Table V. Decomposition Equation Parameters and Formation Enthalpies

	$NaPF_6$	KPF_6	$RbPF_6$	$CsPF_6$
$\Delta H_D°$ kcal mol^{-1} [a]	33.90 ± 0.5 33.44 ± 0.8	41.09 ± 0.3 41.50 ± 0.6	44.79 ± 0.6	49.81 ± 0.5
$\Delta S_D°$, cal K^{-1} mol^{-1} [a]	44.45 ± 1.1 43.32 ± 1.7	35.27 ± 0.4 35.46 ± 0.9	39.09 ± 0.9	45.73 ± 0.8
T range, °K and (median T)	423-516 (486) 411-512 (472)	547-703 (619) 560-694 (620)	576-705 (640)	602-738 (680)
$\Delta H_f°$, kcal mol^{-1}	−548.9 ± 3	−554.6 ± 3	−554.3 ± 3	−555.9 ± 3

[a] D = decomposition according to Equation 5.

mol^{-1} for the decomposition of $RbPF_6$, compared with 39.1 deg^{-1} mol^{-1} from these experiments.

CONCLUSIONS

In this series of compounds, the stability as measured by the compound's $P(PF_5)$ and ΔH_D increases in going from Na to Cs. This trend, paralleling that of oxyanion salts, results from increasing metal atom radius and decreasing electronegativity. Whereas the oxyanion salts of the alkalies vaporize with only partial decomposition, these compounds appear to form no detectable amount of $MPF_6(g)$ on heating.

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Enthalpy of Ruthenium Dioxide to 1200°K by Drop Calorimetry

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A high-precision drop calorimetric system has been used to measure, relative to 298.15°K, the enthalpy of ruthenium dioxide in the temperature range 600–1200°K. The following equation represents the enthalpy of ruthenium dioxide in the temperature range 298–1200°K:

$$(H_T° - H_{298.15}°) = 0.137472\,T + 9.89745 \times 10^{-6}\,T^2 + 4349.59\,T^{-1} - 56.4558 \text{ cal g}^{-1}$$

Values of $(H_T° - H_{298.15}°)$, $C_P°$ and $(S_T° - S_{298.15}°)$ are tabulated.

There is very little high-temperature thermodynamic information for many of the important fission product oxides. As part of a calorimetric study of these materials, the enthalpy of ruthenium dioxide was investigated by us. This compound was chosen because ruthenium is produced in high yields by the fission process, and ruthenium dioxide should be the only stable condensed oxide over the temperature range of the present investigation (*1*). Although there are some low-temperature heat capacity data (*4*) and a calorimetric determination of the heat of formation (*5*), we have been unable to find any previous measurements of the enthalpy of ruthenium dioxide reported in the literature.

EXPERIMENTAL

The ruthenium dioxide used in these studies was a deep blue crystalline solid and was obtained from Alfa Inorganics, Beverly, Mass. Spectrographic analysis of this material showed the only significant metallic impurities to be (in percent); Ag, 0.02; Al, 0.01; Cu, 0.01; and Pt, 0.05. All other metallic impurities were below the detection limits. X-ray diffraction

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analysis indicated ruthenium dioxide only. The lattice parameters were determined to be $a = 4.48$ Å and $c = 3.11$ Å; the crystal structure is tetragonal. This is in agreement with powder diffraction file card No. 18-1139. An analysis for ruthenium was performed by reducing the ruthenium dioxide in a stream of hydrogen gas. The residue was assumed to be virtually pure ruthenium metal since spectrographic analysis did not indicate any major metallic impurities. The oxygen was then calculated from the weight loss in the reduction. Based on three different sample weights, the ruthenium content was 76.03, 76.28, and 75.97 with an average value of 76.09% ruthenium (theoretical 75.95%) and an average of 23.91% oxygen (theoretical 24.05%). Based on the above analysis, the molar ratio O/Ru is 1.98 ± 0.02.

For the calorimetric studies, the ruthenium dioxide was sealed (under vacuum) in a platinum capsule having an internal volume of 5 cc and a 10-mil wall thickness.

The high-precision drop-calorimetric system used for this study and the experimental procedure have been described in detail in a previous publication (*2*). The basic system consists of a resistance-heated vacuum furnace for equilibrating the sample at high temperatures, a copper block calorimeter operating at 25°C, a gate to isolate the calorimeter from the furnace, and a drop mechanism for transfer of the sample capsule from the furnace to the calorimeter. As a check on the accuracy of the calorimetric system, synthetic sapphire supplied by the National Bureau of Standards is run at regular intervals; a typical set of data has been presented in a previous publication (*3*). We have determined the accuracy of the system to be ± 0.15%.

In this study, approximately 75% of the measured heat was due to the ruthenium dioxide, with the remainder accounted for by the platinum capsule. The enthalpy of an empty platinum capsule with identical dimensions and surface appearance was measured in a separate series of experiments, and an empirical expression determined to represent the enthalpy of platinum. This allows one to subtract the contribution for the capsule heat at each experimental temperature.

RESULTS

The experimental enthalpies for ruthenium dioxide are given in Table I. The following equation, with the constants determined by the method of least squares, represents the data over the temperature range 298–1200°K. (Throughout this paper 1 cal = 4.184 J, and all temperatures are based on IPTS-48.)

$$(H_T^\circ - H_{298.15}^\circ) = 0.137472\ T + 9.89745 \times 10^{-6}\ T^2 + 4349.59\ T^{-1} - 56.4558 \text{ cal g}^{-1} \quad (1)$$

Table I. Enthalpy of Ruthenium Dioxide

Temp, K	$(H_T^\circ - H_{298.15}^\circ)$, cal g^{-1}, obsvd	$(H_T^\circ - H_{298.15}^\circ)$, cal g^{-1}, calcd from Eq. 1	% dev, calcd − obsvd
619.4	39.495	39.514	+0.05
699.6	50.762	50.781	+0.04
704.7	51.377	51.508	+0.26
777.7	62.038	62.035	−0.01
778.0	62.042	62.079	+0.06
803.3	65.814	65.777	−0.06
803.6	65.673	65.821	+0.23
871.8	76.200	75.904	−0.39
872.0	76.125	75.934	−0.25
872.0	76.121	75.934	−0.25
1074.0	106.405	106.656	+0.24
1074.1	106.186	106.671	+0.46
1174.6	122.748	122.378	−0.30

Table II. Thermodynamic Functions of Ruthenium Dioxide

Temp, K	$(H_T^\circ - H_{298.15}^\circ)$, cal mol^{-1}	C_p°, cal mol^{-1}°K^{-1}	$(S_T^\circ - S_{298.15}^\circ)$, cal mol^{-1}°$K^{-1}$
298.15	0	12.57	0
300	23.3	12.65	0.08
400	1462.6	15.73	4.20
500	3121.0	17.30	7.89
600	4902.3	18.27	11.14
700	6765.0	18.96	14.01
800	8688.6	19.50	16.57
900	10661.4	19.95	18.90
1000	12676.7	20.35	21.02
1100	14730.0	20.71	22.98
1200	16818.4	21.05	24.79

The standard deviation for Equation 1 is 0.252 cal g^{-1} or 0.27%. The constraint that $(H_T^\circ - H_{298.15}^\circ) = 0$ at 298.15°K has been used in fitting the data. The calculated enthalpy from Equation 1, along with the deviation from the observed values, is shown in Table I. Normally, higher temperatures would have been attained but this was prevented due to traces of residual moisture which caused distortion of the platinum capsule.

The heat capacity for ruthenium dioxide was obtained by differentiating Equation 1 with respect to T and is given by

$$C_P^\circ = 0.137472 + 19.7949 \times 10^{-6}\ T - 4349.59\ T^{-2} \text{ cal g}^{-1} \text{ K}^{-1} \quad (2)$$

The smoothed enthalpies, along with the derived high-temperature heat capacities and entropy increments are given in Table II. The data here are reported as RuO_2, which is within the analytical uncertainty in the O/Ru ratio. The following equation represents the data in column 2:

$$(H_T^\circ - H_{298.15}^\circ) = 18.2926\ T + 1.31742 \times 10^{-3}\ T^2 + 5.78711 \times 10^5\ T^{-1} - 7512.06 \text{ cal mol}^{-1} \quad (3)$$

After the experiments were completed, ruthenium dioxide poured out easily from the capsule and left a shiny surface indicating no interaction with the platinum. An X-ray diffraction pattern of the ruthenium dioxide was identical to that of the starting material. It is therefore assumed that the ruthenium dioxide had not undergone any chemical change in the course of the drop experiments.

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