

ON THE PREPARATION OF PURE XENON TETRAFLUORIDE

by

M. BOHINC AND J. SLIVNIK

J. Stefan Institute and Department of Chemistry,
University of Ljubljana, Ljubljana, Yugoslavia

Received May 8, 1973

Pure xenon tetrafluoride was prepared by the thermal dissociation of the compound formed between sodium fluoride and xenon hexafluoride. The reaction conditions were: Mole ratio $\text{NaF}:\text{XeF}_6$ 6.7:1.0, an initial amount of XeF_6 of 46 m-moles and a dissociation temperature of $350^\circ \pm 5^\circ \text{C}$. The purity of the xenon tetrafluoride produced was determined by checking its melting point and the infrared spectrum of its vapour.

Nowadays preparations of xenon fluorides do not present any appreciable problems. They are in principle similar to the syntheses of some higher fluorides. Of course one should keep in mind that most of the methods described so far yield a small amount of the other two xenon fluorides besides the main product. The amount of these impurities can be as high as a few percent. Yet methods for the preparation of pure xenon difluoride and xenon hexafluoride have been published.

Pure xenon difluoride can be easily prepared by photosynthesis of xenon and fluorine [1—3]. Because of its comparatively higher vapour pressure pure xenon hexafluoride can be separated from mixtures of xenon fluorides by trap to trap sublimation. The methods reported by Malm [4] and Sheft [5], which are based on the selective absorption of xenon hexafluoride at 50°C and desorption at 120°C , are very suitable for the preparation of somewhat larger quantities, up to few grams of xenon hexafluoride.

The preparation of pure xenon tetrafluoride, however, seems to be very difficult, especially so since it forms molecular addition compounds with xenon difluoride [6] even at room temperature. The preparation of pure xenon tetrafluoride involving purification with arsenic pentafluoride in a solution of bromine pentafluoride was reported by Bartlett and Sladky [7]. In 1972 Johnson et al. [8] reported a method of preparation of pure xenon tetrafluoride from xenon and fluorine.

In our experiments very often larger quantities of pure xenon tetrafluoride are needed. Therefore we decided to investigate the possibility of synthesizing larger quantities of xenon tetrafluoride utilizing the experience gained in our study of the thermal dissociation of xenon hexafluoride [9]. At 330°C the dissociation was found to follow the following equation:



It should be emphasized here that under the conditions used we did not observe any indication of the presence of xenon difluoride.

EXPERIMENTAL

Materials

Xenon hexafluoride was prepared at 300°C starting with a mixture of xenon and fluorine having a molar ratio of 1 : 20 at a total pressure amounting 60 atm. The product was purified by the previously mentioned sodium fluoride method [4, 5]. Before use, sodium fluoride was heated at 500°C for 18 hours, then treated with fluorine at 10 atm pressure for 20 hours at 200°C. Subsequently fluorine was thoroughly pumped off, the solid in addition treated with xenon hexafluoride at 150°C and finally pumped off in high vacuum at 350°C.

Apparatus

Reactions were carried out in 120 ml argon-arc welded nickel pressure weighing vessels equipped with brass valves and using an all nickel vacuum system.

Preparation

In a typical experiment 309.5 m-moles of sodium fluoride (treated as mentioned before) was put into the 120 ml nickel reaction vessel and 46 m-moles of xenon hexafluoride were added by sublimation. The reaction vessel was heated in a furnace at 350°C for two and a half hours. The evolved fluorine was pumped off at liquid nitrogen temperature, while sodium fluoride, xenon tetrafluoride and xenon hexafluoride remained in the reaction vessel. The decomposition with subsequent removal of fluorine was repeated seven times. On the basis of the material balance which was followed throughout the decomposition with an accuracy of ± 1 mg, we concluded that the thermal dissociation was practically finished after the seventh run. The experimental data are presented in Fig. 1.

In order to remove possible remaining traces of xenon hexafluoride, the reaction vessel was heated at 50°C overnight and then the volatiles were sublimed away at the same temperature. In the infrared spectrum of the vapour phase, however, a weak absorption band of xenon hexafluoride was observed besides the strong absorption band of xenon tetrafluoride. The product was then purified further by trap to trap sublimation. The purified product had a triple-point of $117.1^\circ \pm 0.05^\circ\text{C}$, exactly the temperature reported by Schreiner and coworkers for xenon tetrafluoride [10]. Also, the infrared spectrum of the vapour revealed no presence of xenon hexafluoride. The yield of the procedure was found to be 89.5 w. %.

Acknowledgement:

This work was financed through the Boris Kidrič Foundation. The help of Mr. T. Ogrin who measured the triple-point, is acknowledged.

REFERENCES

- [1] L. V. Streng, A. G. Streng, *Inorg. Chem.*, **4** (1965), 1370
- [2] J. H. Holloway, *J. Chem. Educ.*, **43** (1966), 202
- [3] J. H. Holloway, *Chem. Commun.*, (1966) 22
- [4] J. G. Malm, F. Schreiner, D. W. Osborne, *Inorg. Nucl. Chem. Lett.*, **1** (1965), 97
- [5] I. Sheft, T. M. Spittler, F. Martin, *Science*, **145** (1964), 701

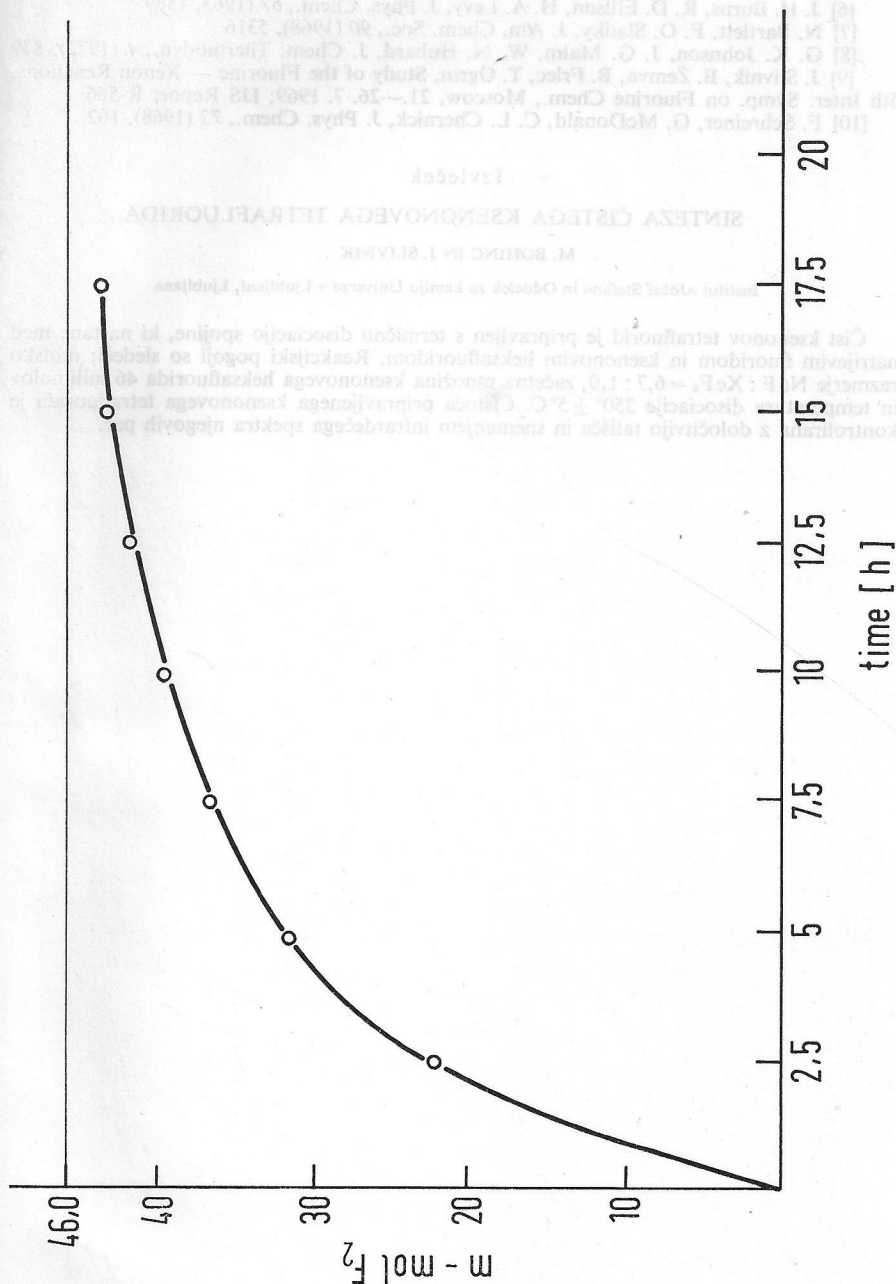


Fig. 1. Time dependence of XeF_6 thermal decomposition at $350^\circ \pm 5^\circ\text{C}$.

- [6] J. H. Burns, R. D. Ellison, H. A. Levy, *J. Phys. Chem.*, **67** (1963), 1569
 [7] N. Bartlett, F. O. Sladky, *J. Am. Chem. Soc.*, **90** (1968), 5316
 [8] G. K. Johnson, J. G. Malm, W. N. Hubbard, *J. Chem. Thermodyn.*, **4** (1972), 879
 [9] J. Slivnik, B. Žemva, B. Frlec, T. Ogrin, *Study of the Fluorine — Xenon Reactions*, 5th Inter. Symp. on Fluorine Chem., Moscow, 21.—26. 7. 1969; IJS Report R-566
 [10] F. Schreiner, G. McDonald, C. L. Chernick, *J. Phys. Chem.*, **72** (1968), 162

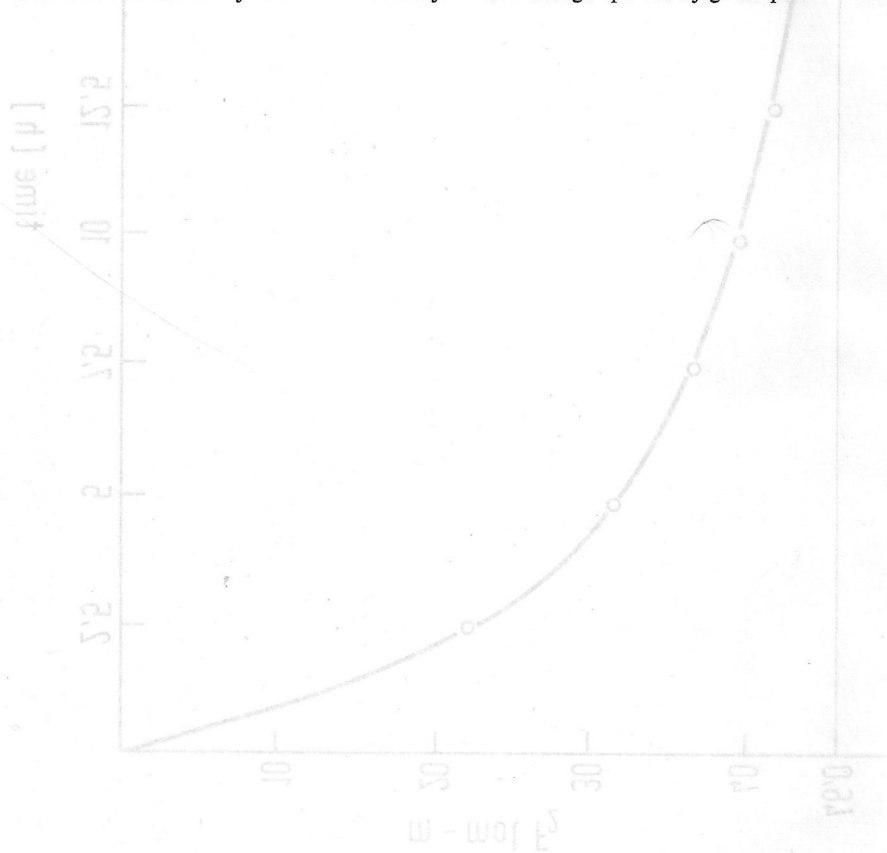
Izvleček

SINTEZA ČISTEGA KSENONOVEGA TETRAFLUORIDA

M. BOHINC IN J. SLIVNIK

Institut »Jožef Stefan« in Oddelek za kemijo Univerze v Ljubljani, Ljubljana

Čist ksenonov tetrafluorid je pripravljen s termično disociacijo spojine, ki nastane med natrijevim fluoridom in ksenonovim heksafluoridom. Reakcijski pogoji so sledeči: molsko razmerje $\text{NaF} : \text{XeF}_6 = 6,7 : 1,0$, začetna množina ksenonovega heksafluorida 46 milimolov in temperatura disociacije $350^\circ \pm 5^\circ \text{C}$. Čistoča pripravljenega ksenonovega tetrafluorida je kontrolirana z določitvijo tališča in snemanjem infrardečega spektra njegovih par.

Fig. 1. Time dependence of XeF_6 thermal decomposition at $350 \pm 5^\circ \text{C}$.