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The Reaction of Neptunium Hexafluoride with Sodium Fluoride[1]

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The equation $3NaF(s) + NpF_6(g) \rightleftarrows 3NaF \cdot NpF_5(s) + {}^1/_2F_2(g)$ was found to represent the equilibrium involved in the reaction of neptunium hexafluoride with sodium fluoride at 250–400°. The partial pressures of fluorine and neptunium hexafluoride in equilibrium with the solid phase formed by reaction of neptunium hexafluoride with sodium fluoride were obtained by measurements of total pressure and ultraviolet absorbance of the gas phase. At a fixed temperature (350°) over a 10-fold variation of fluorine pressure, the value of log p_{NpF_6} was found to depend linearly on log p_{F_2} with a proportionality coefficient of 0.49, comparable to the value of $^1/_2$ expected for the above reaction. Equilibrium constants, $K_p = p_{NpF_6}/p_{F_2}{}^{1/2}$, for the reaction at 250–400°, were expressed by the equation $\log K_p(\text{atm})^{1/2} = [-3.147 \times 10^3/T(°\text{K})] + 2.784$. The X-ray powder diffraction pattern obtained for $3NaF \cdot NpF_5$, sodium octafluoroneptunate(V), was indexed on the basis of a body-centered tetragonal unit cell with lattice constants $a = 5.449 \pm 0.001$ Å and $c = 10.853 \pm 0.003$ Å.

Introduction

The reaction of uranium hexafluoride with sodium fluoride has received much experimental attention. Katz[2] and Malm, *et al.*,[3] who reviewed earlier investigations of this reaction, showed that the stable compounds formed in the reaction are $NaF \cdot UF_6$ and $2NaF \cdot UF_6$ and measured some of the properties of these compounds.

The reaction of the hexafluoride of neptunium, the actinide neighbor of uranium, with sodium fluoride has been the subject of recent experimental investigations in several laboratories including our own. During the course of this work, we have enjoyed the advantage of exchanging information with Katz and Cathers[4] and with Golliher and LeDoux,[5] all of whom have made experimental observations of this reaction. Information has also been presented on removal of neptunium hexafluoride from gaseous fluoride mixtures by reaction with solid sodium fluoride.[6]

We observed that powdered sodium fluoride reacts readily with gaseous neptunium hexafluoride at 150–250° to form a violet-colored solid product and followed these observations with the work described below to obtain information on the stoichiometry of the reaction and the identity, structural properties, and stability of the product.

Experimental Section

Materials.—Reagent grade sodium fluoride powder (−270 mesh) was treated with gaseous fluorine (1 atm at 250° for 15 hr).

Neptunium hexafluoride was prepared by the reaction of fluorine with neptunium dioxide (obtained from the Oak Ridge National Laboratory) that contained 0.13 wt % plutonium, 0.04 wt % uranium, and only minor amounts of other impurities. To prepare neptunium hexafluoride, fluorine was circulated over powdered neptunium dioxide in a tube furnace at 500°, and the neptunium hexafluoride formed was condensed from the gas stream in a trap cooled by a Dry Ice–trichloroethylene slush. The neptunium hexafluoride was purified from low-boiling impurities by several cycles of freezing, removal of supernatant gas, and melting. Comparison of the vapor pressure at the ice point with the literature value[7] was used as an indication of the purity of the neptunium hexafluoride.

Gaseous fluorine was obtained from a commercial source. Small concentrations of hydrogen fluoride were removed from the fluorine by passing it through a tower of sodium fluoride pellets at 100°. Gaseous, dry, high-purity nitrogen was also obtained from a commercial source.

Apparatus and Procedure.—Manipulations of volatile and powdered compounds of neptunium were carried out in a ventilated glove box enclosure to protect personnel from the highly α-radioactive ^{237}Np isotope. Gases were handled in a nickel manifold, equipped with Monel diaphragm valves (valves No. 411 and No. 413, Hoke, Inc., Creskill, N. J.). Gases were circulated by a Monel diaphragm pump (Lapp Pulsafeeder No. CPS-1, Lapp Insulator Co., Inc., Leroy, N. Y.).

Reactions of an excess of neptunium hexafluoride with a thin layer of powdered sodium fluoride were carried out in a tube reactor connected to a calibrated volume and a pressure gauge[8] located in an isothermal enclosure. The reaction of an excess of gaseous neptunium hexafluoride (150–300 torr) with 100-mg samples of powdered sodium fluoride approached completion after 6–15 hr at 150–250°. The change in the number of gas moles as a result of the reaction was determined from the pressure change in the calibrated system. The vapor density of the final gas phase in contact with the solid reaction product was determined by expanding a sample into a calibrated nickel bulb at a known pressure and subsequently weighing the bulb. The weight change of the solid phase as a result of reaction was determined by replacing the gas phase in the tube reactor with nitrogen, cooling the reactor to ambient temperature, and weighing the solid product.

Samples of the solid phases were prepared for X-ray powder diffraction analysis by transferring them from the tube reactor into a polyethylene glove bag filled with dry nitrogen where they were ground and loaded into quartz capillary tubes. X-Ray powder diffraction patterns were obtained with a 114.6-mm Debye–Scherrer camera, using nickel-filtered copper Kα radiation (λ 1.5418 Å). Intensities were obtained with the aid of a densitometer.

The experimental procedure used in determining equilibrium constants for the fluorination of the solid complex $3NaF \cdot NpF_5$ was as follows. A sample of the complex was prepared by circulat-

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[1] Work performed under auspices of the U. S. Atomic Energy Commission.

[2] (a) S. Katz, *Inorg. Chem.*, **3**, 1598 (1964); (b) S. Katz, *ibid.*, **6**, 666 (1966).

[3] J. G. Malm, H. Selig, and S. Siegel, *ibid.*, **5**, 130 (1966).

[4] S. Katz and G. I. Cathers, *Nucl. Appl.*, **5**, 206 (1968).

[5] W. Golliher and R. A. LeDoux, Paducah Plant Laboratory Progress Report, USAEC Report KY-L-437, Paducah, Ky., Oct 1967, pp 12–23.

[6] "Reprocessing of Irradiated Fuels," Quarterly Report No. 26, USAEC Report EURAEC-1832, Center for Study of Nuclear Energy, Mol, Belgium, July 1–Sept 30, 1966, pp 53–56.

[7] B. Weinstock, E. E. Weaver, and J. G. Malm, *J. Inorg. Nucl. Chem.*, **11**, 104 (1959).

[8] S. Cromer, USAEC Report MDDC-803, Columbia University, March 1947.

ing a gaseous mixture of neptunium hexafluoride (20 torr) and fluorine (770 torr) over a thin layer of sodium fluoride for about 15 hr. The gas phase was then replaced with fluorine only, and after an additional 15 hr of circulation at a selected temperature, a sample of the gas phase (a mixture of fluorine and neptunium hexafluoride produced by the reaction of fluorine with the complex) was trapped in a 5-cm spectrometric cell equipped with sapphire windows, and the total absorbance of the gaseous sample was measured in the region 2050–3500 Å using a Cary Model 14B spectrophotometer. The total pressure of the system was measured by a nickel Bourdon gauge (range 0–1500 torr), and the total pressure in the spectrometric cell was measured by a pressure transmitter (range 0–200 torr, Taylor Instrument Co., Rochester, N. Y.).

Calculation of an equilibrium constant was performed as follows. The partial pressure of neptunium hexafluoride was obtained from the measured absorbance at 2210 Å and the relation $p_{NpF_6} = RTA_{NpF_6}/La_{NpF_6}$, where A is the absorbance, a is the molar absorptivity, L is the length of light path, R is the molar gas constant, and T is the Kelvin temperature. The net absorbance of neptunium hexafluoride was obtained by subtracting from the total absorbance at 2210 Å the absorbance of the empty cell at 2210 Å and the absorbance of fluorine at 2210 Å, calculated from $A_{F_2} = a_{F_2}Lp_{total}/RT$. Since in all samples the absorbance of fluorine was small compared to that of neptunium hexafluoride and the partial pressure of neptunium hexafluoride was small compared to that of fluorine, an insignificant error was introduced into the calculations of the equilibrium constants by taking the total pressure as the partial pressure of fluorine.

Results and Discussion

Stoichiometry of the Reaction of Excess Neptunium Hexafluoride with Sodium Fluoride.—The reaction of an excess of gaseous neptunium hexafluoride proceeded with the formation of a solid complex and a net decrease in the total moles of gas in the reaction system. Although the gaseous product of the reaction was not identified by chemical analysis, it was concluded to be fluorine since (1) the product had a vapor density less than that of neptunium hexafluoride, (2) the product did not condense at the temperature of Dry Ice, and (3) the only constituents of the system were sodium, neptunium, and fluorine. This conclusion is also supported by the observations, described below, of the back-reaction in which neptunium hexafluoride is produced by exposing the solid complex to gaseous fluorine.

Stoichiometric information on the reaction was obtained from the loss of neptunium hexafluoride from the gas phase and also from the weight gain and chemical analysis of the solid phase resulting from exposure of sodium fluoride to an excess of neptunium hexafluoride.

The number of moles of fluorine formed by reaction of 1 mol of neptunium hexafluoride was determined from the pressure change and the measurement of vapor density of the gas phase after reaction. The average of five determinations was 0.5 ± 0.1 mol of fluorine. The formation of 0.5 mol of fluorine in the reaction of 1 mol of neptunium hexafluoride would indicate that the reaction product contains pentavalent neptunium.

The number of moles of sodium fluoride reacting with 1 mol of neptunium hexafluoride was determined from the weights of sodium fluoride, the pressure change, and the vapor density of the gas phase after reaction. The average of five determinations was 3.2 ± 0.2.

The ratio of sodium fluoride to neptunium in the solid product was derived from the weight gain of the solid phase during reaction of excess neptunium hexafluoride with sodium fluoride. Because the atomic weight of neptunium is large compared to that of fluorine, the value of this ratio calculated from weight-gain observations was approximately 3 regardless of whether the calculations were made on the assumption that the product contains tetravalent, pentavalent, or hexavalent neptunium. On the basis that the complex is $x\text{NaF}\cdot\text{NpF}_5$, the average value of x, derived from 13 determinations, was 3.03 ± 0.07. The ratio of sodium fluoride to neptunium in the solid product was also derived from the initial weights of sodium fluoride samples exposed to neptunium hexafluoride and the quantities of neptunium found in the solid products by radiochemical analysis. The analyses of ten different samples yielded an average value of 3.1 ± 0.2 mol of NaF/mol of Np. These values agree with the observation of Golliher and LeDoux[5] that the reaction of neptunium hexafluoride with sodium fluoride produces a complex solid with a sodium:neptunium mole ratio of 3:1.

The ratios derived from the reactions of an excess of neptunium hexafluoride with sodium fluoride are the stoichiometric coefficients of the species participating in the reaction. The results indicate that the reaction can be represented by

$$3\text{NaF(s)} + \text{NpF}_6\text{(g)} \longrightarrow 3\text{NaF}\cdot\text{NpF}_5\text{(s)} + {}^1/_2\text{F}_2\text{(g)} \qquad (1)$$

Structure of $3\text{NaF}\cdot\text{NpF}_5$.—A sample of the solid prepared by reaction of neptunium hexafluoride with sodium fluoride at 150° and annealed at 350° produced a well-defined X-ray powder diffraction pattern. This pattern could be indexed on the basis of a body-centered tetragonal unit cell with lattice constants $a = 5.449 \pm 0.001$ Å and $c = 10.853 \pm 0.003$ Å. No evidence of the sodium fluoride pattern was observed. The X-ray data for Na_3NpF_8 recorded in Table I are in excellent agreement with those given by Ruedorff and Leutner[9] for Na_3UF_8 and attest to the fact that Na_3UF_8 and Na_3NpF_8 are isostructural compounds. A similar pattern was obtained by Asprey and coworkers[10] from a compound they have identified as $3\text{NaF}\cdot\text{NpF}_5$.

Equilibrium Constants.—The circulation of nitrogen (1 atm) over the complex solid produced no neptunium hexafluoride detectable by spectrophotometric measurements. The circulation of fluorine over the solid produced partial pressures of neptunium hexafluoride, readily measured by spectrophotometry, that were proportional to the fluorine pressures used. Table II lists the values for the partial pressures of fluorine and neptunium hexafluoride in equilibrium at 350° with the solid. That the values of the ratio $p_{NpF_6}/p_{F_2}^{1/2}$ are similar despite the tenfold variation of the partial

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[9] W. Ruedorff and H. Leutner, *Ann. Chem.*, **632**, 1 (1960).

[10] L. B. Asprey, personal communication, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1967.

Table I

X-Ray Powder Diffraction Data for $3NaF\cdot NpF_5$

	d, Å				d, Å		
hkl	Obsd	Calcd	I_{obsd}	*hkl*	Obsd	Calcd	I_{obsd}
002	5.420	5.426	35	220	1.923	1.926	62
101	4.860	4.870	100	204		1.922	
110	3.851	3.853	26	222	1.814	1.815	12
112	3.138	3.142	70	006		1.809	
103	3.009	3.014	27	301	1.792	1.791	8
200	2.720	2.724	10	310	1.723	1.723	8
004		2.713		312	1.642	1.642	38
202	2.434	2.435	16	116		1.637	
211	2.378	2.378	32	303	1.621	1.623	23
114	2.218	2.218	16	215		1.621	
213	2.020	2.021	37				
105		2.016					

Table II

Partial Pressures of Fluorine and NpF_6 in Equilibrium at 350° with the Solid Phase Formed by Reaction of NpF_6 with NaF

Partial pressure of F_2, atm	Partial pressure of NpF_6, atm		Calcd ratio $p_{NpF_6}/p_{F_2}{}^{1/2}$, $atm^{1/2}$
0.197	2.43×10^{-3}		5.47×10^{-3}
0.428	3.80×10^{-3}		5.81×10^{-3}
0.928	5.17×10^{-3}		5.37×10^{-3}
1.303	6.24×10^{-3}		5.47×10^{-3}
2.000	7.86×10^{-3}		5.56×10^{-3}
		Av	5.53×10^{-3}

pressure of fluorine indicates that the ratio is an equilibrium constant.

The logarithmic form of the equilibrium constant expression for the reverse of eq 1

$$\log p_{NpF_6} = \log K_p + {}^1/_2 \log p_{F_2} \qquad (2)$$

indicates a linear relation between log p_{NpF_6} and log p_{F_2}. The coefficient for the dependence of log p_{NpF_6} on log p_{F_2}, derived by least-squares analysis of the data in Table II, was 0.49, comparable to the expected value of $^1/_2$. These results, indicating that the product of the fluorination of the complex is neptunium hexafluoride and that the equilibrium partial pressure of neptunium hexafluoride is dependent on the one-half power of the partial pressure of fluorine, provide additional evidence that the complex contains neptunium in the pentavalent state.

Figure 1 shows the experimental equilibrium constants obtained at 250–400°. The equilibrium constant for the reverse of eq 1 can be calculated from the expression

$$\log K_p(\text{atm}^{1/2}) = (-3.147 \pm 0.181) \times 10^3/T(°\text{K}) + (2.784 \pm 0.299) \qquad (3)$$

derived by a least-squares fitting of the integrated van't Hoff equation to the data with the assumption that the enthalpy change is constant (the uncertainty values are standard deviations).

The following thermodynamic values are calculated for the reverse of eq 1. The mean enthalpy change, derived from the slope of the line in Figure 1, is $\Delta H° = 14$ kcal (mol of $NpF_6)^{-1}$. The standard free energy change can be calculated from the equation

$$\Delta F°_T = -RT \ln K_p = 14.4 \times 10^3 - 12.7T(°\text{K}) \text{ cal (mol of } NpF_6)^{-1} \qquad (4)$$

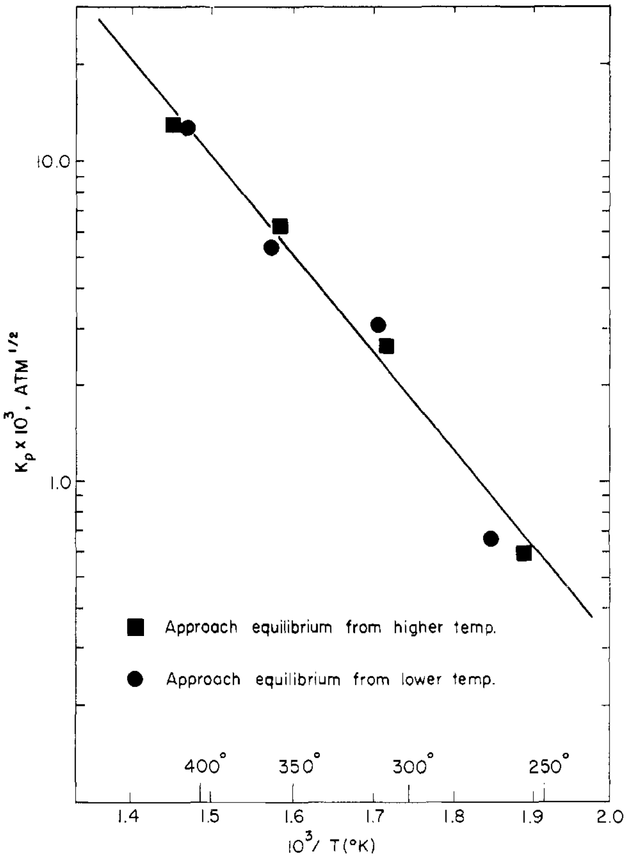

Figure 1.—Temperature dependence of the equilibrium constant for the reaction $3NaF\cdot NpF_5(s) + {}^1/_2F_2(g) \rightleftarrows 3NaF(s) + NpF_6(g)$.

which yields a value of $\Delta F°_{298} = 11$ kcal (mol of $NpF_6)^{-1}$. The mean entropy change, calculated from $\Delta S = (\Delta H - \Delta F)/T$, is $\Delta S° = 13$ cal (mol of $NpF_6)^{-1}$ deg^{-1}.

Possible Formation of Complexes Other Than $3NaF\cdot NpF_5$ in the Reaction of Neptunium Hexafluoride with Sodium Fluoride.—The solid phase resulting from reaction of neptunium hexafluoride and sodium fluoride under the conditions described above is the 3:1 compound of the binary condensed system sodium fluoride–neptunium pentafluoride. For protactinium and uranium, the actinide neighbors of neptunium, both the sodium fluoride–protactinium pentafluoride system[11–13] and the sodium fluoride–uranium pentafluoride system[9,14] form 3:1 compounds and 1:1 compounds, but neither system forms a 2:1 compound. Possibly the 1:1 compound of the sodium fluoride–neptunium pentafluoride system could be formed by the reaction

$$({}^1/_2)3NaF\cdot NpF_5(s) + NpF_6(g) \longrightarrow {}^3/_2NaF\cdot NpF_5(s) + {}^1/_2F_2(g) \qquad (5)$$

Although experimental evidence for formation of this 1:1 compound was not obtained, the limiting conditions necessary for its formation at 250° can be predicted from observations made in the present work.

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[11] D. Brown and J. F. Easey, *Nature*, **205**, 589 (1965).

[12] D. Brown and J. F. Easey, *J. Chem. Soc., A*, 254 (1966).

[13] L. B. Asprey, F. H. Kruse, A. Rosenzweig, and R. A. Penneman, *Inorg. Chem.*, **5**, 659 (1966).

[14] R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *ibid.*, **3**, 126 (1964).

We found that the net reaction of an excess of neptunium hexafluoride with sodium fluoride at 250° stopped with the formation of the 3:1 compound in the presence of an overpressure of about 146 torr of neptunium hexafluoride and 10 torr of fluorine. Therefore, the ratio of $p_{NpF_6}/p_{F_2}^{1/2}$ in the gas phase over $3NaF \cdot NpF_5$ necessary to initiate formation of the 1:1 compound, as expressed by eq 5, is greater than $K_p = (146/760)/(10/760)^{1/2} = 1.68\ atm^{1/2}$.

The results of reaction of sodium fluoride with the hexafluorides of uranium, neptunium, and plutonium reflect the decreasing stability of the hexavalent state across this series of three actinide elements. In the reaction of uranium hexafluoride with sodium fluoride, the stable products are compounds of hexavalent uranium,[1-3] even though some reduction to pentavalent uranium occurs during thermal dissociation of the hexavalent compounds.[15] In the reaction of plutonium hexafluoride with sodium fluoride, plutonium undergoes autoreduction.[16,17] No evidence for a product of this reaction containing hexavalent plutonium has been presented. For the reaction of neptunium hexafluoride with sodium fluoride, Katz and Cathers[4] have reported the formation of a compound containing neptunium in the hexavalent state that readily undergoes reduction to a compound containing neptunium in a lower valence state. All of our observations indicate that, under the conditions described above, the reaction of neptunium hexafluoride with sodium fluoride proceeds with what appears to be direct autoreduction of neptunium and that a complex solid product involving hexavalent neptunium must be relatively unstable compared to $3NaF \cdot NpF_5$.

Acknowledgment.—The authors are indebted to Robert Schablaske and Ben Tani for X-ray powder diffraction analyses.

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[15] G. I. Cathers, M. R. Bennett, and R. L. Jolley, *Ind. Eng. Chem.*, **50**, 1709 (1958).

[16] Chemical Technology Division Annual Progress Report for Period Ending May 31, 1965, USAEC Report ORNL-3830, Oak Ridge, Tenn., Nov 1965, pp 85–87.

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Pentacoordinated Molecules. XII.[1,2] Correlation of Exchange Rates for Some Group V Pentahalide Molecules

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The height of the barrier restricting intramolecular exchange, postulated to be present in PF_5 and related trigonal-bipyramidal molecules, is computed using a vibrational potential function based on normal-coordinate analyses. The barrier height corresponds to a tetragonal pyramid. The latter structure is considered to represent the lowest energy path leading to exchange. Rate constants are calculated for tunneling through the barrier and for activation over the barrier. Although the calculated rates are lower than nmr data indicate, the relative ordering is in agreement with observations ($PF_5 > PClF_4 > PCl_5$). Application to other molecules is made as well as a brief discussion of exchange rates with regard to postulated trigonal-bipyramidal intermediates in substitution reactions.

An intramolecular exchange process has been postulated by Berry,[3] analogous to that established for ammonia, to explain the nmr equivalence of fluorine atoms in PF_5.[4,5] The F^{19} nmr spectrum of PF_5, usually studied below its boiling point of $-85°$, consists of a single fluorine resonance split into a doublet due to P–F coupling. The process involves an internal motion shown in Figure 1 which leaves the molecule in a rotated state compared to the original with equatorial and axial positions exchanged.

Examination of the gas-phase infrared spectrum at room temperature and liquid-phase Raman spectrum of PF_5 at $-100°$[6,7] shows a normal spectrum expected for a trigonal-bipyramidal molecule. A temperature-dependent study of gaseous PF_5 in the far-infrared[8] region between room temperature and $-100°$ has not revealed any features assignable to the presence of an exchange process. Hence the presumed exchange process appears to take place at a rate faster than that detectable in the nmr measurements but slower than that which would affect line widths of vibrational bands.

An electron diffraction study by Hansen and Bartell[9] shows the expected nonequivalence of equatorial and axial bonds. A distance of 1.534 ± 0.004 Å was obtained for the $P–F_{eq}$ bond and 1.577 ± 0.005 Å was

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, Division of Inorganic Chemistry, San Francisco, Calif., April 1968.

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[9] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).