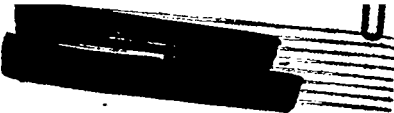


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EQUILIBRIUM CONSTANTS AND HEATS OF REACTION FOR THE  
HYDROFLUORINATION OF URANIUM DIOXIDE AND PLUTONIUM DIOXIDE

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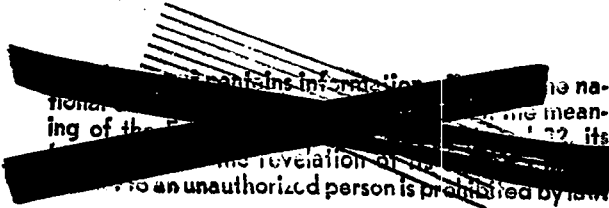
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ABSTRACT

Direct determinations were made of the equilibrium conditions for the reactions of hydrogen fluoride with uranium dioxide at 600°C, 705°C and 800°C and with plutonium dioxide at 400°C and 600°C. From these data the equilibrium constants at these temperatures were calculated. From the change of equilibrium constant with temperature the heats of reaction were calculated. The heat of reaction of hydrogen fluoride on uranium dioxide to yield uranium tetrafluoride was found to be  $-\Delta H = 42080$  cal/mol. This is in fair agreement with the value 45800 cal/mol calculated from the known heats of formation of the compounds involved in the reaction. The heat of reaction of hydrogen fluoride on plutonium dioxide calculated from the equilibrium constants at 400°C and 600°C is 9230 cal/mol.

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EQUILIBRIUM CONSTANTS AND HEATS OF REACTION FOR THE  
HYDROFLUORINATION OF URANIUM DIOXIDE AND PLUTONIUM DIOXIDE

INTRODUCTION

In an earlier report, LA-193, the equilibrium constants for the hydrofluorination of plutonium dioxide at 400°C and at 600°C are given. From these constants the heat of reaction is found to be <sup>10250</sup>~~-9236~~ cal/mol. This value could be calculated from the heats of formation of the compounds involved in the reaction, were these heats known. The heat of reaction of uranium dioxide with hydrogen fluoride has been calculated both from the measured equilibrium constants in the temperature range 600°C to 800°C and from the known heats of formation of the compounds. The agreement between these two independent values lends reliability to the single value obtained for the heat of hydrofluorination of plutonium dioxide.

A direct determination of the equilibrium constant in green salt formation at 800°C is also important because this high temperature is required in the sintering operation. Thus the knowledge of the critical limits of the H<sub>2</sub>O/HF ratio at this high temperature is necessary.

The procedure employed here is the same as that reported in LA-193 except that in the reaction with UO<sub>2</sub> hydrogen is used as the inert gas to insure that the uranium remain in the tetravalent state, while in the reaction with PuO<sub>2</sub> oxygen is necessary for the same purpose.

EXPERIMENTAL PART

The apparatus is shown in Fig. 1. The 200-mg sample of oxide was held in a small platinum bucket weighing about 140 mg. This bucket was suspended by means of a straight 3.8-mil platinum-rhodium wire from the arm of a torsion

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balance (Roller Smith Precision Balance 0 to 500 mg) and hung in a 3/4-inch nickel tube. The tube was wound with resistance wire and was thermally insulated so that temperatures up to 800°C could be attained. Current was supplied by a small Variac. The temperature of the tube at the point where the bucket was suspended was read to 1°C by means of a chromel-alumel thermocouple welded to the tube.

The gases were admitted at the bottom and exhausted at the top through a side arm. The top of the tube was closed with two nickel covers. The wire passed through holes in the covers without touching the sides. Gentle suction from an aspirator drew the gases out of the top section of the tube, drawing off the reacting gases that pass through the lower cover and also drawing in some air through the upper cover. Thus the corrosive gases were removed safely without interfering with the weighing of the bucket.

The rate of flow of anhydrous hydrogen fluoride was regulated by means of a Weinstock Valve (LA-149). The rate was measured accurately by drawing the exit gases through standard alkali for a measured time and then titrating the excess alkali. From the milli equivalents of HF per minute found by titration the partial pressure of HF at the furnace conditions was calculated assuming the gas to be monomolecular at these temperatures.

Hydrogen, in the experiments with  $\text{UO}_2$ , and oxygen, in those with  $\text{PuO}_2$ , was admitted into the bottom of the reactor through a second tube after having passed through a flask where it was saturated with water vapor. From the rate of flow of the dry gas, as measured by a flow meter, and the temperature of the saturator the partial pressures of both the carrying gas ( $\text{H}_2$  or  $\text{O}_2$ ) and the water vapor were calculated.

The reaction was sufficiently rapid even when the experimental conditions

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are close to the equilibrium conditions so that only one or two minutes' observation were required to determine whether the weight was increasing or decreasing under any given set of conditions. By varying either the rate of flow of hydrogen or the temperature of the saturator, the equilibrium could be approached from either side as often as desired.

In Table I are given the data obtained for  $\text{UO}_2$ .

Table I

Equilibrium Conditions for the Reaction:  $\text{UO}_2 + 4\text{HF} \rightarrow \text{UF}_4 + 2\text{H}_2\text{O}$

<u>T, °C</u>	<u>HF, milli equiv/min</u>	<u>H<sub>2</sub>, ml/min</u>	<u>H<sub>2</sub>O</u>	<u>HF, atm</u>	<u>H<sub>2</sub>O, atm</u>
600	8.71	150, 22°C, 592 mm	84°	0.350	0.458
705	4.74	100, 25°C, 592 mm	73°	0.451	0.247
800	8.05	100, 25°C, 592 mm	69°	0.611	0.147

In Table II are given the data obtained for  $\text{PuO}_2$ .

Table II

Equilibrium Conditions for the Reaction:  $\text{PuO}_2 + 4\text{HF} \rightarrow \text{PuF}_4 + 2\text{H}_2\text{O}$

<u>T, °C</u>	<u>HF, milli equiv/min</u>	<u>O<sub>2</sub>, ml/min</u>	<u>H<sub>2</sub>O</u>	<u>HF, atm</u>	<u>H<sub>2</sub>O, atm</u>
400	3.0	109, 22°C, 580 mm	62°	0.384	0.175
600	5.4	104, 22°C, 580 mm	63.5°	0.535	0.141

The equilibrium constants were calculated in the usual way,

$$K_t = \frac{(\text{P}_{\text{H}_2\text{O}})^2}{(\text{P}_{\text{HF}})^4}$$

The values of  $\ln_e K$  are plotted against  $1/T_K^\circ$  in Fig. 2. From the slopes of these lines the heats of reaction were calculated assuming the heat of reaction to be constant over the temperature interval. The values are given in Table III.

Table III

Equilibrium Constants and Heats of Reaction

A. For  $UO_2 + 4HF \rightarrow UF_4 + 2H_2O$

<u>T°C</u>	<u>1000/T<sub>K</sub><sup>°</sup></u>	<u>K</u>	<u>ln K</u>
600	1.145	14.0	2.639
705	1.021	1.47	0.385
800	0.932	0.155	-1.865

$$\ln K = \frac{42080}{RT_K^\circ} - 21.5 \quad - \Delta H = 42080 \text{ cal/mol.}$$

B. For  $PuO_2 + 4HF \rightarrow PuF_4 + 2H_2O$

<u>T°C</u>	<u>1000/T<sub>K</sub><sup>°</sup></u>	<u>K</u>	<u>ln K</u>
400	1.485	1.40	0.336
600	1.145	0.287	-1.249

$$\ln K = \frac{10220}{RT_K^\circ} - 1.91 \quad - \Delta H = 9230 \text{ cal/mol.}$$

Calculation from Known Heats of Formation

In the case of uranium the heat of reaction at the various temperatures can be calculated from the heats of formation of the compounds and known or estimated heat capacities. Most of these values are available in the project literature. For convenience they are listed here.

## Hydrogen fluoride

$$\Delta H_{600}^{\circ} = -64.81 \quad \text{Kcal/mol}$$

$$\Delta H_{705}^{\circ} = -64.89$$

$$\Delta H_{800}^{\circ} = -64.96$$

## Water vapor

$$\Delta H_{600}^{\circ} = -59.00 \quad \text{Kcal/mol}$$

$$\Delta H_{705}^{\circ} = -59.20$$

$$\Delta H_{800}^{\circ} = -59.32$$

## Uranium dioxide

$$\Delta H_{18}^{\circ} = -256.6 \quad \text{Kcal/mol}$$

$$\Delta H_{600}^{\circ} = -254.9$$

$$\Delta H_{705}^{\circ} = -255.6$$

$$\Delta H_{800}^{\circ} = -257.0$$

## Uranium tetrafluoride

$$\Delta H_{18}^{\circ} = -446 \quad \text{Kcal/mol}$$

$$\Delta H_{600}^{\circ} = -442.4$$

$$\Delta H_{705}^{\circ} = -442.5$$

$$\Delta H_{800}^{\circ} = -443.6$$

References: CC-1334, CC-408, CT-385, Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Pub. Co., N.Y. 1936, p. 99.

From these values the heat of reaction has been calculated for the reaction:  $UO_2 + 4HF \rightarrow UF_4 + 2H_2O$  at  $18^\circ$ ,  $600^\circ$ ,  $705^\circ$ , and  $800^\circ C$ .

$$\Delta H_{18^\circ} = -47.28 \text{ Kcal/mol}$$

$$\Delta H_{600^\circ} = -46.26$$

$$\Delta H_{705^\circ} = -45.74$$

$$\Delta H_{800^\circ} = -45.44$$

$$\text{Av. value } 600 - 800^\circ = -45.8$$

The value,  $-42.08$ , calculated from the change in equilibrium constant with temperature is in fair agreement with the above values calculated from heats of formation.

#### SUMMARY AND CONCLUSIONS

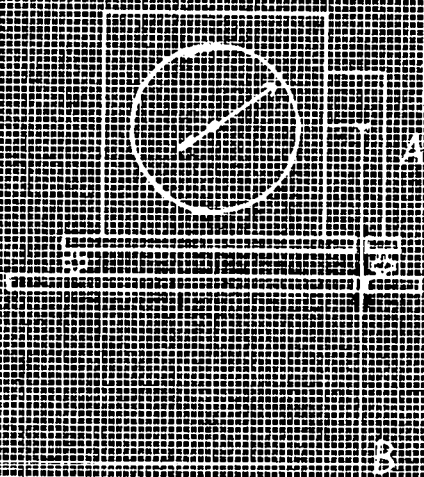
The value of the heat of hydrofluorination of uranium dioxide with anhydrous hydrogen fluoride has been found to be  $-42.08$  Kcal/mol from the equilibrium constants in the temperature range  $600^\circ - 800^\circ C$ .

The value of the heat of hydrofluorination of plutonium dioxide with anhydrous hydrogen fluoride has been found to be  $-9.23$  Kcal/mol by the same method.

At the same temperature ( $600^\circ C$ ) the equilibrium constant for the reaction with  $PuO_2$  is  $0.287$  compared to  $14.0$  for the reaction with  $UO_2$ . This means that the partial pressure of  $H_2O$  allowable in the gas stream is about 7 times lower in the case of plutonium dioxide than it is with uranium dioxide. However, the best anhydrous hydrogen fluoride and commercial compressed oxygen are well below the limit required.



Figure 1  
 Apparatus for Determination of  
 Equilibrium Conditions



- A Roller-Smith Precision Balance
- B No. 10 galv. wire #38 B.S.
- C Pb bucket wt. 130 mg
- D Vented Florence Tube

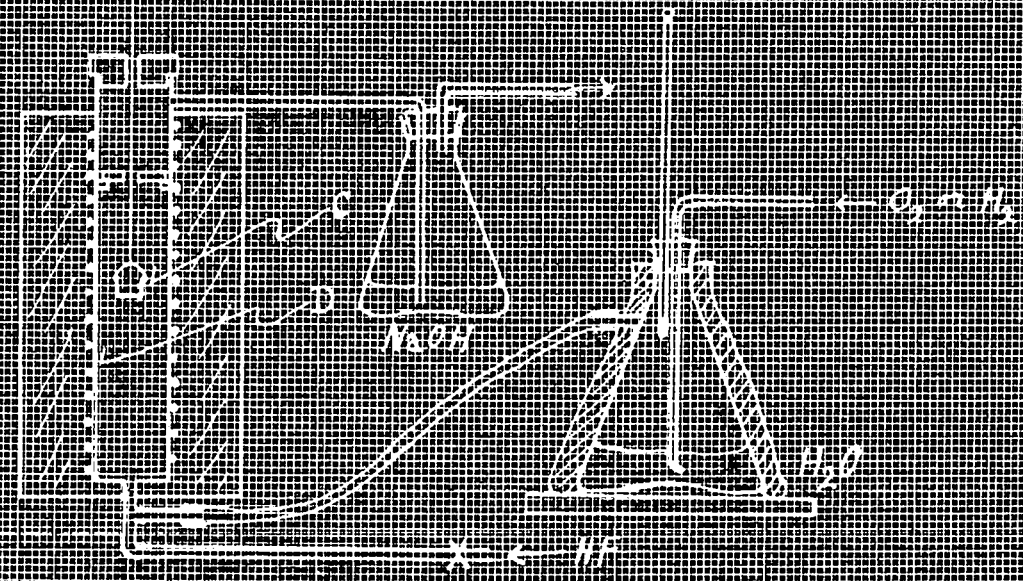
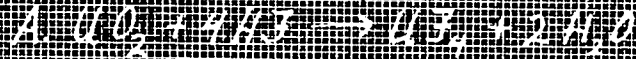


Figure II

Equilibrium Constants for the Reactions

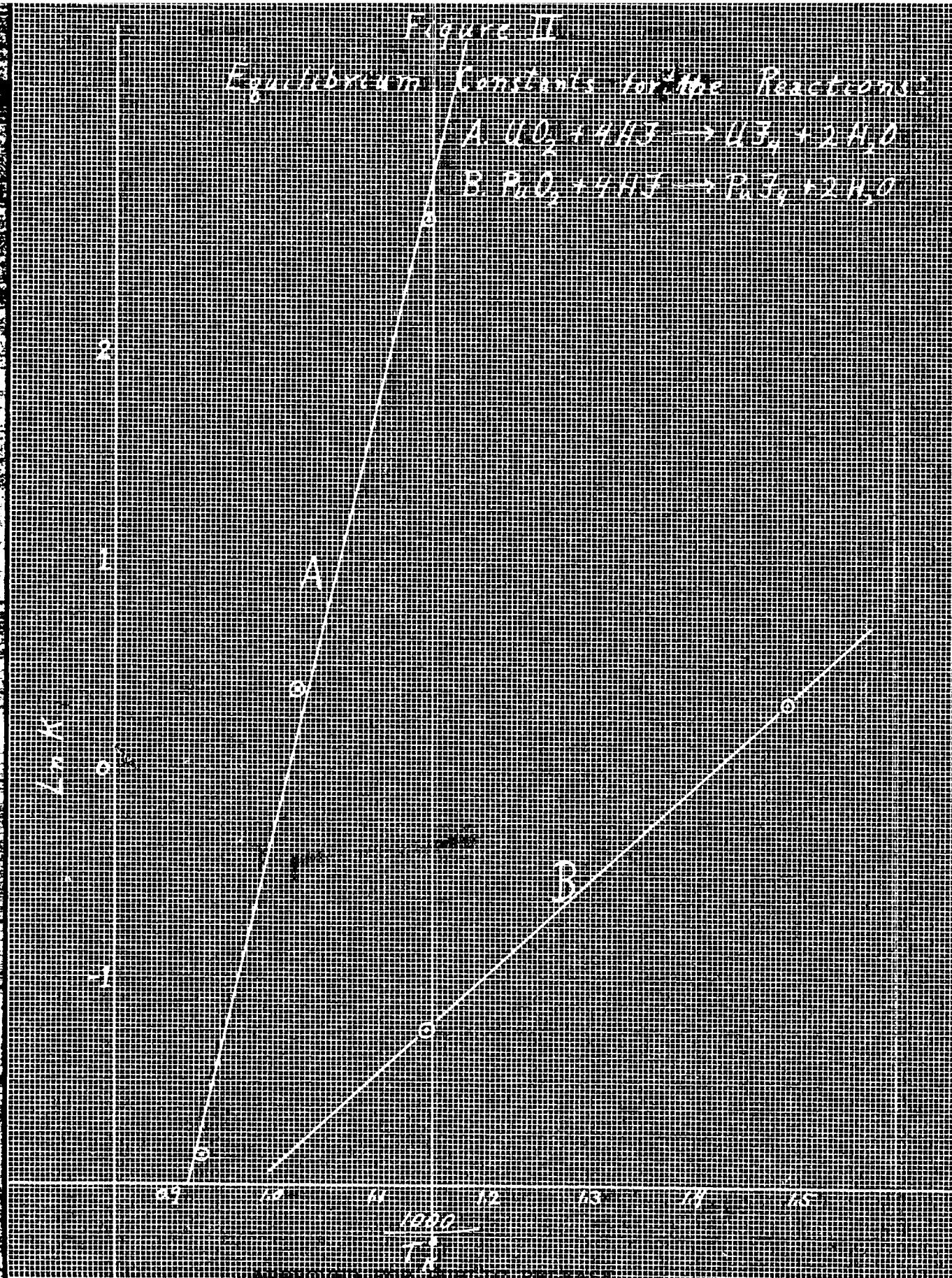


log K

2  
1  
0  
-1  
-2

80 90 100 110 120 130 140 150

$\frac{1000}{T}$



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