[CONTRIBUTION FROM THE SOLID STATE DIVISION, OAK RIDGE NATIONAL LABORATORY[1]]

The Reaction of Uranium Tetrafluoride with Calcium Sulfate

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Uranium tetrafluoride has been observed to react readily with calcium sulfate at temperatures above 630°, forming CaF_2, U_3O_8, SO_2 and SO_3.

Thermodynamic calculations indicate that UF_4 should be oxidized very readily by sulfates, but the nature of the products and the speed of the reaction cannot be predicted. The simple experiments reported here were intended primarily to elucidate the nature of the products in one particular case.

Experimental

Anhydrous $CaSO_4$ was prepared by drying "Baker Analyzed" C.P. $CaSO_4 \cdot 2H_2O$ for about four days at temperatures up to about 730°. When brought to constant weight, two samples lost 20.94 and 20.93% of their initial weights (theor. 20.94%). This material was mixed with pure UF_4 in the amounts required to give a molar ratio $CaSO_4:UF_4$ of 1.99. The light green mixture was loaded into two graphite crucibles. In each experiment, the crucible was placed in a fused silica tube, connected to a Pyrex vacuum system and heated by a small electric furnace. The sample temperature was measured by a Pt–Pt, 10% Rh thermocouple, contained in a silica tube mounted coaxially in the furnace tube. The system was evacuated and flushed thoroughly with tank helium before heating was commenced. Any gases evolved on heating the $CaSO_4$–UF_4 mixtures were condensed in a liquid-nitrogen-cooled trap for subsequent analysis.

In the first experiment, the sample was heated slowly in about 1 atm. of helium. At about 715°, a sudden surge of pressure caused the momentary opening of a ground-glass joint in the vacuum system. A strong odor of SO_2 was noted. The furnace tube was immediately evacuated and pumped out continuously thereafter. After heating for approximately 1.5 hours at 730°, the sample was allowed to cool. The furnace was flushed several times with helium to transfer evolved gases to the cold trap. The second experiment was performed similarly, except that continuous evacuation was employed from the beginning. Accumulation of condensate in the cold trap commenced very slowly at about 530° and increased substantially at 630°. Complete reaction did not occur in 17 hours at the latter temperature, but was reached in about 3 hours at 730°. Pressure measurements at the highest temperature indicated the evolution from the sample of a non-condensable gas.

After completion of each experiment, the condensed gases were allowed to vaporize and were swept with helium into a measured volume of standard NaOH. The excess alkali was titrated with standard HCl to determine total acidity. The neutralized solution was then titrated with standard I_2 to determine SO_2. The gases from the first experiment (from which some gas was lost) contained 52.9 mole % SO_2; those from the second contained 74.8 mole % SO_2. The balance in each case is assumed to be SO_3.

X-Ray diffraction was used to study the solid products remaining in the graphite crucibles after the reactions were complete. The initial materials showed only the diffraction lines of $CaSO_4$ and of UF_4. After reaction, the major constituents found were CaF_2 and U_3O_8. A small amount of $CaUO_4$ was observed and there were probable traces of UO_2F_2. Substances sought but not found included UF_4, $CaSO_4$, $CaSO_3$, CaO, $CaCO_3$ and hydrates of these materials. In the first experiment, the initial mixture lost 24.0% of its weight, and in the second it lost 26.0%.

Discussion

The weight lost by the original $CaSO_4$–UF_4 mixture on heating corresponds accurately to that expected from the reaction

$$6CaSO_4(c) + 3UF_4(c) = 6CaF_2(c) + U_3O_8(c) + 2SO_2(g) + 4SO_3(g) \quad (1)$$

(The theoretical value is 25.5%.) However, the analyses of the gases produced show the presence of substantially more SO_2 than predicted by this equation. Two explanations may be offered for this result. Part of the SO_3 produced may have been reduced by the graphite crucible

$$C(\text{graphite}) + SO_3(g) = CO(g) + SO_2(g) \quad (2)$$

This reduction would have been more important in the second experiment where the $CaSO_4$–UF_4 reaction took place very slowly. Alternatively, UO_3 may have been produced in part and then decomposed to U_3O_8 with the evolution of oxygen. Either CO or O_2 would be consistent with the observation of a non-condensable gas. The presence of UO_3 as a reaction intermediate is supported by the observation of $CaUO_4$ and probably UO_2F_2 among the products. These could have been produced by reactions such as

$$CaSO_4(c) + UO_3(c) = CaUO_4(c) + SO_3(g) \quad (3)$$

or

$$CaF_2(c) + 2UO_3(c) = CaUO_4(c) + UO_2F_2(c) \quad (4)$$

For the calculations which guided this work, it was found necessary to estimate the thermodynamic properties of some of the possible reaction products. It was found that the entropies of sulfates can be estimated from those of the correspond-

TABLE I

ENTROPY CHANGE OF THE REACTION: $M_xSO_4(c) = M_xO(c) + SO_3(g)$

Compd.	$\Delta S°_{298}$ (cal./mole deg.)	Compd.	$\Delta S°_{298}$ (cal./mole deg.)
Na_2SO_4	42.9	$CoSO_4$	44.6
Ag_2SO_4	42.5	$NiSO_4$	51.7
$MgSO_4$	45.7	$CuSO_4$	45.5
$CaSO_4$	45.2	$CdSO_4$	41.5
$SrSO_4$	45.1	$ZnSO_4$	41.9
$BaSO_4$	46.4	$PbSO_4$	43.2
$MnSO_4$	48.8	$^1/_3Al_2(SO_4)_3$	46.2

Mean value: $\Delta S°_{298} = 45.1 \pm 2.7$ (6.0%) cal./mole deg.

TABLE II

ESTIMATED ENTROPIES OF SOME SULFATES

Compd.	$S°_{298}$ (cal./mole deg.)
$BeSO_4$	19.5
$Cr_2(SO_4)_3$	67.8
$Zr(SO_4)_2$	44.3
$U(SO_4)_2$	50.8
UO_2SO_4	39.7

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(1) Operated for the U. S. Atomic Energy Commission by Union Carbide Nuclear Company.

ing oxides due to the approximate constancy of ΔS°_{298} for the reaction

$$M_xSO_4(c) = M_xO(c) + SO_3(g) \qquad (5)$$

This is illustrated in Table I, which includes all of the relevant data given by Rossini, *et al.*[2] Some typical estimated entropy values are given in Table II. It was found also that for 22 pairs of substances given by Rossini, *et al.*, the ratio of the heat of formation of the sulfate to that of the corresponding fluoride—both values adjusted to the same number of metal atoms—was 1.31 ± 0.08. That these results are largely fortuitous is shown by the inconstancy of similar ratios involving the sulfate, nitrate, and chloride.

The assistance of the late G. E. Klein in performing the X-ray diffraction analyses is gratefully acknowledged.

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[2] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Circular Natl. Bureau of Standards 500, 1952.

[CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION, OAK RIDGE NATIONAL LABORATORY, OPERATED BY UNION CARBIDE NUCLEAR COMPANY FOR THE U. S. ATOMIC ENERGY COMMISSION]

A Study of the Reaction: $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$.[1] I. Side Reactions and Thermodynamics

BY L. M. FERRIS

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The reaction of uranium tetrafluoride with dry oxygen has been investigated in the temperature range of 600–900°. In addition to the expected products, uranium hexafluoride and uranyl fluoride, uranium pentafluoride was isolated from the system, and is postulated to be the product of a side reaction between UF_6 and UF_4. Only slight decomposition of uranyl fluoride was observed in this temperature range in accordance with thermodynamic predictions.

Introduction

The reaction of UF_4 with dry O_2 is a convenient laboratory preparation of UF_6. However, the reaction is of interest mainly because it is potentially the basis of a method for the plant-scale production of UF_6 which would eliminate the use of elemental fluorine. Fried and Davidson,[2] who discovered the reaction in 1945, envisioned a process in which the solid product, UO_2F_2, would be continuously recycled and reconverted to UF_4. Such a process utilizing O_2 or air to convert UF_4 to UF_6 appears to have some economic advantage over processes which require the use of fluorine. However, it has been found[3] that the rate of oxidation is not very rapid at temperatures lower than 750°, a fact which could restrict industrial application of the reaction.

The reaction has been the subject of several previous investigations.[2–5] In each case many unexplained observations were reported. Hence, the present investigation was conducted to confirm the results of the previous studies, and to obtain a clearer insight into the nature of the reaction and related phenomena at temperatures between 600 and 900°. The results reported here are essentially qualitative, but will serve as the basis for the interpretation of an extensive study of the kinetics of the reaction.

Experimental Procedure and Observations

Reagents.—Uranium tetrafluoride powder was prepared by hydrogen reduction of UF_6 and contained no more than 2 wt. % UO_2F_2, 0.05 wt. % H_2O, and 0.2 wt. % uranium oxides. Commercially available oxygen and helium were used. The helium contained less than 20 p.p.m. of oxygen. The gases were dried by passage through a train consisting of a fuming sulfuric acid bubbler, a cold trap held at −80° with trichloroethylene–Dry Ice slush, and two Drierite bulbs. After this treatment the dew point of the gases was found to be approximately −30°, corresponding to a moisture content of about 0.05%.

Procedure.—The experiments were performed in long 1-in. diameter quartz tubes heated by means of a 15-in., 750 watt tube furnace with the UF_4 samples contained in platinum boats (100 mm. long; 10 mm. deep; 13 mm. wide). The temperature was maintained within 10° of the specified temperature with a Pyrovane controller utilizing a chromel–alumel thermocouple. Connected to the reaction tubes were 0.5-in. diameter quartz U-tubes which, when immersed in trichloroethylene–Dry Ice slush, served as cold traps for collecting the UF_6.

In a typical experiment, a weighed sample of UF_4 (about 10 g.), which occupied about 3/4 of the capacity of the boat, was heated to the desired temperature in an atmosphere of dry helium. At the desired temperature, the helium was replaced by dry oxygen flowing at a rate of 100–300 standard cc./min. The reaction was allowed to proceed for a predetermined length of time (usually 1 hr.) before cooling in helium. The residue in the boat was then reweighed to determine the weight loss. Chemical and X-ray diffraction analyses[6] were obtained for the residues.

Observations.—At 750–800° evolution of UF_6 and a brown-colored compound (later identified as β-UF_5) was observed shortly after admission of the oxygen. Uranyl fluoride and unreacted UF_4 remained in the platinum boat after an incomplete oxidation. The quartz tubes used to carry out the reactions were severely attacked, particularly in regions of high temperature, and were coated with a series of colored bands of UO_2F_2, UF_4 and U_3O_8 as shown schematically in Fig. 1. In all cases the UF_4 was found in the cooler regions of the tube, while the U_3O_8 and UO_2F_2 were found nearest the hot reaction zone. The solid compounds were

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[1] (a) Research performed under the auspices of the U. S. Atomic Energy Commission; (b) presented in part at the 131st National ACS Meeting, Miami, Florida.

[2] (a) S. Fried and N. R. Davidson, USAEC Report AECD-2981 (1945); (b) summarized in J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 374, 401.

[3] L. M. Ferris, USAEC Report ORNL-2180 (1957).

[4] S. S. Kirslis, T. S. McMillan and H. A. Bernhardt, USAEC Report K-567 (1950).

[5] C. J. Mandelberg and D. Davies, UKAEA Report AERE-C/R-863 (1952).

[6] The author is indebted to the analytical groups of G. R. Wilson and W. R. Laing for the chemical analyses, and to the late Dr. G. E. Klein who performed the X-ray analyses.