consistent with the diffraction symbol mmmB--b. The phase $NdTe_3$[10] shows the same extinctions and has the same space group and similar lattice parameters, $a = b = 4.35$ A, $c = 25.80$ A. A comparison of the relative intensities of corresponding reflections leads to the conclusion that the new phase probably has a structure similar to $NdTe_3$. A tentative formula $LaSnSb_2$ was assigned to this phase, but the exact atomic positions in the structure were not determined.

The LaSb, Sn, and $LaSn_3$ phases were found in the alloy of composition $LaSn_{1.5}Sn_{0.5}$; SmSb, Sn, and $SmSn_3$ phases were likewise found in equilibrium in the alloys of composition SmSnSb and $SmSn_{1.5}Sb_{0.5}$. The alloy of composition LaSnSb showed the equilibrium between LaSb, Sn, and the new ternary phase, while in $LaSn_{0.5}Sb_{1.5}$ the new ternary phase was predominant.

[10] B. K. Norling and H. Steinfink, *Inorg. Chem.*, **5**, 1488 (1966).

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The Systems Xenon Hexafluoride–Germanium Tetrafluoride and Xenon Hexafluoride–Silicon Tetrafluoride

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Received December 20, 1966

Xenon hexafluoride and germanium tetrafluoride, when mixed in the proper proportions, produce the compounds $4XeF_6 \cdot GeF_4$, $2XeF_6 \cdot GeF_4$, and $XeF_6 \cdot GeF_4$. Xenon hexafluoride appears not to react with silicon tetrafluoride.

Formation of compounds by the combination of xenon hexafluoride with stannic fluoride[1] suggests that fluorides of group IV elements other than tin may also combine with xenon hexafluoride. It has now been found that the reaction of excess XeF_6 with GeF_4 proceeds readily at room temperature to yield the white solid $4XeF_6 \cdot GeF_4$. The substance has a dissociation pressure of the order of 1 mm at 22°. When the complex is pumped at 0°, XeF_6, but practically no GeF_4, is slowly lost. After half of the combined XeF_6 has been removed, further loss is very slow. The substance remaining in the reactor, $2XeF_6 \cdot GeF_4$, is a white, crystalline solid. When $2XeF_6 \cdot GeF_4$ is pumped at 22°, XeF_6 and GeF_4 are removed in a 2:1 molar ratio at a rate of about 100 mg/hr in the system employed. At 0° the rate is much slower. The low rate of sublimation of $2XeF_6 \cdot GeF_4$ indicates that its dissociation pressure at 22° is only a small fraction of that of $4XeF_6 \cdot GeF_4$.

The reaction of excess GeF_4 with XeF_6 proceeds at room temperature to form the white, crystalline solid $XeF_6 \cdot GeF_4$. When pumped at 22°, a sample of this compound decomposed under vacuum in a somewhat complicated manner. The XeF_6 and GeF_4 were lost at a molar ratio of about 3:4 until about 61% of the sample had been removed. While the next 23% was removed, the XeF_6 to GeF_4 molar ratio in the sublimate rapidly increased to 2:1. During removal of the last 16% of the sample, the XeF_6 and GeF_4 were lost at a constant molar ratio close to 2:1. This behavior indicates that pumping from a mixture of $XeF_6 \cdot GeF_4$ and $2XeF_6 \cdot GeF_4$ gives the gases GeF_4 and XeF_6 in a ratio of about 4:3. As the process continues more $2XeF_6 \cdot GeF_4$ is formed. When the proportion of $XeF_6 \cdot GeF_4$ in the solid becomes low, the composition of the gas being removed changes and becomes 2:1 for the XeF_6 to GeF_4 ratio after only $2XeF_6 \cdot GeF_4$ remains in the solid phase. Equilibria which probably are involved are represented by

$$[4XeF_6 \cdot GeF_4] = [2XeF_6 \cdot GeF_4] + 2XeF_6(g)$$

$$[2XeF_6 \cdot GeF_4] = 2XeF_6(g) + GeF_4(g)$$

$$2[XeF_6 \cdot GeF_4] = [2XeF_6 \cdot GeF_4] + GeF_4(g)$$

The physical and chemical properties of the GeF_4 complexes are in many ways similar to those of the SnF_4 complexes. The compounds react violently with water to give a nearly quantitative yield of Xe(VI) in solution. Neither $2XeF_6 \cdot GeF_4$ nor $XeF_6 \cdot GeF_4$ melts under an atmosphere of nitrogen up to temperatures of 98 and 135°, respectively.

Attempts to prepare adducts of xenon hexafluoride with silicon tetrafluoride have been unsuccessful.

Experimental Section

Reagents.—Xenon hexafluoride was prepared by the combination of the elements under pressure at about 225°. Germanium tetrafluoride was prepared by passing fluorine over germanium dioxide at 300°. Ten grams of GeO_2 contained in a nickel boat was placed inside a nickel tube that could be heated electrically. A flow rate of about 1 l./hr of fluorine was used, and the GeF_4 was collected in a copper trap cooled to −183°. Silicon tetrafluoride was prepared by the reaction of silica with sodium fluoride and sulfuric acid.

Equipment.—Prefluorinated Monel and stainless steel reactors equipped with brass Hoke valves were used for the reactions. The reactors could be opened to allow the solid adducts to be re-

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[1] K. E. Pullen and G. H. Cady, *Inorg. Chem.*, **5**, 2057 (1966). Further detail will be included in the thesis of the junior author, to be published in 1967.

moved for study. The XeF_6 was handled in a prefluorinated metal vacuum line.

Preparation and Decomposition of $4XeF_6 \cdot GeF_4$ and $2XeF_6 \cdot GeF_4$.—In a typical experiment 0.7516 g (3.06 mmoles) of XeF_6 was distilled into a reactor containing 0.0990 g (0.666 mmole) of GeF_4 (molar ratio, 4.6:1). The reactants were contacted at room temperature for 22 hr. When the product was then subjected to pumping, the weight decreased as shown in Figure 1. The material pumped away was collected in a trap at −196° and at intervals was removed and analyzed for xenon. On pumping for just 3 min at 0° a weight loss of 86.1 mg occurred. The analysis for Xe showed that only XeF_6 had been pumped away. *Anal.* Calcd for XeF_6: Xe, 53.5. Found: Xe, 53.2. The weight of the product remaining in the reactor, 0.7645 g, corresponded to a composition of $4.07XeF_6.GeF_4$. Further weight loss was slow for the next 6.5 hr. During this period 0.3442 g was lost. Analysis for Xe at four nearly equally spaced intervals indicated that essentially only XeF_6 was being pumped away. *Anal.* Found: Xe, 52.9, 52.3, 52.1, 53.2. The weight of the product remaining in the reactor, 0.4203 g, corresponded to a composition of $1.97XeF_6 \cdot GeF_4$. Further loss in weight was so slow at 0° that only 12 mg was removed by pumping for 2.5 hr. The pumping was, therefore, continued at ambient room temperature (22°). All but 10 mg of the material remaining in the reactor was then removed during 4 hr of pumping. Analysis for Xe at four random intervals indicated that XeF_6 and GeF_4 were being pumped away in a 2:1 molar ratio. *Anal.* Calcd: Xe, 41.1. Found: Xe, 41.4, 40.4, 40.7, 41.5. While subliming $2XeF_6 \cdot GeF_4$ under vacuum, the sublimate was condensed in a trap at −196°. When the trap was later warmed to −78°, a substantial fraction of the GeF_4 could be removed as vapor by pumping. This means that much of the GeF_4 was present uncombined with XeF_6. The sublimation of $2XeF_6 \cdot GeF_4$ must have involved its dissociation into GeF_4 and XeF_6.

Preparation of $XeF_6 \cdot GeF_4$.—In a typical experiment 0.3686 g (1.50 mmoles) of XeF_6 was allowed to react with 0.3139 g (2.11 mmoles) of GeF_4 (molar ratio 1:1.4). The reactants stood at room temperature for 8 hr. At the end of this time the unreacted GeF_4 was removed by pumping while the reactor was held at −78°, a temperature at which XeF_6 is practically nonvolatile. After pumping to constant weight, the molar ratio of XeF_6 to GeF_4 in the remaining material was 1.57. An additional 362 mg of GeF_4 was then added, and the reactor was allowed to stand at 22° for another 4 hr. The unreacted GeF_4 was then pumped away at −78°. The solid product then weighed 0.5397 g corresponding to a molar ratio of XeF_6 to GeF_4 of 1.31. GeF_4 (483 mg) was again added, and the reactor was allowed to remain at 22° for 6 hr. After pumping away the unreacted GeF_4 at −78°, the weight of the product in the reactor, 0.5900 g, corresponded to a composition of $1.01XeF_6 \cdot GeF_4$. Allowing another 483 mg of GeF_4 to stand over the solid for an additional 12 hr caused no further increase in weight, indicating that the reaction was complete. In general, the reaction of excess GeF_4 to form $XeF_6 \cdot GeF_4$ seemed to proceed much more slowly than the reaction of excess XeF_6 to form $4XeF_6 \cdot GeF_4$.

Decomposition of $XeF_6 \cdot GeF_4$.—The $XeF_6 \cdot GeF_4$ used in the decomposition study consisted of 1.0906 g of XeF_6 combined with 0.6421 g of GeF_4 to give a product having a composition of $1.03XeF_6 \cdot GeF_4$. As in the cases of $4XeF_6 \cdot GeF_4$ and $2XeF_6 \cdot GeF_4$, the decomposition was studied by collecting the products removed by pumping and by analyzing them for xenon. In each sample collected, the weight of XeF_6 was calculated from the amount of Xe found, and the weight of GeF_4 was determined by difference.

In Figure 2 the composition of each fraction analyzed is plotted as a function of loss in weight of the sample. The pumping was done at 22°. While the first 1.056 g of material was pumped away, the molar ratio of XeF_6 to GeF_4 remained nearly constant and close to 0.75. The ratio then increased until the total loss in weight was 1.449 g. At this point the ratio in the sublimate was close to 2.0. The molar ratio remained close to 2.0 while the rest of the volatile material in the reactor was pumped away. Weight was lost at a rate of about 135 mg/hr while the molar ratio of the products being collected was 0.75. The total Xe found in all of the samples analyzed, 0.5797 g, corresponded to a weight of 1.0830 g of XeF_6 and agreed closely to the original weight, 1.0906 g, of XeF_6.

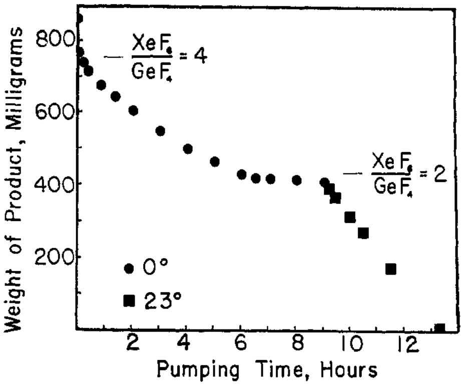

Figure 1.—Illustration of the preparation and subsequent decomposition under vacuum of $4XeF_6 \cdot GeF_4$. The reactor initially contained 751.6 mg of XeF_6 and 99.0 mg of GeF_4 (molar ratio, 4.6:1). The graph shows the rapid loss at 0° of unreacted XeF_6 to give $4XeF_6 \cdot GeF_4$ followed by further slow loss at 0° of XeF_6 to yield $2XeF_6 \cdot GeF_4$ eventually. On pumping at 23° XeF_6 and GeF_4 are then lost in a 2:1 molar ratio.

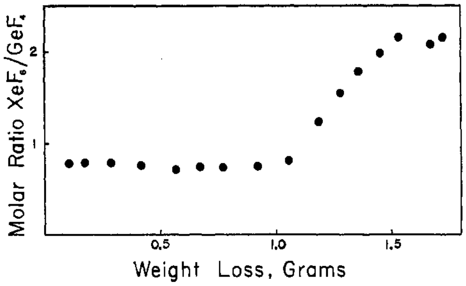

Figure 2.—Illustration of the course of the decomposition of a 1.732-g sample of $XeF_6 \cdot GeF_4$ under vacuum at 22°. The composition of the products removed by pumping is plotted against loss of weight.

Properties of $4XeF_6 \cdot GeF_4$.—On the basis of crude measurements made with a mercury manometer, the 4:1 complex was estimated to have a dissociation pressure of the order of 1 mm at room temperature. This relatively high pressure of XeF_6 makes handling of the substance in glass inconvenient.

Properties of $2XeF_6 \cdot GeF_4$.—The 2:1 complex was found to be a white, crystalline solid which attacked dry glass only slowly and was very hygroscopic. (*Caution:* the reaction of complexes of XeF_6 with SiO_2 or H_2O should be regarded as capable of yielding explosive XeO_3.)

The substance was observed to react violently with water, but no O_2 could be detected as a product of reaction. When a solution of KI was added to the hydrolyzed material, another vigorous reaction occurred resulting in the liberation of I_2 and Xe. Titration of the iodine with sodium thiosulfate indicated a liberation of 11.7 equiv of I_2/mole of $2XeF_6 \cdot GeF_4$ (theoretical, 12.0).

An attempt was made to measure a melting point of $2XeF_6 \cdot GeF_4$ under an atmosphere of dry nitrogen in a glass vessel. Sublimation to cooler parts of the vessel was observed at temperatures as low as 50°. No melting was observed up to 98°, the temperature at which the last portion of the solid sublimed from the heated zone.

Properties of $XeF_6 \cdot GeF_4$.—Like the 2:1 complex, $XeF_6 \cdot GeF_4$ was found to be a white, crystalline solid which was very hygroscopic but attacked dry glass only slowly.

When the solid was flooded with water, a vigorous reaction occurred. No oxygen was observed as a product but the solution contained an oxidizing agent capable of liberating iodine in the proportion of 6.01 equiv/mole of $XeF_6 \cdot GeF_4$ consumed (theoretical, 6.00).

The 1:1 complex did not melt in glass under an atmosphere of nitrogen up to a temperature of 135°. The substance sublimed readily at temperatures above 50°. At 110° a yellow vapor (presumably XeF_6) could be seen above the solid. The yellow color increased in intensity as the sample was heated to 135°. The heating was discontinued at this point because there was considerable attack on the glass.

X-Ray Powder Patterns.—The X-ray powder photographs were taken using samples contained in 0.2-mm Lindemann glass capillaries which were filled as previously described[1] and loaded into a 114.6-mm diameter Debye–Scherrer powder camera. Nickel-filtered copper radiation (λ 1.5418 A) was used, and exposures of 4–6 hr were made.

The *d* spacings found for $2XeF_6 \cdot GeF_4$ and $XeF_4 \cdot GeF_4$ are given in Tables I and II, respectively. The visually estimated relative intensity of each measured line is listed as strong (s), medium (m), or weak (w).

Powder patterns were taken at some random compositions corresponding to XeF_6 to GeF_4 molar ratios between 2.0 and 1.0. These powder patterns showed only those lines attributable to $2XeF_6 \cdot GeF_4$ and $XeF_6 \cdot GeF_4$ suggesting that there are no other compounds in this molar ratio range.

Table I

X-Ray Powder Diffraction Data for $2XeF_6 \cdot GeF_4$

d, A	Intens	*d*, A	Intens	*d*, A	Intens
7.6	w	2.45	w	1.731	w
4.65	w	2.40	w	1.711	w
4.55	s	2.29	m	1.668	m
4.32	w	2.23	w	1.633	w
4.22	w	2.18	w	1.585	w
4.01	w	2.13	w	1.554	w
3.93	w	2.09	m	1.531	w
3.83	w	2.03	w	1.498	w
3.54	w	2.01	m	1.473	w
3.32	m	1.98	w	1.431	w
3.15	w	1.96	w	1.409	w
2.94	w	1.91	w	1.388	w
2.85	w	1.89	w	1.364	w
2.72	w	1.87	w	1.306	w
2.64	m	1.799	m	1.273	w
2.60	w	1.768	w		
2.54	w	1.743	m		

Table II

X-Ray Powder Diffraction Data for $XeF_6 \cdot GeF_4$

d, A	Intens	*d*, A	Intens	*d*, A	Intens
6.4	m	2.08	w	1.365	w
5.23	w	2.01	w	1.343	w
5.08	m	1.98	w	1.324	w
4.86	s	1.90	w	1.308	w
4.76	s	1.86	w	1.291	w
3.74	s	1.84	w	1.274	w
3.56	m	1.82	w	1.261	w
3.46	w	1.786	m	1.232	w
3.31	w	1.735	w	1.215	w
3.21	w	1.707	w	1.196	w
3.12	s	1.678	w	1.173	w
2.97	w	1.646	w	1.158	w
2.88	w	1.627	w	1.144	w
2.82	w	1.610	s	1.118	w
2.75	w	1.594	w	1.041	w
2.62	w	1.561	w	0.890	w
2.57	w	1.511	w	0.867	w
2.52	w	1.489	w	0.837	w
2.43	w	1.473	w	0.828	w
2.30	m	1.442	w	0.822	w
2.23	m	1.413	w	0.7941	w
2.17	w	1.396	w	0.7892	w
2.13	w	1.379	w	0.7800	w

Attempted Reaction of XeF_6 with SiF_4.—All attempts to prepare a complex between XeF_6 and SiF_4 were unsuccessful. Three preparations were attempted on a millimole scale at different temperatures. In all of the cases about equimolar amounts of XeF_6 and SiF_4 were used. After allowing the reactants to stand for several hours, the mixtures were pumped at −78°. Complete and rapid removal of the SiF_4 was taken as evidence that no reaction had occurred. Reactions were tried at 67, 22, and −78°. The low-temperature reaction was attempted by slowly cooling the reactants to −78° over a 30-min period and then allowing the reactants to stand 16 hr at that temperature. In every case all of the SiF_4 was removed in 3–5 min on pumping at −78°.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research.

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Kinetics of the Reaction between Plutonium(III) and Xenon Trioxide

By J. M. CLEVELAND

Received December 21, 1966

The kinetics of the reaction between Pu(III) and XeO_3, according to the equation $6Pu(III) + XeO_3 + 6H^+ \rightarrow 6Pu(IV) + Xe + 3H_2O$, have been studied in perchlorate media by following the rate of disappearance of Pu(III) spectrophotometrically at 600 mμ. The rate law for the reaction is: $-d[Pu(III)]/dt = k[Pu(III)][XeO_3]$. The reaction rate is independent of acidity in the 0.5–2 *M* range. From the variation of the reaction rate with temperature, the following thermodynamic quantities of activation at 25° were calculated: $\Delta H^{\ddagger} = 15.3 \pm 2.1$ kcal/mole; $\Delta F^{\ddagger} = 20.2 \pm 0.1$ kcal/mole; $\Delta S^{\ddagger} = -16.0 \pm 6.9$ eu. The mechanism of the reaction appears to involve either successive one-electron changes or a two-electron change to form a Pu(V) species other than PuO_2^+, which then reacts with Pu(III) to form Pu(IV).

The preparation and identification of xenon trioxide by Koch and Williamson[1] indicated that this compound is a powerful new oxidizing agent with a six-electron change. The xenon–xenon(VI) potential has been estimated to be −1.8 v in acid solution,[2] placing xenon

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(1) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(2) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).