delta H_f(Am^{+4}) = -161.3 + 34.16 + 14.9 = -112.2 \text{ kcal/mol.}$$

It is now possible to calculate the heat of reaction for

$$(4) \quad Am^{+3} + H^+ = Am^{+4} + 1/2\ H_2 \qquad \Delta H_4$$
$$\Delta H_4 = -112.2 + 161.3 = 49.1 \text{ kcal/mol.}$$

It was assumed that ΔS_{298} for reaction (4) was the same as for the reaction with plutonium

$$Pu^{+3} + H^+ = Pu^{+4} + 1/2\ H_2 \qquad \Delta S_{298} = -32.4 \text{ e.u.}^5$$
$$\Delta F_4 = \Delta H_4 - T\Delta S_4$$
$$= 49.1 + 298.16(32.4) = 58.8 \text{ kcal/mol.}$$
$$E_4 = -\frac{\Delta F_4}{nF} = -\frac{58.8}{23.07} = -2.55 \text{ v.}$$

This value is in close agreement with the value of -2.6 v. estimated by Eyring[5] for the Am^{+3}-Am^{+4} potential.

IV. HEAT OF FORMATION OF AmO_2^+

It had been observed[23] that addition of 0.1M Na_2SO_3 to Pu(VI) in 35% K_2CO_3 solution resulted in the precipitation of a gray compound which was identified spectrophotometrically and by x-ray analysis as $K_2Pu_2O_6 \cdot xH_2O$. The compound $Na_2Pu_2O_6 \cdot xH_2O$ had also been prepared by adding NaOH to a Pu(VI) nitrate solution and allowing the latter to stand for a prolonged period of time.

Werner and Perlman[3] investigated the preparation of the analogous compound of americium as a method for a rapid separation of americium and curium. They found that addition of 1% NaOCl to a 30% solution of K_2CO_3 containing Am^{+3} at about 80°C. resulted in the precipitation of a gray compound. Werner[24] carried out a reduction experiment by titrating the supposed Am(V) with Fe^{+2} ion. In an initial reduction he calculated that one equivalent of Fe^{+2} ion had reduced 1.5 equivalents of americium. Later experiments increased this to 1.9 equivalents of americium per equivalent of Fe^{+2} ion. This evidence indicated that the americium initially had been in the five state. The compound was assumed to be $K_2Am_2O_6 \cdot xH_2O$, analogous to $K_2Pu_2O_6 \cdot xH_2O$.

Preparation of $Na_2Am_2O_6 \cdot xH_2O$

The oxidation of Am^{+3} was carried out as described above by addition of 1% NaOCl to a 30% solution of Na_2CO_3 containing the Am^{+3}. After about a half an hour at 80°C., a gray precipitate began forming. When the precipitate had settled, it was washed several times with 0.01M NaOH and dried at reduced pressure.

The resulting compound was loaded directly into glass calorimeter bulbs for heat of solution measurements. The samples were not weighed, but the amount of americium was determined after completion of the runs by assaying aliquots of the calorimeter solutions in a low-geometry alpha counter. The value 3.61×10^6 counts per minute per microgram at 52% geometry was used as the specific activity[28] of Am^{241}.

Heat of Reaction of $Na_2Am_2O_6 \cdot xH_2O$

The purpose of the present investigation was to determine the heats of the following reactions:

(1) $Na_2Am_2O_6 \cdot xH_2O + 4H^+ = 2Na^+ + 2AmO_2^+ + (x+2)H_2O$ ΔH_1

(2) $AmO_2^+ + 4H^+ + 2Fe^{+2} = Am^{+3} + 2Fe^{+3} + 2H_2O$ ΔH_2

It was decided to determine the heat of solution of the americium compound in 1.50M $HClO_4$ which would give a value for ΔH_1. A subsequent measurement of the heat of reaction of $Na_2Am_2O_6 \cdot xH_2O$ in 1.50M $HClO_4$ containing 0.01M $Fe(ClO_4)_2 \cdot 6H_2O$ would give a value of $\Delta H_1 + 2\Delta H_2$. With these data, it would be possible to calculate the heat of formation of AmO_2^+.

Table 10 lists the values obtained for the heat of reaction of the americium compound with Fe^{+2} ion:

Table X

Heat of Reaction of $Na_2Am_2O_6 \cdot xH_2O$ With 0.01M $Fe(ClO_4)_2$ in 1.50M $HClO_4$ at 25°C.

Sple No.	Weight Am--Mg.	Heat Evolved-Calories	-ΔH (kcal/mol)
1	0.5688	0.0444	18.9
2	0.5355	0.0359	16.3
			17.6 ± 1.3

Treatment of Data

If one considers reactions of the type

(3) $Mo_2^+ + 2H^+ + H_2 = M^{+3} + 2H_2O$ ΔH_3

for U, Np, and Pu,[18,19,20] it can be seen that the corresponding reaction for Am would have an estimated ΔH_3 of about -78 kcal/mol. Using this information with the heats of formation of Fe^{+2} and Fe^{+3} ions,[22] the reaction

(2) $AmO_2^+ + 4H^+ + 2Fe^{+2} = Am^{+3} + 2Fe^{+3} + 2H_2O$ ΔH_2

would have a calculated heat of reaction of about -58 kcal/mol. Therefore, it is

likely from the experimental value of -17.6 kcal/mol that either the proposed mechanism given for the reaction of $Na_2Am_2O_6 \cdot xH_2O$ in acid solution is in error or the compound measured was not all in the five state initially.

An experiment was therefore carried out to determine the ratio of the weight of americium in the prepared compound to the weight of the compound. This information possibly would give an indication of the formula of the prepared material. Two separate oxidations of Am^{+3} were carried out and one sample of each preparation was weighed on the Kirk-Craig-Gullberg microbalance[10] in a small glass cone. This material was then dissolved in acid and an aliquot was counted in the low geometry alpha counter to determine the amount of americium present in the sample. The data obtained are given in Table XI.

Table XI

Results of Weight-Assay Experiment

Sple No.	Sple Weight-Mg.	Weight Am-Mg.	(Wt.Am)/(Wt.Sple)	$2Am/Na_2Am_2O_6$
1	0.0206	0.0157	0.76	0.77
2	0.0481	0.0348	0.72	0.77

This information is not of much value, however, although it does indicate that if the compound were indeed $Na_2Am_2O_6 \cdot xH_2O$, x is probably not greater than two. It is more reasonable to expect that, at the most, only part of the material was in the five state and that the remaining americium had been reduced to the three state before the calorimeter run was made. For example, if a basic carbonate such as $Am(OH)CO_3$ were present, the heat evolved would be much less than the theoretical value expected from reactions (1) and (2) above. Also, it is of interest to note that the ratio $Am/Am(OH)CO_3$ is 0.76.

Since there is a great deal of doubt as to just what the reason is for the apparent discrepancy in the heat of reaction of the five state, it is impossible

to give an experimental value for the heat of formation of AmO_2^{+} at this time.

V. HEAT OF FORMATION OF AmO_2^{++} (Aq.)

The existence of the plus six state of americium has recently been discovered at Los Alamos by Asprey, Stephanou, and Penneman.[4] They found that addition of $(NH_4)_2S_2O_8$ to an acid solution (0.1M H^+) of Am^{+3} at about 80°C. results in the slow appearance of a dark rum-colored solution of AmO_2^{++}, identified by spectrophotometric analysis.

The compound, $NaAmO_2(C_2H_3O_2)_3$, has also been prepared and has been shown to be isomorphous with $NaPuO_2(C_2H_3O_2)_3$ by crystallographic analysis.[4]

Preparation of $NaAmO_2(C_2H_3O_2)_3$

Sodium americyl acetate was chosen as the starting compound for investigation of the heat of formation of AmO_2^{++}. Am^{+3} was oxidized to the six state at 80°C. as described above and the resulting solution was made 0.6M in $HC_2H_3O_2$, 0.2M in $NaC_2H_3O_2$ and 5.0M in $NaNO_3$. This method of preparation is the same as that used in the preparation of $NaPuO_2(C_2H_3O_2)_3$.[23] After waiting for 1-1/2 hours, the white precipitate was centrifuged and washed several times with water, after which time it was dried at reduced pressure and loaded into a glass calorimeter bulb. The weight of americium was determined later by assay of the calorimeter solution, using a low geometry alpha counter.

The precipitate obtained appeared to be only very slightly soluble in the water used for washing. The analogous plutonium compound is reported to be soluble to the extent of 10 grams per liter of water at 25°C.[23]

Heat of Reaction of $NaAmO_2(C_2H_3O_2)_3$

The following reactions are of interest in the determination of the heat of formation of AmO_2^{++}:

(1) $NaAmO_2(C_2H_3O_2)_3 = Na^+ + AmO_2^{++} + 3C_2H_3O_2^-$ ΔH_1

(2) $AmO_2^{++} + 3Fe^{+2} + 4H^+ = Am^{+3} + 3Fe^{+3} + 2H_2O$ ΔH_2

It was decided to measure the heat of solution of $NaPuO_2(C_2H_3O_2)_3$ in 0.15M $HClO_4$ and use this observed heat as the value for ΔH_1 above. A measurement of the heat of reaction of $NaAmO_2(C_2H_3O_2)_3$ in 0.15M $HClO_4$ and 0.01M $Fe(ClO_4)_2 \cdot 6H_2O$ would give an experimental value for $\Delta H_1 + \Delta H_2$. These data would permit the subsequent calculation of the heat of formation of AmO_2^{++}.

Unfortunately, however, it was found that only an insignificant amount of heat was liberated when the supposed $NaAmO_2(C_2H_3O_2)_3$ dissolved in the calorimeter.

X-ray analysis of a sample of the material prepared showed that it was not isomorphous with $NaPuO_2(C_2H_3O_2)_3$ as the Am(VI) compound is reported to be.[4] This information, together with the fact that no heat was evolved upon solution of the sample, is evidence that the prepared compound was not $NaAmO_2(C_2H_3O_2)_3$.

Further investigations are being carried out in the laboratory in order to determine successfully the heat of formation of AmO_2^{++}.

VI. DISCUSSION

Summary of the Thermodynamic Properties of the Aqueous Americium Ions

	ΔH_{298}	ΔS_{298}*	ΔF_{298}	E
$Am + 3H^+ = Am^{+3} + 3/2\ H_2$	-161.3	3.8	-162.4	2.35
$Am + 4H^+ = Am^{+4} + 2H_2$	-112.2	-28.2	-103.8	1.12
$Am^{+3} + H^+ = Am^{+4} + 1/2\ H_2$	49.1	-32.4	58.8	-2.55

*ΔS_{298} taken as same as for analogous reactions for Pu[17,5].

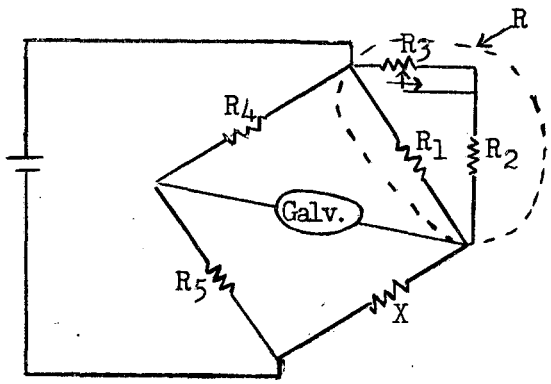
ΔF and ΔH values are in kcal/mol, ΔS values are in calories per degree and E values are in volts.

The values given above for the thermodynamic properties of the aqueous americium ions depend upon the value for the heat of formation of Am^{+3}. It is of interest to note that the heat of formation of Pu^{+3} is given as -141.9 kcal/mol.[20]

Measurements of the heats of vaporization of plutonium and americium metals[25,26,27] indicate that the value for americium is from twenty to thirty kcal/mol more negative than that for plutonium. The results found in the present investigation appear consistent with these measurements.

VII. APPENDICES

Appendix A
Proof That $\Delta\theta/t$ is Almost a Linear Function of $\bar{\theta}$



R_1 = 1000 ohm resistance
R_2 = 33,300 ohm resistance
R_3 = decade resistance box (0-9999 ohms)
X = resistance thermometer (calorimeter) unprimed resistances are initial resistances; primed resistances are new resistances corresponding to change ΔX in X
$\theta = 1/(R_2 + R_3)$
q = average rate of energy input
t = time
$\bar{\theta} = 1/2\ (\theta + \theta')$
$\Delta\theta = \theta - \theta'$

(1) $R_4/R_5 = R/X = R'/X' = \text{constant} = k$

(2) $R = kX$

(3) $R' = kX'$

(4) $1/R = 1/R_1 + 1/(R_2 + R_3) = 1/R_1 + \theta$

(5) $1/R' = 1/R_1 + 1/(R_2 + R_3') = 1/R_1 + \theta'$

Subtracting Equation (5) from Equation (4)

(6) $1/R - 1/R' = \theta - \theta' = \Delta\theta = 1/(kX) - 1/(kX') = (R' - R)/(RR')$

Assume the change in resistance of resistance thermometer is proportional to the input of energy. Then

(7) $X' - X = \Delta X = bqt$ where b is constant of proportionality

From Equations (2) and (3)

(8) $(R' - R)/(RR') = (X' - X)/(kXX')$

Combining this result with Equations (6) and (7)

$\Delta\theta = (R' - R)/(RR') = (X' - X)/(kXX') = (bqt)/(kXX')$

(9) $\Delta\theta/t = (bq)/(kXX')$

Adding Equations (4) and (5) and utilizing Equations (2) and (3)

(10) $1/R + 1/R' = 2/R_1 + \theta + \theta' = 2/R_1 + 2\bar{\theta} = (R + R')/(RR') = (R + R')/(k^2XX')$

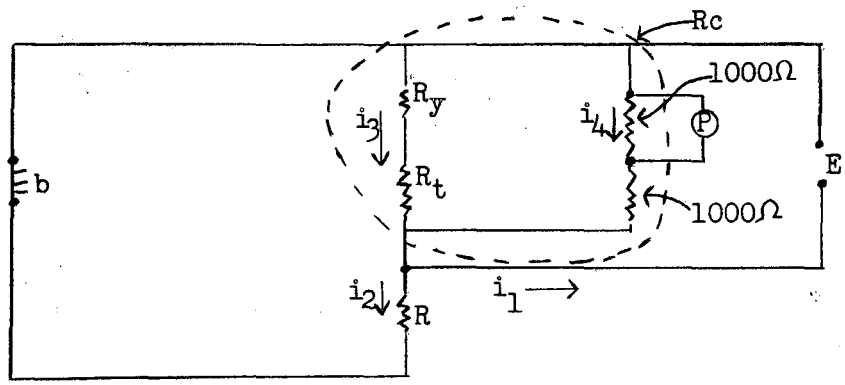
(11) $\Delta\theta/t = (2bqk)(1/R_1 + \bar{\theta})/(R + R')$ (by combining Equations (9) and (10))

It can be seen from Equation (11) that a plot of $\Delta\theta/t$ vs. $\bar{\theta}$ should give a straight line, because all the other values in the equation are constants except R and R'. However, over the entire range of the resistance decade box (0-9999 ohms), the maximum change the quantity $1/(R + R')$ can experience is between the limits 5.1502×10^{-4} ohm^{-1} and 5.1328×10^{-4} ohm^{-1}, or a percentage change of only 0.34%. In practice, the range of the resistance decade box employed in a run is not over 2500 ohms; therefore, the actual deviation from linearity is smaller by a factor of at least four.

Appendix B

Sample Calculation of Energy Equivalent of Microcalorimeter

(Energy Input No. IV, Mg Metal Run No. 1 in 1.0M HCl at 25°C.)



E_b' = 1.42012 v. (Measured value of potential across resistance bridge)

E' = 0.90957 v. (Measured value of potential across resistance thermometer)

$E_b = 2.00188^{*}E_b'$ = 2.84291 v. (True potential across resistance bridge)

$E = 1.99882^{*}E'$ = 1.81807 v. (True potential across resistance thermometer)

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*Conversion factors to convert measured potentials to true potentials. Potentials are measured across potential dividers.

$\Delta E = E_b - E = 1.02484$ v.

$E^2 = 3.30538$ v.

$R_o = 2010$ ohms (Setting of decade resistance box during energy input)

$R = (33{,}300 + R_o)(10^3)/(34{,}300 + R_o) = 972.46$ ohms

$i_2 = \Delta E/R = 0.001054$ amp.

$i_1 = B_2/R9$ (See circuit diagram, Fig. 8) $= 0.034135$ amp. (constant for all runs)

$i = i_1 + i_2 = 0.035189$ amp.

Total $p = Ei = 0.063976$ watt

$p_4 = E^2/2000 = 0.001653$ watt

$p_{t+y} = p - p_4 = 0.062323$ watt

$p/E^2 = 1/R_c = 0.0193551$ ohm^{-1}

$1/(R_y + R_t) = 1/R_c - 1/2000 = 0.0188551$ ohm^{-1}

$R_t + R_y = 53.036$ ohms

R_y = Resistance of manganin leads (See C, Fig. 9) plus one-half resistance of loose ends of calorimeter windings (assumed that one-half of power generated in loose ends does no useful heating) $= 1.944$ ohms

R_t = Resistance of calorimeter $= 51.092$ ohms

$p_t = (p_{t+y})(R_t)/(R_t + R_y) = 0.060039$ watt

$p_t - 0.00038^{**} = 0.059659$ watt $= 0.8557$ calorie/minute (Energy equivalent of calorimeter)

**Correction for thermometric current.

VIII. ACKNOWLEDGMENTS

Appreciation is offered to those who assisted the author in the performance of this research. Mrs. Winifred Heppler was instrumental in preparing the lanthanum and praseodymium metal samples used in the heat of solution measurements; she also assisted in other operations involved in carrying out this work. Dr. David H. Templeton, Carol Dauben, and Lee Jackson performed the x-ray diffraction work; spectrographic analyses were carried out by John Conway and Milton Moore. The group operating under Professor Leo Brewer was responsible for preparing the TaC crucibles used in metal production. Herman P. Robinson offered helpful advice and assistance in the solution of various electronic problems connected with the microcalorimeter. The Health Chemistry group aided in the handling of radioactive materials.

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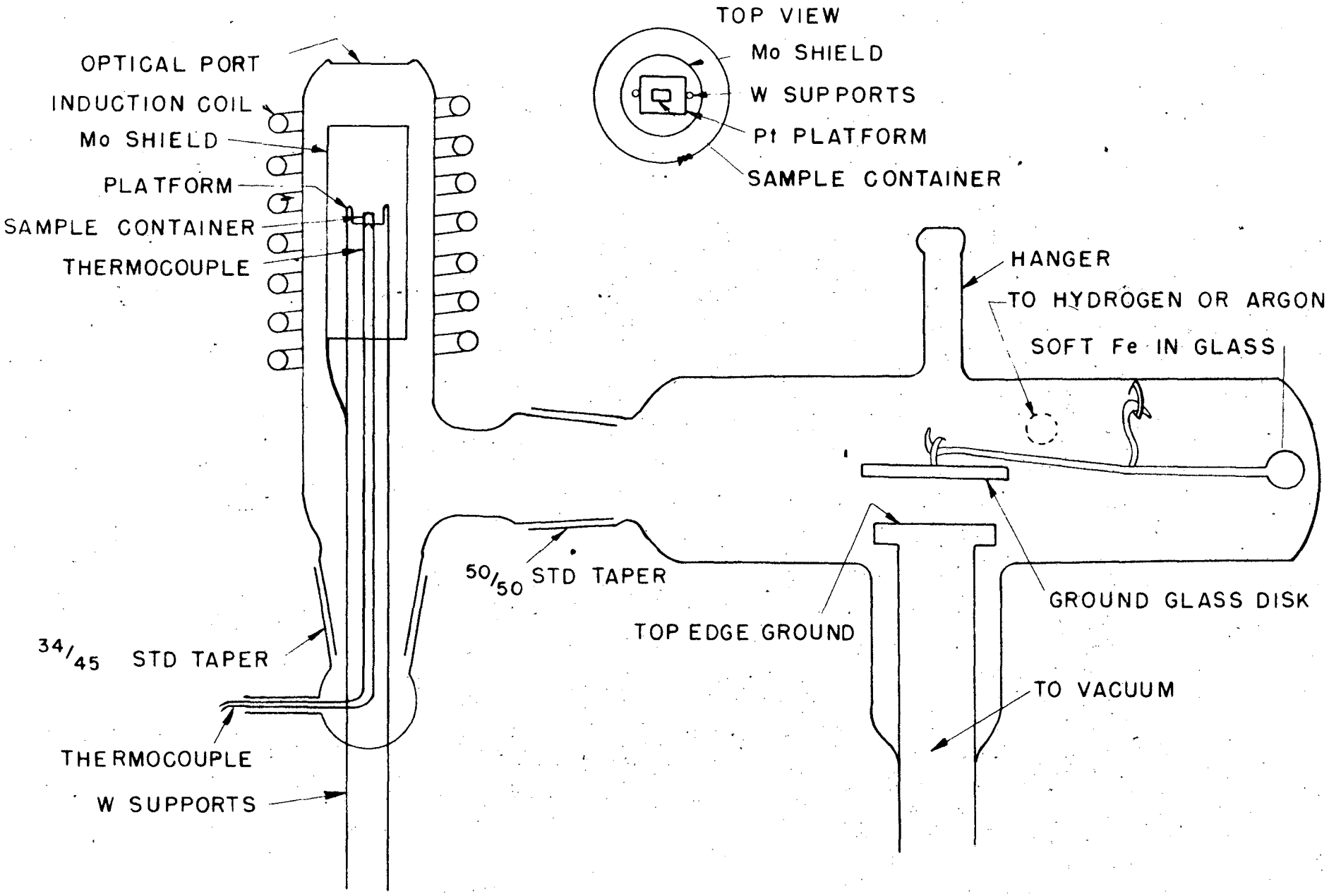


FIG. 1

HYDROGEN REDUCTION APPARATUS

13636-1

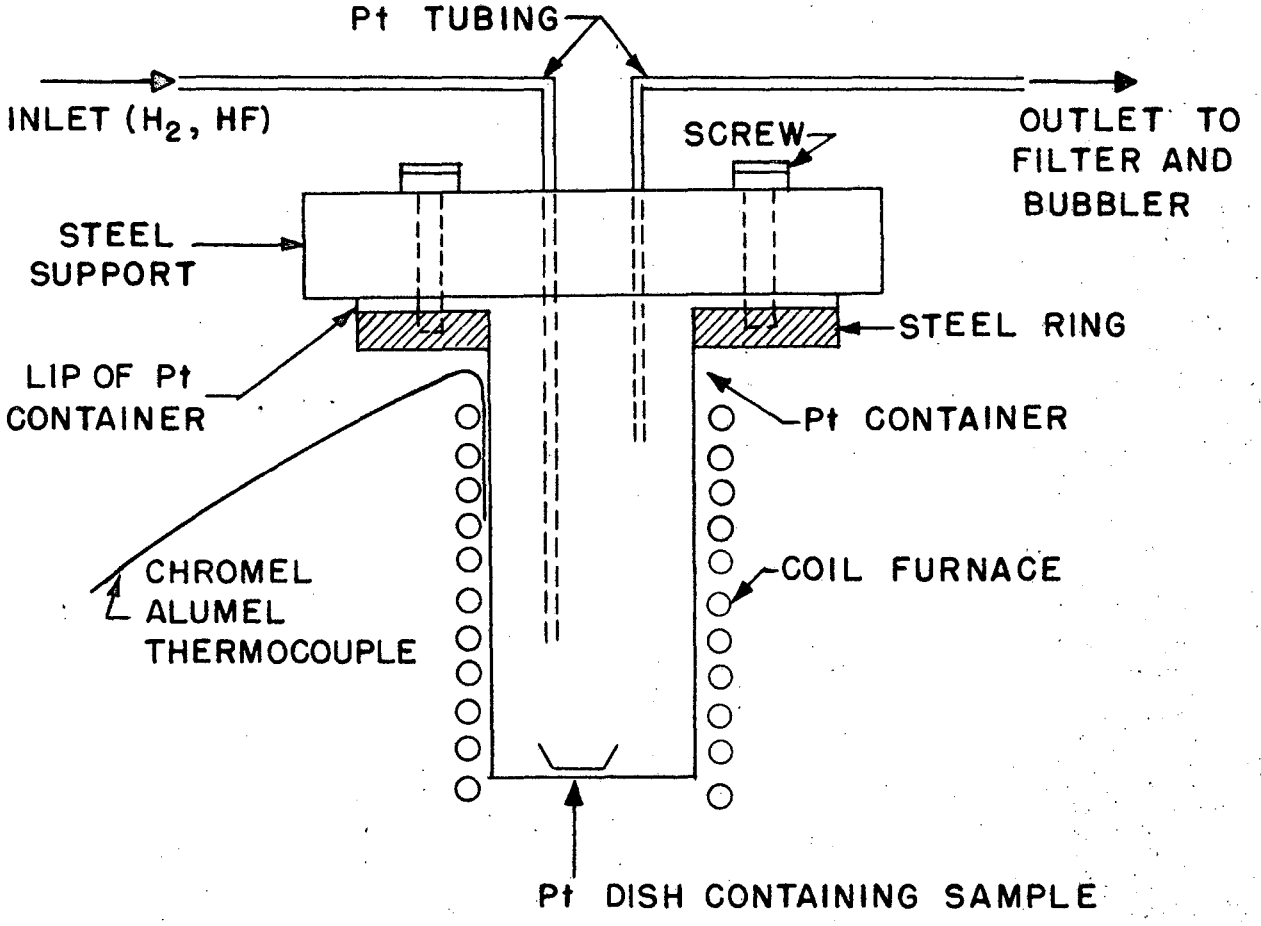


FIG. 2

FLUORINATION APPARATUS

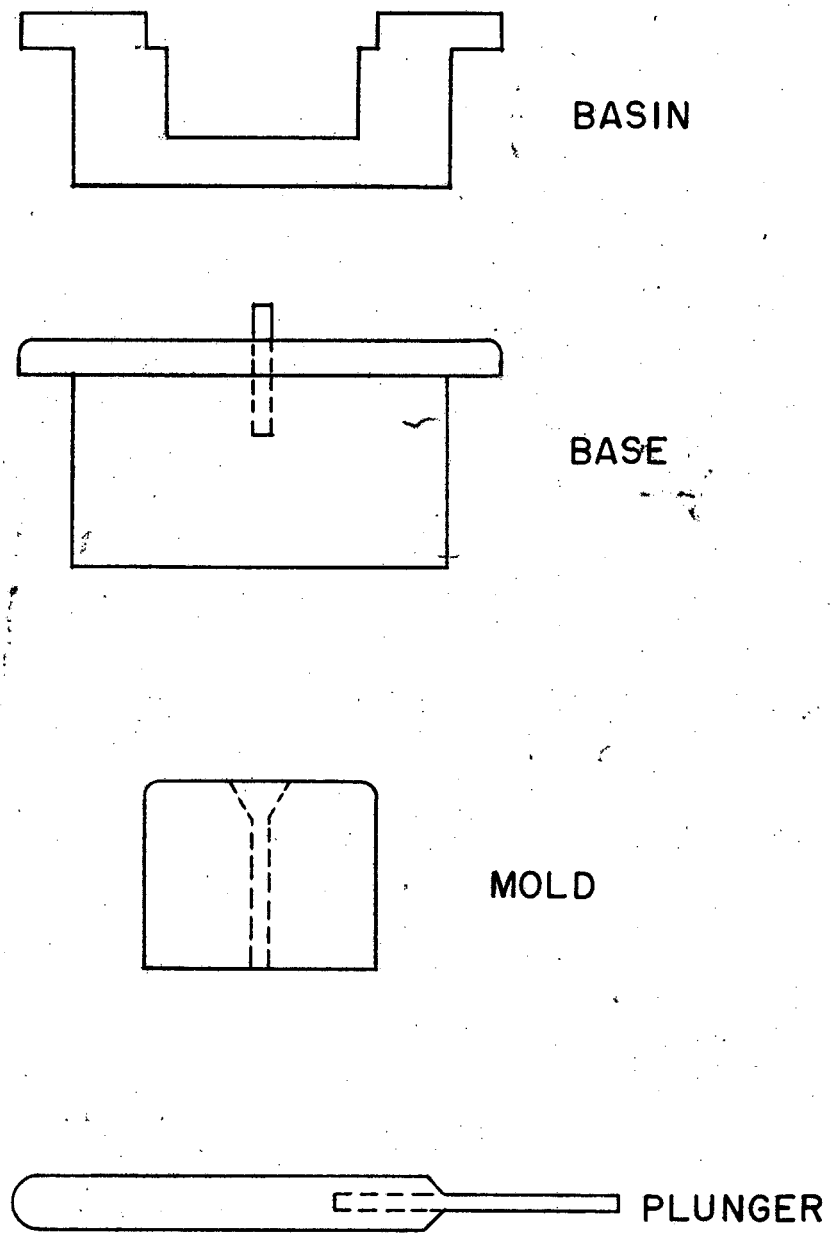


FIG. 3
PELLET PRESS

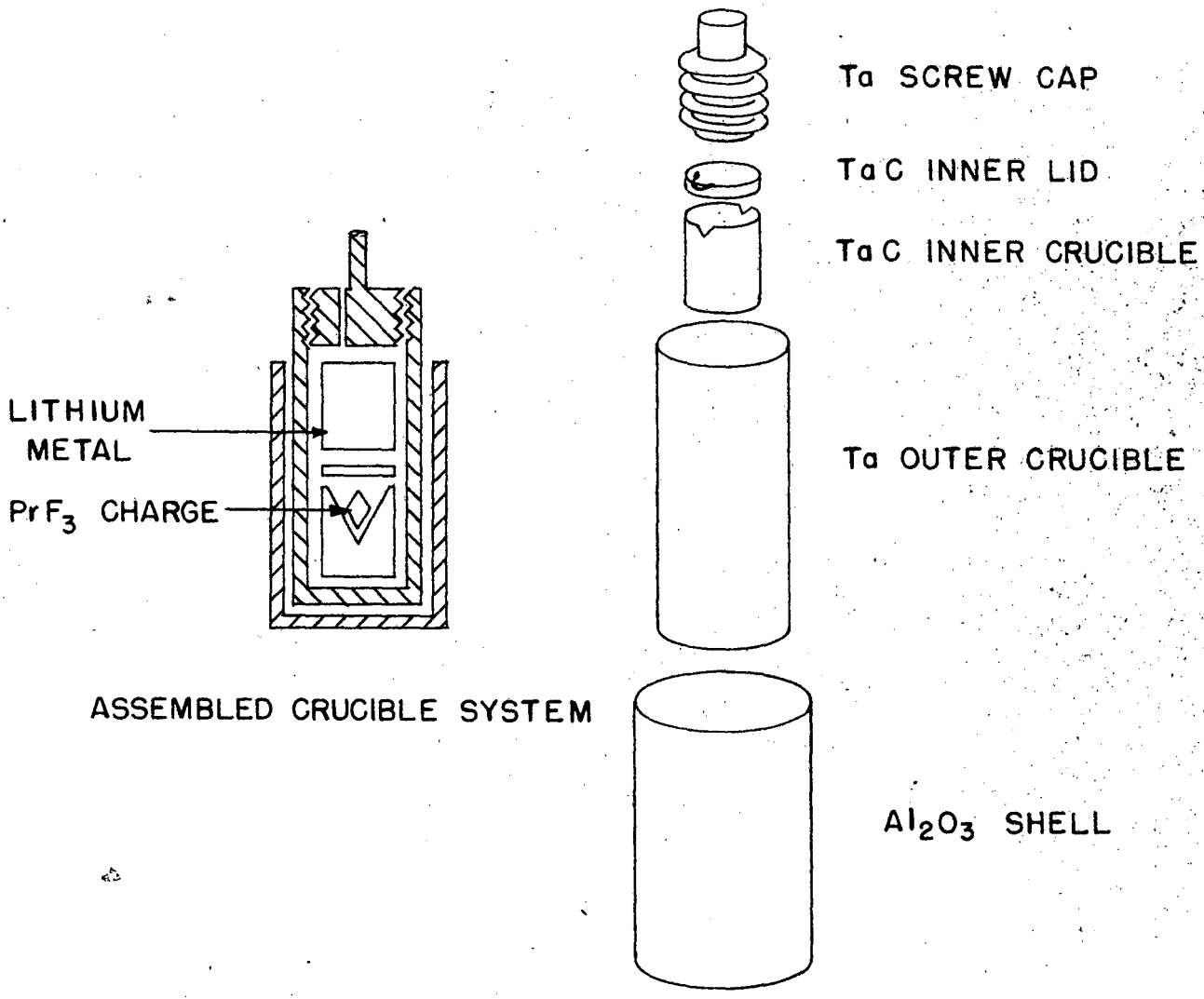


FIG. 4
TaC CRUCIBLE SYSTEM

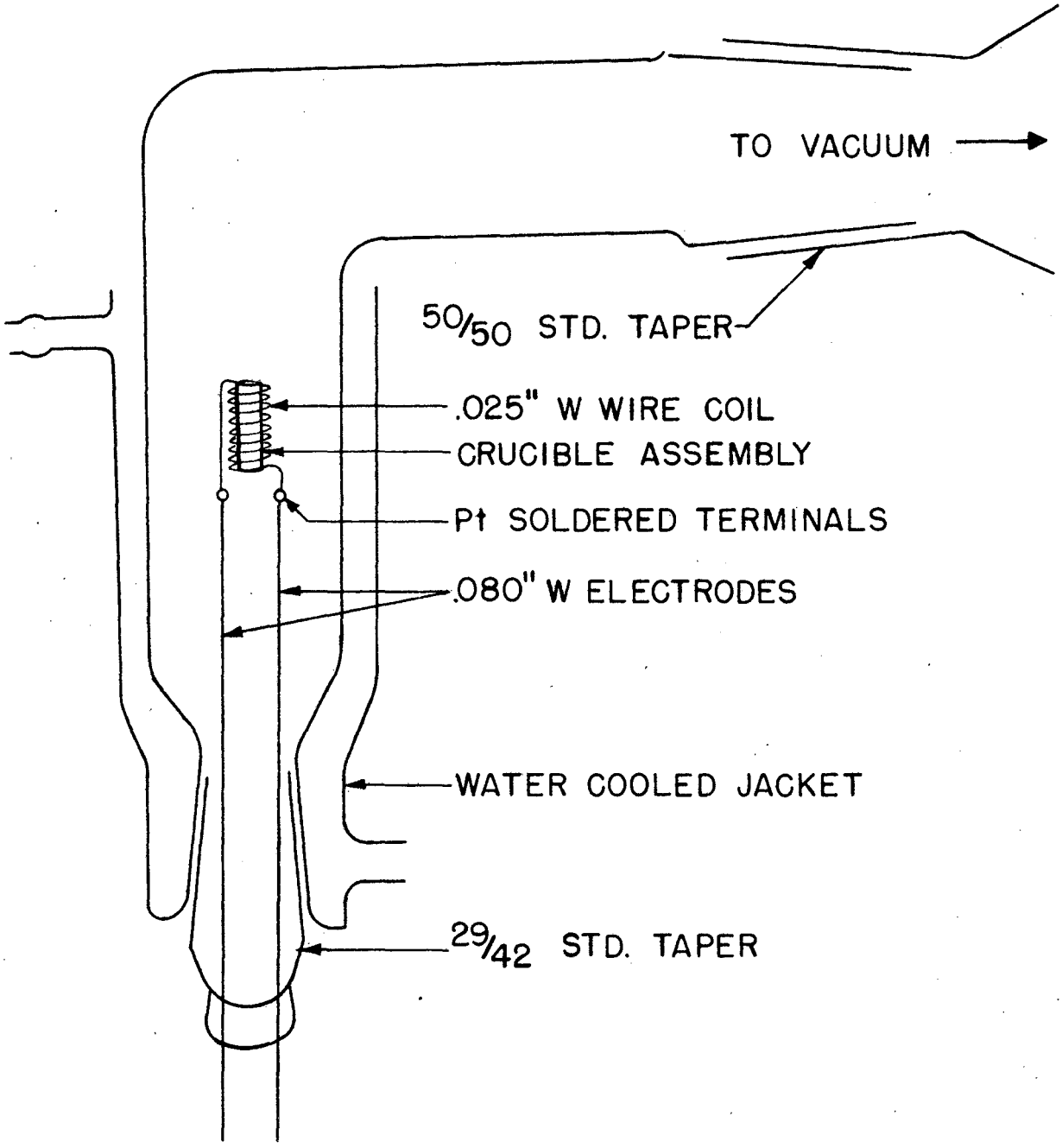


FIG. 5

TUNGSTEN COIL FURNACE ASSEMBLY

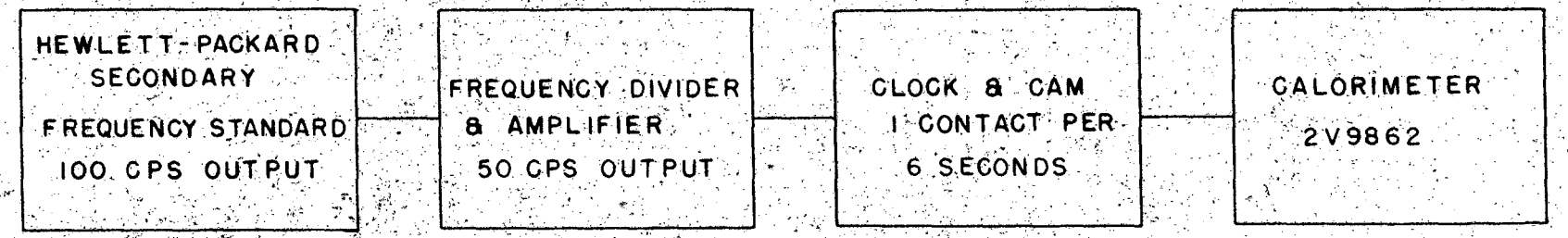


FIG. 6

MICROCALORIMETER
TIME STANDARD
BLOCK SCHEMATIC

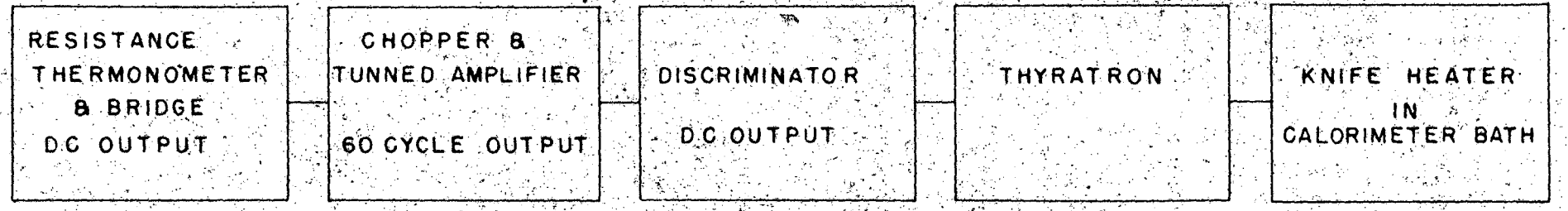


FIG. 7

MICROCALORIMETER
TEMPERATURE CONTROL
BLOCK SCHEMATIC

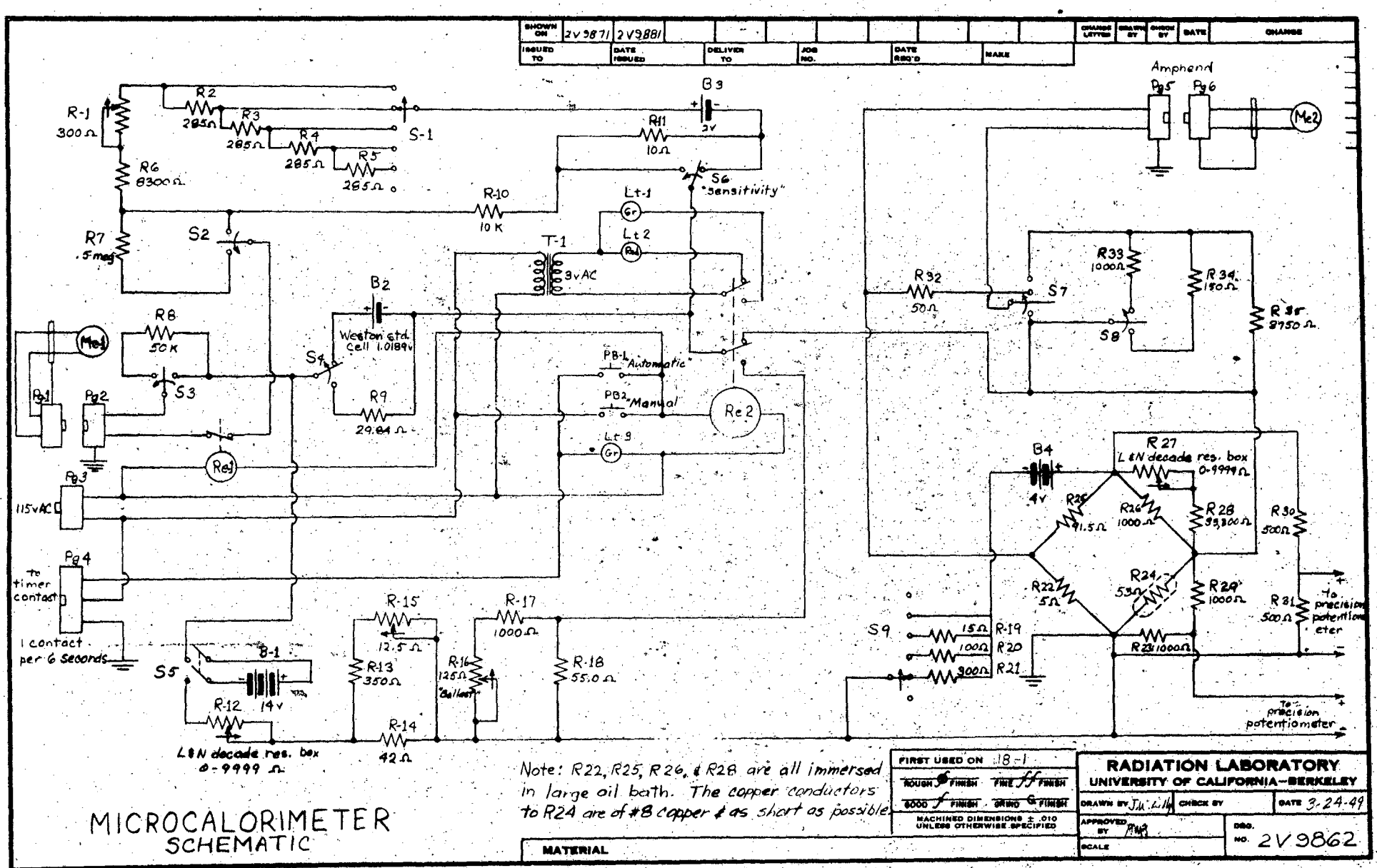
Microcalorimeter Parts List for Figure 8

Designation	Quantity	Specifications
R-1	1	300 ohms, 25 watts, W.W. potentiometer
R2,R3,R4,R5	4	285 ohms, consisting of 400 ohms, 10 watts, W.W. in parallel with 1000 ohms, 10 watts, W.W.
R6	1	8300 ohms, W.W.
R7	1	.5 megohms manganin
R8	1	50,000 ohms manganin
R9	1	29.84 ohms (IRC precision manganin, non-inductively wound on ceramic core, immersed in oil bath) "standard resistor"
R-10	1	10,000 ohms manganin
R-11	1	10 ohms manganin
R-12, R27	2	0-9999 ohms, L & N decade resistance box
R-13	1	350 ohms manganin
R-14	1	42 ohms manganin
R-15	1	12.5 ohm potentiometer, W.W.
R-16	1	125 ohm potentiometer, W.W.
R-17,R23,R26,R29 R33	5	1000 ohms manganin (R26 immersed in oil bath)
R-18	1	55.0 ohms manganin (immersed in oil bath)
R-19	1	15 ohms, manganin
R20	1	100 ohms manganin
R21	1	300 ohms manganin
R22	1	5 ohms manganin (immersed in oil bath) ~53 ohms at 25°C, copper resistance thermometer, non-inductively wound with manganin leads
R25	1	91.5 ohms, manganin (immersed in oil bath)
R28	1	33,300 ohms manganin (immersed in oil bath)
R30,R31	2	500 ohms manganin
R32	1	50 ohms copper damping resistor
R34	1	150 ohms manganin
R35	1	3750 ohms manganin

Note: All manganin resistors are IRC type WW-4 or equivalent. Some values are made by paralleling two or more resistors.

Microcalorimeter Parts List for Figure 8

Designation	Quantity	Specifications
B-1	1	14 volts: 7 heavy duty lead storage cells
B2	1	1.0189 volts: Weston standard cell
B3	1	2 volts: lead storage cell
B4	1	4 volts: 2 lead storage cells
PB-1,PB2	2	Push-button contacts, normally open
Lt-1	1	6 volt pilot light, green
Lt2	1	6 volts pilot light, red
Lt3	1	110 volt pilot light, green
Re-1	1	SPST relay, 115 volts a.c., normally closed
RE2	1	DPDT impulse relay Advance type 904A, 115 volts a.c., silver contacts
Me-1	1	Rubicon galvanometer, .006 μa/mm 368 ohm coil, cal. 3402 HH
Me2	1	Leeds & Northrup high sensitivity galvanometer. Sensitivity .077 μv/mm, C.D.R.X. 28 ohms, coil resistance 21 ohms, period 8.8 seconds
S-1, S9	2	6-position, single circuit tap-switch
S2,S3,S8	3	SPDT copper knife-switch
S4,S6	2	SPDT toggle-switch
S5	1	DPST toggle-switch
S7	1	SPDT copper knife-switch with pole added so that R-32 is connected before remainder of circuit
S10	1	SPST SWITCH
T-1	1	Pri. 115 V a.c., Sec. 6.3 v, 1 amp. C. T.



MICROCALORIMETER SCHEMATIC

Note: R22, R25, R26, & R28 are all immersed in large oil bath. The copper conductors to R24 are of #8 copper & as short as possible.

FIRST USED ON 18-1

ROUGH f FINISH FINE ff FINISH

6000 f FINISH GRIND G FINISH

MACHINED DIMENSIONS ± .010 UNLESS OTHERWISE SPECIFIED

MATERIAL

RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA—BERKELEY

DRAWN BY J.M.L.H. CHECK BY DATE 3-24-49

APPROVED BY E.M.M.

SCALE

DWG. NO. 2V9862

"ALBANENE" REG. U. S. PAT. OFF.

FIG. 8

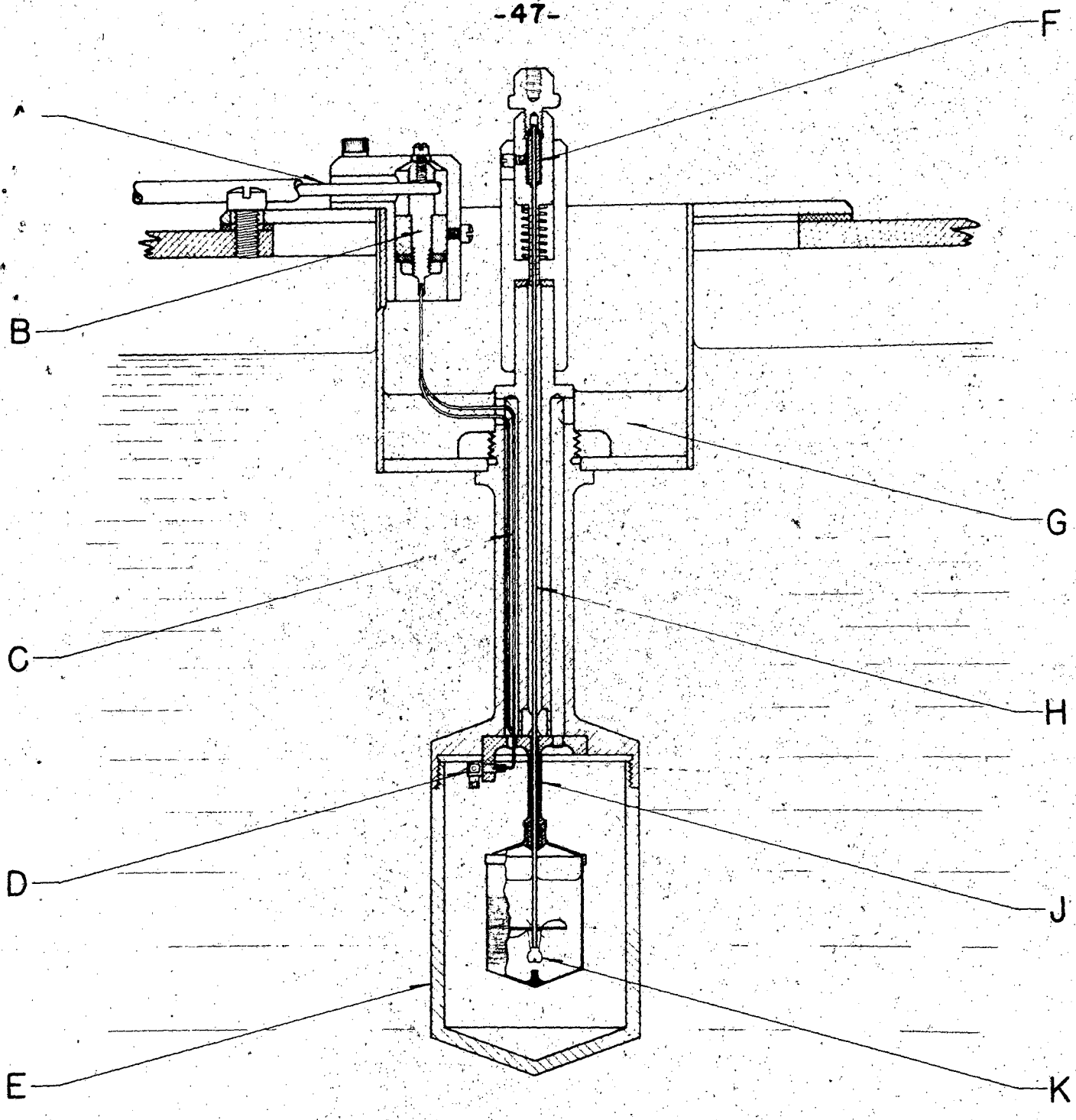


FIG. 9

MICROCALORIMETER CROSS SECTION

A. HEAVY COPPER LEAD
B. COPPER TERMINAL POST
C. MANGANIN LEAD
D. COPPER JACK
E. STAINLESS STEEL SUBMARINE SHELL
F. BAKELITE COLLET
G. PARAFFIN
H. STIRING SHAFT
J. LUCITE HANGER
K. SAMPLE BULB

CM 0 1 2 3 4 5

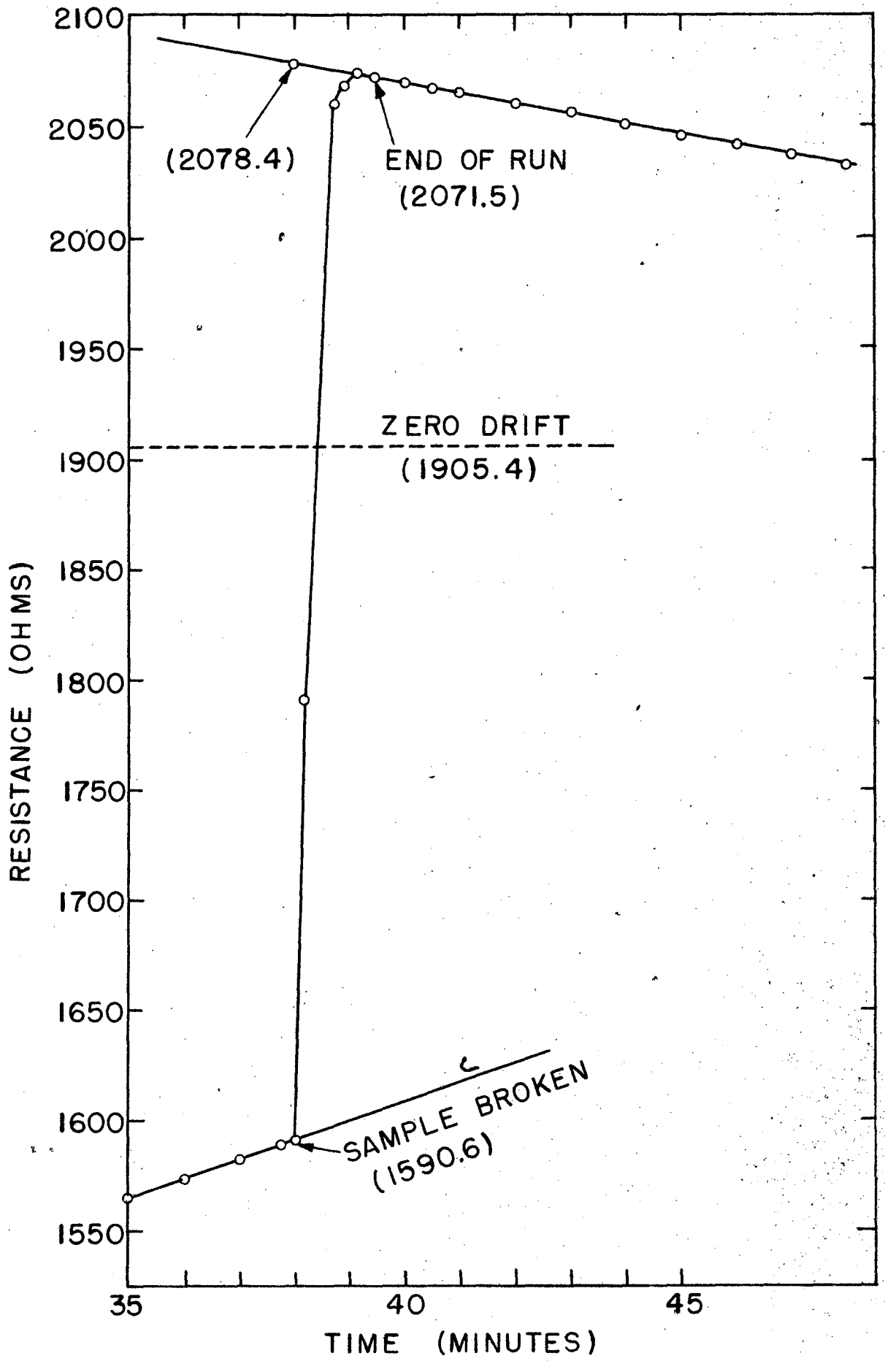


FIG. 10

HEAT OF SOLUTION CURVE, Mg METAL RUN NO. I
1.0 M HCl AT 25° C.

14895-I

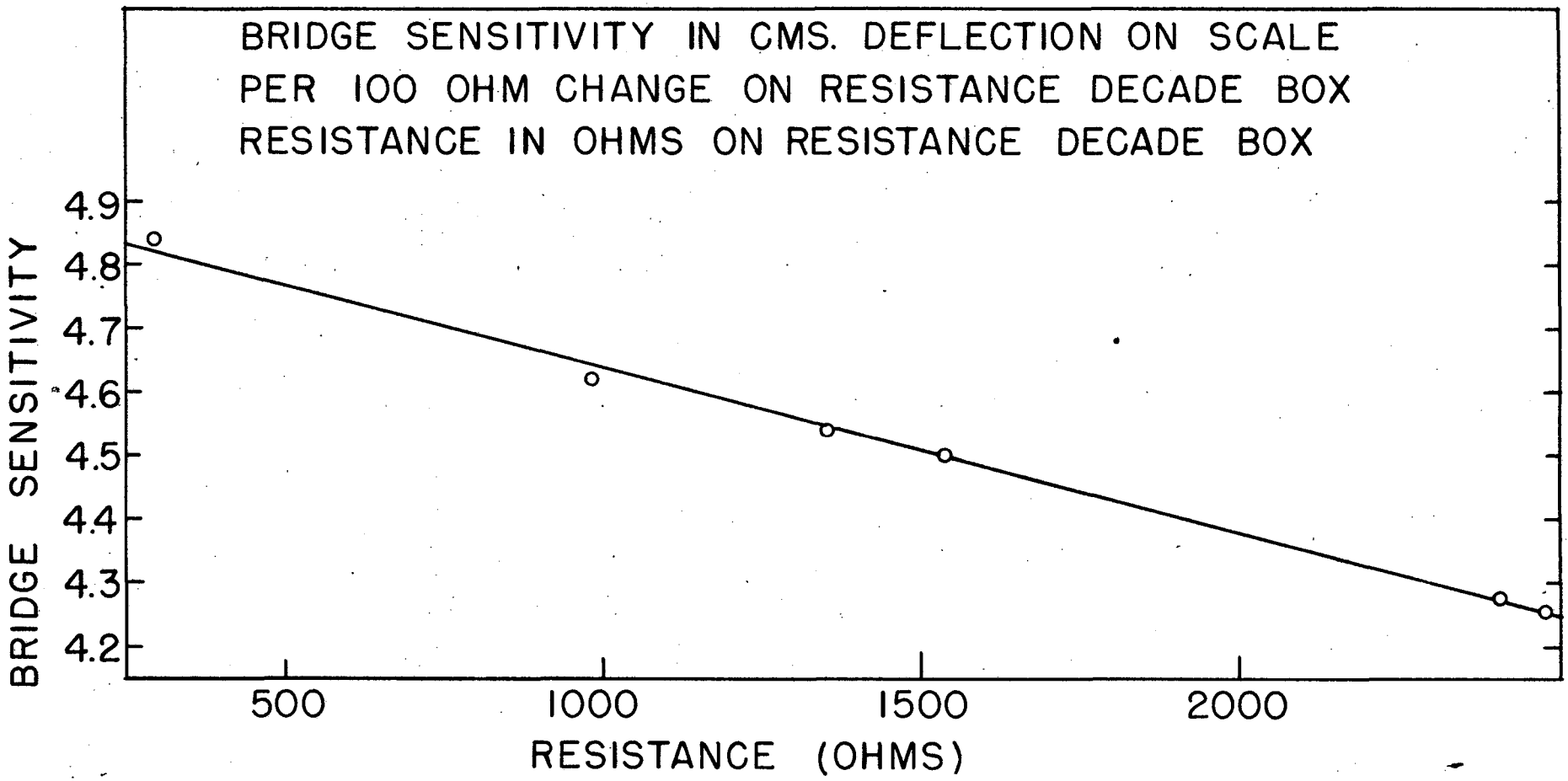


FIG. II

BRIDGE SENSITIVITY VS RESISTANCE

MAGNESIUM METAL RUN NO. I

1.0 M HCl AT 25° C.

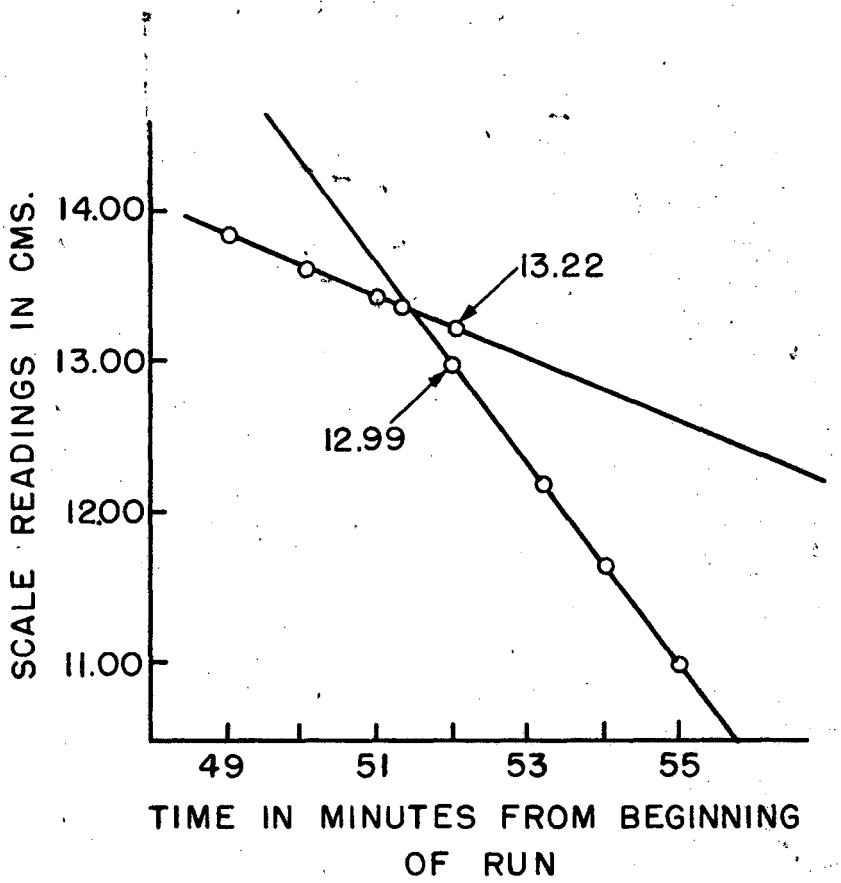


FIG. 12
PLOT OF DATA TAKEN DURING ENERGY INPUT NO. IV, Mg METAL RUN NO. I IN 1.0 M HCl AT 25° C.

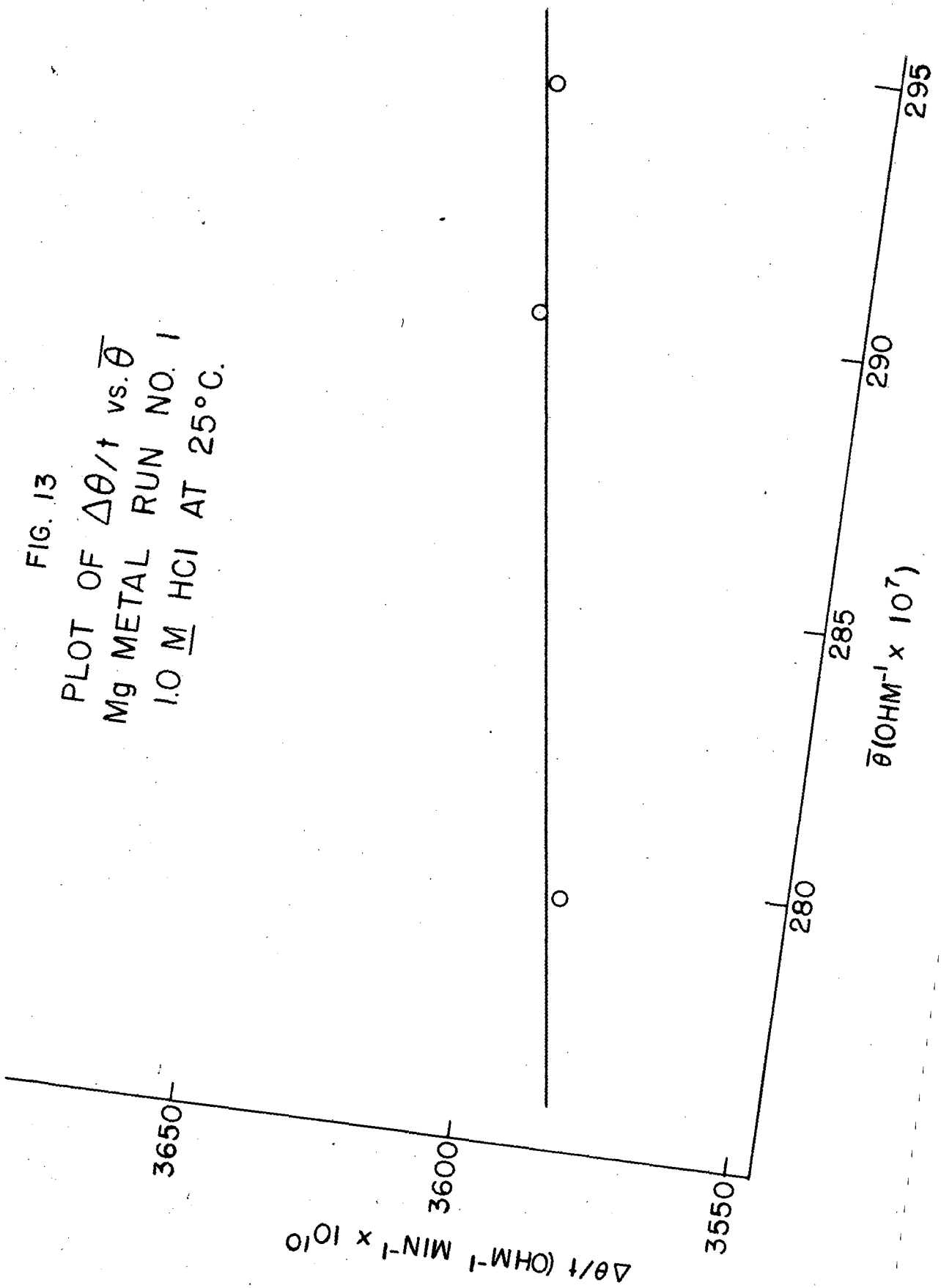


FIG. 13
PLOT OF $\Delta\theta/t$ vs. $\bar{\theta}$
Mg METAL RUN NO. 1
1.0 M HCl AT 25°C.

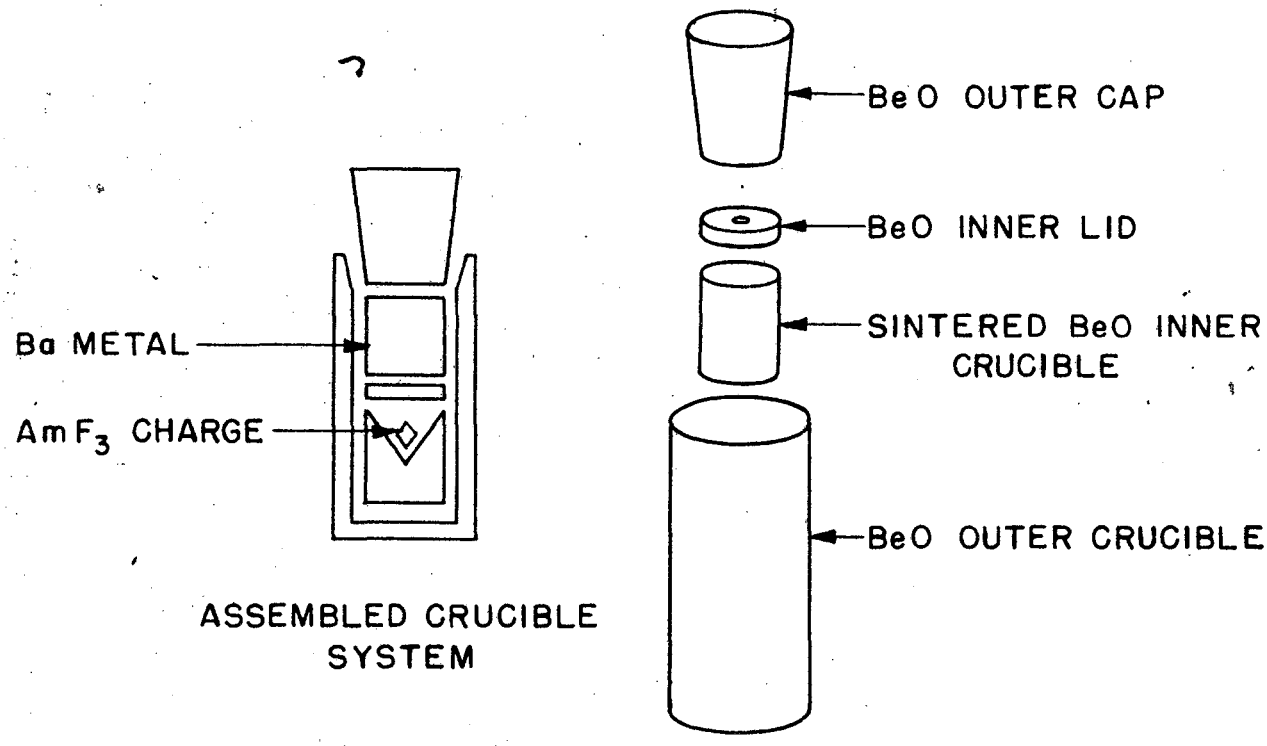


FIG. 14

BeO CRUCIBLE SYSTEM