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Note

On the Synthesis of Xenon Di-, Tetra-, and Hexafluoride

J. Slivnik, A. Šmalc, B. Žemva, and A. N. Mosevič*

Nuclear Institute »Jožef Stefan«, Ljubljana, Slovenia, Yugoslavia

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Among the methods so far described for the synthesis of xenon fluorides the most common is the heating of a xenon-fluorine mixture in closed reaction vessels under pressure. Using this system it is possible to prepare xenon difluoride, tetrafluoride, and hexafluoride.

Recently Falconer¹ reported the synthesis of xenon difluoride by heating a xenon and fluorine mixture with xenon in excess. With a molar ratio of 1 : 5 at 400° C, as reported by the Argonne group², the product was said to be the tetrafluoride. The starting pressure in this gaseous mixture was 6 atm at 20° C. It appears that the hexafluoride is produced when molar ratios of xenon and fluorine from 1 : 16 to 1 : 20 and pressures from 60 to 200 atm are used³⁻⁶. The conditions for all the above mentioned syntheses were found empirically. The first systematic investigation of the thermal reaction of xenon and fluorine was by Weinstock *et al.*⁷ who determined the equilibrium constants for the formation of each of the fluorides. From his measurements it is evident that the synthesis reported for the tetrafluoride and hexafluoride yield a product contaminated with other xenon fluorides. As a further extension of this work we decided to carry out a systematic investigation by continuous pressure measurements of the gaseous mixtures during the reaction and by measuring the pressure differences at 22° C before and after the heating.

EXPERIMENTAL

Fluorine of $99 \pm 0.5\%$ purity was prepared and purified as described elsewhere^{8,9}. Xenon of 99.5% purity was obtained from L'Air Liquide, Paris. Reactions were carried out in 100 ml. nickel reaction vessels equipped with pressure gauges of the class 2.5. Since no Monel Bourdon gauges were at our disposal, pressure transmitters with copper bellows were made. These were used in conjunction with oil filled brass Bourdon gauges.

Fluorine was admitted into the reaction vessels from a manifold capable of withstanding fluorine pressures up to 160 atm. Xenon was metered from a reservoir of known volume into a 10 ml. metal can at -196° C. It was then transferred into the reaction vessel.

Reaction vessels were heated up to 160° C using a thermostated glycerine bath. Higher temperatures were achieved using an electrical furnace which embodied a large aluminum block. At temperatures up to 160° C both the vessel and the pressure transmitter were heated, but at higher temperatures the pressure transmitter, which accounted for 10% of the total volume, was maintained at room temperature.

* On leave from University of Leningrad, USSR.

After the completion of the reaction the reactor was cooled to -196°C , then warmed up to 22°C and the pressure was measured. The reaction products were separated by sublimation and distillation techniques.

Preliminary experiments between 200° and 450°C showed that the reaction proceeded too quickly for accurate determination of its rate⁹. When the reaction vessel was plunged into the already heated furnace, as much as 40% of xenon was consumed before the temperature equilibrium was reached. The fact that 10% of the total volume was outside of the heated zone also contributed to the error of the measurements. Therefore we decided to carry out measurements between 90° and 160°C .

Three identical reaction vessels were simultaneously placed in a thermostat at 120°C . The molar ratio of the xenon-fluorine mixture was 1:10 and the starting pressure at 22°C was 33 atm. When the reaction had equilibrated, the three vessels were cooled to 22°C and the pressure was measured. The contents of one were analysed while the other two were heated at 150°C until the pressure was constant. The procedure was repeated and the third vessel was heated at 200°C to constant pressure. Finally this vessel was cooled and the contents were analysed.

Fig. 1 shows the pressure measurements at 120° , 150° and 200°C . The pressures measured at 150° and 200° , reduced to 120°C , are shown by the dotted

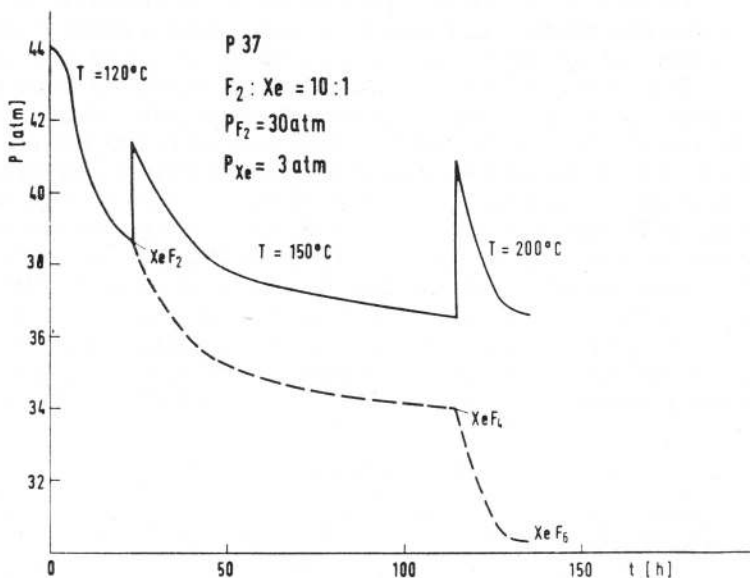


Fig. 1. Pressure-time dependence at various reaction temperatures (120 , 150 and 200°C).

line. The differences in pressure measured at 22°C before and after the reaction are summarized in Table I. Since the vapor pressures of xenon fluorides are negligible at room temperature as compared with the total pressure, the pressure measured at 22°C is caused only by unreacted reactants. The reaction products were hydrolyzed and the fluoride was determined by thorium nitrate titration. The results of the analyses are given in Table I.

Our observations indicate that xenon difluoride, tetrafluoride and hexafluoride can be formed stepwise from the same reaction mixture depending only upon temperature.

TABLE I

The Differences in Pressure of Reaction Mixture Before and After the Reaction

Temperature (°C)	Pressure at 22° C (atm)		Pressure drop (atm)	Product composition	
	Before experiment	After		Calc'd.*	Fluorine content (%)
120	33.0	27.3	5.7	XeF _{1.90}	22.2 ± 0.3
150	33.0	23.9	9.1	XeF _{4.04}	37.0 ± 0.3
200	33.0	20.9	12.1	XeF _{6.05}	46.4 ± 0.3

* on the basis of the pressure drop.

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IZVLEČEK

Sinteza ksenonovega di-, tetra- in heksa-fluorida

J. Slivnik, A. Šmalc, B. Žemva in A. N. Mosevič

Opisan je način za pripravo ksenonovega difluorida, tetrafluorida in heksafluorida iz zmesi ksenona in fluora v molskem razmerju 1 : 10 in pri začetnem pritisku 33 atm (pri 22° C). Ugotovili smo, da je mogoče reakcijo voditi postopoma preko difluorida oz. tetrafluorida do heksafluorida.

NUKLEARNI INŠTITUT »JOŽEF STEFAN«
LJUBLJANA

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