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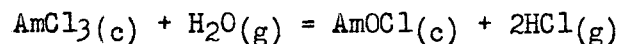| Route to	Noted by	Date	Route to	Noted by	Date
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Heat and Free Energy of the Reaction:

$$AmCl_3(c) + H_2O(g) = AmOCl(c) + 2HCl(g)$$

A. Broido and B. B. Cunningham

July 14, 1950

Berkeley, California

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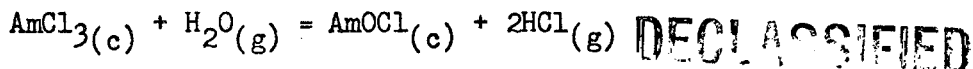
$$AmCl_{3(c)} + H_2O_{(g)} = AmOCl_{(c)} + 2HCl_{(g)}$$ DECLASSIFIED

A. Broido and B. B. Cunningham
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

ABSTRACT

Equilibrium constants at various temperatures in the range $400°C.-575°C.$ have been determined for the vapor phase hydrolysis of americium trichloride. The reaction was studied by a flow method in which mixtures of HCl and H_2O gases were passed over the solid material 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 ΔC_p of the hydrolysis reaction, values were calculated for the heats and entropies of the reaction. The entropy change in the hydrolysis reaction was calculated to be $\Delta S_{298}° = 36.7$ cal. deg.$^{-1}$ mole^{-1}. The heat of reaction obtained was $\Delta H_{298}° = 23.0$ kcal. mole^{-1}.

The heat of formation of $AmOCl_{(c)}$ is calculated to be -251.3 ± 2.7 kcal. mole^{-1} at $298°K.$

DECLASSIFIED

HEAT AND FREE ENERGY OF THE REACTION:

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

A. Broido[*] and B. B. Cunningham
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

July 14, 1950

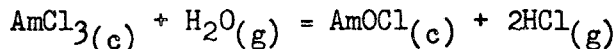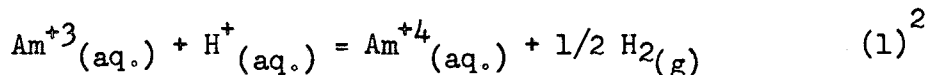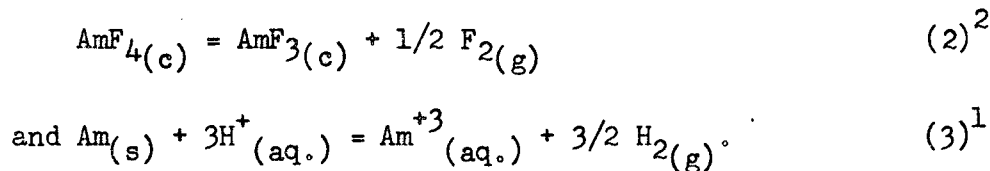The work described here represents a continuation of a systematic investigation of the thermodynamics of americium and its compounds. Values for the heats of formation at $298^{\circ}K$. of $AmO_{2(c)}$, $AmCl_{3(c)}$, and $Am^{+3}_{(aq.)}$ have been reported previously,[1] as have estimates of the free energies of the reactions:

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(1) Lohr and Cunningham, to be published.

$$Am^{+3}_{(aq.)} + H^{+}_{(aq.)} = Am^{+4}_{(aq.)} + 1/2\ H_{2(g)} \qquad (1)[2]$$

---

(2) Eyring, Cunningham, and Lohr, to be published.

$$AmF_{4(c)} = AmF_{3(c)} + 1/2\ F_{2(g)} \qquad (2)[2]$$

$$\text{and}\ Am_{(s)} + 3H^{+}_{(aq.)} = Am^{+3}_{(aq.)} + 3/2\ H_{2(g)}. \qquad (3)[1]$$

Our interest in the thermodynamics of the reaction:

$$AmCl_{3(c)} + H_2O_{(g)} = AmOCl_{(c)} + 2HCl_{(g)} \qquad (4)$$
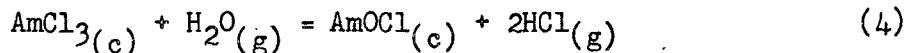
is due in part to the fact that the corresponding plutonium reaction has been

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[*]Present address: Naval Radiological Defense Laboratory, Hunters Point, San Francisco, California. The data presented here were included in a dissertation submitted by A. Broido to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

investigated[3] and comparison of the two is of interest in developing the systematics

(3) Sheft and Davidson, National Nuclear Energy Series, Plutonium Project, Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.25 (McGraw-Hill Book Co., Inc., New York, 1949).

of the thermochemistry of the actinide elements, and in part to the fact that the

technical problem of preparing the pure halides of the actinide and rare earth

elements frequently is complicated by the formation of oxyhalide impurities. A
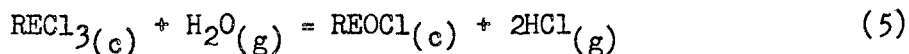
knowledge of the thermodynamics of the formation of the oxyhalides may be ex-

pected to be of value in avoiding such complications.

A concomitant investigation of the thermodynamics of the reaction:

$$RECl_3(c) + H_2O(g) = REOCl(c) + 2HCl(g) \tag{5}$$

where RE stands for La, Pr, or Sm, has also been carried out by us and is reported

elsewhere.[4]

(4) Broido and Cunningham, to be published.

EXPERIMENTAL

Preparation of Americium Stock

The americium used in these experiments was prepared by the sequence of

nuclear reactions:[5]

$$Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241} \xrightarrow{\beta^-} Am^{241}$$
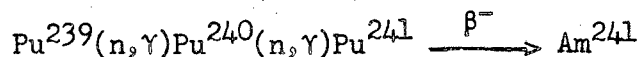
(5) Seaborg, Phys. Rev., 78, 472 (1950).

The americium prepared in this way was separated, concentrated and purified as

described previously.[6] A spectrographic analysis of the americium used in these

(6) Cunningham and Asprey, to be published.

experiments was carried out by Mr. John Conway and Mr. Milton Moore of the Radiation Laboratory. This analysis 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.

Apparatus

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 AmO_2 of about 0.5 mg. weight was mounted on the platinum pan which rested in the ring bent into the quartz fiber. The furnace was 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 was converted to the trichloride or the oxychloride the weight on the pan increased and the fiber was bent downward. The motion of the free end of the fiber was followed with the aid of a microscope.

The operation of the cantilever type quartz fiber microbalance has been described elsewhere.[7]

_____

(7) Cunningham, Nucleonics, 5, No. 5, 62 (1949).

GAS
EXHAUST

┌THERMOCOUPLE

┌Pt. PAN SET IN LOOP
  OF QUARTZ FIBRE

QUARTZ FIBER

GAS INLET

13 m.m. (O.D.)

OPTICAL
PORT

QUARTZ BRACKET
CEMENTED TO PYREX
FLOOR WITH Ag Cl

MICROSCOPE WITH
OCULAR MICROMETER

SARGENT TUBE FURNACE

18 cm.
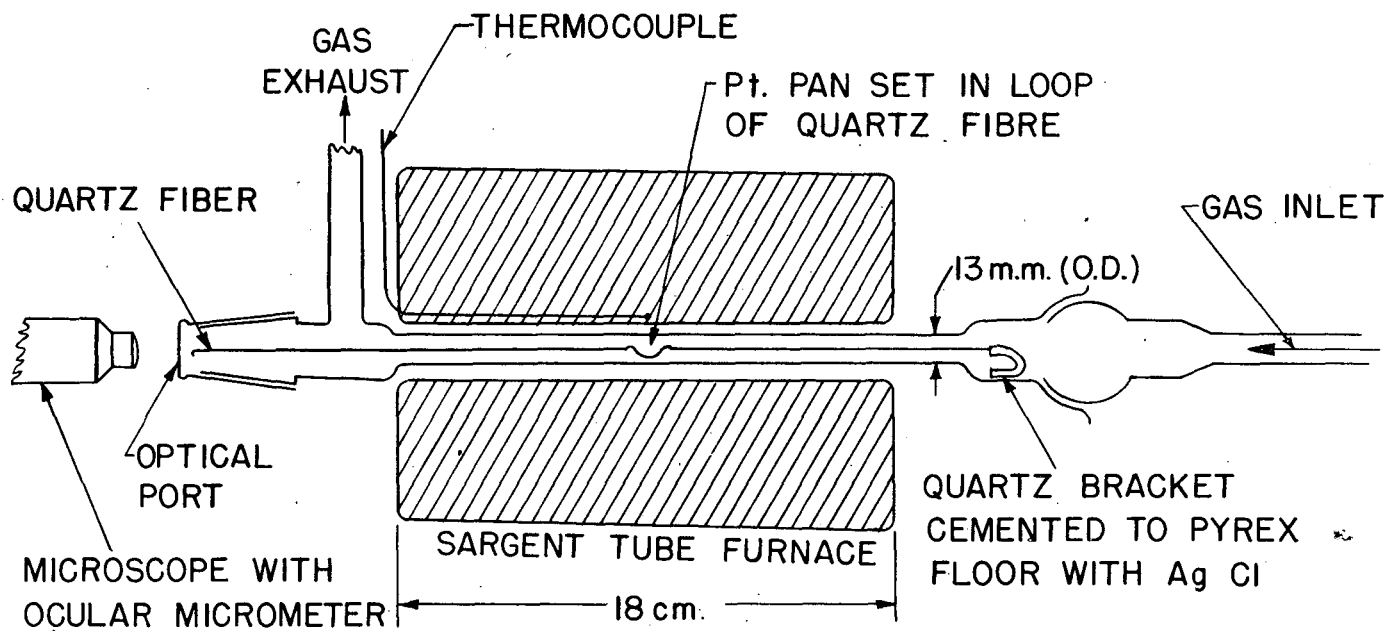
FIG. I - APPARATUS FOR THE DETERMINATION OF THE EQUILIBRIUM CONSTANTS FOR THE REACTION
$$RCl_{3(s)} + H_2O_{(g)} = ROCl_{(s)} + 2 HCl_{(g)}$$
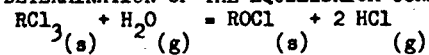
The beam of the balance used in our experiments with americium was about 130 microns in diameter and 12 cm. in length. The diameter of the pointer was about one-half that of the beam, and its length was about 16 cm. The pan, made of half-mil platinum, was approximately 0.5 cm. in diameter and was tied on to the fiber with 2-mil gold wire. The sensitivity of the balance was about 16 mm. per mg. With the particular microscope and ocular micrometer used, this corresponded to about 80 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.

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

An external thermocouple was sealed into place with Sauereisen Insalute
high temperature cement, the end of the couple being placed directly over the
balance pan on the outside of the tube. At this position the temperature dif-
fered quite markedly from that in the center of the tube, the difference in
temperature varying with the temperature. Fig. 2 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. The cold ends of the thermocouple wires were attached
to the potentiometer through copper contacts kept at the melting point of ice.

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.[8] For the

(8) International Critical Tables, (McGraw-Hill Book Co., Inc., New York, 1926).

titrations, standard solutions of HCl and NaOH were made up, with concentrations
of about 0.2M. The concentration of the NaOH solution was at first determined

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

OZ 93
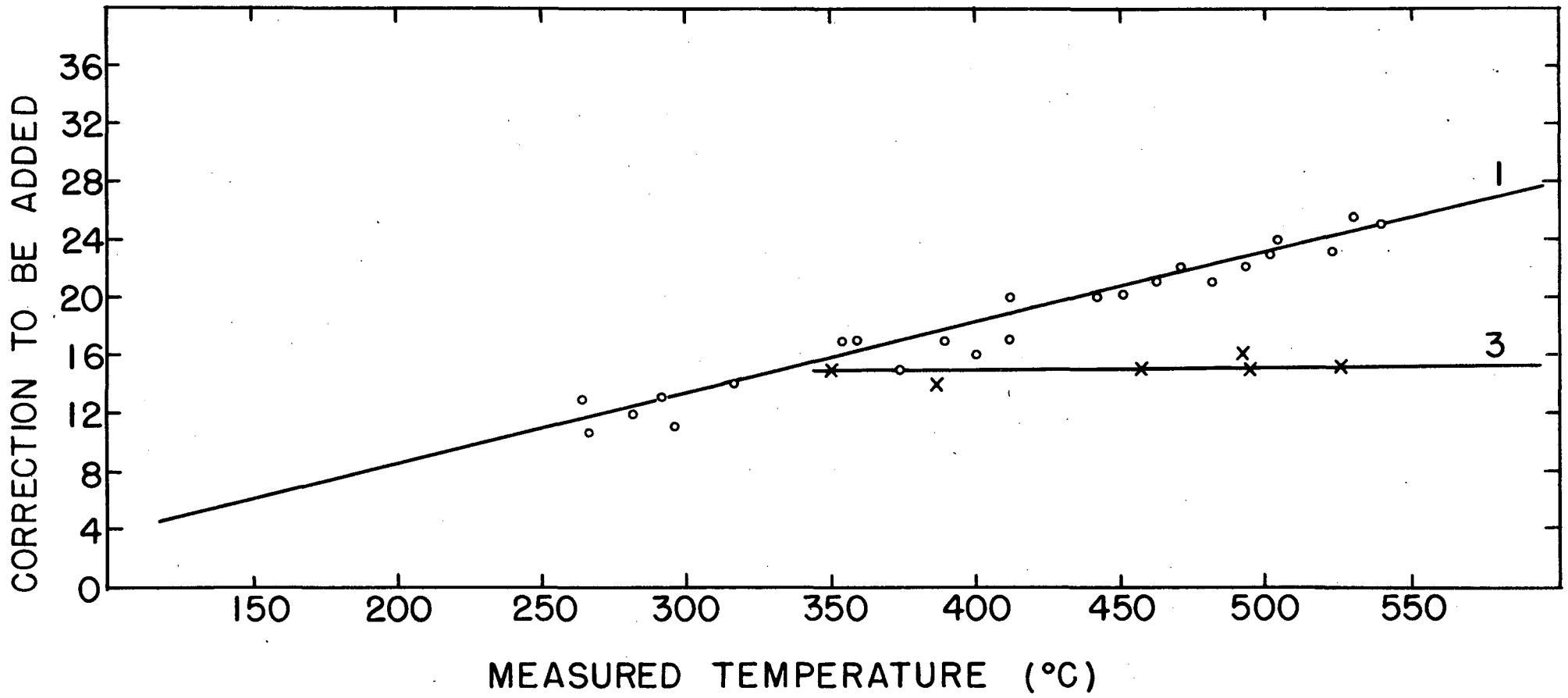
using potassium acid phthalate as the standard. The HCl solution was then standardized against the NaOH solution. During the course of these experiments the HCl and NaOH concentrations were compared frequently. Upon completion of the experiments, a final check was made by means of a gravimetric determination, as AgCl, of the concentration of the HCl solution. All standardizations agreed to within less than $\pm 0.1\%$.

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.[8]

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 II.

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[9] it has been found that, because of thermal diffusion effects,

(9) Brewer and Lofgren, U. S. Atomic Energy Commission Declassified Document AECD-1834 (Jan. 2, 1948).

Table II

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

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, values of the

equilibrium constant for the americium hydrolysis were determined, at flow

rates which 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, one point was determined using argon, rather than nitrogen, as the

inert gas with no apparent effect resulting from this change.

Equilibrium Measurements

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. 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 identity of the solid phases, $AmCl_3$ and AmOCl, obtained in these measurements was verified by x-ray diffraction analysis in separate experiments. It has been pointed out by Giauque[10] that the heat content of finely-divided solid

(10) Giauque, J. Am. Chem. Soc., 71, 3192 (1949).

materials may be considerably different from that of the same materials in the form of macro crystals. In the case of our measurements, Dr. D. H. Templeton has estimated from the x-ray diffraction pictures that our crystals were of the order of 1000 $\overset{o}{A}$ in diameter, and hence not significantly different from macro crystalline preparations.

The values obtained for the equilibrium constant for the vapor phase hydrolysis of americium trichloride are summarized in Table III. 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.[8] 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.

Table III

The Variation with Temperature of the Equilibrium Constant for the Reaction

$$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$$
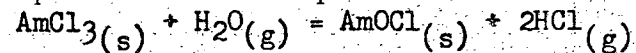
Experiment No.	Reaction Temp. ($^\circ$K)	1000/T	Conc. of HCl Soln. (% HCl)	Temp. of HCl Soln. ($^\circ$C)	P_{HCl} (mm)	P_{H_2O} (mm)	$K = \dfrac{P_{HCl}^2}{P_{H_2O} \times 760}$ (atm^{-1})	Mean K	$\Delta F_{Experimental}$ (Kilocalories)	$\Delta F_{Calculated}$ (Kilocalories)
1	846	1.182	39.42	20.0	330	2.17	>66.2	68.1	-7.09	-7.07
				22.3	369	2.56	<70.0			
2	828	1.208	39.24	19.5	301	2.13	>55.9	57.1	-6.65	-6.45
				20.5	319	2.29	<58.4			
3	818	1.222	38.96	19.0	266	2.10	>44.3	46.5	-6.24	-6.12
				21.0	302	2.46	<48.8			
4	809	1.236	38.30	21.0	249	2.65	>30.8	32.4	-5.59	-5.82
				23.0	280	3.03	<34.0			
5	786	1.272	37.88	20.0	202	2.53	>21.2	22.7	-4.87	-5.03
				23.0	242	3.19	<24.2			
6	756	1.323	37.02	22.5	180	3.40	>12.5	13.4	-3.90	-4.01
				25.0	207	3.98	<14.2			
7	741	1.350	37.00	20.2	152	2.81	>10.9	11.7	-3.62	-3.51
				23.5	186	3.65	<12.5			
8	720	1.389	36.28	22.2	133	3.48	> 6.7	7.1	-2.80	-2.78
				24.1	153	4.03	< 7.6			
9	700	1.429	35.76	22.0	114	3.70	> 4.6	4.9	-2.21	-2.09
				24.0	128	4.22	< 5.1			
10	679	1.473	34.92	22.9	88	4.33	> 2.4	2.5	-1.24	-1.38
				25.0	97	4.85	< 2.6			

DISCUSSION AND CONCLUSIONS

The use of the cantilever type quartz fiber microbalance to follow the
progress of the hydrolysis reaction has proved to be extremely convenient.
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 partic-
ularly advantageous at the lower temperatures. At the higher temperatures,
about $500^{\circ}C.$, the reaction usually proceeded quite rapidly, frequently going
essentially to completion in a matter of minutes. At the lower temperatures,
about $350^{\circ}C.$, 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
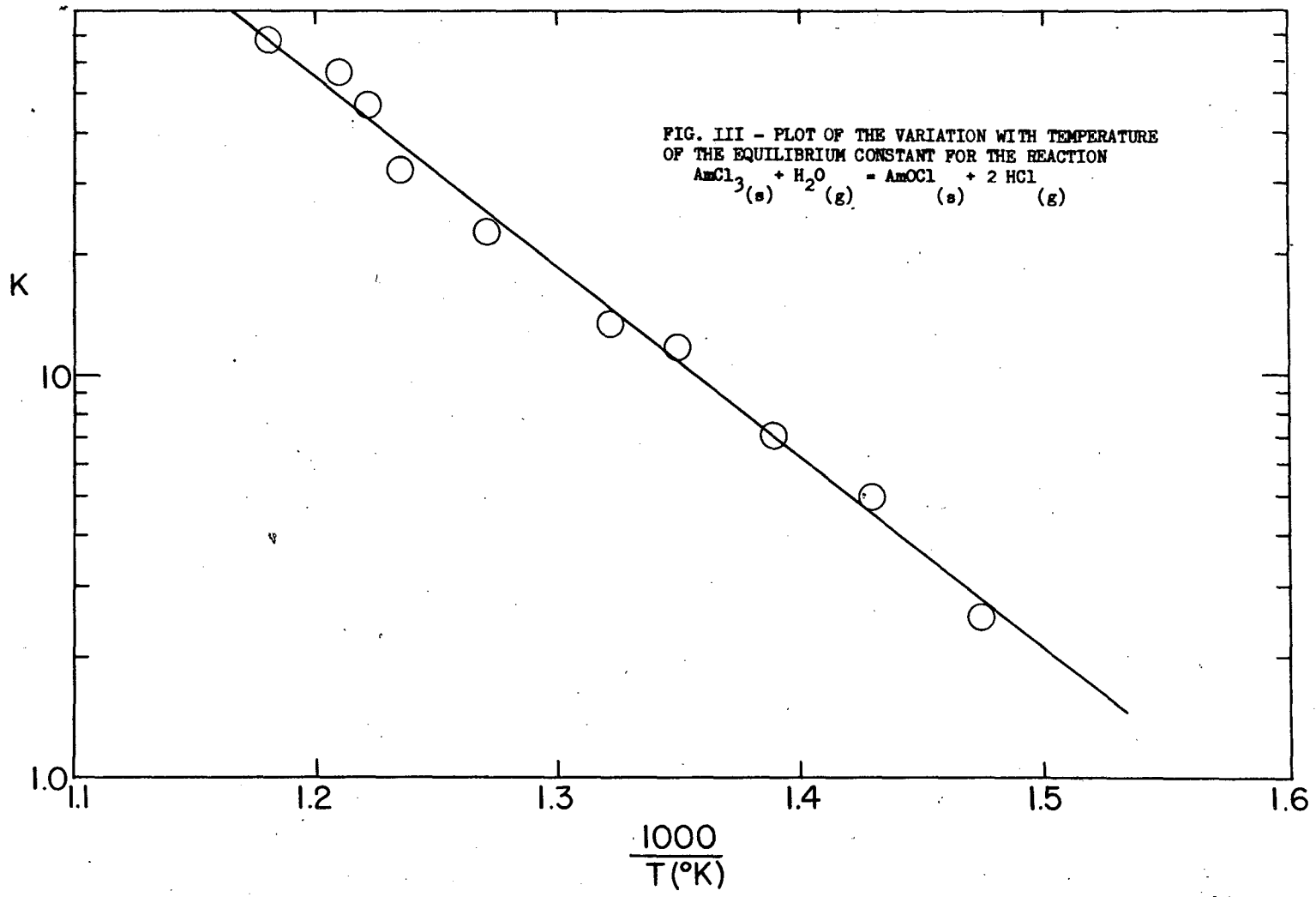for each observation.

C_p equations for the gases are readily available, but it is necessary to
estimate values of the heat capacity of the solids. The heat capacity of the
solids may be estimated by use of the additivity principle discussed by Lewis
and Randall.[11] Using the values recommended for temperatures of about $400^{\circ}C.$,

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(11) Lewis and Randall, "Thermodynamics," (McGraw-Hill Book Co., Inc.,
New York, 1923).

---

namely 7.1 for elements heavier than oxygen and 5.9 for oxygen, the result is
-8.3 cal. mole^{-1} deg.$^{-1}$. Combining this value with the equations for the gases
one obtains

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

The experimental data are plotted in Fig. 3.

K

10

1.0

$$\frac{1000}{T(^\circ K)}$$

1.1   1.2   1.3   1.4   1.5   1.6

FIG. III - PLOT OF THE VARIATION WITH TEMPERATURE
OF THE EQUILIBRIUM CONSTANT FOR THE REACTION
$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2 HCl_{(g)}$

-16-

With the aid of the heat capacity equation, a curve was calculated giving the best fit with the experimental points. From this the thermodynamic properties listed in Table IV were calculated.

Table IV

Thermodynamic Properties of the Reaction:
$$AmCl_{3(c)} + H_2O_{(g)} = AmOCl_{(c)} + 2HCl_{(g)}$$

ΔH_0^o kcal.	ΔH_{298}^o kcal.	ΔS_{298}^o cal./deg.	ΔH_{785}^o kcal.	ΔS_{785}^o cal./deg.	K_{785}
+24.1	+23.0	+36.7	+21.69	+34.00	24.7

The probable errors of the three values on the right, ΔH_{785}^o, ΔS_{785}^o, and K_{785}, in the experimental region, are considered to be less than ± 0.1 kcal., ± 0.1 e.u., and $\pm 10\%$, respectively.

Sheft and Davidson[3] have investigated the corresponding reaction for $PuCl_{3(c)}$, using a static method and approaching equilibrium from one side only. As a result the scatter in their points is much greater than that observed here. Using an estimated ΔC_p of 2.4 cal./mole/^{o}C. they report for the plutonium reaction:

$$\Delta H_{298}^o = +22.2 \pm 0.7 \text{ kcals. and } \Delta S_{298}^o = -32.7 \text{ cal./deg.}$$

The same authors also investigated the hydrolysis of plutonium tribromide by $H_2O_{(g)}$, for which they report:

$$\Delta H_{298}^o = +24.1 \text{ kcal. and } \Delta S_{298}^o = +35.7 \text{ e.u.}$$

Broido and Cunningham[4] have investigated the analogous reaction for $LaCl_{3(c)}$, $PrCl_{3(c)}$, and $SmCl_{3(c)}$ and have found ΔS_{298}^o to be $+36.7 \pm 0.1$ e.u. in all cases.

In view of the relatively large experimental error of the measurements by Sheft and Davidson we believe that ΔS_{298}^o for the plutonium trihalide reactions

investigated by them is 36.7 ± 0.1 e.u. In particular, the difference of 3 e.u. between the entropy of the trichloride and that of the tribromide reaction, which Sheft and Davidson accept as being real, seems to us to be improbable.

Consequently, we have recalculated their results, using our ΔC_p equation and a value of $\Delta S_{298}^{\,\circ} = 36.7$ e.u. We then get for the reaction:

$$PuCl_{3(c)} + H_2O_{(g)} = PuOCl_{(c)} + 2HCl_{(g)}$$

$\Delta H_0^{\,\circ} = 26.1$ kcals. and $\Delta H_{298}^{\,\circ} = 25.0$ kcals.

$\Delta H_{298}^{\,\circ}$ for the americium reaction is thus two kilocalories less positive than that for plutonium. A similar trend, in order of decreasing ionic radius, has been noted for the analogous hydrolysis of the rare earth trichlorides, although here the change in ΔH for a corresponding change in ionic radius appears to be only about half as great.

Lohr and Cunningham[1] report the heat of formation of $AmCl_{3(c)}$ to be -251.3 ± 2.7 kcal. at $298^{\circ}K$. Whence we calculate for the heat of formation of $AmOCl_{(c)}$ at $298^{\circ}K$.

$$\Delta H_{f(298)}^{\,\circ} = -252.6 \pm 2.7 \text{ kcal.}$$

SUMMARY

A convenient method of investigating equilibria of the type:

$$RCl_{3(c)} + H_2O_{(g)} = ROCl_{(c)} + 2HCl_{(g)},$$
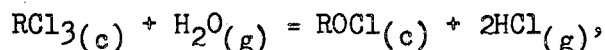
using submilligram quantities of solid trichlorides, is described in detail.

The heats and entropies for the reaction:

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

were found to be:

$$\Delta H_0^{\,0} = +24.1 \text{ kcal./mole}, \quad \Delta H_{298}^{\,0} = +23.0 \text{ kcal./mole},$$

$$\Delta H_{785}^{\,0} = +21.69 \text{ kcal./mole}; \quad \Delta S_{298}^{\,0} = +36.7 \text{ cal./deg./mole},$$

$$\Delta S_{785}^{\,0} = +34.00 \text{ cal./deg./mole and } K_{785} = 24.7.$$

The heat of formation of $AmOCl_{(c)}$ is calculated to be -251.3 ± 2.7 kcal./mole at $298^{\circ}K$.

ACKNOWLEDGMENT