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.

OAK RIDGE, TENNESSEE

(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.

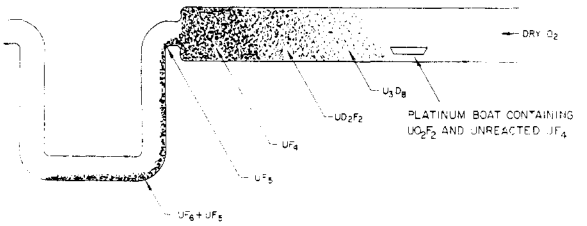

Fig. 1.—Distribution of compounds inside a quartz reactor after reaction of UF_4 with dry oxygen.

scraped from the surface of the quartz and were identified by X-ray analysis. Weight losses produced by complete reaction of the UF_4 were found to be greater than expected from the stoichiometry. For the case of incomplete reaction of UF_4 it was determined from the chemical analyses that the amount of UO_2F_2 produced was less than expected from the corresponding UF_4 consumption. These observations will be discussed in greater detail later. However, it is recognized at this point that several phenomena can be postulated to account for the weight loss anomaly and the deposition of uranium compounds on the walls of the reaction vessel. Among these are (1) vaporization of UF_4, (2) thermal decomposition and/or vaporization of UO_2F_2,[2] and (3) a side reaction which consumes UF_4. Hence an attempt was made to explain the observations by considering each of the above phenomena separately.

Vaporization of UF_4.—The rate of vaporization of UF_4 was found to be exceedingly low in the temperature range of 600–900° in accordance with reported vapor pressures.[7] At each temperature the rate of vaporization was at least one-fiftieth that of the corresponding rate of reaction of UF_4 with oxygen.[3] As a consequence the observed anomalies cannot be accounted for on the basis of UF_4 vaporization.

Decomposition of UO_2F_2.—The rate of decomposition of pure UO_2F_2 was measured in dry helium at 700 and 800° using a thermobalance[8] which continuously recorded the weight change of a decomposing sample. Only small amounts of U_3O_8 were found as a decomposition product. A number of reactions have been proposed[2b] for the decomposition, but all are thermodynamically unfavorable at the temperatures of interest (see Fig. 2). The best choice on the basis of the free energy estimates[9] and the reaction product is $3UO_2F_2 \rightarrow UF_6 + {}^2/_3\, U_3O_8 + {}^1/_3\, O_2$. Using this reaction, material balances of greater than 98% could be obtained indicating vaporization to be negligible. First-order rate constants calculated with the above stoichiometry from the thermobalance weight-loss curves are given in Table I.

Table I

First-order Rate Constants for the Reaction $3UO_2F_2 \rightarrow UF_6 + {}^2/_3\, U_3O_8 + {}^1/_3\, O_2$

Temperature (°C.)	k (min.$^{-1}$)
700	7.62×10^{-5}
700	6.76×10^{-5}
800	7.67×10^{-4}
800	7.83×10^{-4}

The rate constants are seen to be very low and are approximately one-fiftieth of those for the reaction of UF_4 with oxygen.[3] An activation energy of about 50 kcal./mole is calculated from these data. Since UO_2F_2 was found to be quite stable at temperatures lower than 800° its decomposition cannot explain deviations from the stoichiometry $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$.

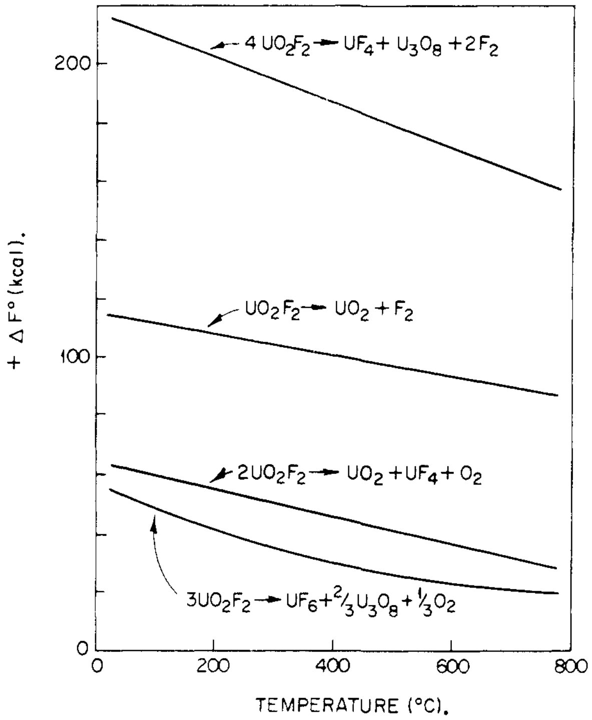

Fig. 2.—Estimates of the temperature dependence of standard free energy changes for the decomposition of UO_2F_2.

Formation of UF_5 by a Side Reaction.—The existence of UF_5 was discovered when it was noticed that a brown-colored substance was collected in the cold trap instead of the expected snow-white UF_6. At first this coloration was thought to be due to traces of impurities in the UF_6. However, when the contents of the cold trap were contacted with water, a significant amount of green UF_4 was precipitated. Only a yellow solution of UO_2F_2 would be expected from pure UF_6. The UF_6 was separated from the UF_5 by passage of a dry gas over the two compounds while they were held at a temperature near 60°. The UF_6 was sublimed (sublimation point 57°[10]) leaving brown solid UF_5 in the vessel. The brown solid was loaded into thin-walled quartz capillary tubes inside a dry-box and was identified as β-UF_5 by X-ray analysis.[6]

As already implied, UF_5 is extremely sensitive toward moisture, rapidly hydrolyzing to UO_2F_2 and UF_4 at room temperature with chemical analyses suggesting the ratio to be 1-to-1 (see Table II).

Table II

Analysis of the Product of Hydrolysis of UF_5

	Compound or mixture	U^{+4} (wt. %)	F^- (wt. %)
1.	UF_4	75.8	24.2
2.	UF_5	35.7	28.6
3.	UO_2F_2	0.0	12.3
4.	1-to-1 mixture of UO_2F_2 and UF_4	37.9	18.25
5.	Hydrolysis product	38.9	17.8

Since UF_5 is a known[11] product of the low temperature reaction of solid UF_4 and gaseous UF_6, it seemed reasonable to expect its formation by the same route at high temperatures. Estimated free energy changes for the reaction $UF_4 + UF_6 \rightarrow 2UF_5$ (Fig. 3) supported this contention. A vapor phase reaction is ruled out due to the low rate of vaporization of UF_4. Also, it appears certain that UF_5 is a vapor at high temperatures. Hence, this side reaction is

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[7] A. D. Ryon and L. P. Twichell, USAEC Report H-5.385.2 (1947).

[8] L. M. Ferris and E. G. Carter, USAEC Report ORNL-2216 (1957).

[9] These and subsequent thermodynamic quantities were obtained from the following sources: all uranium compounds except UO_2F_2 and UF_5 from L. Brewer, *et al.*, USAEC Report MDDC-1543 (1945); UF_5 from A. Glassner, USAEC Report ANL-5107 (1953); the free energy of formation of UO_2F_2 at various temperatures was calculated using the above sources and the $\Delta F°$ for the reaction $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$ as given in a private communication by R. P. Metcalf of the ORNL Chemistry Division.

[10] J. Katz and E. Rabinowitch, ref. 2b, p. 411.

[11] J. Katz and E. Rabinowitch, ref. 2b, p. 383.

proposed to explain the weight loss anomalies encountered in the reaction of UF_4 with dry oxygen.

The extent to which this side reaction occurs during a UF_4 oxidation may be obtained from chemical analyses and weight losses. Since UO_2F_2 was found to be quite stable at the temperatures of interest, it was used as a measure of the UF_4 consumed by the reaction $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$. However, more UF_4 was consumed during an experiment than could be accounted for by UO_2F_2 formation. Hence, the amount of UF_4 involved in the side reaction was obtained by difference. Table III contains data for oxidations at various temperatures calculated on this basis. As seen from these data a considerable fraction of UF_4 is consumed by the side reaction. The scatter at each temperature is perhaps due to differences in packing of the individual powdered UF_4 samples.

TABLE III

EFFECT OF THE SIDE REACTION $UF_4 + UF_6 \rightarrow 2UF_5$ AT VARIOUS TEMPERATURES

Run	Temp. (°C.)	Initial UF_4 (g.)	UO_2F_2 produced (g.)	UF_4 consumed by reaction with O_2 (g.)	Total UF_4 consumed (g.)	UF_4 consumed by side reaction	
						Grams	%
1	900	12.1122	4.1491	8.4310	10.8205	2.3895	22.1
2	800	6.4019	0.8789	1.7859	2.1064	0.3205	15.2
3	800	12.5406	3.0497	6.1970	8.8085	2.6115	29.6
4	800	11.0964	3.5233	7.1593	9.4626	2.3033	24.3
5	800	12.3706	1.8925	3.8456	7.8283	3.9827	50.9
6	800	18.4868	5.1336	10.4315	15.3103	4.8788	31.9
7	800	9.8120	2.7951	5.6796	7.7115	2.0319	26.3
8	800	17.2728	2.0876	4.2420	6.4917	2.2497	34.6
9	750	9.8170	2.8849	5.8621	7.8402	1.9781	25.2
10	750	5.9361	0.1186	0.2410	0.3582	0.1172	32.7
11	700	4.1478	0.3303	0.6712	0.7009	.0297	4.2
12	700	14.4736	4.5541	9.2539	9.9503	.6964	7.0
13	700	11.9810	2.9116	5.9164	8.3630	2.4466	29.2
14	700	5.9359	0.3701	0.7520	0.9977	0.2457	24.6
15	650	5.9325	.0142	0.0288	0.0924	.0636	68.8
16	600	12.9860	.6108	1.2411	1.7171	.4760	27.7
17	600	8.6912	.1089	0.2213	0.3297	.1084	32.9
18	600	10.0843	.1114	0.2264	0.7544	.5280	70.0
19	600	10.9064	.3773	0.7667	1.5500	.7833	50.5

Material balances show that neither of the following reactions accurately describes the consumption of the UF_4.

$$2UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6 \qquad (1)$$

$$3UF_4 + O_2 \longrightarrow 2UF_5 + UO_2F_2 \qquad (2)$$

The observed stoichiometry lies somewhere between the case of no side reaction (eq. 1) and that of a complete back reaction with UF_6 (eq. 2).

It is also seen from Fig. 3 that UF_5 is expected to be relatively unstable in the region of 600°. Its disproportionation has been reported previously.[11] This property of UF_5 can help explain the observed deposits of uranium compounds inside a reaction vessel. UF_5 formed at high temperature by the postulated side reaction apparently decomposes at a fairly rapid rate as it is being swept out of the reaction vessel. UF_4 is deposited initially by this mechanism. However, at temperatures greater than 600°, UF_4 may be reoxidized[3] to UO_2F_2. Use of a thermocouple probe indicated that little UO_2F_2 was deposited in regions where the temperature was lower than 600°.

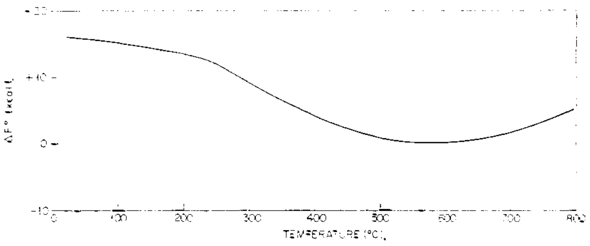

Fig. 3.—Estimates of the temperature dependence of standard free energy change for the reaction $2UF_5 \rightarrow UF_4 + UF_6$.

Deposition of UF_4 as a result of the dissociation of UF_6 is a thermodynamic impossibility.[12]

The U_3O_8 found in the system was a product of the reaction of UF_6 with quartz. This was verified by oxidizing UF_4 in a quartz reaction vessel which was lined with a protective Pt tube. In these experiments only traces of U_3O_8 were found.

Acknowledgment.—The author is indebted to Dr. R. G. Wymer and to Mr. R. E. Blanco for their helpful suggestions and discussions, and to Mr. J. F. Land and Mr. J. F. Talley who performed much of the experimental work.

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[12] L. Brewer, *et al.*, USAEC Report MDDC-1543 (1945).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Cyanide-1,10-Phenanthroline Complexes of Iron(II)

BY ALFRED A. SCHILT

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Iron(II) has been shown to form the tetracyano-mono-(1,10-phenanthroline)-ferrate(II) ion and the neutral dicyano-bis-(1,10-phenanthroline)-iron(II) complex. The visible absorption characteristics of these complexes have been determined, and a spectrophotometric investigation of the equilibria involved in their formation has been made.

Introduction

The interference of cyanide ion in the colorimetric determination of iron by 1,10-phenanthroline and related compounds[1,2] constitutes a limitation to such applications. The following investigation was carried out in order to establish the nature of this interference and to provide information useful for the development of analytical procedures suitable for the determination of iron and cyanide ions in the presence of each other.

Experimental

Apparatus and Materials Used.—All spectrophotometric measurements were made employing a Cary Recording Spectrophotometer (Model 11), matched silica stoppered cells of path length 1.000 ± 0.001 cm., and slit widths ranging from 0.01 to 0.02 mm. over the wave length region scanned.

The 1,10-phenanthroline monohydrate was obtained from the G. Frederick Smith Chemical Company. Eastman Kodak Company (white label) *m*-dinitrobenzene and hydroxylamine hydrochloride were used without further purification. All other chemicals were reagent grade.

Identification of Dicyano-bis-(1,10-phenanthroline)-iron (II).—Preliminary studies disclosed that a dark violet precipitate is gradually produced from aqueous solutions con-

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[1] W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 60 (1938).

[2] A. A. Schilt and G. F. Smith, *Anal. Chem.*, **28**, 809 (1956).