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The enthalpy of formation of UPd_3 by fluorine bomb calorimetry[a]

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The energy of the reaction between $F_2(g)$ and $UPd_3(c)$ to give $Pd(PdF_6)(c)$, about 15 mass per cent Pd(c) and $UF_6(g)$, has been measured in a bomb calorimeter. After removal of $F_2(g)$ and $UF_6(g)$, but without dismantling the combustion bomb, the energy of the reaction between gaseous $PF_3(g)$ and the $\{Pd(PdF_6)(c)+Pd(c)\}$ left in the bomb, to give Pd(c) and $PF_5(g)$, has been measured in the calorimeter. Combining these reactions, the standard enthalpy of formation : $\Delta H_f^\circ(UPd_3, c, 298.15\ K) = -(524\pm31)\ kJ\cdot mol^{-1}$ has been derived.

1. Introduction

The intermetallic compound UPd_3 is of immediate interest because of its formation during fission of nuclear fuel in a reactor. The (U, Pu)Me_3 phases, in which Me = Ru, Rh, and Pd, were detected in carbide and even in oxide fuel.(1) To understand the formation of (U, Pu)Pd_3 phases in irradiated nuclear fuel, thermodynamic quantities for the binary UMe_3 compounds are very useful.

Very little is known about the thermochemical properties of UPd_3. Only one thermodynamic value has been reported, the standard Gibbs energy of formation $\Delta G_f^\circ(UPd_3, c, 1673\ K) = -259\ kJ\cdot mol^{-1}$ which was obtained by mass-spectrometric measurements.(3) Here, the determination of the enthalpy of formation of UPd_3, using the fluorine bomb calorimetric method, will be described.

2. Experimental

The reaction of UPd_3 with fluorine according to:

$$2UPd_3+(15-3x)F_2(g) = 2UF_6(g)+(3-x)\{Pd(PdF_6)(c)\}+2xPd(c), \qquad (1)$$

in which x is the mole fraction of Pd metal ($=0.5\pm0.2$), was chosen because almost the entire UPd_3 sample reacts with F_2 to form UF_6 and a mixture of $Pd(PdF_6)$ and Pd.

Since there are two unknowns in reaction (1): $\Delta H_f^\circ(UPd_3, c, 298.15\ K)$ and x, it is necessary to find a proper "analytical" method accurately to determine x in

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reaction (1). A second reaction:

$$(3-x)\{\mathrm{Pd(PdF_6)(c)}\}+(9-3x)\mathrm{PF_3(g)} = (9-3x)\mathrm{PF_5(g)}+(6-2x)\mathrm{Pd(c)}, \qquad (2)$$

was chosen because $PF_3(g)$ reduces the $Pd(PdF_6)$ in the $\{Pd(PdF_6)+Pd\}$ mixture, left over after the first reaction, spontaneously. $\Delta H_f^\circ\{Pd(PdF_6), c, 298.15\ K\}$ and $\Delta H_r^\circ(298.15\ K)$ for the reaction $PF_3+F_2 = PF_5$, are known and the energy released in reaction (2) can be measured, thus x can be calculated from reaction (2). By using this result for x in reaction (1), the enthalpy of formation of UPd_3 can be derived.

CALORIMETRIC SYSTEM

The calorimetric system consisted of a nickel combustion bomb similar to that described previously(7) and a bomb calorimeter, laboratory designation ANL-R-2, similar to that described by Hubbard *et al.*(8) The calorimetric temperatures were measured by quartz-crystal thermometry.(9) The system was calibrated by the combustion in oxygen of National Bureau of Standards benzoic acid (sample 39i), which has a certified energy of combustion under prescribed conditions of $-(26.434\pm0.003)\ \mathrm{kJ\cdot g^{-1}}$. A series of calibration experiments, some before, some in between, and some following, the UPd_3 combustions, were performed. The energy equivalent ε(calor), of the calorimetric system, was determined to be $(13853.4\pm2.2)\ \mathrm{J\cdot K^{-1}}$ for the first four UPd_3 combustions, and $(13844.4\pm4.2)\ \mathrm{J\cdot K^{-1}}$ for the last two UPd_3 combustions.

MATERIALS

The starting materials for the preparation of UPd_3 were palladium sponge of high purity (99.99 mass per cent, Johnson Matthey Chemicals Limited), and uranium nitride (UN). UN was prepared by the reaction of finely divided uranium powder with nitrogen. At 975 K, uranium sesquinitride (U_2N_{3+x}) is formed; it is decomposed in vacuum or inert atmosphere to UN at 1650 K.

Before use, the palladium sponge was dried in vacuum at 775 K to remove any adsorbed moisture. UPd_3 was prepared by heating mixtures of UN with palladium in the stoichiometric composition at 1350 K. A high-frequency induction furnace was used to heat the samples.(2)

Tantalum carbide was used as the container material. The reaction products were ground in a dry box and reheated; this was done until the reaction was complete as indicated by X-ray diffraction analysis.

UPd_3 is a grey solid; it reacts with moisture when exposed to air, as can be concluded from a change in the lattice parameters. The X-ray diffraction results of the UPd_3 sample, used for the combustion experiments, showed the presence of only hexagonal UPd_3 with $a = (577.3\pm0.1)$ pm and $c = (962.7\pm0.2)$ pm. This result is in good agreement with the X-ray diffraction results found in the literature.(10) A small amount of UO_2 was visible in the X-ray diffraction results of the UPd_3 sample. Chemical analyses of UPd_3 are given in table 1.

TABLE 1. Analysis and impurity corrections of UPd_3: mass fractions w

Impurities present in UPd_3						
Element	10^2w(total)	Impurity	10^2w	Δh_c° / $J \cdot g^{-1}$	10^2w(U, total) as UPd_3	10^2w(Pd, total) as UPd_3
U	42.48				42.48	
Pd	57.27					57.27
O	0.0660	UO_2	0.5570	22.84	−0.4910	
C	0.0205	UC	0.4268	51.61	−0.4063	
N	0.0140	UN	0.2519	18.99	−0.2379	
H	<0.0010	—	—	—		
Al	0.0005	Al(sol)	0.0005	0.28		
Si	0.0020	USi	0.0190	2.66	−0.0170	
Fe	0.0019	Fe(sol)	0.0019	0.33		
Ni	0.0011	Ni(sol)	0.0011	0.12		
Ta	0.0085	$TaPd_3$	0.0235	0.75		−0.0150
total	99.8655		1.2817	97.58	41.3278	57.2550

Graphite felt (sheets of thickness 5.23 mm, National Grade WDF) used as a combustion aid for the UPd_3 sample, was purchased from Union Carbide Corporation. A series of combustion experiments with this graphite felt in fluorine was performed previously,(11) and a value and standard deviation of the mean of $-(77769.3 \pm 18.4)\ J \cdot g^{-1}$ was obtained for the standard energy of combustion of the graphite sample $\Delta U_c^\circ/M$(sample). Hexagonal black selenium shot was taken from the same batch that was used for the determination of $\Delta H_f^\circ(SeF_6, g)$.(12) Purified fluorine (99.99 moles per cent) was prepared by distillation of commercial fluorine in a low-temperature still.(13) The phosphorus trifluoride gas, used in the reduction experiments, was obtained from Ozark Mahoning Co. Removal of the small amounts of oxygen and nitrogen in the PF_3 gas was done by condensing the PF_3 in a steel trap with liquid nitrogen and pumping off the solid, as described previously.(6)

PRELIMINARY EXPERIMENTS

To establish the conditions under which UPd_3 could be completely fluorinated or oxidized, several preliminary combustion experiments were done. Combustion experiments with UPd_3 in oxygen showed incomplete combustion of UPd_3; under calorimetric conditions only about 15 per cent of the UPd_3 had reacted. It was found by X-ray analyses that Pd and U_3O_8 were formed on the outside of a molten residue. The temperature rise caused by the reaction:

$$3UPd_3 + 4O_2 = U_3O_8 + 9Pd$$

had evidently melted the palladium which in turn covered the UPd_3. The use of auxiliary combustion aids, such as graphite cloth on which UPd_3 powder was spread, and magnesium powder, mixed with UPd_3, did not improve the results of the combustions. It was therefore decided to continue combustion experiments of UPd_3

in fluorine. If no auxiliary was used, combustion of UPd_3 in fluorine was incomplete, presumably because the palladium fluoride reaction product (PdF_2, "PdF_3", and Pd) melted and covered unreacted UPd_3, thereby quenching the reaction. Both thin and massive nickel containers were attacked by the reaction mixture, the latter much less. Thus contact between UPd_3 and the nickel container material had to be avoided. Different auxiliary combustion aids were tested, including tungsten foil, AlF_3 powder, graphite cloth, and graphite felt. Graphite felt was selected because its high specific energy of combustion caused UPd_3 to burn nearly completely to UF_6 and a mixture of Pd, $Pd(PdF_6)$, and a small amount of PdF_2. Complete fluorination of UPd_3 could be obtained only by carefully spreading powdered UPd_3 on graphite felt, which provided about 85 per cent of the total energy evolved. The felt could easily be cut into thin layers and weighed. To prevent spattering of the UPd_3 on to the bomb surfaces, the graphite felt was arranged so as completely to cover the UPd_3. This was done by carefully spreading the UPd_3 in between three graphite-felt disks. Selenium shot was put on the top disk as an ignitor.

High fluorine pressures up to 2375 kPa were used. Under these conditions more than 60 mass per cent of the palladium fluoride reaction product which was found by X-ray diffraction to be pure $Pd(PdF_6)$, sublimed. On the bottom of the nickel container several small metal drops were found; X-ray diffraction results showed the metal to be pure palladium (about 15 mass per cent of the total palladium involved in the experiments). The palladium fluoride reaction product in the nickel container was mainly $Pd(PdF_6)$; however, a small amount of PdF_2 was found, estimated between 2 and 8 mass per cent of the total $Pd(PdF_6)$. The best way to "analyze" the amount of palladium fluoride $Pd(PdF_6)$ in the experiments was to reduce the $Pd(PdF_6)$, left over after the fluorination of UPd_3, with $PF_3(g)$ and to measure the energy of reduction. From this result the amount of fluorinated palladium can be calculated.

PROCEDURES

A preliminary combustion of a piece of carbon in fluorine served to pre-fluorinate the combustion bomb, as well as the cylindrical thick-bottomed nickel container. During the calorimetric experiments, the bomb was opened only in a helium-atmosphere glove box, so as to reduce adsorption of moisture on the bomb walls and consequent reaction with fluorine. The calorimetric procedure was as follows. The bomb was taken into the glove box and dismantled. The nickel support container (about 40 g), four pieces of graphite felt, and the UPd_3 and selenium, were accurately weighed (figure 1). The bottom piece of carbon was cut cross-shaped, so as to avoid the formation of unreacted UF_4 on the bottom of the nickel container. The UPd_3 was carefully spread in between the remaining three cylindrical disks of graphite. A little selenium was put on the top piece. The nickel container with contents was placed on the bomb head, the bomb was assembled, connected with the tank, which had been charged to 2375 kPa with fluorine, and taken out of the glovebox. The bomb and connecting tube were evacuated, and the system was placed in the calorimeter.

After the forerating period, the combustion of the sample was started by opening the tank valve. After the combustion, the bomb was removed from the calorimeter,

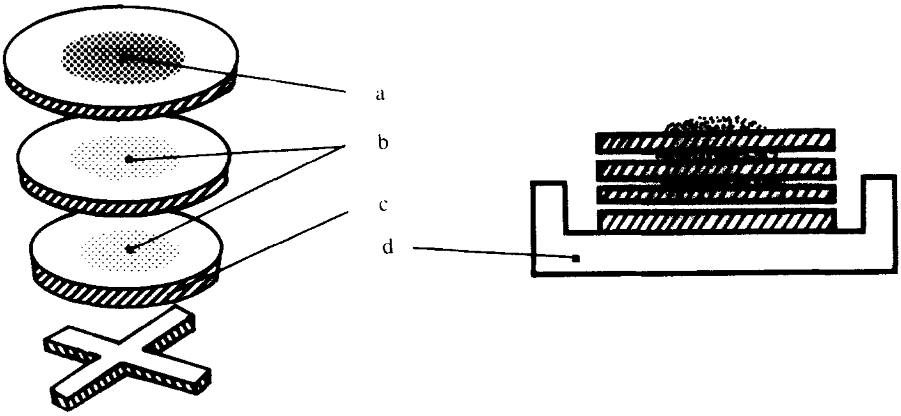

FIGURE 1. The nickel support container and contents.

dried, and the bomb gases were condensed into a liquid-nitrogen-cooled trap and fluorine was pumped off the condensate. Analyses of the residual gas for C_2F_6 and C_3F_8 by g.c. showed that the mole percentage of C_2F_6 was less than 0.02 per cent of the CF_4, and of C_3F_8 was less than 0.005 per cent of the total CF_4.

The evacuated bomb was returned to the glove box; the tank was disconnected, charged with PF_3 up to 1830 kPa, and again connected with the bomb. During this procedure the bomb was not dismantled. The system was taken out of the glovebox, evacuated, and placed in the calorimeter. The energy of reduction of the unknown amount of $Pd(PdF_6)$, left in the bomb after the fluorination of UPd_3, was measured. After the reduction, the bomb gases were condensed into a liquid-nitrogen-cooled trap. Analyses of the gas, a mixture of PF_3 and PF_5, by a mass-spectrometric method showed yields of PF_5 ranged between 1.68 and 1.86 volume per cent of the PF_3, depending on the amount of $Pd(PdF_6)$ involved in the experiments. The post-reduction residue was identified by X-ray analysis as palladium metal. This residue was washed in $0.6\,mol \cdot dm^{-3}$ HCl for about 30 min at room temperature, the solution was then filtered to remove palladium, and analyzed for uranium and fluorine. Total uranium (ascribed to UF_4) was found to be 0.26 mg or less, and total fluorine (ascribed to UF_4 and $Pd(PdF_6)$) 0.61 mg or less. The palladium residue was then dissolved in a mixture of concentrated H_2SO_4 and concentrated HNO_3. To dissolve all the palladium, the mixture was heated and some water was added. This solution was analyzed for uranium. Total uranium (ascribed to unreacted UPd_3) was found to be 0.38 mg or less. No black graphite fibers were found in the residues.

3. Results

The results of six combustions of UPd_3 in fluorine according to reaction (1), immediately followed by the reduction of the $Pd(PdF_6)(c)$ with PF_3 according to reaction (2) are presented in tables 2 and 3. Since an amount of PdF_2 was found by X-ray analysis in some interrupted experiments (after the fluorination step), the estimate

TABLE 2. Results of UPd_3 composition experiments[a]

Experiment no.	2	4	5	6	11	12
$m^i(UPd_3)/g$	0.51341	0.53204	0.55797	0.51332	0.54602	0.53160
$m^f(UPd_3)/g$	0.00070	0.00089	0.00035	0.00042	0.00089	0.00077
$m(UPd_3\ \mathrm{reacted})/g$	0.51271	0.53115	0.55762	0.51290	0.54513	0.53083
$m(C\ \mathrm{reacted})/g$	0.28745	0.26561	0.28291	0.28619	0.27894	0.28647
$m(Se\ \mathrm{reacted})/g$	0.05846	0.05344	0.04704	0.07398	0.05366	0.04593
$n(C_2F_6\ \mathrm{formed})/\mu mol$	4.41	4.41	5.37	4.08	5.71	2.47
$n(C_3F_8\ \mathrm{formed})/\mu mol$	1.08	1.08	0.96	0.74	1.34	1.26
$m(UF_4\ \mathrm{formed})/g$	0.00016	0.00016	0.00010	0.00011	0.00035	0.00016
$\Delta\theta_c/K$	1.85987	1.73499	1.83704	1.86976	1.81672	1.84525
$\varepsilon(\mathrm{calor})(-\Delta\theta_c)/J$	−25765.5	−24035.5	−25449.2	−25902.5	−25151.5	−25546.5
$\Delta U(\mathrm{contents})/J$	−43.7	−40.8	−43.2	−43.9	−42.6	−43.3
$\Delta U(\mathrm{gas})/J$	−1.1	−1.0	−1.1	−1.1	−1.0	−1.1
$\Delta U(C)/J$	22354.8	20656.3	22001.7	22256.8	21693.0	22278.6
$\Delta U(Se)/J$	823.0	752.4	662.3	1041.5	755.5	646.6
$\Delta U(F_2,\ \mathrm{blank})/J$	−15.8	−15.8	−15.8	−15.8	−15.8	−15.8
$\Delta U(C_2F_6+C_3F_8)/J$	−3.4	−3.4	−3.8	−2.9	−4.4	−2.6
$\Delta U(UF_4)/J$	−0.1	−0.1	−0.1	−0.1	−0.3	−0.1
$\Delta U\{Pd(PdF_6)\}/J^b$	1123.7	1069.3	1175.5	1128.8	1119.7	1083.1
$\Delta U(PdF_2)/J^b$	65.0	61.9	68.0	65.3	64.8	62.7
$\{\Delta U_c^\circ/m(\mathrm{sample})\}/(J\cdot g^{-1})$	−2853.7	−2930.8	−2879.6	−2873.7	−2903.0	−2897.9

$\langle\Delta U_c^\circ/m(\mathrm{sample})\rangle = -(2889.8 \pm 10.9)\ J\cdot g^{-1\,c}$
mass correction (table 1) = (0.012817 ± 0.001345)
impurity correction (table 1) = $(97.6 \pm 3.0)\ J\cdot g^{-1\,c}$
mass and impurity correction for $UPd_{3.099}$:
$(1-0.012817)$ g of $UPd_{3.099}$: $-(2889.8-97.6)\ J\cdot g^{-1}$
$\Delta U_c^\circ/M(UPd_{3.099}) = -(2828.5 \pm 12.0)\ J\cdot g^{-1\,c}$
other uncertainties (PdF_2 analysis) = $(\pm 24.6)^c$
$\Delta U_c^\circ/M(UPd_{3.099}) = -(2828.5 \pm 54)\ J\cdot g^{-1\,d}$
$\Delta U_c^\circ = -(1605.9 \pm 30.7)\ kJ\cdot mol^{-1\,d,e}$
$\Delta H_c^\circ = -(1610.9 \pm 30.7)\ kJ\cdot mol^{-1\,d,e}$
$\Delta H_f^\circ(UPd_{3.099}) = -(536.7 \pm 30.8)\ kJ\cdot mol^{-1\,d,e}$

[a] For the reaction $UPd_{3.099}(c)+3F_2(g) = UF_6(g)+3.099Pd(c)$.
[b] Masses of $Pd(PdF_6)$ and PdF_2 are given in table 3.
[c] Standard deviation of the mean.
[d] Uncertainty interval equal to twice the final overall standard deviation.(30)
[e] The molar mass of $UPd_{3.099}$ was taken to be 567.763 $g\cdot mol^{-1}$.

has been made that the $Pd(PdF_6)$ phase in the bomb contains (5 ± 3) mass per cent of PdF_2. From the total energy $\Delta U(\mathrm{total})$ involved in the reduction experiments the masses of palladium fluorides, $m\{Pd(PdF_6),\ \mathrm{total}\}$ and $m(PdF_2)$, can be calculated according to

$$\Delta U(\mathrm{total}) = (0.05x)\{\Delta U_c^\circ/M(PdF_2\} + [0.95x - m\{Pd(PdF_6),\ \mathrm{unreacted}\}]\Delta U_c^\circ/M\{Pd(PdF_6)\}. \qquad (3)$$

where x is total mass of PdF_2 and $Pd(PdF_6)$. The item $m\{Pd(PdF_6),\ \mathrm{unreacted}\}$ represents a small mass of unreduced $Pd(PdF_6)$ as was found by chemical analysis (table 3). By combining the energies of reduction of the palladium fluorides,

TABLE 3. Results of PF_3 reduction experiments

Experiment no.	2	4	5	6	11	12
$\Delta\theta_c/K$	0.07544	0.07154	0.07927	0.07582	0.07529	0.07253
$\varepsilon(\text{calor})(-\Delta\theta_c)/J$	−1045.1	−991.1	−1098.2	−1050.4	−1042.3	−1004.1
$\Delta U(\text{contents})/J$	−2.1	−2.0	−2.2	−2.1	−2.1	−2.0
$\Delta U(\text{gas})/J$	0.1	0.1	0.1	0.1	0.1	0.1
$\Delta U(PF_3, \text{blank})/J$	−72.6	−72.6	−72.6	−72.6	−72.6	−72.6
$\Delta U(\text{total})/J$	−1119.7	−1065.6	−1172.9	−1125.0	−1116.9	−1078.6
$m\{Pd(PdF_6)\text{unreacted}\}/g$	0.00150	0.00138	0.00101	0.00143	0.00107	0.00166
$m\{Pd(PdF_6)\text{total}\}/g^a$	0.38253	0.36400	0.40016	0.38427	0.38116	0.36870
$m(PdF_2)/g^a$	0.02013	0.01916	0.02106	0.02022	0.02006	0.01941

[a] From equation (3)

$\Delta U_c^\circ/M(PdF_2) = -1156.5\ J \cdot g^{-1}$ and $\Delta U_c^\circ/M\{Pd(PdF_6)\} = -2877.5\ J \cdot g^{-1}$, respectively (see table 4), with $\Delta U(\text{total})$, $m(PdF_2)$, and $m\{Pd(PdF_6)\}$ have been calculated (table 3). The corrections to standard states were applied in the usual manner.(14) The auxiliary data used in the calculations are all in table 4.

Additional explanation of some entries in tables 2 and 3 is as follows: For the calculations of $\Delta U(\text{gas})$, μ in the equation of state $pV = nRT(1-\mu p)$ and $(\partial U/\partial p)_T$ were estimated by the method of Hirschfelder *et al.*,(24) from the intermolecular-force constants for PF_3 and PF_5, and for UF_6,(25) CF_4,(24) SeF_6,(26) and F_2.(27) The volume of the empty bomb was $0.3131\ dm^3$, and the volume of the tank was $0.2361\ dm^3$. $\Delta U(PF_3, \text{blank})$ is the correction for the expansion of PF_3 from the tank into the empty bomb. An average value and standard deviation of $\Delta U(PF_3, \text{blank}) = -(72.6 \pm 5.1)\ J$ was obtained. The term $\Delta U(F_2, \text{blank})$ is a combined correction for

TABLE 4. Auxiliary data at 298.15 K

$c_p/(J \cdot K^{-1} \cdot g^{-1})$	$UPd_3(c)$, 0.183;(28) Ni(c), 0.4439;(15) Se(c), 0.3213;(16) C(graphite), 0.7100;(16) Pd(c), 0.243.(15)
$\rho/(g \cdot cm^{-3})$	Ni(c), 8.907;(17) Se(c), 4.804;(18) Pd(c), 11.4;(29) $PdF_3(c)$, 5.06;(29) C(graphite), 2.27;(19) $UPd_3(c)$, 13.39.(10)
$C_V/(J \cdot K^{-1} \cdot mol^{-1})$	$F_2(g)$, 22.983;(15) $UF_6(g)$, 121.3;(20) $SeF_6(g)$, 102.17;(12) $CF_4(g)$, 52.76;(15) $PF_3(g)$, 50.38;(21) $PF_5(g)$, 74.85.(21)
$\{\Delta U_c^\circ/M\}/(J \cdot g^{-1})$	Se(c), $-(14078.7 \pm 2.5)$;(12) C(graphite), $-(77769.3 \pm 18.4)$;(11) U(c), $-(9199.64 \pm 7.7)$;(4) $UF_4(c)$, $-(875.8 \pm 8.4)$;(34) $Pd(PdF_6)(c)$, $-(2937.7 \pm 22)$;(6) $PdF_2(c)$, $-(3230.7 \pm 291)$.(35)
$\{\Delta U^\circ/M(F_2)\}/(J \cdot g^{-1})$	$PF_3 + F_2$ reaction: $-(16670.3 \pm 7.5)$.(5)
$\Delta H_f/(kJ \cdot mol^{-1})$	$UF_6(g)$, $-(2147.6 \pm 1.8)$;(4) $CF_4(g)$, $-(933.20 \pm 0.8)$;(22) $C_2F_6(g)$, $-(1343.9 \pm 5.0)$;(23) $C_3F_8(g)$, $-(1754.8 \pm 20.0)$;(23) $SeF_6(g)$, $-(1116.92 \pm 0.59)$;(12) $Pd(PdF_6)(c)$, $-(967.4 \pm 7.3)$;(6) $PdF_2(c)$, $-(469 \pm 42)$.(35)
$\Delta H_r/(kJ \cdot mol^{-1})$	$PF_3 + F_2$ reaction: $-(635.9 \pm 0.3)$.(5)
$\{\Delta U_c^\circ/M(PdF_2)\}/(J \cdot g^{-1})$	$PF_3 + PdF_2$ reaction: $-(1156.5)$.(5,6)
$[\Delta U_c^\circ/M\{Pd(PdF_6)\}]/(J \cdot g^{-1})$	$PF_3 + Pd(PdF_6)$ reaction: $-(2877.5)$.(5,6)

the endothermic expansion of F_2 into the combustion bomb and the exothermic reaction of F_2 with surfaces in the bomb. An average value and standard deviation of $\Delta U(F_2, \text{blank}) = -(15.8 \pm 2.7)$ J was obtained. The expansion experiments were interspersed with the fluorination/reduction experiments of tables 2 and 3. ΔU(C) and ΔU(Se) are the corrections for the combustion in fluorine of graphite and selenium, respectively.

The correction $\Delta U(C_2F_6 + C_3F_8)$ accounts for the formation of variable small amounts of C_2F_6 and C_3F_8, which are itemized as $n(C_2F_6$ formed) and $n(C_3F_8$ formed); $\Delta U(C_2F_6 + C_3F_8)$ represents the additional energy change had C_2F_6 and C_3F_8 been completely fluorinated to CF_4. The calculated energy of the reactions is based on auxiliary values of ΔH_f° for CF_4, C_2F_6, and C_3F_8. $\Delta U(UF_4)$ accounts for the formation of a very small amount of UF_4; its energy of fluorination is based on the auxiliary value of $\Delta U_c^\circ/M$. $\Delta U\{Pd(PdF_6)\}$ and $\Delta U(PdF_2)$ are the corrections for the combustion in fluorine of $Pd(PdF_6)$ and PdF_2, based on the auxiliary values of $\Delta U_c^\circ/M$ in table 4. The masses of $Pd(PdF_6)$ and PdF_2 are calculated in table 3. The chemical analyses of the calorimetric UPd_3 sample are given in table 1. The impurity corrections in UPd_3 are based on the assumption that the mole-fraction solid solubilities of the elements O, C, N, Si, and Ta will be very small; less than 20×10^{-6}. These elements will be present mainly as UO_2, UC, UN, USi, and $TaPd_3$, respectively. The impurity correction applied in table 2 was calculated from the total mass fraction of impurities (1.2817 mass per cent) with its total specific enthalpy of combustion ($97.6\ \text{J} \cdot \text{g}^{-1}$). The large uncertainty attached to the impurity correction reflects mainly the uncertainty in the estimated amount of PdF_2 in the experiments.

The excess Pd in the sample will be present in solution and has been calculated from the total uranium and palladium present as UPd_3. The unreacted UPd_3, $m^f(UPd_3)$, found in the post-reduction palladium residues, was subtracted from the original UPd_3 weighings, $m^i(UPd_3)$, and itemized as $m(UPd_3$ reacted). The average energy of combustion of $UPd_{3.099}$ in table 2: $\langle \Delta U_c/M(UPd_{3.099})\rangle = -(2828.5 \pm 54)\ \text{J} \cdot \text{g}^{-1}$, has been determined for the reaction:

$$UPd_{3.099}(c) + 3F_2(g) = UF_6(g) + 3.099Pd(c). \qquad (4)$$

From the average energy of combustion of $UPd_{3.099}$, the enthalpy of combustion (table 2) has been calculated to give $\Delta H_c^\circ(UPd_{3.099}) = -(1610.9 \pm 30.7)\ \text{kJ} \cdot \text{mol}^{-1}$. By subtracting the enthalpy of formation of $UF_6(g)$, $-(2147.6 \pm 1.8)\ \text{kJ} \cdot \text{mol}^{-1}$ (table 4) the standard enthalpy of formation of

$$UPd_{3.099}, \Delta H_f^\circ\{UPd_{3.099}, c, 298.15\ \text{K}\} = -(536.7 \pm 30.8)\ \text{kJ} \cdot \text{mol}^{-1},$$

was derived.

The amount of fluorinated palladium in the reduction experiments according to reaction (2) has also been determined in a different way by analyzing the amount of PF_3 converted to PF_5 after the reduction experiments. The results of four determinations are given in table 5. PF_5 in PF_3 was measured mass-spectrometrically in volume per cent and recalculated to mole per cent. The tank was charged with 0.19651 mol of PF_3 from which $n(PF_5)$ could be calculated. Since for the reaction: $PF_3(g) + F_2(g) = PF_5(g)$, $n(PF_5) = n(F_2)$, the mass $m(F_2)$ of fluorine which has been

TABLE 5. Determinations of PF_5 in PF_3 after reduction experiments; ϕ denotes volume fraction and x mole fraction

Experiment no.	4	5	6	11
$10^2\phi(PF_5 \text{ in } PF_3)$	1.68	1.72	1.83	1.86
$10^2x(PF_5 \text{ in } PF_3)^a$	1.743	1.785	1.899	1.930
$n(PF_5)/mol^b$	0.003425	0.003508	0.003732	0.003793
$m(F_2)/g$	0.13104	0.13329	0.14180	0.14412
$\Delta U(F_2)/J$	2184.5	2222.0	2363.8	2402.5
$\Delta U(\text{total})/J^c$	-1065.6	-1172.9	-1125.0	-1116.9
$\Delta U\{Pd(PdF_6)\}/J^d$ $\Delta U(PdF_2)/J$	1118.9	1049.1	1238.8	1285.6
$\{\Delta U_c^\circ/m(\text{sample})\}/(J \cdot g^{-1})$	-2954	-3228	-2787	-2718

$\langle \Delta U_c^\circ/m(\text{sample})\rangle = -(2922 \pm 113)\ J \cdot g^{-1\,e}$
mass and impurity correction for $UPd_{3.099}$ (table 2):
$\Delta U_c^\circ/M(UPd_{3.099}) = -(2861 \pm 226)\ J \cdot g^{-1\,f}$
$\Delta U_c^\circ = -(1624 \pm 128)\ kJ \cdot mol^{-1\,f}$
$\Delta H_c^\circ = -(1629 \pm 128)\ kJ \cdot mol^{-1\,f}$
$\Delta H_f^\circ(UPd_{3.099}) = -(519 \pm 128)\ kJ \cdot mol^{-1\,f}$

[a] The densities of PF_3 and PF_5 were taken to be 3.907 and 5.805 $g \cdot dm^{-3}$, respectively.
[b] Total amount of PF_3 in reaction vessel: 0.19651 mol.
[c] From table 3.
[d] Inserted in table 2 to recalculate $\{\Delta U_c^\circ/m(\text{sample})\}$.
[e] Standard deviation of the mean.
[f] Uncertainty interval equal to twice the final overall standard deviation.[30]

connected with palladium can be calculated. The energy of the reaction $PF_3 + F_2 = PF_5$ is known from table 4, $-16670.3\ J \cdot g^{-1}$, and $\Delta U(F_2)$ can be calculated. From the total energy $\Delta U(\text{total})$ involved in the reduction experiments and $\Delta U(F_2)$, $\Delta U\{Pd(PdF_6)\} + \Delta U(PdF_2)$ can be calculated:

$$\Delta U(\text{total}) + \Delta U(F_2) = \Delta U\{Pd(PdF_6)\} + \Delta U(PdF_2).$$

These values for $[\Delta U\{Pd(PdF_6)\} + \Delta U(PdF_2)]$ were inserted in table 2 to calculate the values for $\Delta U_c^\circ/m(\text{sample})$ in table 5. From the average enthalpy of combustion of $UPd_{3.099}$ in table 5, $\langle \Delta U_c^\circ/M(UPd_{3.099})\rangle = -(2861 \pm 226)\ J \cdot g^{-1}$, the standard enthalpy of formation of

$$UPd_{3.099}, \Delta H_f^\circ\{UPd_{3.099}, c, 298.15\ K\} = -(519 \pm 128)\ kJ \cdot mol^{-1},$$

has been derived, in the same way as for table 2. Although this result must be regarded as tentative, due to the large uncertainty in the analysis of $PF_5(g)$, it supports the value derived above. An advantage of this method is that we do not need to know the enthalpies of formation of $Pd(PdF_6)$ and PdF_2, as well as their amounts in the mixture of palladium fluorides.

4. Discussion

The standard enthalpy of formation of $UPd_{3.099}(c)$ $\Delta H_f^\circ(UPd_{3.099}, c, 298.15\ K)$, has been determined to be $-(536.7 \pm 30.8)\ kJ \cdot mol^{-1}$. To calculate the enthalpy of formation of the stoichiometric compound we assume that excess of palladium is entirely in solid solution, as is justified by solid solubility measurements of Pd in UPd_3.(2) We then find to a good approximation:

$$(4/4.099)\{\Delta H_f^\circ(UPd_{3.099})\} = \Delta H_f^\circ(UPd_3, c, 298.15\ K) = -(524 \pm 31)\ kJ \cdot mol^{-1}.$$

The only previous value for the enthalpy of formation of UPd_3 is an estimate of $-251\ kJ \cdot mol^{-1}$.(31) The enthalpy of formation of UPd_3 is comparable with the very negative enthalpies of formation of $ZrPt_3$: $-(517 \pm 33)\ kJ \cdot mol^{-1}$,(32) and $HfPt_3$: $-(552 \pm 48)\ kJ \cdot mol^{-1}$,(32) in accordance with the predictions of the Engel–Brewer theory.

The only experimental thermochemical value that has been published for UPd_3 is the standard Gibbs energy of formation $\Delta G_f^\circ(UPd_3, s, 1673\ K) = -259\ kJ \cdot mol^{-1}$. This value was obtained from mass-spectrometric measurements, however, without any detail of the experiments.(3) When we extrapolate the thermodynamic functions of UPd_3, as published(2) and based on the enthalpy of formation, the entropy, and the heat-capacity measurements,(28) we arrive at a value $\Delta G_f^\circ(UPd_3, s, 1673\ K) = -527\ kJ \cdot mol^{-1}$. An explanation for the large discrepancy cannot be given.

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