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THE VAPOR PHASE HYDROLYSIS OF THE TRICHLORIDES OF LANTHANUM, PRASEODYMIUM, SAMARIUM, AND AMERICIUM

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The Vapor Phase Hydrolysis of the Trichlorides of Lanthanum, Praseodymium, Samarium, and Americium

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by

Abraham Broido
B.S. (University of Chicago) 1943

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THE VAPOR PHASE HYDROLYSIS OF THE TRICHLORIDES OF LANTHANUM, PRASEODYMIUM, SAMARIUM, AND AMERICIUM

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ABSTRACT

Equilibrium constants at various temperatures in the range 350°C.-550°C. have been determined for the vapor phase hydrolysis of the trichlorides of lanthanum, praseodymium, samarium, and americium. The reactions were studied by a flow method in which mixtures of HCl and H_2O gases were passed over the solid materials mounted on a cantilever-type quartz fiber microbalance. The progress of the reaction could be determined by observing the weight change in the solid.

From the data obtained and an estimate of the ΔCp of the hydrolysis reactions, values were calculated for the heats and entropies of the reactions. The entropy change in the four hydrolysis reactions was calculated to be $\Delta S_{298}^{\circ} = 36.7$ cal deg^{-1} mol^{-1}. The heats of reaction at 25°C. obtained were as follows: $\Delta H_{La}^{\circ} = 28.5$ kcal mol^{-1}, $\Delta H_{Pr}^{\circ} = 25.5$ kcal mol^{-1}, $\Delta H_{Sm}^{\circ} = 21.9$ kcal mol^{-1}, and $\Delta H_{Am}^{\circ} = 23.0$ kcal mol^{-1}.

In addition, the heat of formation of $LaCl_3$, -254.9 kcal mol^{-1}, was obtained by determining the heat of solution of La metal in 1.5<u>M</u> HCl, and from this value and the ΔH° of the corresponding hydrolysis reaction, the heat of formation of LaOCl was found to be -240.1 kcal mol^{-1}.

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THE VAPOR PHASE HYDROLYSIS OF THE TRICHLORIDES OF LANTHANUM, PRASEODYMIUM, SAMARIUM, AND AMERICIUM

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I. INTRODUCTION

Notably absent from standard compilations of thermochemical data (such as those of Bichowsky and Rossini[1] or those of Brewer, Bromley, Gilles and Lofgren[2]) are data pertaining to the rare earth oxyhalides. The oxyhalides, nevertheless, constitute an important class of compounds. The ease of formation of the oxychlorides and oxybromides, for example, is a major source of difficulty in the attempted preparation of pure samples of the corresponding trihalides. The presence of oxyhalide impurities not only introduces an element of uncertainty in all observations on the properties of the trihalide sample, but may have a deleterious effect on some of the chemical reactions of the trihalide - the reduction to metal by metallic reductants, for example.

Existing methods for the preparation of the oxyhalides are all based on purely empirical procedures. It was felt, therefore, that the determination of the thermodynamic properties of some of the rare earth oxyhalides was desirable. The method chosen as the most promising in yielding some of the desired information involved a systematic investigation of the reaction

$$RCl_{3(s)} + H_2O_{(g)} = ROCl_{(s)} + 2HCl_{(g)},$$

in which R symbolizes a rare earth or actinide cation, by measurement of the equilibrium constants at various temperatures. Since some of the elements to be studied were available only in extremely small quantities and since the reaction can conveniently be investigated using small quantities of the solid materials, all experiments were performed using of the order of 1 mg. of cation. It was hoped that the measurement of these constants would be sufficiently accurate, and the differences between values for the individual rare earths and actinides sufficiently great, that the reaction would also provide an insight into differences in the chemical behavior of these various elements. It would be of interest, for example, to compare differences between lanthanide and actinide elements in their reactions in the dry state, such as the one discussed here, and their reactions in solution, such as their elution from ion exchange columns.

The method that was chosen for the investigation of the equilibria is, because of its convenience and wide applicability, perhaps worthy of special note. The method is based on the fact that a weight change of about twenty percent results when a rare earth trichloride is converted to the oxychloride. The sample to be investigated is mounted on a cantilever-type quartz fiber microbalance contained inside of the reaction tube and maintained at the desired temperature by an electrically heated tube furnace (Fig. I). Fixed concentrations of HCl and H_2O gases, carried by a stream of nitrogen gas which is bubbled through an aqueous solution of HCl of carefully established composition, are passed over the sample. If the HCl^2/H_2O ratio exceeds the value of the equilibrium constant at a particular temperature, the sample should be converted to the trichloride; if not, the oxychloride should result.

It is obvious that if the ΔF, ΔH, and ΔS of the reaction are determined, and the free energies, heats, and entropies of formation of the trichloride, HCl, and H_2O are known, the corresponding values for the oxychloride may readily be determined. Although the thermodynamic properties of the two gases involved in the reaction are well known,[3] recent experiments at this laboratory cast some doubt upon the generally accepted values for the heats of formation of the rare earth trichlorides. As a result, it was deemed advisable to check this value for at least one rare earth. To do this, the heat of solution of lanthanum metal in hydrochloric acid solution was determined in the Westrum-Eyring microcalorimeter available at this laboratory.

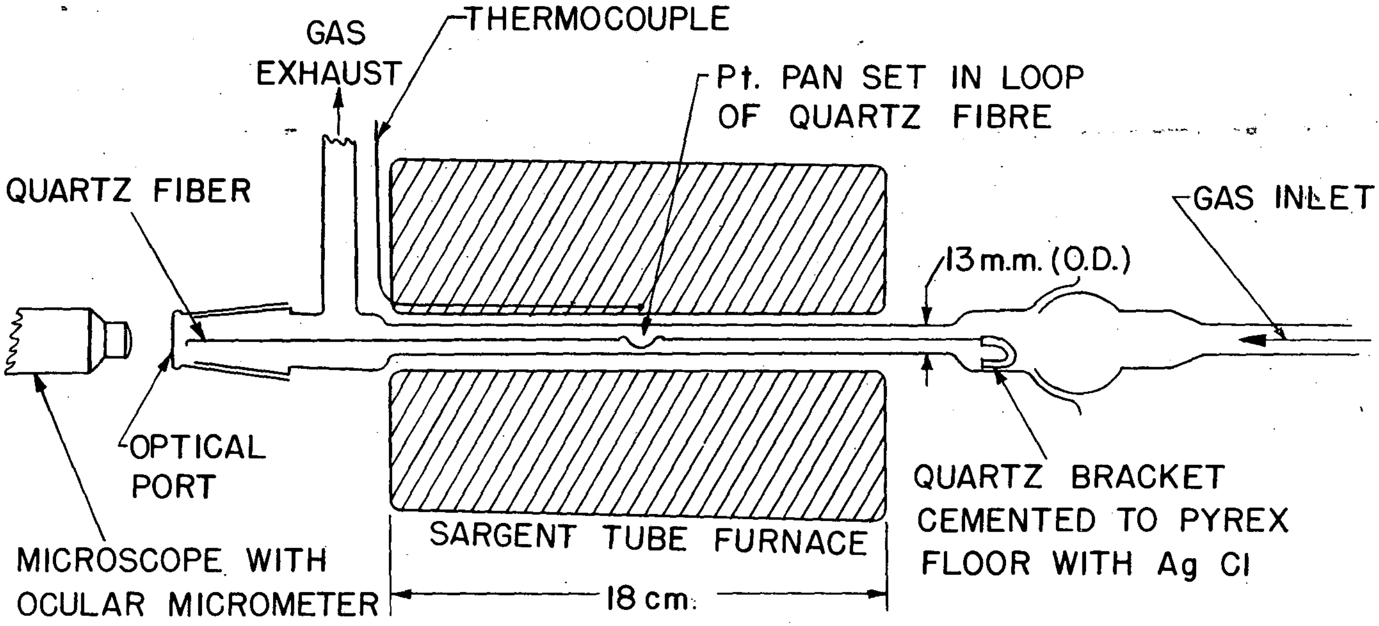

FIG. I - APPARATUS FOR THE DETERMINATION OF THE EQUILIBRIUM CONSTANTS FOR THE REACTION

$$RCl_{3(s)} + H_2O_{(g)} = ROCl_{(s)} + 2\,HCl_{(g)}$$

Finally, as a check upon the validity of this method of evaluating the heat of formation of the oxychlorides, it was hoped that it would be possible to determine this value independently, by calorimetrically obtaining the heat of solution of one of the oxychlorides in aqueous HCl. Unfortunately, in the short time that was available in which to attempt this experiment it was found impossible to prepare a sample of lanthanum or praseodymium oxychloride which could be dissolved rapidly enough to make this determination possible.

II. DESCRIPTION OF APPARATUS

A. Apparatus for Following the Hydrolysis Reaction

1. General.-- The essential features of the apparatus that was used in following the progress of the hydrolysis reaction are illustrated in Fig. 1. The figure indicates the relative positions of the reaction vessel containing the cantilever-type, quartz fiber microbalance, the Sargent tube furnace used to heat the sample, the thermocouple used to measure the reaction temperature, and the optical system used to detect the deflection of the balance pointer. Additional apparatus not shown in the figure includes gas bubblers, flow meters, Dewar flasks, and the potentiometer to which the thermocouple is attached.

At the start of a series of experiments, a sample of an oxide of the element to be studied is mounted on the platinum pan which sits in a ring bent into the quartz fiber. The furnace is brought to the desired temperature and the flow of nitrogen gas started through the bubblers containing the HCl solution and through the reaction tube. As the sample is converted to the trichloride or the oxychloride the weight on the pan increases and the fiber is bent downward. The motion of the free end of the fiber may be detected with the aid of a microscope.

2. Weight Measurements.-- The operation of the cantilever type quartz fiber microbalance has been described elsewhere.[4] For a given load, the deflection, d, of the end of the pointer may be calculated from the following equation:

$$d = \frac{MgL^2}{3\pi E_y r^4}(4L + 6P)$$

In this equation M is the load in grams, g is the gravitational constant, L is the distance from the fixed end of the beam to the load, P is the length of the pointer (the distance from the load to the free end of the fiber), E_y is the value of Young's modulus for the beam, and r is its radius.*

The beam of the balance used in the experiments with the rare earth compounds was about 200 microns (ca. 8 mil) in diameter and 12 cm. in length. The diameter of the pointer was about one-half that of the beam, and its length was about 16 cm. The pan, made of half-mil platinum, was approximately 0.5 cm. in diameter and was tied on to the fiber with 2-mil gold wire. The sensitivity of the balance, measured by converting a known quantity of lanthanum from the trichloride to the oxychloride was about 4 mm. per mg. With the particular microscope and ocular micrometer used, the sensitivity was 21 divisions per mg., and the position of the pointer could be measured to the nearest 0.2 division. Except when external disturbances occurred which also affected much larger equipment, the balance was quite stable and remarkably free of vibration.

In the case of the lanthanum experiments, 0.024 millimoles of lanthanum (3.9 mg. of La_2O_3) were used. The weight change produced by converting this sample from trichloride to oxychloride is 1.32 mg., and this corresponded to a total deflection of 27.3 divisions. The experiments with praseodymium and samarium were performed with comparable quantities and on the same balance. The americium experiments were performed with approximately 0.5 mg. Am, using a balance with a beam diameter of about 130 microns.

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*For small silica fibers, the value of Young's modulus varies appreciably with the diameter (but only very slightly with temperature). Exact values may be found in Chapter V of "Procedures in Experimental Physics," by J. Strong et al. (Prentice-Hall, Inc., New York, 1943).

3. Temperature Measurements.-- The temperature of the sample was determined by use of an external iron vs. constantan thermocouple. Each thermocouple used was standardized against a platinum vs. platinum-rhodium thermocouple mounted inside a reaction tube. The platinum vs. platinum-rhodium thermocouple was itself standardized against the boiling point of water, and the freezing points of lead and aluminum. The results of this standardization are summarized in Table I.

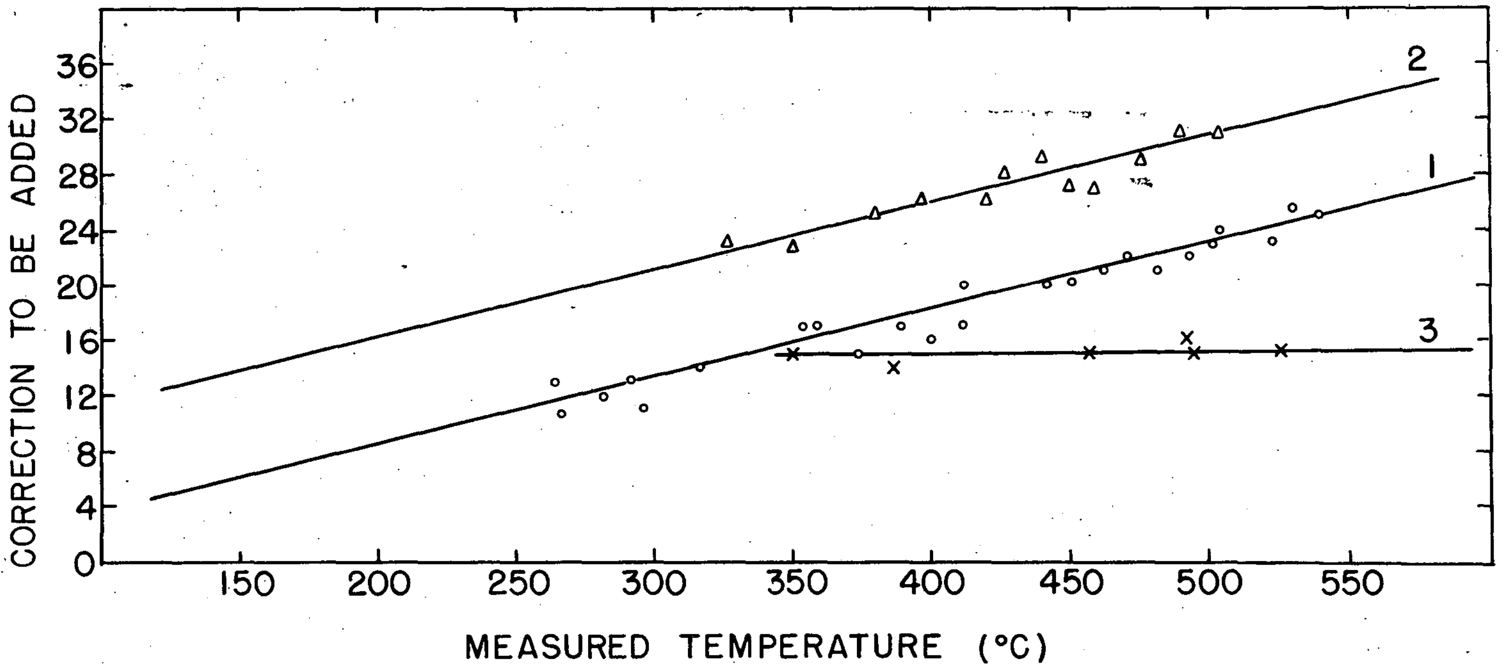
Table I

Standardization of Pt vs. Pt-Rh Thermocouple

Thermometric Fixed Point	True Temp.	Measured Temp.
1. Boiling point of water	100°C.	98°C.
2. Freezing point of Pb (>99.99% pure)	327.3	326
3. Freezing point of Al (>99.99% pure)	660.1	658.5

In the first few experiments (with lanthanum), the external thermocouple was placed in loose contact with the reaction tube, directly above the sample. In this position the temperature measured was always within two degrees of the internal temperature. However, because of the uncertainty in the placing of the thermocouple it was decided to permanently mount a thermocouple into the furnace. The thermocouple was sealed into place with Sauereisen Insa-lute high temperature cement, the end of the couple being placed directly over the balance pan, but about 2 mm. outside of the furnace ring. At this position the temperature differed quite markedly from that in the center of the tube, the difference in temperature varying with the temperature. Curve 1 in Fig. II shows the relation between the true temperature in the tube (as measured with the platinum vs. platinum-rhodium thermocouple) and the temperature indicated by the mounted iron vs. constantan thermocouple.

FIG. II - CALIBRATION CURVES FOR THE EXTERNAL IRON VS CONSTANTAN THERMOCOUPLES



For the early experiments the cold ends of the thermocouple wires were sealed to each other, the potentiometer being attached at a break in one of the wires. Before completion of the lanthanum experiment, however, this was modified by attaching the individual wires to the potentiometer through copper contacts kept at the melting point of ice. When the system was changed, the calibration of the thermocouple also changed, and the new calibration is shown in curve 2 of Fig. II. This thermocouple was used for several months with no apparent change in calibration. Finally, for the americium experiments, a new thermocouple was installed. This couple was closer to the surface of the tube and as a result the correction to be applied was not only less than in the previous cases, but appeared to be quite constant with changes in temperature (curve 3, Fig. II).

4. Measurement of Gas Concentrations.— The flow of HCl and H_2O gases through the reaction tube was controlled by bubbling nitrogen gas (purity >99.9%) through several (two at low concentration of HCl, three at higher concentrations) 250 ml bubblers containing HCl solutions of C.P. reagent grade, fortified if necessary, by prior saturation with HCl gas. Since the experiments were performed in an air conditioned room in which the temperature varied by not more than a degree or two, it was found necessary to place only the final bubbler in a large Dewar flask containing water at a known temperature in the range 20-25°C. Early experiments indicated that one bubbler was sufficient to saturate the gas with HCl and H_2O vapors, the other bubblers serving only to minimize the depletion of HCl from the final bubbler.

The pressures of HCl and H_2O in the reaction tube were determined by titrating the HCl in the final bubbler and using the values for the corresponding vapor pressures reported in the International Critical Tables.[5] For the titrations, standard solutions of HCl and NaOH were made up, with concentrations of about 0.2<u>M</u>. The concentration of the NaOH solution was at first determined using potassium acid phthalate as the standard. The HCl solution was then standardized against the NaOH solution. During the course of these experiments the HCl and NaOH concentrations were compared frequently. On the two occasions that this ratio deviated from the expected value, the standardization with acid phthalate was repeated. Each time it was the NaOH concentration which had changed (probably because of introduction of CO_2). Upon completion of the experiments, a final check was made by means of a gravimetric determination, as AgCl, of the concentration of the HCl solution. A summary of all the standardizations is given in Table II.

Table II

Standardization of HCl and NaOH Solutions

Date	Method of Standardization	Conc. of NaOH	Conc. of HCl
1. 4-9-49	$KH(C_8H_4O_4)$	0.2086	0.2322
2. 6-5-49	"	0.1984	0.2321
3. 2-10-50	$KH(C_8H_4O_4)$	0.1976	0.2322
4. 3-18-50	AgCl	---	0.2320

The procedure followed in determining the concentration of the HCl solutions in the bubbler was to pipet approximately 500λ of the solution into a weighed micropipet, obtaining the exact quantity of solution by weighing, then to transfer this solution into a flask containing carbonate-free water and to titrate with standard NaOH to a phenolphthalein end point. Thus the HCl content of the solution was obtained directly as percent HCl and the respective pressures of HCl and H_2O could be obtained directly from the tables in the International Critical Tables. Those portions of the tables which are pertinent are reproduced in Table III.

Table III

Partial Vapor Pressures of Aqueous Solutions of HCl

% HCl	Partial Pressure of H_2O mm.Hg		Partial Pressure of HCl mm.Hg	
	20°C.	25°C.	20°C.	25°C.
20	10.3	14.1	0.205	0.32
22	9.30	12.6	0.45	0.68
24	8.30	11.4	1.00	1.49
26	7.21	9.95	2.17	3.20
28	6.32	8.75	4.90	7.05
30	5.41	7.52	10.6	15.1
32	4.55	6.37	23.5	32.5
34	3.81	5.35	50.5	68.5
36	3.10	4.41	105.5	142
38	2.51	3.60	210	277
40	2.00	2.88	399	515
42	1.56	2.30	709	900

To look for any gross error in this method of determining the respective gas pressures, the HCl pressure was occasionally checked by passing the gas mixture through a final bubbler containing a known quantity of standard NaOH solution. With the aid of the flow meters in the line it was possible to calculate the volume of gas passed through the bubbler in a given time with an accuracy of about 10 percent. By titrating the excess NaOH in the bubbler it was possible to calculate the quantity of HCl gas absorbed by the NaOH solution. A comparison of the observed values with those calculated from the International Critical Tables is given in Table IV.

Table IV

Comparison of Observed and Calculated HCl Pressures

HCl Content (% HCl)	Time of Flow minutes	Total Volume (at S.T.P.) ml.	P_{HCl}(exp'l) mm.	P_{HCl}(I.C.T.) mm.
29.68	170	5100	11	12.2
33.16	120	3970	52	49
33.65	240	3780	48	51
33.76	780	4400	57	62
33.83	795	3770	61	63
34.16	90	3590	67	71
37.24	60	1220	162	169

One further point should be mentioned in connection with the determination of the pressures of HCl and H_2O in the reaction tube. In experiments of a similar nature it has been found[6] that, because of thermal diffusion effects, the ratio of pressures of several gases going into, or coming out of, a hot tube is not necessarily the same as the ratio of these pressures in the center of this tube. As a check on possible thermal diffusion effects, when the values of the equilibrium constant for the lanthanum hydrolysis at the higher temperatures were determined, the flow rates were varied from a minimum of 1-2 cc. per minute to a maximum of about 60 cc. per minute with no noticeable change in equilibrium constant. Finally, as will be noticed in Table V giving the experimental results for the lanthanum trichloride hydrolysis, one point was determined using argon, rather than nitrogen, as the inert gas with no apparent effect resulting from this change.

B. Apparatus Used in the Determination of the Heat of Solution of Lanthanum Metal

1. Heat Measurements.-- The Westrum-Eyring microcalorimeter used in the determination of the heat of solution of lanthanum metal has been described previously.[7] A diagram of the calorimeter circuit and a cross-sectional view of the calorimeter may be found in Fig.III. The calorimeter chamber is mounted by means of a machined Lucite tube in a stainless steel submarine submerged in a bath thermostated with a toluene-thyratron proportional controller. The chamber itself is made of tantalum, has a capacity of 8 ml, and a wall thickness of less than 0.2 mm. A winding of copper wire over the cylindrical surface provides an integrating resistance thermometer sensitive to 10^{-5} degrees as well as a heater for the input of electrical energy. Stirring and fracture of the small sample bulb are achieved by use of the slender quartz or pyrex shaft. The thermal leakage modulus of the calorimeter was found to be 0.025 degrees per minute. The heat of stirring and the thermometric current total 10^{-4} calories per minute. In use, the calorimeter has been found to give values reproducible to one or two kilocalories for heats of solutions of the order of 160 kilocalories per mole using samples of the order of 2-5 micromoles.[8]

2. Weight Measurement.-- The samples used in the microcalorimeter were of the order of 0.5 mg. in mass and were weighed in a Kirk-Craig-Gullberg quartz fiber torsion microbalance.[4] This instrument was calibrated against several one mg. Bureau of Standards weights, each accurate to 0.1 percent, and had a sensitivity of 5786.4 divisions per milligram. It could be read to the nearest 0.05 division and with care was reproducible to 0.1-0.2 divisions.

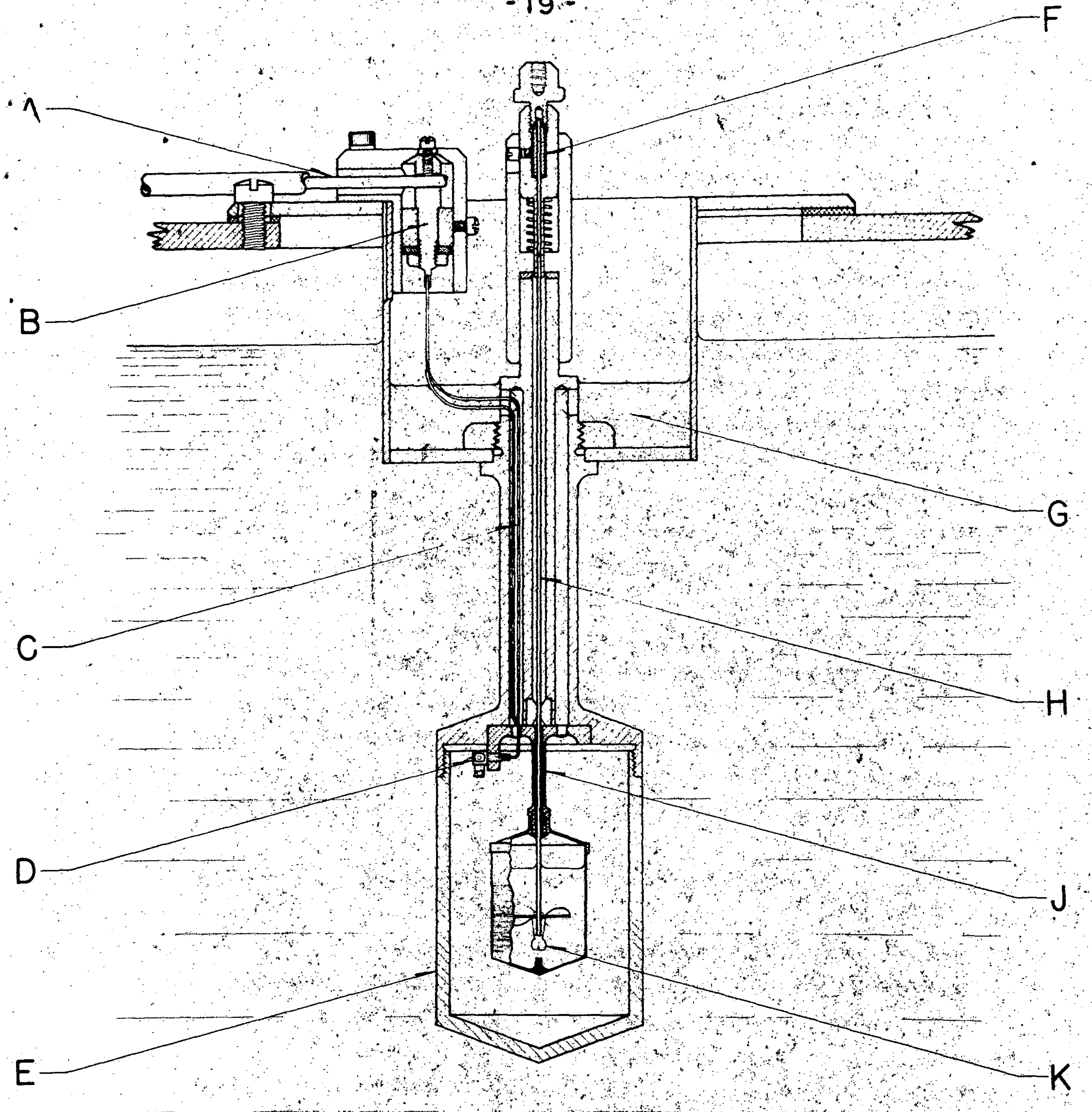
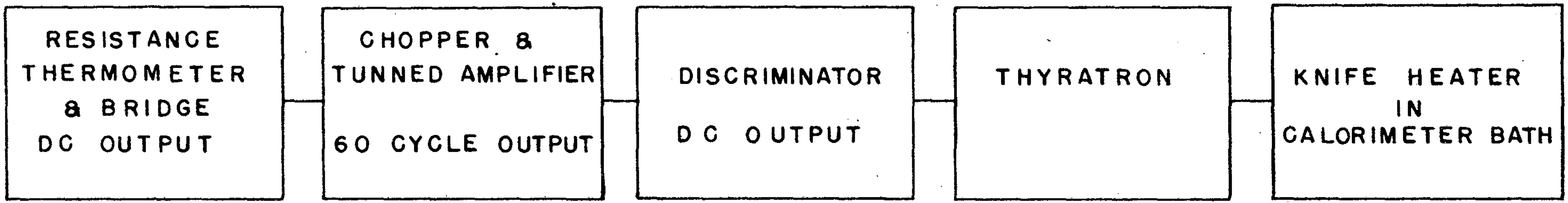


FIG. III - a

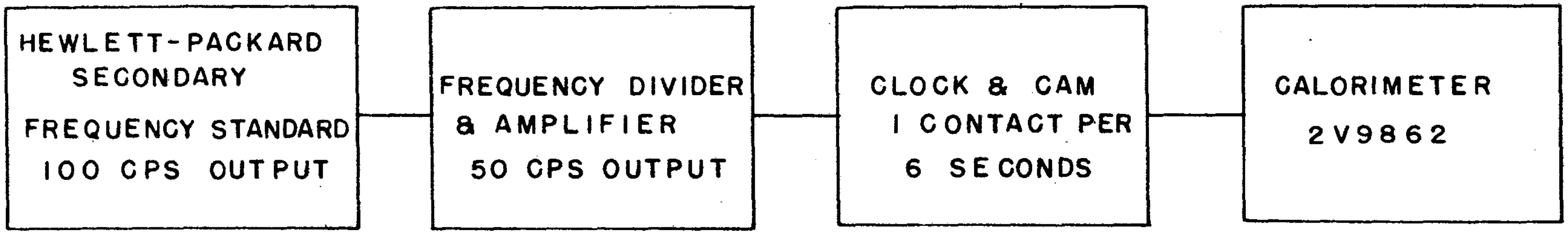
MICROCALORIMETER CROSS SECTION

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



MICROCALORIMETER
TEMPERATURE CONTROL
BLOCK SCHEMATIC

FIG. III - b



MICROCALORIMETER
TIME STANDARD
BLOCK SCHEMATIC

FIG. III - c

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 megohm 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 magnanin
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)
R24	1	~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

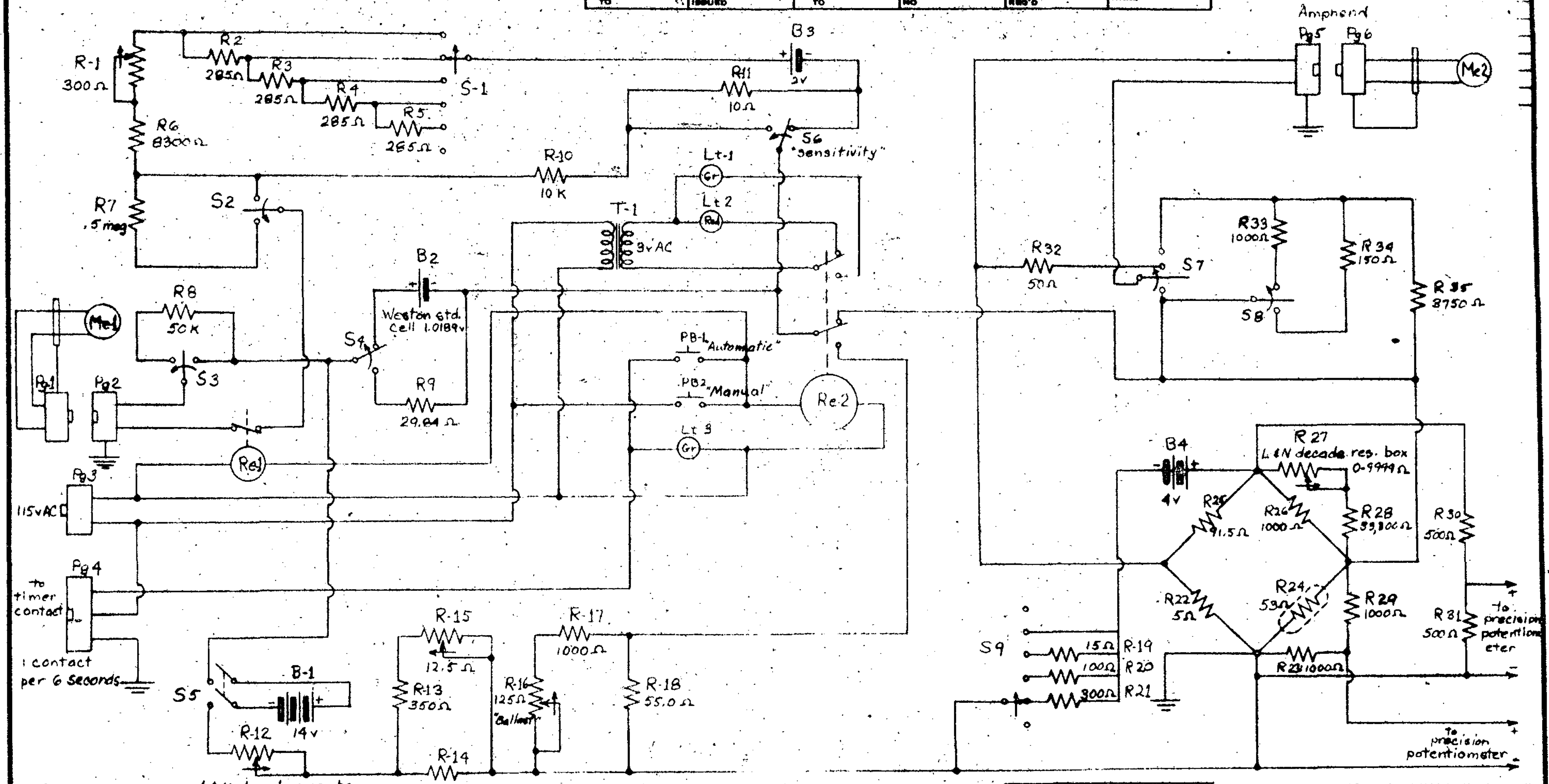
Note: All manganin resistors are IRC type WW-4 or equivalent. Some values are made by paralleling two or more resistors.

Fig. III-d1

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 AC, 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.

Fig. III-d2

SHOWN ON	2V9871	2V9881								CHANGE LETTER	DRAWN BY	CHECK BY	DATE	CHANGE
ISSUED TO		DATE ISSUED		DELIVER TO		JOB NO		DATE REC'D	MAKE					



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 8-1

ROUGH ▽ FINISH FINE ▽▽ FINISH
GOOD ▽ FINISH GRIND G FINISH
MACHINED DIMENSIONS ± .010 UNLESS OTHERWISE SPECIFIED

RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA—BERKELEY

DRAWN BY J.H. Lilly CHECK BY DATE 3-24-49
APPROVED BY
SCALE
DWG. NO 2V9862

MATERIAL

MICROCALORIMETER
SCHEMATIC

FIG. IV-e

OZ 42

III. EXPERIMENTAL RESULTS

A. The Hydrolysis of Lanthanum Trichloride

1. X-ray Diffraction Experiments.— The starting material for the lanthanum hydrolysis experiments was La_2O_3 of greater than 99.95 percent purity obtained from the Atomic Research Institute at Iowa State College. Before any experiments were undertaken using the microbalance technique described above (Sec. IIA), several experiments were performed using standard x-ray diffraction techniques for the identification of the solid phase. In these experiments the sample was mounted in a platinum boat which was attached to an iron-cored glass tube. The boat was introduced into a reaction tube which had a side arm which could be drawn down into a thin-walled capillary tube. Upon completion of the reaction the boat was magnetically pushed into position over the side arm and tilted sufficiently to drop a portion of its contents into the capillary tube. The tube was then sealed off and its contents examined by the x-ray diffraction group under Dr. D. H. Templeton.

The structures of the $LaCl_3$ and LaOCl crystals were confirmed, the $LaCl_3$ crystal being hexagonal with lattice constants $a = 7.483 \pm 0.003 A^o$ and $c = 4.375 \pm 0.003\ A^o$, while the LaOCl crystal is tetragonal with constants $a = 4.111 \pm 0.002\ A^o$ and $c = 6.868 \pm 0.004\ A^o$. Although several samples submitted for x-ray diffraction analyses contained mixtures of oxychloride and trichloride, in no case was there observed any change in lattice constants which might indicate appreciable solid solution formation. No high temperature x-ray diffraction data was obtained, but the room temperature results, together with the fact that the same value was obtained for the equilibrium constant whether one started with oxychloride and increased the HCl/H_2O ratio until the trichloride formed or started with the trichloride and decreased the HCl/H_2O ratio until the oxychloride resulted, were taken to indicate that there was no appreciable solubility of one of the materials in the other.

2. Microbalance Experiments.-- In determining the equilibrium constant for the hydrolysis reaction with the microbalance technique, the concentration of the HCl solution and the furnace temperature were adjusted until the gas pressures were close to the equilibrium pressures and the solid sample existed partly as trichloride and partly as oxychloride. In every case except the first (Experiment No. 7, Table V), final adjustments were made by changing the temperature of the HCl solution. The reaction was seldom followed to completion, being continued at one temperature of the HCl solution only long enough to ascertain the direction of motion of the balance pointer. The temperature of the HCl solution was then changed sufficiently to cause motion of the balance in the other direction. Thus, equilibrium was always approached from both sides, and while the equilibrium constant was never obtained exactly, it was always bracketed.

The values obtained for the equilibrium constant for the vapor phase hydrolysis of lanthanum trichloride are summarized in Table V. In this table, column 1 gives the experiment number (in order of decreasing temperature, not necessarily in chronological order), column 2 gives the corrected temperature inside the reaction tube while column 3 gives the reciprocal of this temperature (times 10^3). Column 4 gives the HCl content of the acid solution, column 5 the temperature of this solution, columns 6 and 7 the pressures of HCl and H_2O gases, respectively, as obtained from the International Critical Tables. In column 8 are listed the limits on the equilibrium constant for the reaction, while column 9 lists the midpoints of the two limits for each experiment. Column 10 gives the values of ΔF_T^o for the reaction as calculated from the figures in column 9. The significance of column 11, the calculated values of ΔF_T^o is discussed in section IV of this paper.

Table V

The Variation with Temperature of the Equilibrium Constant for the Reaction
$LaCl_{3(s)} + H_2O_{(g)} = LaOCl_{(s)} + 2HCl_{(g)}$

Experiment No.	Reaction Temp. (°K)	1000/T	Conc. of HCl Soln. (% HCl)	Temp. of HCl Soln. (°C.)	P_{HCl} (mm)	P_{H_2O} (mm)	$K = \frac{P_{HCl}^2}{P_{H_2O} \times 760}$ (atm^{-1})	Mean K	$\Delta F_{Experimental}$ (Kilocalories)	$\Delta F_{Calculated}$ (Kilocalories)
1	838	1.193	35.38	19.2 20.0	82 86	3.1 3.3	>2.85 <2.95	2.90	-1.77	-1.31
2	798	1.253	34.04	22.2 25.0	60 70	4.4 5.3	>1.08 <1.21	1.14	-0.21	0.05
3	764	1.309	33.07	22.5 23.5	41 44	5.0 5.4	>0.44 <0.47	0.45	1.21	1.21
4	760	1.316	33.15	22.4 23.8	41 45	4.9 5.3	>0.45 <0.50	0.47	1.14	1.35
5*	759	1.318	33.07	19.8 21.5	35 39	4.2 4.7	>0.38 <0.42	0.40	1.38	1.38
6	720	1.389	31.55	22.6 24.0	23.2 26.4	5.7 6.2	>0.124 <0.149	0.136	2.86	2.71
7	683	1.464	29.73 30.02	25.0 24.6	13.8 14.8	7.6 7.3	>0.036 <0.039	0.036	4.51	3.98
8**	641	1.560	28.83	16.0 20.0	4.2 6.6	3.9 5.8	>0.006 <0.010	(0.008)	(6.14)	5.44

---

*Argon was used as the inert gas in this experiment.

**This value is only approximate because of the very slow rate at this temperature.

B. The Determination of the Heat of Solution of Lanthanum Metal

Before 1940, very little was known of the thermochemical data of the rare earth compounds. Only scattered results were available, and in most cases even those measurements were carried out on materials whose purity was highly questionable. Thus, when Bommer and Hohmann published their data on a systematic study of the heats of solution of carefully purified rare earth metals[9] and rare earth halides,[10] these values were quite generally accepted as being the best data available. While the heat of solution of lanthanum trichloride obtained by Bommer and Hohmann agreed quite well with the value accepted by Bichowsky and Rossini,[1] the heat of solution of the metal was higher by some 9 kcal than the previously accepted value. Some recent work done at this laboratory[8] had indicated that, in the case of praseodymium, at least, the Bommer and Hohmann value for the heat of solution of the metal was in error. Since the techniques used by Bommer and Hohmann in their determinations made it appear likely that a systematic error had been introduced by them, it was decided to redetermine the heat of solution of lanthanum metal.

The lanthanum metal used in these experiments came from three sources. The purity of the sample obtained from Johnson,Matthey was found by spectrographic analysis to be greater than 95 percent. The sample of metal obtained from the Atomic Research Institute of Iowa State College was found to be better than 99 percent pure. Finally, some lanthanum metal was prepared by Mrs. Winifred Heppler of this laboratory, using as starting material a sample of lanthanum ammonium nitrate obtained from Lindsay Light and Chemical Company and reportedly better than 99.5 percent pure.

Before undertaking the experiments in the microcalorimeter, an approximate value for the heat of solution of lanthanum metal in 1.5M HCl was obtained using a Dewar flask and Beckman thermometer. The heat capacity of this crude calorimeter was obtained by measuring the known heat of solution of magnesium metal.[8]

The results obtained for lanthanum are summarized in Table VI.

Table VI

Approximate Heat of Solution of Lanthanum Metal in 1.5M HCl Solution

Source of Material	Size of Sample (mg.)	Temperature Rise (°C.)	Heat of Solution (kcal)
Iowa State	142.8	1.087	-164.2
Johnson, Matthey	130.3	1.000	-165.5

Since these results were considerably lower than the value -176.5 reported by Bommer and Hohmann for very dilute acid solutions, it was decided to determine the amount of hydrogen liberated by the material, to see if perhaps an appreciable fraction had been oxidized before use. Two samples of the Iowa State material were dissolved in dilute HCl which had previously been saturated with hydrogen gas. The results of these experiments are summarized in Table VII.

Table VII

Hydrogen Liberated by Lanthanum Metal

Weight of Sample (mg.)	Millimoles of Hydrogen Liberated	Expected
70.48	0.760	0.761
53.23	0.572	0.575

Finally, four determinations of the heat of solution at 25°C. of lanthanum metal from the various sources were made in the microcalorimeter. The results are summarized in Table VIII.

Table VIII

Heat of Solution at 25°C. of Lanthanum Metal in 1.5M HCl

Source of Material	Size of Sample (ug)	Calories Liberated	Heat of Solution (kcal)
Iowa State	242.79	0.286	-163.5
Iowa State	865.85	1.034	-165.9
Berkeley	548.61	0.662	-167.8
Berkeley	639.62	0.769	-167.3
		avg.	-166.1

It may be seen that our value for the heat of solution is considerably different from that of Bommer and Hohmann and, indeed, shows fair agreement with the value -167.7 kcal for about 2.7M HCl given in Bichowsky and Rossini. From the data in Table VII it appears that, unless the sample contains compensating amounts of hydride and oxide impurities, the material is essentially pure metal. Further, if such a fortuitous mixture of impurities did occur in the Iowa State material, it must also have resulted in the metal obtained from the other two sources since the metal obtained from the three different sources gave, within experimental error, the same heat of solution.

The heat of formation of solid lanthanum trichloride may be obtained from the heat of solution reported above by adding three times the heat of formation of 1.5M HCl and subtracting the heat of solution in 1.5M HCl of $LaCl_3$. The heat of formation of 1.5M HCl is given in the National Bureau of Standards Tables[3] as -39.5 kcal. Bommer and Hohmann obtained the value -31.6 kcal for the heat of solution at 25°C. of lanthanum trichloride in water, and this is in good agreement with the value -31.3 kcal listed by Bichowsky and Rossini for 16°C. Bommer and Hohmann also obtained for the heat of solution of the trichloride in 14.1 percent HCl, the value -26.4 kcal. Confirmation of the validity of a linear interpolation to 1.5$\underline{M}$ HCl comes from the work of Robinson and Westrum[11] on the heat of solution of $PuCl_3$ in varying concentrations of HCl. They found that the heat of solution increased linearly upon dilution from 6.0$\underline{M}$ HCl down to 0.1$\underline{M}$ HCl and extrapolated the value -31.9 kcal for the heat of solution of $PuCl_3$ at infinite dilution.

For $LaCl_3$ the interpolation to 1.5$\underline{M}$ HCl gives -29.7 kcal for the heat of solution at 25°C. Combining the above values one obtains for the heat of formation of solid lanthanum chloride the value -254.9 kcal.

C. The Hydrolysis of Praseodymium Trichloride

The praseodymium used in these experiments was obtained from Dr. E. R. Tompkins of the Clinton Laboratories, Monsanto Chemical Company, and had been highly purified by him, using ion exchange techniques. Spectrographic analysis indicated its purity to be greater than 99.99 percent. The values obtained for the equilibrium constant for the vapor phase hydrolysis of praseodymium trichloride are summarized in Table IX. In this table the headings have the same interpretation as those discussed under lanthanum (Sec. III A2).

D. The Hydrolysis of Samarium Trichloride

The samarium used in these experiments was obtained as oxide from the Atomic Research Institute of Iowa State College. Spectrographic analysis indicated its purity to be greater than 99.99 percent. The values obtained for the equilibrium constant for the vapor phase hydrolysis of samarium trichloride are summarized in Table X. In this table the headings have the same significance as those discussed under lanthanum (Sec. III A2).

E. The Hydrolysis of Americium Trichloride

The americium used in these experiments was Am^{241}, an isotope of half-life about 500 years, produced by beta-decay of Pu^{241}. This material was separated from plutonium by a series of peroxide and hydroxide precipitations and additional

Table IX

The Variation with Temperature of the Equilibrium Constant for the Reaction
$PrCl_{3(s)} + H_2O_{(g)} = PrOCl_{(s)} + 2HCl_{(g)}$

Experiment No.	Reaction Temp. (°K)	1000/T	Conc. of HCl Soln. (% HCl)	Temp. of HCl Soln. (°C.)	P_{HCl} (mm)	P_{H_2O} (mm)	$K = \frac{P_{HCl}^2}{P_{H_2O} \times 760}$ (atm^{-1})	Mean K	$\Delta F_{Experimental}$ (Kilocalories)	$\Delta F_{Calculated}$ (Kilocalories)
1	842	1.188	37.19	21.5 23.2	180 200	3.08 3.46	>13.8 <15.2	14.5	-4.47	-4.47
2	817	1.224	36.56	22.0 24.0	150 170	3.38 3.86	> 8.8 < 9.8	9.3	-3.62	-3.62
3	771	1.297	35.46	22.0 24.0	100 112	3.84 4.38	> 3.43 < 3.77	3.60	-1.96	-2.05
4	743	1.346	35.01	20.0 22.0	74 84	3.44 4.12	> 2.09 < 2.25	2.17	-1.14	-1.10
5	727	1.375	34.80	18.3 20.0	59 68	3.00 3.55	> 1.52 < 1.71	1.61	-0.68	-0.56
6	700	1.429	33.58	22.7 25.0	51 58	4.83 5.53	> 0.70 < 0.80	0.75	0.40	0.37

Table X

The Variation with Temperature of the Equilibrium Constant for the Reaction
$SmCl_{3(s)} + H_2O_{(g)} = SmOCl_{(s)} + 2HCl_{(g)}$

Experiment No.	Reaction Temp. (°K)	1000/T	Conc. of HCl Soln. (% HCl)	Temp. of HCl Soln. (°C.)	P_{HCl} (mm)	P_{H_2O} (mm)	$K = \frac{P_{HCl}^2}{P_{H_2O} \times 760}$ (atm^{-1})	Mean K	$\Delta F_{Experimental}$ (Kilocalories)	$\Delta F_{Calculated}$ (Kilocalories)
1	785	1.274	38.98	20.6 22.1	302 326	2.37 2.68	>50.6 <52.8	51.7	-6.15	-6.15
2	769	1.300	38.49	21.7 23.1	277 298	2.72 2.98	>37.1 <39.2	38.1	-5.56	-5.60
3	741	1.350	38.04	20.0 22.0	213 241	2.51 2.91	>23.8 <26.3	25.0	-4.74	-4.66
4	710	1.408	37.27	19.6 22.6	159 190	2.64 3.33	>12.6 <14.2	13.4	-3.66	-3.59
5	709	1.410	37.09	20.8 22.0	166 179	2.95 3.24	>12.3 <13.0	12.7	-3.58	-3.55
6	676	1.479	35.82	22.5 25.0	119 135	3.72 4.47	> 5.0 < 5.4	5.2	-2.22	-2.42

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chemistry was performed to remove impurities such as iron and chromium. Spectrographic analysis then indicated the only impurities to be aluminum, calcium, and magnesium. Before use, the sample was further purified by precipitating twice as the fluoride (with $HClO_4$ metatheses) and finally as the hydroxide with subsequent ignition to the oxide. The values obtained for the equilibrium constant for the vapor phase hydrolysis of americium trichloride are summarized in Table XI. In this table the headings have the same interpretation as those discussed under lanthanum (Sec. III A2).

IV. DISCUSSION AND CONCLUSIONS

A. The Heats and Entropies of the Hydrolysis Reactions

The use of the cantilever type quartz fiber microbalance to follow the progress of the hydrolysis reaction has proved to be an extremely effective tool. Repeated observations can be made without ever removing the sample from the reaction vessel. It is not necessary to follow the reaction itself by a lengthy analytical procedure on the sample to determine the results obtained. In fact, it is not even necessary to follow the reaction to completion in either direction, the direction of motion of the balance being sufficient to indicate whether or not the equilibrium constant has been exceeded. This latter fact proved particularly advantageous at the lower temperatures. At the higher temperatures, about 500°C., the reaction usually proceeded quite rapidly, frequently going essentially to completion in a matter of minutes. At the lower temperatures, about 350°C., it took several days to ascertain the direction of motion of the balance (say, 10 percent of the way to completion of the reaction). To follow the reaction to completion at the low temperatures would have taken several weeks for each observation.

One effective check on the validity of the results obtained using this method is to calculate heats and entropies for the reaction, and to consider the

Table XI

The Variation with Temperature of the Equilibrium Constant for the Reaction
$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl$

Experiment No.	Reaction Temp. (°K)	1000/T	Conc. of HCl Soln. (% HCl)	Temp. of HCl Soln. (°C.)	P_{HCl} (mm)	P_{H_2O} (mm)	$K = \frac{P_{HCl}^2}{P_{H_2O} \times 760}$ (atm^{-1})	Mean K	$\Delta F_{Experimental}$ (Kilocalories)	$\Delta F_{Calculated}$ (Kilocalories)
1	846	1.182	39.42	20.0 22.3	330 369	2.17 2.56	>66.2 <70.0	68.1	-7.09	-7.07
2	828	1.208	39.24	19.5 20.5	301 319	2.13 2.29	>55.9 <58.4	57.1	-6.65	-6.45
3	818	1.222	38.96	19.0 21.0	266 302	2.10 2.46	>44.3 <48.8	46.5	-6.24	-6.12
4	809	1.236	38.30	21.0 23.0	249 280	2.65 3.03	>30.8 <34.0	32.4	-5.59	-5.82
5	786	1.272	37.88	20.0 23.0	202 242	2.53 3.19	>21.2 <24.2	22.7	-4.87	-5.03
6	756	1.323	37.02	22.5 25.0	180 207	3.40 3.98	>12.5 <14.2	13.4	-3.90	-4.01
7	741	1.350	37.00	20.2 23.5	152 186	2.81 3.65	>10.9 <12.5	11.7	-3.62	-3.51
8	720	1.389	36.28	22.2 24.1	133 153	3.48 4.03	> 6.7 < 7.6	7.1	-2.80	-2.78
9	700	1.429	35.76	22.0 24.0	114 128	3.70 4.22	> 4.6 < 5.1	4.9	-2.21	-2.09
10	679	1.473	34.92	22.9 25.0	88 97	4.33 4.85	> 2.4 < 2.6	2.5	-1.24	-1.38

reasonableness of the results obtained. For one thing, it would be expected that the entropy change in the hydrolysis reaction would be essentially the same regardless of rare earth or actinide used. In order to calculate values of ΔH^o and ΔS^o from the data obtained, it is necessary to have information on ΔCp for the reaction

$$RCl_{3(s)} + H_2O_{(g)} = ROCl_{(s)} + 2HCl_{(g)}.$$

Cp equations for the gases are readily available, but it is necessary to estimate values of the heat capacity of the solids. This may be done in several ways all of which agree fairly well. Sheft and Davidson[12] have estimated ΔCp for the hydrolysis of plutonium tribromide by analogy with other compounds, as follows:

$$-\Delta Cp = C_{H_2O} - 2C_{HBr} + 1/2C_{UCl_4} - 1/2C_{UO_2} + 2C_{KBr} - 2C_{KCl} = 2.6 \text{ cal/mole/}^oC.$$

$$-\Delta C_p = C_{H_2O} - 2C_{HBr} + C_{PbBr_2} - C_{PbO} = 2.2 \text{ cal/mole/}^oC.$$

$$\text{Average} = 2.4 \text{ cal/mole/}^oC.$$

and they have used this same value in considering the plutonium trichloride hydrolysis.[13]

Although the assumption that the difference in heat capacity of the two solids is essentially constant is reasonably good, it is probably somewhat more accurate to include the complete equations given in Lewis and Randall[14] for the heat capacity of the gases involved. The heat capacity of the solids may be estimated by use of the additivity principle discussed by Lewis and Randall. Using the values suggested as applicable about room temperature, namely, 6.4 cal mol^{-1} deg^{-1} for lanthanum and chlorine and 4.0 cal mol^{-1} deg^{-1} for oxygen, one obtains for $C_{LaOCl}-C_{LaCl_3}$ the value -8.8 cal mol^{-1} deg^{-1}. Using the values recommended for temperatures of about 400°C., namely 7.1 for lanthanum and chlorine and 5.9 for oxygen, the result is 8.3 cal mol^{-1} deg^{-1}. Combining this later value with the equations for the gases one obtains

$$\Delta Cp = -4.11 + 0.0039T - 0.00000222T^2.$$

In the temperature range of the experiments, this equation is in excellent agreement with the value chosen by Sheft and Davidson. The equation, however, probably gives a better extrapolation to 298.1°K.

With the aid of the heat capacity equation, curves were calculated giving the best fit with the experimental points (Figures IV, V, VI, VII, and VIII). When this was done, the praseodymium, samarium, and americium results gave essentially identical values for ΔS° for the respective reactions, while the best fit of the lanthanum data gave results that differed considerably (Fig. IV). Since the lanthanum experiments were the first ones performed and thus subject to greater experimental uncertainty, it was decided that this difference was probably not real. All experiments have thus been calculated using the same values of ΔS_T°. The values for ΔF_T°, calculated from these values of ΔS_T° and the best corresponding values of ΔH_T° obtained for each element, are listed in the last column of Tables V, IX, X, and XI. Even including the lanthanum experiments, the mean deviation in ΔF° of all the results is of the order of 0.1 kcal.

In Table XII have been summarized for the elements studied the values of ΔH_0°, ΔH_{298}°, ΔS_{298}° and ΔH°, ΔS°, and K at a representative temperature in the range of the experiments. As far as is known to the author, the only study made of a similar reaction is that made on plutonium trichloride and tribromide by Sheft and Davidson. In this work these authors used a non-flow method and thus for each point approached equilibrium from only one side. As a result, the scatter in their points is much greater than that observed here. Table XII and Fig. VII include also an estimate of the heat of the plutonium trichloride hydrolysis made by assuming the same values of ΔS° obtained for the elements discussed above. It is of interest to note that the values calculated in this way are in good agreement with those determined by Sheft and Davidson for the plutonium tribromide hydrolysis.

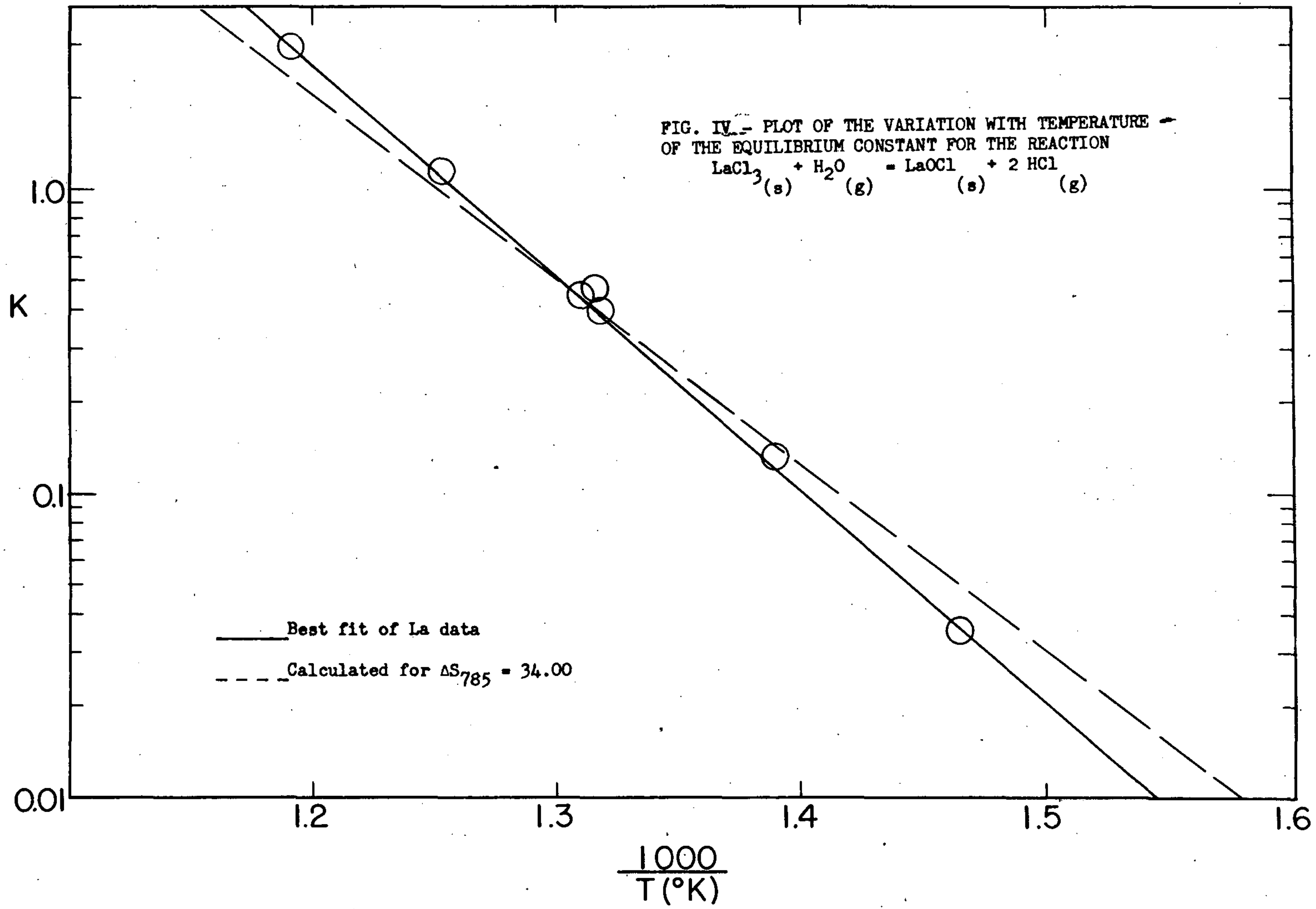

FIG. IV - PLOT OF THE VARIATION WITH TEMPERATURE OF THE EQUILIBRIUM CONSTANT FOR THE REACTION

$LaCl_{3(s)} + H_2O_{(g)} = LaOCl_{(s)} + 2\ HCl_{(g)}$

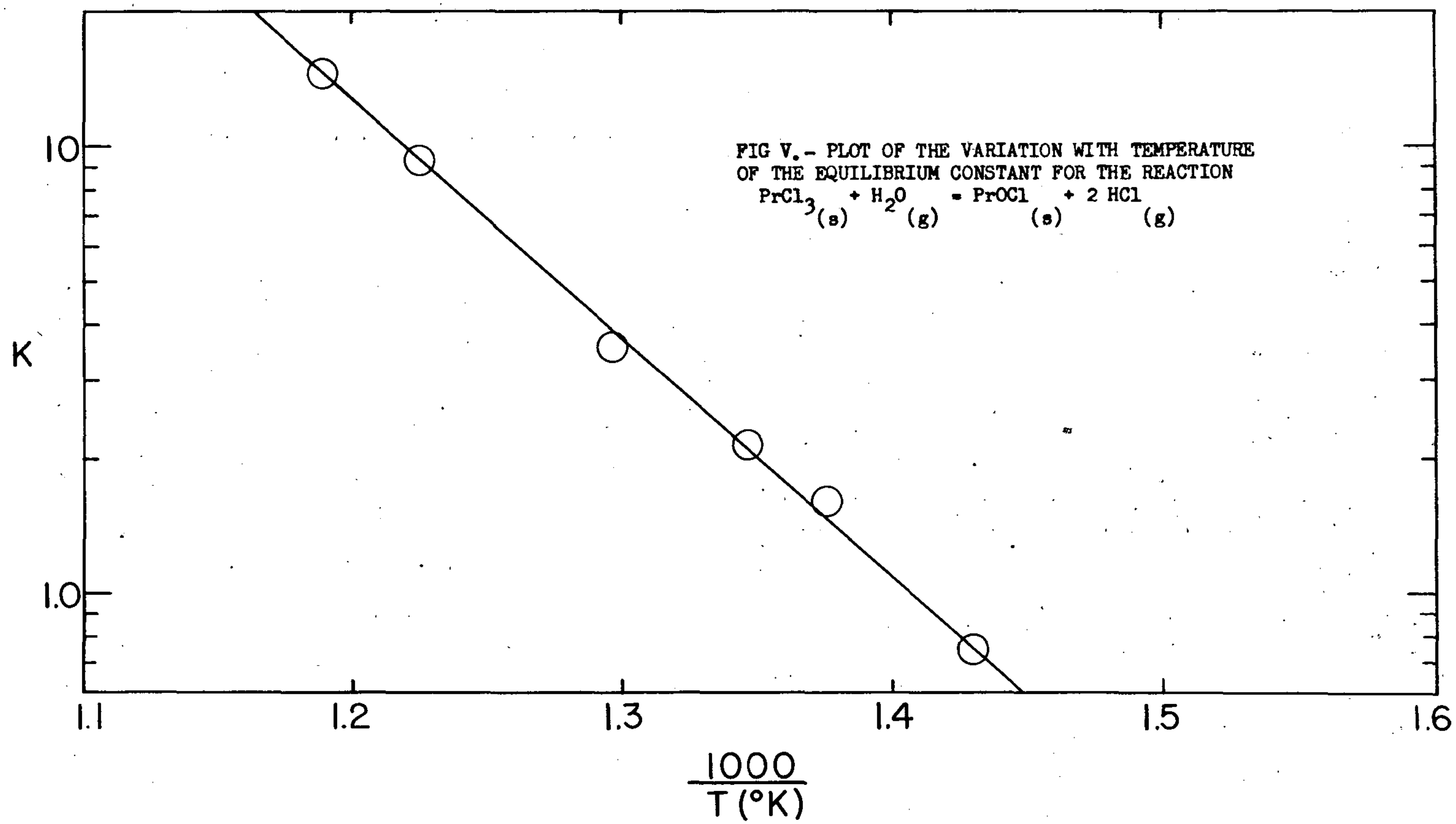

FIG V.- PLOT OF THE VARIATION WITH TEMPERATURE OF THE EQUILIBRIUM CONSTANT FOR THE REACTION
$PrCl_{3(s)} + H_2O_{(g)} = PrOCl_{(s)} + 2\ HCl_{(g)}$

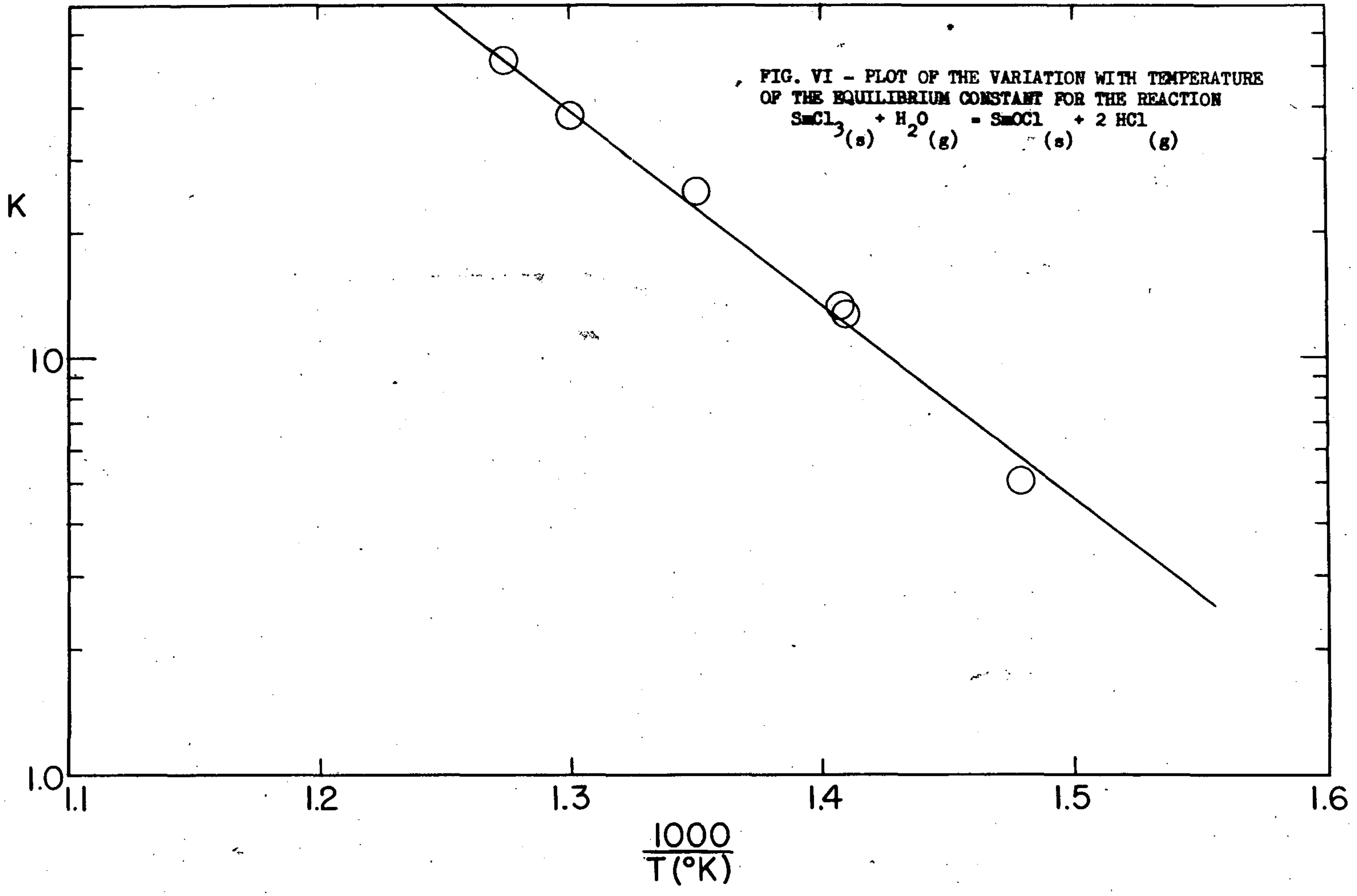

FIG. VI - PLOT OF THE VARIATION WITH TEMPERATURE OF THE EQUILIBRIUM CONSTANT FOR THE REACTION
$SmCl_{3(s)} + H_2O_{(g)} = SmOCl_{(s)} + 2\,HCl_{(g)}$

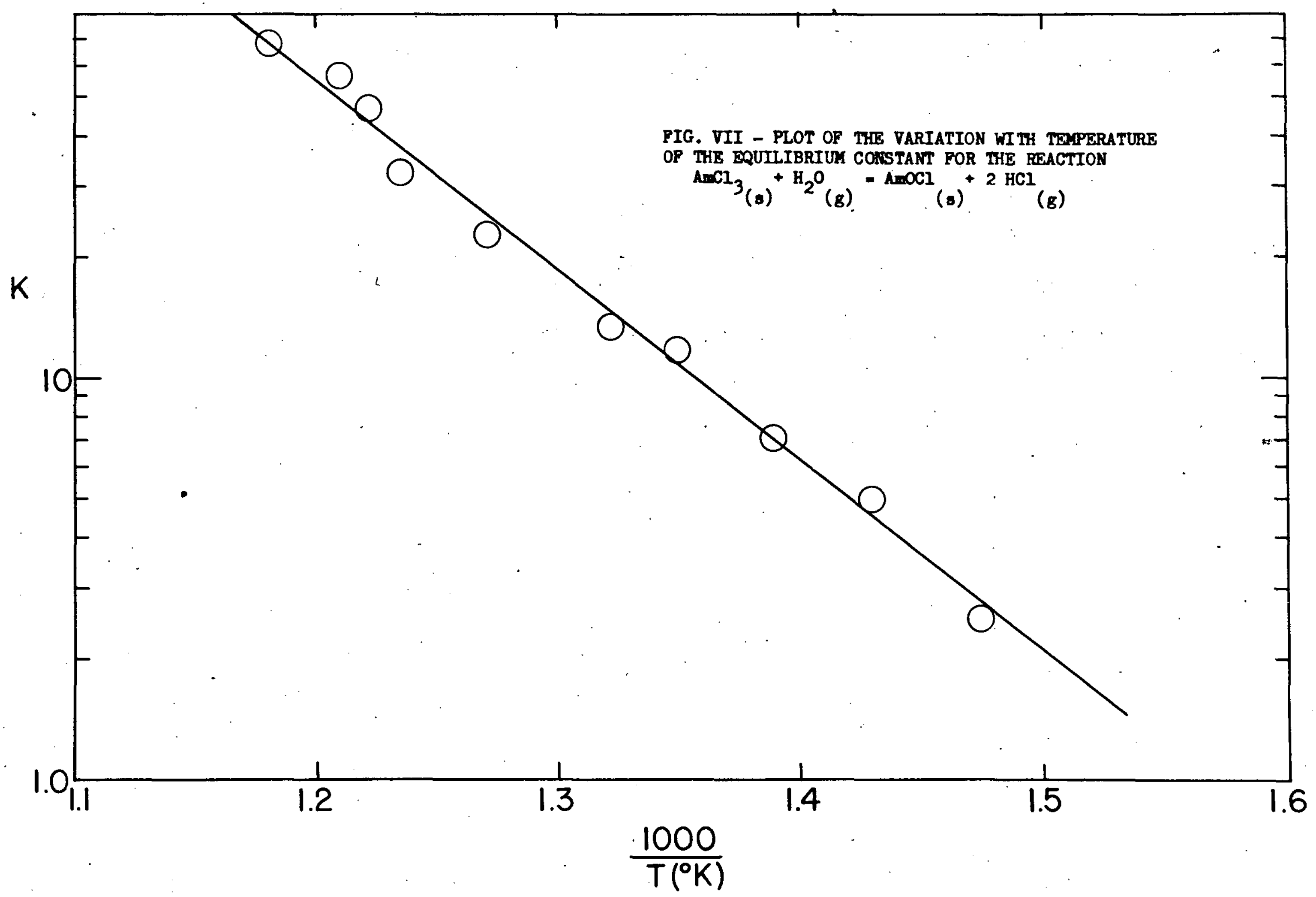

FIG. VII - PLOT OF THE VARIATION WITH TEMPERATURE OF THE EQUILIBRIUM CONSTANT FOR THE REACTION

$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2\ HCl_{(g)}$

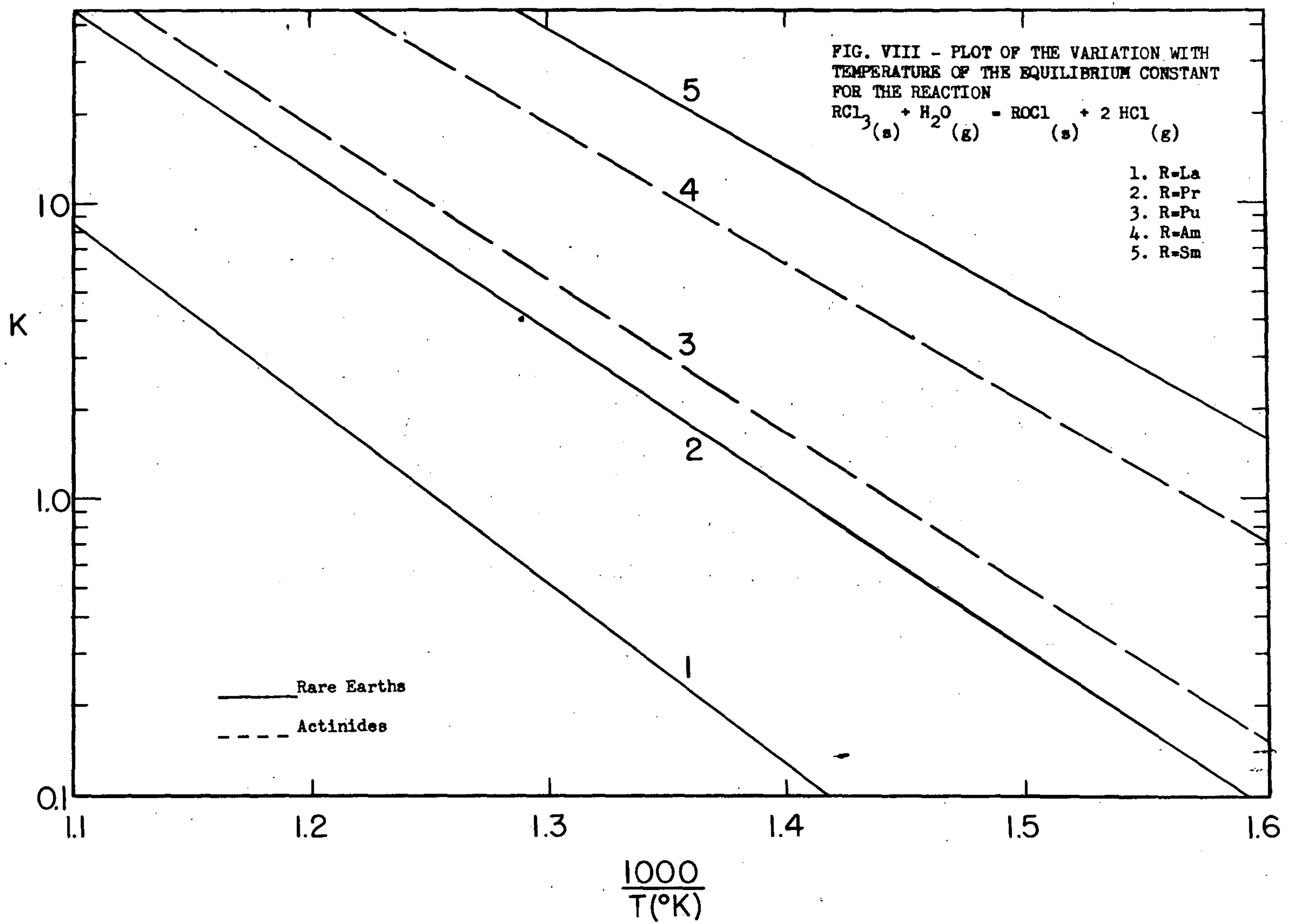

FIG. VIII - PLOT OF THE VARIATION WITH TEMPERATURE OF THE EQUILIBRIUM CONSTANT FOR THE REACTION

$RCl_{3(s)} + H_2O_{(g)} = ROCl_{(s)} + 2\ HCl_{(g)}$

Table XII

Heats and Entropies of the Trichloride Hydrolysis Reactions

Element	ΔH_0°	ΔH_{298}°	ΔS_{298}°	ΔH_{785}°	ΔS_{785}°	K_{785}
Lanthanum	29.6	28.5	36.7	27.18	34.00	0.73
Praseodymium	26.5	25.5	36.7	24.15	34.00	5.10
Plutonium	(26.1)	(25.0)	36.7	(23.7)	(34.00)	(7.6)
Americium	24.1	23.0	36.7	21.69	34.00	24.7
Samarium	22.9	21.9	36.7	20.54	34.00	51.5

B. The Heats and Entropies of Reactions Involving Lanthanum Oxychloride

With the aid of the values obtained for the hydrolysis reaction, reaction (1) in Table XIII, it is possible to calculate heats and entropies of several other reactions of interest. Additional information needed for these calculations include values for the heats and entropies of $LaCl_3$ and La_2O_3 and of the various gases involved in the reactions discussed. Values for HCl, H_2O, Cl_2, O_2, and H_2 may be found in the National Bureau of Standards Tables, which also include values for the heats of formation of the oxide and chloride of lanthanum. However, it was felt that the value reported in this paper for the heat of formation of lanthanum trichloride was more nearly correct, and this value was used in the calculations. Although the entropies of the solids are not accurately known, values for both the oxide[15] and the chloride[2] have been estimated.

Of primary interest in the reactions listed is, of course, reaction (2) which gives the heat and entropy of formation of lanthanum oxychloride. Reaction (3) illustrates the stability of the oxychloride against disproportionation to the trichloride and oxide. Reaction (4) shows the further hydrolysis of the oxychloride to the oxide. Reactions (5), (6), and (7) give several methods of forming the oxychloride.

Table XIII

Reactions Involving Lanthanum Oxychloride

Reaction	ΔH_{298}^{o} (kcal)	ΔS_{298}^{o} (e.u.)
(1) $LaCl_{3(s)} + H_2O_{(g)} = LaOCl_{(s)} + 2HCl_{(g)}$	+28.5	+36.7
(2) $La_{(s)} + 1/2\ O_{2(g)} + 1/2\ Cl_{2(g)} = LaOCl_{(s)}$	-240.1	-35.5
(3) $LaOCl_{(s)} = 1/3\ La_2O_{3(s)} + 1/3\ LaCl_{3(s)}$	+2.4	-5.5
(4) $LaOCl_{(s)} + 1/2\ H_2O_{(g)} = 1/2\ La_2O_{3(s)} + HCl_{(g)}$	+17.9	+10.1
(5) $LaCl_{3(s)} + 1/2\ O_{2(g)} = LaOCl_{(s)} + Cl_{2(g)}$	+14.8	+21.5
(6) $1/2\ La_2O_{3(s)} + 1/2\ Cl_{2(g)} = LaOCl_{(s)} + 1/4\ O_{2(g)}$	-11.1	-2.5
(7) $La_{(s)} + HCl_{(g)} + H_2O_{(g)} = LaOCl_{(s)} + 3/2\ H_{2(g)}$	-160.2	-27.2

V. ACKNOWLEDGMENTS

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