Reports

Xenon Fluorosilicate and Related Compounds

Abstract. *The reaction product of Xe, F_2, and SiF_4 in a glow discharge has been shown to have a composition approximating Xe_2SiF_6. It and a similar hexafluorophosphate are unstable at room temperature. A stable hexafluoroantimonate is formed from Xe, F_2, and SbF_5 at 250°C.*

The initial announcement of the preparation of a salt of xenon(I), $XePtF_6$ (*1*), was followed by reports of the preparation of $XeRhF_6$ by Bartlett (*2*) and of the "adduct" Xe-RuF_6 by Chernick *et al.* (*3*). These were prepared by combination of the noble gas with the noble metal hexafluoride. On the basis of the magnetic susceptibility the first of these was characterized as $Xe^{I}Pt^{V}F_6$, although in the absence of electron-spin resonance data there appeared to be no good reason for preferring this formulation over $Xe^{II}Pt^{IV}F_6$. More recently Bartlett (*4*) has provided more evidence for the $Xe^{I}Pt^{V}F_6$ formulation by metathetical reactions in IF_5. Bartlett (*2*) has also reported the formation of brick red $Xe(PtF_6)_2$ by the action of Xe on excess solid PtF_6 or by pyrolysis of $XePtF_6$. More recently Peacock and co-workers (*5*) have reported the formation of yellow, diamagnetic $XeF_2 \cdot 2SbF_5$ by reaction of XeF_2 or XeF_4 with SbF_5 and of straw-colored $XeF_2 \cdot 2TaF_5$ from XeF_4 and TaF_5. These are suggested to be covalent compounds of xenon(II).

We have prepared a salt of xenon which appears with little doubt to be a compound of xenon(I). When a 2:1 mole ratio of xenon and fluorine at a total pressure of less than 10 mm was passed in glass apparatus at −78°C through a 6500- to 7000-volt glow discharge, a white crystalline solid was deposited on the walls of the vessel. This solid was stable at −78°C, but upon warming to room temperature slowly decomposed to gaseous products among which Xe and SiF_4 were found by mass spectral analysis. The gaseous decomposition products were hydrolyzed in 10-percent aqueous KOH, and the silicon and fluorine content of the solution was determined by standard analytical methods. These, combined with the volume of xenon liberated, in a typical case gave a composition for the solid of $Xe_{2.3}SiF_{5.8}$. A similar run carried out with a 2:1:1 mole ratio of xenon, fluorine and silicon tetrafluoride gave a product having a 2.2:1 atom ratio of xenon to silicon. In the case of the 2:2:1 ratio about 0.35 g of product was obtained. Although it is possible to obtain molecular addition compounds under conditions such as these—as has, indeed, been suggested for the Xe-RuF_6 "adduct"—it is a little more difficult to imagine a ternary Xe-F_2-SiF_4 adduct of proportions so fortuitously close to the composition Xe_2SiF_6 and the formulation $(Xe^+)_2SiF_6^{--}$ seems to be the most reasonable.

A similar reaction with xenon, phosphorus pentafluoride, and fluorine produced a white-to-yellow solid, unstable at room temperature and containing both Xe and PF_5 as judged by mass spectral and infrared analyses of the decomposition products. On the other hand, heating a mixture of the gases at 220°C for 10 hours in a nickel bomb and passing the gases into a trap at −78°C produced nothing containing xenon.

However, when 0.153 mole of SbF_5, 0.0435 mole of Xe, and 0.0410 mole of F_2 were heated in a nickel bomb at 250°C for 12 hours, a xenon-containing, pale yellow solid resulted which reacted vigorously with water with release of xenon. This did not sublime below 100°C, whereas the compound reported by Peacock (*5*) sublimed at 60°C in vacuum. Our compound is presumed to be $XeSbF_6$.

If the radius of the Xe^+ cation is similar to that for Na^+ (*6*) and the lattice energy for Xe_2SiF_6 is similar to that for Na_2SiF_6 (*7*), the molar enthalpy for the reaction

$$2\,Xe(g) + F_2(g) + SiF_4(g) \rightarrow Xe_2SiF_6(c)$$

is about −40 kcal. If it is assumed that the entropy of Xe_2SiF_6 is the same as that of Cs_2SiF_6, ΔS for for the reaction is about −134 entropy units and ΔF is about 0 at 298°K. Since the reverse of this reaction is the expected decomposition reaction, the calculations correspond to the qualitatively observed stability. Similar calculations indicate that $XeBF_4$ should be stable up to about 150°C, but that $KrBF_4$ should be unstable down to within a few degrees of absolute zero.

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References and Notes

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2. See p. 38, *Chem Eng. News* **63**, 36 (1963).
3. C. Chernick *et al.*, *Science* **138**, 136 (1962); H. H. Claasen, J. G. Malm, H. H. Selig, Conference on Noble Gas Compounds (Argonne National Laboratory, 22–23 Apr. 1963).
4. N. Bartlett and N. K. Jha, *Noble Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 23.
5. A. J. Edwards, J. H. Holloway, R. D. Peacock, *Proc. Chem. Soc.* **1963**, 275 (1963).
6. The radii of the noble gas cations (for example, Xe^+) were estimated from the ratio of the halogen van der Waals radii to the ionic radii calculated by Bell and Gelles, *J. Chem. Soc.* **1951**, 2734 (1951), and the van der Waals radii of the noble gases—2.07 Å for Xe, as determined from the crystal structure of XeF_2 [P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, D. F. Smith, *Science* **139**, 842 (1963)].
7. There should be no crystal field stabilization energy for the noble gas + 1 cations as contrasted to the halogen + 1 cations [J. Arotsky and M. C. R. Symons, *Quarterly Reviews* **16**, 282 (1962)].

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Origin of Diamonds in the Ureilites

Abstract. *Diamonds in two of the three diamantiferous stony meteorites (ureilites) show a pronounced crystallographic orientation. This suggests that the diamonds were produced by shock during breakup of the meteorite's parent body rather than by high gravitational pressure.*

In previous papers (*1, 2*) on the origin of meteoritic diamonds (Table 1) I concluded that the diamonds in the Canyon Diablo iron were formed by conversion of graphite as a result of the shock of impact of the meteoroid with the earth. The subsequent finding of coesite and stishovite (*3*) in the sandstone around the Canyon Diablo crater indicates shock pressures of at least 100 kbar. The successful shock-induced conversion of graphite to diamond in the laboratory (*4*) also lends strong support to the shock origin of Canyon Diablo diamonds.

Diamonds also occur in a rare type