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THERMAL DECOMPOSITION OF THE COMPOUND URANIUM TETRAFLUORIDE-
AMMONIUM FLUORIDE

H. A. Bernhardt, R. A. Gustison, J. C. Posey

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Title: THERMAL DECOMPOSITION OF THE
COMPOUND URANIUM TETRAFLUORIDE
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Author: H. A. Bernhardt
R. A. Gustison
J. C. Posey

CARBIDE AND CARBON CHEMICALS CORPORATION
K-25 Laboratory Division

A B S T R A C T

The compound uranium tetrafluoride-ammonium fluoride ($\text{UF}_4 \cdot \text{NH}_4\text{F}$) may be completely decomposed into uranium tetrafluoride and gaseous ammonium fluoride by heating in vacuo for 100 minutes at 375°C . It was found that the variation of decomposition rate with the temperature is given by the formula:

$$\log \frac{1}{t} \log \frac{W_0}{W} = 2.42 \pm 0.10 - (2.67 \pm 0.38) \left(\frac{1000}{T} \right), \text{ where}$$

t = time in minutes.
W₀ = ratio of ammonia to uranium in original material.
W = ratio of ammonia to uranium after time t.
T = temperature in degrees Kelvin.

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THERMAL DECOMPOSITION OF THE COMPOUND URANIUM TETRAFLUORIDE-AMMONIUM FLUORIDE

H. A. Bernhardt, R. A. Gustison, and J. C. Posey

INTRODUCTION

For the conversion of uranium compounds to uranium hexafluoride, uranium tetrafluoride is the most convenient intermediate. In the recovery of uranium from certain solutions, the compound uranium tetrafluoride-ammonium fluoride ($UF_4 \cdot NH_4F$) is obtained. The purpose of this work was to determine optimum conditions for the thermal decomposition of the compound uranium tetrafluoride-ammonium fluoride to uranium tetrafluoride.

EXPERIMENTAL

Preparation of the Compound Uranium Tetrafluoride-Ammonium Fluoride. The compound uranium tetrafluoride-ammonium fluoride was prepared by the following procedure:

A solution of uranyl sulfate was prepared containing 100% excess of ammonium fluoride. The pH was adjusted to 3.3 and a 100% excess of ferrous sulfate was added. The bright green crystalline precipitate was filtered and washed. After thorough washing with distilled water, and drying at 50°C, the mole ratio of ammonia to uranium was 1.15.

Thermal Decomposition. The apparatus used for the thermal decomposition study is shown in figure 1. A pyrex distillation flask was used as the reaction cell. The bulb of the flask was placed in the furnace, which was a clay cup wound with nichrome wire. The side-arm of the flask was connected to a Welch vacuum pump through a cold trap.

A sample of the compound uranium tetrafluoride-ammonium fluoride weighing between 2 and 5 gm was sealed into the distillation flask. The system was evacuated and the furnace turned on. The distillation flask was maintained at the desired temperature while evacuating continuously. The pressure of the system was maintained below 10 microns by the Welch pump. Decomposition temperatures from 151 to 385°C and reaction times from 95 to 250 min were studied. The mole ratio of ammonia to uranium in the product was determined by analysis. This ratio was a measure of the completeness of decomposition.

FIGURE 1

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THERMAL DECOMPOSITION APPARATUS	
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DATE: MAY 17, 1949	DWG NO: LD-B854

EXPERIMENTAL RESULTS

The thermal decomposition of the compound uranium tetrafluoride-ammonium fluoride could be observed visually by the generation of a white sublimate (ammonium fluoride) which condensed in the side-arm of the distillation flask. As a temperature of the reactor was raised, the generation of the white sublimate was first noted at a temperature of 130°C.

The mole ratios of ammonia to uranium in the products for a number of decomposition runs are given in table I.

TABLE I

RATE OF THERMAL DECOMPOSITION OF THE COMPOUND URANIUM TETRAFLUORIDE-AMMONIUM FLUORIDE

Temperature, °C	Reaction Time, min	Final Mole Ratio of Ammonium to Uranium
151	100	1.120
196	95	1.012
216	250	0.7188
243	90	0.8279
271	90	0.3249
302	190	0.2526
306	100	0.1672
365	120	0.00736
376	150	0.01284
285	108	0.01272

Note: Mole ratio of ammonia to uranium in starting material was 1.15.

These results were correlated by postulating normal first order dependence of reaction rate upon concentration and by assuming a variation of the first order reaction rate constant with temperature according to the Arrhenius equation.

The first order rate dependence is expressed by equation (1):

$$\log \frac{W_0}{W} = \frac{k \cdot t}{2.303}, \text{ where} \quad (1)$$

W_0 = ratio of ammonia to uranium in original material.

W = ratio of ammonia to uranium after time t .

t = time in minutes.

k = reaction rate constant.

The Arrhenius equation was used in the form:

$$\log k = \frac{-E}{4.567 T} + C, \text{ where} \quad (2)$$

k = reaction rate constant

E = energy of activation of the reaction.

T = temperature in degrees Kelvin.

C = integration constant.

Values of k were obtained for each temperature from the data recorded in table I by using equation (1) and making a rough correction for amount of reaction while the reactor was reaching final temperature. The least mean squares plot of $\log k$ vs $1/T \times 10^3$ is shown in figure 2 (solid line). Shown as dotted lines on the graph are the 95% confidence limits of the line.

From the slope of the line in figure 2, it was calculated that the activation energy of the decomposition is 12.23 ± 1.75 k cal/mole at the 95% confidence level. Using the values of E and C determined from figure 2, equation (2) may be put in the form:

$$\log k = 2.78 \pm 0.10 - (2.672 \pm 0.38) \cdot \frac{1000}{T}, \text{ where} \quad (3)$$

the limits of accuracy are expressed at the 95% confidence level.

DISCUSSION OF RESULTS

Composition of the Compound Uranium Tetrafluoride-Ammonium Fluoride.

The mole ratio of ammonia to uranium in the compound uranium tetrafluoride-ammonium fluoride is greater than one to one. Since the observed mole ratio, 1.15, is not integral nor half-integral, it is unlikely that chemical bonding alone is involved. It is more probable that the ammonium fluoride in excess of a one to one mole ratio became attached by some mechanism of coprecipitation, such as occlusion or adsorption.

LEGEND:

- Least mean squares line.
 --- 95 per cent confidence limits of the line.

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DECOMPOSITION RATE CONSTANT AS A FUNCTION OF TEMPERATURE	
K-25 PLANT CARBIDE & CARBON CHEMICALS CORP	
DRWN <u>B. Hammer</u>	APPV'D <u>JCB</u>
DATE: MAY 17, 1949	DWG NO: LD-8853

The effect of loosely bound excess ammonium fluoride would be to increase disproportionately the rate of decomposition at the lower temperatures. Thus, the observed activation energy of the decomposition is probably lower than that for uranium tetrafluoride-ammonium fluoride in which the mole ratio of ammonia to uranium is exactly one to one.

Decomposition of the Compound Uranium Tetrafluoride-Ammonium Fluoride.

The application of the least mean squares method to the calculation of the mean value of the graph, figure 2, is not entirely rigorous. That portion of the variance which is due to analytical error is not constant but should approach infinity at either extremity of the line. This may be seen from the nature of the function $\log \log \frac{W_0}{W}$. However, since the analytical con-

tribution to the total variance is not known and there is no evidence in the data of this effect, all points were given equal weight.

The reaction times and temperatures given in table I and figure 2 were corrected to allow for the decomposition which took place during the heating of the samples to the temperature of the run. The reaction time was counted from the time when the reaction rate constant reached half the value finally attained. The average temperature was calculated from the expression:

$$\text{Average temperature} = \frac{\sum (\text{temperature} \times \text{time})}{\text{total time}} \quad (4)$$

These corrections had only a slight effect on the calculated values of the reaction rate constant and the activation energy. Without correction, the activation energy was calculated as 11.88 $\pm$ 1.73 k cal/mole as compared with the corrected value, 12.23 $\pm$ 1.75 k cal/mole.

Interpretation of Results. It may be seen by inspection of table I and figure 2 that the rate of decomposition increases with the temperature. At a temperature of 375°C, the decomposition is 99% complete in 100 minutes. The degree of decomposition for other temperatures and reaction times may be calculated from equation (3).

It should be noted that these results would not apply directly to operations in which the rate of diffusion of ammonium fluoride through the bed of salt was slow enough to affect the reaction rate.

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SUMMARY

When uranium tetrafluoride is precipitated from a solution containing ammonium fluoride, the precipitate contains slightly more than one mole of ammonium fluoride per mole of uranium tetrafluoride. The thermal decomposition in vacuo of this additional compound was studied over the temperature range 151 to 385°C. At a temperature of 375°C, the decomposition may be carried practically to completion in 100 minutes. From the experimental data, an equation was derived relating decomposition rate and temperature.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Special Analysis Section of the Works Laboratory for all analyses made in connection with this problem.

LABORATORY REFERENCE

Notebook No. HL-720, issued to J. C. Posey, October 31, 1946, pages 285 to 299.

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