Reports

Fluorine Compounds of Xenon and Radon

Abstract. Xenon and fluorine combine readily. Xenon tetrafluoride is a colorless crystalline material, stable at room temperature. The existence of at least one other fluoride and two oxyfluorides has been demonstrated. The heaviest "inert gas," radon, also reacts with fluorine, yielding a compound less volatile than xenon tetrafluoride.

The existence in the atmosphere of gaseous species less reactive than nitrogen was recognized by Cavendish in 1785. Systematic studies leading to the isolation and characterization of the inert gases, however, began with the isolation of argon by Rayleigh and Ramsay in 1894 (*1*). For the group of gases, helium, neon, argon, krypton, xenon, and finally radon, the most characteristic chemical property was taken to be the absence of chemical reaction.

As concepts of valence based on the distribution of electrons in atomic orbitals were developed, the inert gases with filled shells played an important role (*1*). But our observations (*2*) may require revision of previous concepts.

A number of compounds whose existence could not be confirmed have been reported at various times for one or another of these gases (*3*). Some weak molecular associations of the inert gases (hydrates and clathrates) have been unequivocally demonstrated, but these associations involve a stable molecule as the other combining species; and the combinations have been attributed to secondary valence forces and favorable geometry (*1*). Band spectra recently observed in electrical discharges and ascribed to XeO and KrO suggest some binding, but stable compounds were not reported (*4*).

A chemical reaction of xenon with platinum hexafluoride vapor was reported in June 1962 by Bartlett (*5*), who suggested that $Xe^+PtF_6^-$ is the most likely formula for the yellow powder resulting from this reaction.

In the light of this interesting observation (*6*), Claassen, Selig, and Malm (*7*) decided to explore the possibility of a direct reaction between xenon and fluorine. After heating a mixture of these gases (with fluorine in moderate excess) for 1 hour at 400°C and then cooling to −78°C, they found, surprisingly, no unreacted xenon. The reaction product was recovered in high yield as a colorless crystalline material, stable at room temperature. The formula XeF_4, derived from the ratio of fluorine to xenon consumed in the reaction, was confirmed by reaction with hydrogen:

$$XeF_4 + H_2 \rightarrow Xe + 4HF$$

and analysis of the products.

Claassen *et al.* noted that xenon tetrafluoride can be sublimed readily at room temperature in an evacuated glass system and that crystals up to a few millimeters across grow in a few hours. The vapor pressure was negligible at −78°C and perhaps 3 mm-Hg at room temperature.

Hydrolysis studies were initiated. The results are not well understood and the observations are discussed more fully below. An infrared absorption band at wave number 590 cm^{-1} was found in a vapor sample. Limited observations were also reported on the compound's insolubility in *n*-perfluoro heptane and on the probable existence of a lower fluoride.

Direct determinations of molecular weight, further confirming the formula XeF_4 and also providing conclusive evidence for the existence of other xenon compounds, have now been made by analyzing samples of xenon fluoride in a time-of-flight mass spectrometer (*8*). Samples from two preparations of the tetrafluoride were studied. In one the xenon tetrafluoride had been made from highly purified fluorine. When the sample was held at room temperature, vapor admitted to the spectrometer yielded the scan shown in Fig. 1. When the sample was cooled to −78°C, all the xenon fluoride species were frozen out, but as the sample warmed slightly, XeF and XeF_2 masses appeared, as shown in Fig. 2. It is evident that XeF_2 exists as a stable species and is more volatile than XeF_4. XeF_3 is probably a fragment derived from XeF_4, and XeF may be a fragment derived largely from XeF_2.

The other sample was taken from the residue left in a container from which most of the xenon tetrafluoride had been removed. This batch had been made with ordinary fluorine containing a few tenths of a percent of oxygen. A more complicated pattern resulted. Ion masses were observed corresponding to the following species: XeF, XeF_2, XeF_3, XeF_4, XeO, XeOF, $XeOF_2$, $XeOF_3$, $XeOF_4$ (*9*). The species containing the XeO group appear to originate in $XeOF_3$ and $XeOF_4$. These two have an independent existence, with no very great difference in volatility. The volatility of these oxyfluorides of xenon is comparable to that of XeF_4 rather than to that of XeF_2.

Xenon and fluorine combine when irradiated at room temperature with the full light of a high-pressure quartz mercury arc. These experiments were carried out in silica vessels at approximately atmospheric pressure with a 2:1 mole ratio of fluorine to xenon. Attack of the silica by fluorine during irradiation introduced a complication, and experiments with sapphire windows are planned. The fact that xenon and fluorine react photochemically provides a valuable approach for studying the mechanism of the xenon-fluorine reaction.

An investigation of the crystal structure of XeF_4 is in progress. Samples suitable for powder or single-crystal studies have been prepared by condensation from the vapor phase. Crystals develop with either monoclinic or orthorhombic symmetry, the monoclinic probably being the higher temperature modification.

A preliminary study of the infrared absorption spectrum of the XeF_4 vapor gave an intense band at 586 cm^{-1}, a weaker one at 290 cm^{-1}, and very weak ones at 1100 and 1130 cm^{-1}. The Raman spectrum of the solid has very intense bands at 502 and 543 cm^{-1} and probably a weak one at 235 cm^{-1}. It must be emphasized that this is a preliminary report and that some of these bands may be due to impurities, but the observations to date are consistent with a square planar model, and not with a tetrahedral one. A preliminary, inconclusive analysis of the x-ray data is consistent with this picture.

When xenon tetrafluoride was treated with either dilute sodium hydroxide solution or water, a yellow color developed and the solid phase slowly dissolved to give a clear, pale yellow solution. All the fluorine in the original compound could be accounted for as fluoride. While there was some evolution of xenon and oxygen, the gas recovered was much less than would result from total hydrolysis according to the following equation:

$$XeF_4 + 2H_2O \rightarrow Xe + O_2 + 4HF$$

The yellow alkaline solution prepared as above can be evaporated to dryness under a heat lamp without loss of xenon (*10*). If, however, the solution is first acidified, the xenon is lost upon evaporation. These observations indicate that the hydrolysis of XeF_4 is complex and demonstrate that a xenon compound, perhaps an ionic species, can exist in aqueous solution.

Xenon tetrafluoride is insoluble in n-C_7F_{16} and is soluble, with reaction, in benzene. Xenon tetrafluoride is readily soluble in anhydrous hydrogen fluoride, with no evidence of reaction. At −78°C the solubility is less than 1 mg/ml. At 60°C the solubility exceeds 100 mg/ml. The electrical conductivity of the resulting solution is low. Hydrogen fluoride is a good ionizing solvent, and the low conductivity tends to reduce the probability that ionic reactions can be observed and to rule out ionic mechanisms for fluorinating reactions such as those described below.

Observations of the absorption spectrum (50,000 cm^{-1} to 400 cm^{-1}) of a dilute (0.2*M*) solution of xenon tetrafluoride in hydrogen fluoride revealed no significant difference from the spectrum of pure hydrogen fluoride except for an absorption in the ultraviolet that increased steadily with decreasing wavelength. The molar absorption (A_m) found at 33,300 cm^{-1} (300 $m\mu$) was 30, rising to 100 at about 35,400 cm^{-1} (285 $m\mu$).

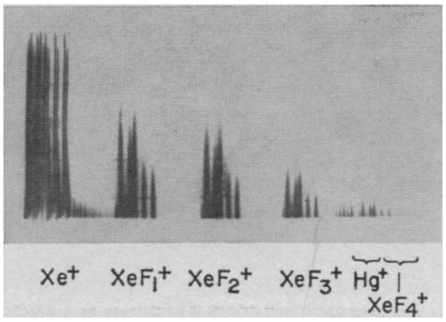

Fig. 1. Mass spectra of xenon fluorides. Vapor was admitted to spectrometer from sample at room temperature. The peaks are off scale in the Xe^+ spectrum, thereby distorting the xenon isotope abundance pattern.

Xenon tetrafluoride, when dissolved in hydrogen fluoride, is a moderately strong fluorinating agent. Bright platinum is fluorinated to PtF_4 with quantitative release of the combined xenon. The course of fluorination reactions with benzene and uranium tetrafluoride suggests a fluorination potential comparable to that of uranium hexafluoride rather than to that of chlorine trifluoride.

Samples of xenon tetrafluoride have shown no evidence of reaction or decomposition after 6 weeks' storage in Pyrex vessels at room temperature. Solutions of xenon tetrafluoride in anhydrous hydrogen fluoride have been similarily stored in polychlorotrifluoroethylene (Kel-F) for 2 weeks.

No attack has been noted on silver chloride by either dry xenon tetrafluoride or a hydrogen fluoride solution.

A number of minor explosions occurred while we were manipulating these xenon compounds. They have occurred mostly in liquid nitrogen traps protecting vacuum pumps when these traps have been allowed to warm up to room temperature at the end of an active operating interval. These explosions may result from the reaction of fluorinating substances with traces of organic matter, or they may be due to unstable oxides as found in similar manipulations with chlorine trifluoride.

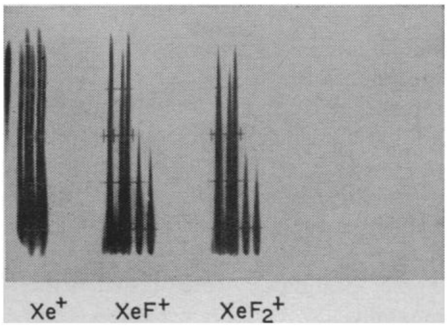

Fig. 2. Mass spectra of XeF and XeF_2. These were the first species to appear after removal of the dry ice bath.

The results with xenon led us to examine the reactivity of radon (*11*). The most stable isotope of radon has only a 3.8-day half-life, and the manipulation of even microgram quantities requires elaborate shielding.

In tracer experiments with 5 to 100 microcurie amounts of Rn^{222}, it has been shown that a radon fluoride of low volatility exists. The position of Rn^{222} in a vacuum line is conveniently determined by observing the 1.8-Mev gamma emission of the daughter Bi^{214} (19.7-minute half-life), which grows into equilibrium with the radon in each new site it occupies and decays in each previous site, within several hours. In a prefluorinated metal vacuum line, it was demonstrated that unreacted radon could be transferred from one site to another with negligible loss, simply by cooling the receiving vessel with liquid nitrogen and maintaining the supply vessel at room temperature or even lower (−78°C, for example). However, when fluorine was added to a vessel containing radon and the mixture was heated to 400°C, the volatility of the radon was greatly reduced. The active deposit no longer moved at room temperature and only began to move at approximately 250°C in a 10^{-6} mm-Hg vacuum.

In another experiment a trace amount of radon mixed with several milligrams of xenon was fluorinated. The xenon fluoride product sublimed from the reaction vessel at 50°C, but the radon fluoride again remained fixed until a temperature of 250°C was reached.

Radon fluoride is reduced with hydrogen at 500°C to yield elemental radon. In trace amounts, the compound shows no evidence of decomposition induced by alpha particles, but this does not necessarily indicate radiation stability since most of the energy from very small samples is absorbed by the container. The preparation of quantities of radon fluoride large enough for conventional analysis may be difficult in view of the associated radioactivity, but samples large enough for analysis in the time-of-flight mass spectrometer should be feasible.

Research in this interesting field will proceed rapidly. As group VIII-A of the Periodic Table, the "inert gases," because of their presumed nonreactivity, have occupied an isolated position, apart from the other groups of chemical elements. Discovery that at least two of these elements readily form stable compounds opens the door to investigations which should more closely integrate this group with the rest of the Periodic Table.

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References and Notes

1. See for example, Mellor's *Modern Inorganic Chemistry*, G. D. Parkes, Ed. (Longmans, Green, London, 1961).
2. Based on work performed under the auspices of the U.S. Atomic Energy Commission.
3. A. Van Antropoff, K. Weil, H. Fraüenhof, [*Naturwissenschaften* **20**, 688 (1932)] claimed the synthesis of a krypton chlorine compound with the aid of an electric discharge. O. Ruff and W. Menzel [*Z. Anorg. Allgem. Chem.* **213**, 206 (1933)] attempted to make the fluorine compound by an analogous technique and found no evidence of reaction. D. Yost and A. L. Kaye [*J. Am. Chem. Soc.* **55**, 3890 (1933)] found no reaction between krypton and chlorine under ultraviolet irradiation and between xenon and fluorine in an electric discharge. Yost and Kaye pointed out that Pauling and others had suggested the possibility of such reactions and that their results were only tentative. However, Antropoff [A. Van Antropoff, H. Frauenhof, K. H. Krüger, *Naturwissenschaften* **21**, 315 (1933)] conceded a partial misinterpretation of his earlier results, and there has been little subsequent research.
4. C. D. Cooper, G. C. Cobb, E. L. Tolnas, *J. Mol. Spectry.* **7**, 223 (1961).
5. N. Bartlett, *Proc. Chem. Soc.* **1962**, 218 (1962).
6. At Argonne National Laboratory the reaction with platinum hexafluoride was duplicated and xenon was shown to react at room temperature with ruthenium hexafluoride, but not with uranium, neptunium, or iridium hexafluorides. When the ruthenium hexafluoride system was studied quantitatively, a larger than equimolar consumption of the hexafluoride was observed, and some reduction of the ruthenium seemed to occur. This suggested the role of a hexafluoride as a fluorine carrier and led to the studies with xenon and fluorine. Xenon also reacts with plutonium hexafluoride. The course of this reaction, however, has not yet been elucidated (M. Steindler and J. Fischer, Argonne Chem. Eng. Div., private communication).

→ H. H. Claassen, H. Selig, J. G. Malm, *J. Am. Chem. Soc.* **84**, 3593 (1962).

8. M. H. Studier and E. N. Sloth, *J. Phys. Chem.*, in press.
9. Other species found (for example, Xe, O_2, H_2F_2) can be explained without reference to xenon compounds.
10. Xenon which had been irradiated with slow neutrons in a nuclear reactor was used to prepare the xenon tetrafluoride used in the hydrolysis experiment described. The behavior of the xenon was followed by observing the gamma activity associated with the resulting mixture of radioactive xenon isotopes.
11. P. R. Fields, L. Stein, M. H. Zirin, submitted for publication.

2 October 1962

Azeotropic Freeze-Drying

Abstract. Spheres of comminuted frozen meat were freeze-dried by boiling in toluene under reduced pressure. The dehydration was performed at 30°C and apparently took place without melting the ice. The dried product rehydrated readily and showed all the characteristics of freeze-dried defatted meat.

Freeze-drying is possible without vacuum, so long as the water vapor pressure of the medium surrounding a frozen specimen is below the vapor pressure of ice at that temperature. This process was demonstrated in the dry air freeze-drying experiments of Meryman (*1*) and Lewin and Mateles (*2*).

Azeotropic mixtures are composed of two or more compounds that distill together without decomposition or reaction. The boiling point of an azeotropic mixture is constant, and is lower than the boiling point of its constituents. The composition of the azeotropic vapor depends upon the molecular weight and vapor pressures of the mixture components at a given temperature. The purpose of our work was to test the feasibility of azeotropic freeze-drying.

At 0°C water and toluene form an azeotrope with a vapor pressure of 12.1 mm-Hg. Of this pressure 4.6 mm represents the vapor pressure of ice and 7.5 mm the vapor pressure of toluene. The composition of the azeotrope is 10.7 percent water and 89.3 percent toluene. If the temperature is increased, but the water is still frozen, the composition of the azeotrope changes. The vapor pressure of the solvent increases, while the vapor pressure of water depends on the temperature of ice. The azeotropic mixture becomes unsaturated. The degree of saturation depends on the rate of heat supply to sublimate the ice, and on the rate of vapor removal from the boiling flask. The vapor pressure at the solvent-ice contact is greater than the vapor pressure of solvent in other parts of the flask. Thus, violent boiling occurs around a frozen specimen. Due to the temperature difference between the condensor and the boiling flask, the azeotrope is rapidly removed. Heat of 620 cal is necessary to sublimate 1 g of ice at 0°C, and since the vapors are rapidly removed, it is not likely that the ice will melt. These postulates were tested experimentally.

Approximately 300 ml of toluene were placed in a 700-ml round bottom flask and heated to 30°C. The flask was fitted with an insulated Bidwell-Sterling receiver arm, a condensor, a manometer and a vacuum line. A 7-g sphere of frozen (−15°C) comminuted meat, about 1.5 cm in diameter, was placed in the flask and a vacuum was drawn immediately. When the pressure reached 33 mm-Hg (in approximately 60 seconds) the contents of the flask surrounding the meat sample came to a vigorous boil. Vapors rose to the condensor, where they separated into water and toluene. Water settled in the Bidwell-Sterling receiver while toluene returned to the flask. At the end of 90 minutes, 4.8 ml of water had accumulated in the receiver, and the boiling subsided. At that time air was allowed to enter the system. The sample was withdrawn and placed for 45 minutes in an air oven at 101°C to dry off the solvent.

After drying in the oven, the sample had the typical porous structure of freeze-dried meat. The weight of the dry material was 1.5 g and its dimensions appeared unchanged. Upon immersion in water, the material promptly rehydrated to the consistency and appearance of very lean, raw, ground meat. Its taste was that of uncooked beef.

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1. H. T. Meryman, *Science* **130**, 628 (1959).
2. L. M. Lewin and R. I. Mateles, *Food Technol.* **16**, 94 (1962).

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Simple Apparatus for Ultrafiltration

Abstract. A rapid and highly efficient ultrafiltration apparatus has been devised from readily available laboratory materials costing less than $5. Employing a fritted glass tube to support an evacuated dialysis bag, it accommodates as little as 1 milliliter and is ideally suited to dialysis of small volumes and concentration of macromolecules for chromatography and electrophoresis.

In our laboratory it is routinely necessary to concentrate protein solutions for electrophoretic analysis and to remove protein from an amino acid solution for chromatographic analysis. These two operations are carried out simultaneously with the apparatus shown in Fig. 1. The grommet (Walsco Electronics, No. 7034-F; inside diameter, 1/4 in.; mounting hole, 3/8 in.) is