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The Preparation of UF_6 from UF_4 and O_2

In connection with another problem we have had occasion to examine the reaction of UF_4 with oxygen at elevated temperatures. We have found that UF_4 reacts with dry oxygen at $800^\circ C$ according to the equation:

The yield of UF_6 in this reaction is forty per cent of the theoretical or greater. Consideration of the available thermodynamic data indicates that this reaction should take place under these conditions.

In one experiment, a platinum boat containing 5.97 g UF_4 was placed in a nickel tube which was heated by a furnace and connected to two glass "U" tubes in series. Dry oxygen was passed over the UF_4 at a rate of about 35 cc per min. and at a temperature of $800^\circ C$ for 1 hour. A white condensate collected in the first "U" which contained 35 mg. KF and which was cooled with liquid O_2 . There was some etching and deposition on the glass leading from the nickel tube to the "U" tube. The "U" tube was sealed off from the nickel tube, and the liquid O_2 removed and the white condensate sublimed in vacuo into the second "U" tube which was maintained at -78° . This "U" tube was sealed off and the melting point of the contents determined as $65.3-65.8^\circ C$. The triple point of UF_6 is $64.05^\circ C$. There was considerable etching of the glass. There can be no doubt that the volatile solid was UF_6 . The resublimed material weighed 1.30 g, corresponding to a 39% yield. The whitish yellow residue (UO_2F_2 -identified in a previous experiment by x-ray analysis) in the platinum boat weighed 2.09 g, or 71.4% of theoretical.

In an earlier experiment using 4.31 g of UF_4 , the UF_6 was collected in a "U" tube (at $-180^\circ C$) and then treated with aqueous ammonia. A yellow precipitate of ammonium diuranate formed. The contents of the "U" were analyzed by C-IV and found to contain 0.260 g of U and 0.133 g of F, corresponding to an F to U ratio of 6.41. The yield based on the U recovery is 16%. The residual UO_2F_2 was 1.56 gm. or 74% of theoretical. The low weight of the residue in these experiments is probably due to the slow volatilization of UO_2F_2 as such.

In both these experiments there was considerable attack of the inside of the nickel tube in the hot region but little or none in the cool regions. Green UF_4 flakes (identified by the x-ray method) were found in the hot part of the tube. This is probably due to reduction of UF_6 by the nickel tube, since UF_4 itself would not sublime in appreciable quantity at $800^\circ C$. The platinum boat was not attacked.

In our first experiment, 0.0747 g of UF_4 was treated with a slow stream of oxygen at 800° in a quartz tube for 1 hour. A black substance deposited on the walls of the tube inside the furnace and this was shown to be U_3O_8 by x-ray analysis by Dr. Zachariasen. The whitish yellow residue was identified by the x-ray method as UO_2F_2 . Its weight was 0.0343 g, or 102% of theoretical. This residue was heated in O_2 to $1000^\circ C$ in quartz for 1 hour, and there were 5.5 mg residue of U_3O_8 . Some of

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the UO_2F_2 must have sublimed out of the boat as such; the small residue of U_3O_8 may have been due to the reaction:

taking place to some extent. In CC-1717, the group at Brown University reports similar experiments on the treatment of UF_4 with O_2 in "Vycor" tubes. They observed some weight loss in their residues and some sublimate and suggested the possibility that UF_6 was being formed.

From a thermodynamic point of view, we may consider the reactions:

The thermodynamic values for the uranium compounds used in our calculations are listed in Table I.

Table I

Thermodynamic Values for Some Uranium Compounds

Substance	$-\Delta H_{2980}^\circ(\text{formation})$	S_{2980}°	$C_{P,2980}^\circ$
UF_4 (c)	450	36	28
UF_6 (g)	505	91	31
UO_2F_2 (c)	385	36	28
U_3O_8 (c)	845	22	18

The data in Table I are all available in the project literature except that for UO_2F_2 . The entropy and heat capacity of UO_2F_2 were taken as the same as for UF_4 , and the heat of formation was estimated on the assumption that the heat of solution of UO_2F_2 is 10 kcal per mol.

Using this data one may calculate the free energy equations for reactions A) and B) as

A) $\Delta F = 11,200 + 9.21 T \log T - 32.8 T.$

B) $\Delta F = 91,500 + 34.55 T \log T - 143.7 T.$

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Table II lists the calculated pressures of UF_6 in equilibrium with one atmosphere of O_2 and UF_4 and UO_2F_2 , respectively.

Table II

Equilibrium Pressures of UF_6 for Reactions A and B

A	$T^{\circ}K$	300°	600°	900°	1100°
	p(mm) of UF_6	8.1×10^{-4}	2.5	28	46.7
B	$T^{\circ}K$	300°	800°	1100°	1300°
	p(mm) of UF_6	10^{-51}	$10^{-12.6}$	1.3×10^{-7}	2.8×10^{-5}

The calculations would indicate that reaction A) should proceed readily at $600^{\circ}K$ and that B) would proceed quite slowly even at $1300^{\circ}K$. Actually reaction A) did not appear to go appreciably at temperatures below $1073^{\circ}K$, suggesting that the free energy of this reaction may be 10 kilocalories greater than calculated. The uncertainties in the various thermo-chemical quantities appear to be greater than 10 kcal.

To assess the relative amounts of the competing reactions:

we need consider only their difference

The ratio of F_2 to UF_6 in equilibrium at $1100^{\circ}K$ is of the order of magnitude of 10^{-14} and this measures the relative extent to which reaction C) will proceed with respect to reaction A. Reaction B) was discussed in MUC-GTS-1012, and is still less likely than C).

Conclusions

1. It is possible to prepare UF_6 from UF_4 in fair yield by the action of O_2 at $800^{\circ}C$. We are not in a position to assess the technical possibilities of a synthesis of UF_6 that does not require fluorine, however, the following considerations seem pertinent. The system might be a cyclic one according to the equations:

It may be that reaction A proceeds quantitatively at 800°C and the non-quantitative yield is due to destruction of the UF_6 by the hot nickel tube. Possibly the yield would be improved by using a superior material of construction for the hot reactor, perhaps a CaF_2 tube or a platinum tube or a prefluorinated nickel tube. At least this reaction serves as a convenient laboratory preparation of UF_6 when F_2 is not available.

2. The failure to obtain a quantitative yield of the residue of UO_2F_2 is due to the volatilization of UO_2F_2 under the conditions of the experiment.

3. It is common analytical procedure to convert UF_4 to U_3O_8 by ignition in air. Our results demonstrate that this conversion must be due to moisture in the air and suggest that caution must be observed with respect to free access of moist air, etc., so that some of the U is not lost by volatilization as UF_6 or UO_2F_2 .

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