tion and the necessary limiting binary and infinite dilution values, interpolated when necessary, which define the ternary system from −75° to − 175°F. The system is defined at lower temperatures by the binary data (*7*, *8*). Simple expressions for the linear region, which represents almost all of the data, are

$$\log K_{\mathrm{M}} = \log K_{\mathrm{M(P)}} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{M(P)}}/K_{\mathrm{M(E)}}] \quad (1)$$

$$\log K_{\mathrm{E}} = \log K_{\mathrm{E(MP)}}^{\infty} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{E(MP)}}^{\infty}/K_{\mathrm{E(M)}}] \quad (2)$$

$$\log K_{\mathrm{P}} = \log K_{\mathrm{P(M)}} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{P(M)}}/K_{\mathrm{P(ME)}}^{\infty}] \quad (3)$$

$$\text{for } 0 \leq x_{\mathrm{E}} \leq x_{\mathrm{E}}'$$

Values for $K_{\mathrm{M(P)}}$, $K_{\mathrm{P(M)}}$, $K_{\mathrm{M(E)}}$, and $K_{\mathrm{E(M)}}$ can be easily found from the pressure temperature cross-plots of the binary data (*7*, *8*); x_{E}' has to be determined from the methane–ethane data (*8*); values for $K_{\mathrm{E(MP)}}^{\infty}$ and $K_{\mathrm{P(ME)}}^{\infty}$ are found from cross-plots of ternary data extrapolated to boundary concentrations. The extrapolation is justified because it is not extensive. These plots must be carefully constructed on large-scale engineering paper to retain the accuracy of the data.

The linearity of the *K*-values in the low temperature region was not evident in the data of Price and Kobayashi (*4*). Significant deviations from this investigation were found at temperatures below −50°F, especially for the methane–propane system. The most probable explanations are improper sampling and lack of analytical sensitivity. At the time of the older work, analysis could only be made to a mole fraction of ±0.001; now, with the improvements that have been made in chromatographic analysis, it is possible to determine amounts less than 0.001% with a good accuracy and reproducibility. Improvements in the sampling system (*7*, *8*) are also highly significant. The effect of a small amount of the less volatile component in the vapor phase becomes more pronounced as the temperature and pressure decrease.

The construction of pressure temperature cross-plots is helped by using data of other investigators (*1*, *2*, *4*, *5*) at higher temperatures than this investigation.

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NOMENCLATURE

All values are determined at the same temperature and pressure.

K_{M}, K_{E}, K_{P} = *K*-values of methane, ethane, and propane, respectively, in the ternary system

$K_{\mathrm{A(B)}}$ = *K*-value of A in the A-B binary system

$K_{\mathrm{A(BC)}}^{\infty}$ = *K*-value of A at infinite dilution in the B-C binary

x_{E}' = ethane mole fraction in the liquid phase in the methane–ethane system

x_{E} = ethane mole fraction in the liquid phase in the ternary system

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Thermal Decomposition of Alkali Metal Hexafluorophosphates

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The thermal decomposition of $NaPF_6$, KPF_6, $RbPF_6$, and $CsPF_6$ has been studied using mass spectrometric–effusion cell and differential thermal analysis techniques. All evolve PF_5 when heated under effusion conditions. The PF_5 decomposition pressure equations and first values for the formation enthalpies have been determined.

The hexafluorophosphates of the alkali metals present an interesting study of the variation in stability with cation size and are commercially important as well. Because stability data were not available, we conducted mass spectrometric and thermal analysis studies of the decomposition of these compounds.

EXPERIMENTAL

All compounds were used as received without further purification. According to the manufacturer the fluorine contents were 99.6, 97.1, and 101.0% of theoretical for the Na, Rb, and Cs salts, respectively. The PF_6^- content was 100.2 and 96.7 of theoretical for the Na and K salts, respectively (*13*). For our experiments, volatile impurities would contribute to the total weight loss measurements upon which the decomposition pressure calibrations are based while nonvolatile substances would be troublesome only if they altered the sample's activity.

The extent of both problems can be evaluated from our data since volatiles would be mass spectrometrically observed while activity variations would be seen as variations in the sample's vapor/decomposition pressure with time at a constant temperature. The compounds are stable enough not to require unusual precautions for handling. Differential thermal analyses were performed under vacuum with a Du Pont 900 DTA in-

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strument using Pt sample cells. The effusion cell-mass spectrometry equipment described earlier (*5*) was used to identify the gaseous species and to determine the pressure-temperature equation. For this work the molecular beam source was modified to avoid large pressure differentials between the molecular beam source and ionization regions for noncondensable gases.

In this way the attenuation of an ion current signal occurring when the direct path from effusion cell to ionizer is blocked is an accurate measure of the molecular beam intensity. A gold-plated nickel effusion cell was used for all samples. Its orifice diameter and Clausing factor were 0.022 in. and 0.89, respectively. The cell temperature-control apparatus described earlier was also modified by placing another heating filament directly below the cell. With this, we reduced axial temperature gradients, a common source of error in mass spectrometric studies of thermal properties, to 2.5°K or less. The cell and sample were weighed together to ±20 μg before placing the cell in the mass spectrometer. As before, temperatures were measured at two points in the cell top and two in its base using Chromel-Alumel thermocouples and a Honeywell 2732 potentiometer. The emf data were converted to temperatures using published tables with corrections supplied by the thermocouple wire manufacturer. The amount of sample used was sufficient to assure a sample area to orifice area ratio >100, thus negating errors due to a small condensation coefficient.

The decomposition data were taken as follows: After loading a weighed amount of sample into the effusion cell, the cell was placed in the mass spectrometer's molecular beam furnace. The sample temperature was then raised until vaporization or decomposition products were detectable. After we focused on the most intense ion from the vapor, a continuous record was made of the time Δt_i spent at each temperature T_i while measuring the ion current I_i. The Δt_i times were made long compared to the time needed to change temperatures. Sets of T_i, Δt_i, I_i points were taken over the largest T range possible, corresponding roughly to 10^{-11} atm, the limit of detectable signal, and 10^{-4} atm, the limit of the effusion equation in this experiment. The cell was then removed and sample reweighed. From these data the decomposition pressures were calculated.

The effusion equation is

$$P = \frac{\Delta W}{44.33\ aK\Delta t}\left(\frac{T}{M}\right)^{1/2} \qquad (1)$$

where P is the pressure in atmospheres of molecules of mass M, amu, escaping through an orifice of area a, cm², and Clausing factor K, from an effusion cell at temperature T, °K, giving a rate of weight loss $\Delta W/\Delta t$, g sec⁻¹. This equation was used to find the sensitivity constant k in the mass spectrometer equation (*3*).

$$P = kI_iT_i \qquad (2)$$

as

$$\sum_i \Delta W_i = 44.33\ aKM \sum_i (I_iT_i^{1/2}\Delta t_i)k \qquad (3)$$

since $\sum_i \Delta W_i$ is merely the total weight lost during the entire experiment. Through Equation 2, then, each IT point was converted to the corresponding pressure. Finally the PT data were analyzed by the method of least squares for the best fit to the equation

$$R \ln P \text{ (atm)} = \frac{-\Delta H^\circ}{T} + \Delta S^\circ \qquad (4)$$

An early version of this procedure was successfully applied to a study of the sublimation of Mn (*4*) and of Cd and Ag (*8*).

RESULTS AND DISCUSSION

Sodium Hexafluorophosphate. The first DTA scan exhibited an exotherm at 413°K which, by thermogravimetry, accompanied at 2% wt loss. Subsequent scans showed only a continuous endotherm beginning at 558°K. Comparison of the mass spectrum with that for PF_5(g) (*12*) showed the PF_5 evolution accompanied both endotherms. For the mass spectrometric studies PF_4^+, the most abundant PF_x^+ species, was used as the measure of the PF_5 decomposition pressure. At a constant temperature we could find no trend in the PF_4^+ intensity indicating the sample activity was not altered by the NaF residue or by traces of impurities. POF_3(g) was clearly present in the spectrum although the POF_x^+ species were attenuated 25% or less by blocking the molecular beam-to-ion source path, indicating the precursor originated largely outside the molecular beam source.

Our interpretation, supported by the absence of the P—O stretching absorption in the sample's ir spectrum, is that POF_3 formed *in situ* when PF_5 scavenged surface absorbed H_2O from the mass spectrometer parts. In any event, comparison of the combined POF_x^+ intensities indicated a negligible weight loss would have occurred as POF_3. No sodium-containing species were observed. Table I gives the data and derived PF_5 pressures from the two experiments. One may estimate from temperature, weight loss, time, and orifice dimension uncertainties that derived pressures may be uncertain by ±30% in the absolute sense and by ±20% in the relative sense. As shown, the agreement is within 5% except at low temperatures.

Potassium Hexafluorophosphate. Small endotherms were observed at 456° and 474°K on the first DTA scans with fresh samples but they did not appear on subsequent scans unless the sample was exposed to air. The chemical cause is not apparent since KPF_6 is very resistant to hydrolysis and oxidation. A broad, continuous endotherm beginning at approximately 698°K characterized the DTA curve. Superimposed was a small endotherm at 703°K which was consistently reproduced and must be assumed to represent a phase transition.

Mass spectrometric analysis showed conclusively that KPF_6 evolves PF_5 when heated under effusion conditions. If one assumes the decomposition forms KF at near unit activity, one should observe ions derived from KF(g) since the vapor pressure of KF reaches 10^{-9} atm in this temperature range (*2*). The only potassium-containing species observed was K^+; how-

Table I. PF_5 Decomposition Pressure over $NaPF_6$

Time, Δt_1, sec.	Temp, T_i, °K	Current, I_i, A	Pressure, P_i, atm
	Run 1		
1960	493	1.80×10^{-8}	5.15×10^{-6}
9640	515	8.00×10^{-8}	2.39×10^{-5}
2560	499	2.30×10^{-8}	6.66×10^{-6}
1920	486	1.01×10^{-8}	2.85×10^{-6}
2180	463	1.75×10^{-9}	4.70×10^{-7}
1140	445	4.35×10^{-10}	1.12×10^{-7}
1620	423	7.00×10^{-11}	1.72×10^{-8}
$\sum_i \Delta W_i = 0.01267$ gram			
	Run 2		
6120	462	5.55×10^{-9}	6.22×10^{-7}
2290	472	9.30×10^{-9}	1.07×10^{-6}
1680	483	1.70×10^{-8}	1.99×10^{-6}
2670	499	4.85×10^{-8}	5.87×10^{-6}
9360	512	1.36×10^{-7}	1.69×10^{-5}
4950	491	3.00×10^{-8}	3.58×10^{-6}
1980	455	1.95×10^{-9}	2.15×10^{-7}
1080	438	4.95×10^{-10}	5.26×10^{-8}
1740	411	5.00×10^{-11}	4.99×10^{-9}
$\sum_i \Delta W_i = 0.00972$ gram			

Table II. PF_5 Decomposition Pressure over KPF_6

Time, Δt_i, sec.	Temp., T_i, °K	Current, I_i, A	Pressure P_i, atm
	Run 1		
1620	547	2.74×10^{-10}	2.11×10^{-9}
2460	555	4.14×10^{-10}	3.23×10^{-9}
2460	564	7.46×10^{-10}	5.91×10^{-9}
2160	589	3.77×10^{-9}	3.12×10^{-8}
2160	606	8.38×10^{-9}	7.14×10^{-8}
4020	619	1.75×10^{-8}	1.52×10^{-7}
2040	638	4.58×10^{-8}	4.11×10^{-7}
2520	654	1.06×10^{-7}	9.74×10^{-7}
2220	673	2.63×10^{-7}	2.49×10^{-6}
3000	686	4.52×10^{-7}	4.36×10^{-6}
2340	703	8.22×10^{-7}	8.12×10^{-6}
$\sum_i \Delta W_i = 0.00173$ gram			
	Run 2		
1800	603.6	1.30×10^{-9}	4.28×10^{-8}
1980	621.9	3.70×10^{-9}	1.26×10^{-7}
1380	632.6	6.60×10^{-9}	2.28×10^{-7}
1200	645.6	1.41×10^{-8}	4.97×10^{-7}
600	646.9	1.47×10^{-8}	5.19×10^{-7}
2280	654.9	2.20×10^{-8}	7.86×10^{-7}
1500	664.6	3.50×10^{-8}	1.27×10^{-6}
1380	680.9	7.20×10^{-8}	2.67×10^{-6}
4320	694.6	1.29×10^{-7}	4.89×10^{-6}
2100	643.1	1.35×10^{-8}	4.74×10^{-7}
1800	618.6	4.30×10^{-9}	1.45×10^{-7}
1740	601.6	1.70×10^{-9}	5.58×10^{-8}
3120	619.1	4.20×10^{-9}	1.42×10^{-8}
1800	597.3	1.23×10^{-9}	4.01×10^{-8}
1680	575.6	3.10×10^{-10}	9.73×10^{-9}
1680	560.0	1.10×10^{-10}	3.36×10^{-9}
$\sum_i \Delta W_i = 0.00133$ gram			

Table III. PF_5 Decomposition Pressure over $RbPF_6$

Time, Δt_i, sec.	Temp., T_i, °K	Current, I_i, A	Pressure, P_i, atm
8830	705.3	4.30×10^{-8}	5.35×10^{-6}
600	690.9	1.80×10^{-8}	2.20×10^{-6}
900	663.4	5.10×10^{-9}	5.97×10^{-7}
600	636.4	1.22×10^{-9}	1.37×10^{-7}
540	639.5	1.40×10^{-9}	1.58×10^{-7}
1500	607.4	2.68×10^{-10}	2.87×10^{-8}
1200	594.4	1.14×10^{-10}	1.20×10^{-8}
6000	576.1	3.60×10^{-11}	3.66×10^{-9}
$\sum_i \Delta W_i = 0.00269$ gram			

Table IV. PF_5 Decomposition Pressure over $CsPF_6$

Time, Δt_i, sec	Temp., T_i, °K	Current, I_i, A	Pressure, P_i, atm
6300	738	2.46×10^{-7}	1.60×10^{-5}
1140	720	1.12×10^{-7}	7.13×10^{-6}
1080	700	4.92×10^{-8}	3.04×10^{-6}
1500	681	1.83×10^{-8}	1.10×10^{-6}
3120	661	5.70×10^{-9}	3.33×10^{-7}
3000	641	1.94×10^{-9}	1.10×10^{-7}
900	612	3.00×10^{-10}	1.62×10^{-8}
1500	602	1.40×10^{-10}	7.45×10^{-9}
$\sum_i \Delta W_i = 0.00597$ gram			

ever, it has been reported that K^+ is over 500 times more abundant than KF^+ in the spectrum of KF(g) using 75-V electrons (*1*). Since there was no evidence for gaseous KPF_6, it is certain that K^+ arose entirely from KF. The KF contribution to the weight losses observed in the two experiments on KPF_6 summarized in Table II was negligible. Again, there was no evidence of varying KPF_6 activity, and the results of the second run are within 5% of the first's data except at low temperatures.

Rubidium Hexafluorophosphate. The DTA curve consisted of a continuous endotherm beginning at 693°K superimposed on which was a small endotherm at 823°K and a small exotherm at 848°K. The continuous endotherm was again mass spectrometrically shown to be caused by PF_5 loss, but nothing could be learned about the other features since these were well above the effusion experiment range. The only rubidium species observed was Rb^+. Since the vapor pressure of RbF is high enough—e.g., 1.4×10^{-9} atm at 700°K (*2*)—and since Rb^+ is by far the most abundant ion in the RbF mass spectrum (*9*), one can conclude that Rb^+ arose from RbF(g) only. A pair of peaks, roughly equal in intensity, at approximately 314 and 316 amu could not be identified. Although definitely originating in the effusion cell, these ions did not appear to represent species contributing significantly to the sample weight loss. If $RbPF_6$(g) exists, an upper limit to $P(RbPF_6,g)$ at 700°K would be 0.1% of $P(PF_5)$. The activity of $RbPF_6$ appeared to be constant throughout the experiment. The data are summarized in Table III.

Cesium Hexafluorophosphate. The only feature of the DTA curve was the continuous decomposition or sublimation endotherm beginning at 748°K. Mass analysis of the sample vapors showed the process accompanied evolution of PF_5. In addition, the presence of peaks at 285 and 133 amu were clearly indicative of vapor phase CsF, since its most abundant ions are Cs_2F^+ and Cs^+ (*9*). The loss in sample weight as CsF was negligible. The $P(PF_5)$ data are summarized in Table IV. As in the other samples, $P(PF_5)$ was not time dependent at a constant temperature indicating neither CsF nor any traces of impurities form solutions with $CsPF_6$.

DERIVED DATA

The best values for $\Delta H_D°$ and $\Delta S_D°$(D means decomposition according to Equation 5) for the decomposition reactions

$$MPF_6(s) \rightarrow MF(s) + PF_5(g) \qquad (5)$$

where M = Na, K, Rb, and Cs are tabulated in Table V.

As mentioned above, MF(s) has been assumed to form at unit activity. Supporting this, one notes that if a solid or liquid solution formed, the Phase Rule would permit $P(PF_5)$ and therefore composition to vary with time in an effusion experiment at a constant temperature; such behavior was not, in fact, observed. From the $\Delta H_D°$ data, $\Delta H_f°(MPF_6,s)$ has been calculated for each compound using $\Delta H_f°$ for NaF, and PF_5 and $C_p°(PF_5,g)$ from the *JANAF* tables (*6*), $\Delta H_f°$ for RbF and CsF from NBS *Circular 500* (*11*), and $C_p°$ data from Kelley (*7*). Where more than one ΔH value was available, an average was taken, ignoring the small differences in median temperatures, and twice the larger of the standard deviations was assigned to the average ΔH. An approximate check on the validity of the data can be made through S° and C_p data available for KPF_6 and $RbPF_6$ (*10*).

For KPF_6 $S_{600°K}° \simeq 82.6 \pm 3$ cal deg^{-1} mol^{-1}. When combined with available PF_5 and KF data (*6*), one obtains $\Delta S_{600°K}° \simeq 29.5 \pm 3$ cal deg^{-1} mol^{-1} for the decomposition according to Equation 5. At 600°K, the Table II data give $P(PF_5) = 4.9 \times 10^{-8}$ atm so using $\Delta H_{600°K}° = 41.3 \pm 1.2$ kcal mol^{-1} gives $\Delta S_{600°K}° = 35.3 \pm 2$ cal deg^{-1} mol^{-1}. The probable cause for this difference, if it is in fact real, is that the correct ΔH_D lies at the lower limit of the uncertainty range cited—i.e., near 40 kcal mol^{-1}. In the same manner, we estimate $S_{600°K}°$ $(RbPF_6,s) = 77.4 \pm 2$ cal deg^{-1} mol^{-1} and $\Delta S_D° = 37.8 \pm 3$ cal deg^{-1}

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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