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UNITED STATES ATOMIC ENERGY COMMISSION

**THE THERMODYNAMIC PROPERTIES OF SOME
FLUORIDES OF U AND Pu**

By
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September 18, 1944

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The University of Chicago

Metallurgical Laboratory

DATE September 18, 1944

To G. T. Seaborg

DEPARTMENT

FROM N. R. Davidson

DEPARTMENT

IN RE: The Thermodynamic Properties of Some Fluorides of U and Pu

Some experiments of Heath, Florin, and Meyer, (CK-1701) have suggested that it is possible to oxidize PuF_3 or PuF_4 with oxygen to PuO_2 . Furthermore, it is a common analytical procedure to ignite UF_4 to U_3O_8 at ca. 800°C . This reaction might be considered to be due to oxidation by atmospheric oxygen. The replacement of fluorine by oxygen is a rather unusual reaction. I have therefore collected some of the existing data on the thermodynamic properties of oxides and fluorides of U and Pu in order to more precisely consider these questions. At the same time I am recording some estimates of the probable values of the heats and free energies of several reactions involving the plutonium fluorides.

We first consider the equilibrium constants for the reactions

The heat of formation of UF_4 has been determined as 446 kcal/mol (CL-697, Chap. IV, Sec.B). The low temperature specific heats and entropies of UF_4 (up to 350°K) are given in CCA-201, and I estimate the equation $C_p = 29.4 + 5 \times 10^{-4}(T - 350)$ for the heat capacities at higher temperatures. The low temperature heat capacities and entropies of UO_2 and UO_3 are given in CPA-329. The high temperature heat capacities are reported in CPA-502. Bickowsky and Rossini give values for the heats of formation of UO_2 and $\text{UO}_{8/3}$. The other thermodynamic properties have been estimated from those of UO_2 and UO_3 . Using these various sources, Table I, listing some of the high temperature thermodynamic properties of UF_4 , UO_2 , and $\text{UO}_{8/3}$ has been assembled.

Table I

Heats of Formation and Entropies of UF_4 , UO_2 and $\text{UO}_{8/3}$ at High Temperatures

	UF_4		UO_2		$\text{UO}_{8/3}$	
$\Delta H_f, 298.1^\circ (\text{kcal.})$	446		257		282	
$S_{298.1^\circ} (\text{eu})$	36.0		18.6		22	
$T^\circ\text{K}$	$\text{H}-\text{H}_{298.1^\circ} (\text{eu})$	$\text{S}-\text{S}_{298.1^\circ}$	$\text{H}-\text{H}_{298.1^\circ}$	$\text{S}-\text{S}_{298.1^\circ}$	$\text{H}-\text{H}_{298.1^\circ}$	$\text{S}-\text{S}_{298.1^\circ}$
500°	6	15	3	8	4	9
800°	13	29	9	18	10	20
1100°	23	39	15	24	16	26
1300°	36*	49*	19	28	21	30

* UF_4 melts at ca. 1233°C . I have estimated the entropy of melting as 5 e.u.

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On the basis of this data, the free energy changes for reaction A and B are calculated and are listed in Table II. Data for the thermodynamic properties of the common gases used in this report have been taken from Brewer's tables in CC-1334. The quantity $\sqrt{K}=P(F_2)$ represents the pressure of fluorine in equilibrium with one atmosphere of oxygen in the presence of UF_4 and UO_2 or $UO_{8/3}$.

Table II

The Oxidation of UF_4 by Oxygen

Reaction	T°K	ΔH	ΔF	$\sqrt{K}=P(F_2)$
A	298.1°	189	180	10^{-66}
	1100°	188	157	$10^{-15.6}$
	1300°	181	152	$10^{-12.8}$
B	298.1°	164	159	10^{-58}
	1100°	162	150	$10^{-14.9}$
	1300°	155	145	$10^{-12.4}$

It is evident from the data for reaction B that below 1000°C, UF_4 cannot be oxidized by air to U_3O_8 and F_2 . The available thermochemical data for F_2O indicate that it is unstable above room temperature and therefore the equilibrium cannot be shifted to the right by the formation of a fluorine oxide. I believe that the ignition of UF_4 to U_3O_8 must be due to the presence of H_2O vapor in the atmosphere, hydrolyzing the UF_4 to give HF.

The data for reaction A are included because they are analogous to a reaction which it is claimed will proceed for plutonium.

It is interesting to calculate the equilibrium constant for the hydrolytic reaction

Calculations of the equilibrium constant for this reaction are summarized in Table III. The columns $p(H_2O)$ and $p(HF)$ refer to the pressure of H_2O or HF respectively in equilibrium with one atmosphere of HF or H_2O in the presence of UF_4 and UO_2 .

Table III

The Hydrolysis of UF_4 by H_2O Vapor

T°K	$\Delta F(kcal.)$	$p(H_2O)$	$p(HF)$
298.1°	36	2×10^{13}	2×10^{-7}
800°	2	1.9	0.73
1300°	-11	0.14	2.6

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September 18, 1944

It is evident that the hydrolysis of UF_4 is a much easier reaction to carry out than is the oxidation of UF_4 . The change in sign of ΔF is of interest in connection with the actual problem of the conversion of UO_2 to UF_4 by HF .

It is my contention that the reactions,

can be proved to be impossible by considering the fact that PuO_2 is converted to PuF_4 or PuF_3 by the action of anhydrous HF .

These reactions are known to go at ca. $550^\circ C$. It has not actually been carried out at $300^\circ C$ (the temperature of the "oxidations" described above) but it is highly probable that the reactions are exothermic and proceed more readily at lower temperatures. Calculations are presented for both $600^\circ K$ and $800^\circ K$. Milligram quantities of PuO_2 are converted to PuF_4 in a few hours. If one liter of HF gas slowly passed over one mg of PuO_2 will convert it to PuF_4 , the H_2O pressure in equilibrium with one atmosphere of HF in the presence of PuO_2 and PuF_4 cannot be less than 10^{-4} atmospheres. Allowing a safety factor, we assume the equilibrium water pressure in the presence of unit activity of HF gas cannot be less than 10^{-5} atmospheres (.0076 mm. Hg) for reaction E. Therefore ΔF must be less than 27.4 and 36.6 kcal. at 600° and 800° respectively. By combining this equation with the equation (G) $2F_2 + 2H_2O \rightleftharpoons 4HF + O_2$, $\Delta F_{600^\circ} = -159$ kcal., $\Delta F_{800^\circ} = -167$ kcal., we find that for reaction C, $\Delta F_{600^\circ} > 132$ kcal., $\Delta F_{800^\circ} > 131$ kcal., i.e., the equilibrium F_2 pressures in the presence of an atmosphere of O_2 are less than 10^{-24} atmospheres at 600° and 10^{-18} atmospheres at $800^\circ K$. At $800^\circ K$ and a flow rate of O_2 of 10 cc/min, the rate of conversion of PuF_4 to PuO_2 is less than 2×10^{-9} micrograms per hour.

For the case of reaction D, one must also consider the free energy change for the reaction $\frac{1}{2}H_2 + \frac{1}{4}O_2 \longrightarrow \frac{1}{2}H_2O$, and one thus obtains that the equilibrium fluorine pressures at temperatures of 600° and 800° are less than 5×10^{-10} atmospheres and 5×10^{-8} atmospheres respectively. Actually if use is made of the fact that PuF_4 is reduced to PuF_3 by a trace of hydrogen, these limits can be lowered considerably.

I think the calculations presented above throw sufficient doubt on the experimental results on the oxidation of UF_4 , PuF_3 , and PuF_4 to make it necessary to reexamine these questions with improved experiments.

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Fried has recently observed that PuF_4 decomposes in vacuo in PuF_3 at temperatures as low as 1173°K with an appreciable rate. If we assume that for the reaction $(\text{H}) \text{PuF}_4 \rightleftharpoons \text{PuF}_3 + \frac{1}{2}\text{F}_2$, $p(\text{F}_2) = 10^{-7}$ atmospheres at 1173°K , then $\Delta F = 19$ kcal. The entropy of F_2 is known and the entropy difference between PuF_4 and PuF_3 may be estimated from the entropy for UF_4 as 15 e.u. So I estimate for this reaction, $\Delta S = 15$ e.u., and $\Delta H = 37$ kcal.

It is important to see whether these estimates are consistent with the fact that the reaction

proceeds at 800°K . Assuming ΔH and ΔS constant for reaction H and combining this data with the data for reaction G, we find for reaction K, $\Delta F_{800^\circ} = 13$ kcal, $\Delta H = 2$ kcal., and the equilibrium constant is 3×10^{-4} . Therefore, in the presence of half an atmosphere of both HF and O_2 , the equilibrium water pressure is calculated as ca. 7.6 mg. Hg. It is seen therefore that the instability of PuF_4 relative to decomposition into PuF_3 and F_2 is consistent with the oxidation of PuF_3 to PuF_4 by O_2 in the presence of HF. However this latter reaction is expected to be readily reversed by H_2O vapor.

We may also calculate that the free energies for the reaction

on the basis of the estimates for reaction H. The results are $\Delta F_{800^\circ} = -40$, $\Delta H_{800^\circ} = -27$.

The similar reaction for UF_4 has been studied by British workers, whose results are reported in BR422 (CT). Their results differ considerably from those reported by various American workers, but seem to be carefully done and valid. They report that at 1000°C the equilibrium pressure of HF in the presence of one atmosphere of hydrogen is probably .05 to .1 atmosphere. (The experiments were made in a flowing system and the HF pressure may be low.) However, we calculate $\Delta F_{1273^\circ\text{K}} = 5.8$ kcal for the reaction

On the basis of the data for UF_4 in table 1, I estimate the entropy difference between UF_4 and UF_3 as -21, and ΔS for the reaction is estimated as 10. Therefore $\Delta H_{1273} = 18.5$ kcal. For the reduction of solid UF_4 at 1273°C , I calculate $\Delta H = 24.5$ kcal, and $\Delta S = 15$ e.u. Assuming $\Delta C_p = -3$, $\Delta H_{298.1^\circ} = 26.6$ kcal, $\Delta S_{298.1} = 19$ e.u. At 800°K we calculate an equilibrium pressure of 0.4 mm of Hg HF pressure for one atmosphere of H_2 , and therefore the reaction might be expected to proceed slowly even at this temperature. The British workers claim that the reaction does not take place below 1000°C , and this must be attributed to rate factors. 60
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