Reports

Krypton Difluoride: Preparation and Handling

Abstract. *Krypton difluoride was prepared by irradiation of krypton and fluorine in an electron beam (1.5 Mev) at −150°C. The compound is a white crystalline solid, stable only at temperatures below about −30°C.*

The compound KrF_4 has been prepared by Grosse *et al.* (*1*) by passing an electric discharge through the elements at −196°C. Evidence for formation of KrF_2 has been obtained (*2*) by ultraviolet irradiation of the elements frozen into an inert gas matrix at −253°C. With an electron beam to irradiate krypton and fluorine at −150°C, KrF_2 has been prepared in 100-mg amounts and some of its properties have been examined.

The preparations were made in a cylindrical 3-liter nickel vessel, 15 cm in diameter, which was previously used for preparation of XeF_2 by a similar method (*3*). The 1.5-Mev electron beam entered through a 0.013-cm nickel window welded on the inner end of a re-entrant tube projecting 3.1 cm into the vessel. Such an arrangement diminishes the radiation intensity at the front wall of the vessel, and should permit accumulation of products there which otherwise might decompose in the main part of the beam. Cooling to −150°C was accomplished by means of two heavy copper straps wrapped around the vessel and soft-soldered to it, their ends dipping into liquid nitrogen. In three successful experiments, the pressures of the reactants at room temperature were approximately 1 atm each, with fluorine in modest excess.

After the irradiations, excess krypton and fluorine were pumped away while the reaction vessel slowly warmed up. The vessel was then connected to a glass vacuum system containing a fused quartz U-tube and the product was frozen out in the U-tube while pumping continued. Small amounts of KrF_2 began to come out while the vessel was at −60°C, but the bulk of it was obtained between −40° and −30°C. When trapped by dry ice or liquid nitrogen, this compound is a finely divided white solid. It sublimes without appreciable decomposition as its container warms up, and has been transferred back and forth several times between the quartz U-tube and a nickel tube. In one experiment, after the product had sublimed out of the U-tube, a colorless crystal almost 1 mm across was found on the wall of the quartz tubing above the U-tube. This crystal survived apparently without change for about 5 minutes at room temperature, then suddenly disappeared with a mild explosion. While dry XeO_3 is violently explosive (*4*), there has been no report that KrF_4 or any of the xenon fluorides are at all explosive, even though KrF_4 is unstable at room temperature.

Attempts to obtain vapor pressure measurements were only partly successful, since the compound decomposes fairly rapidly well below room temperature. Volatility apparently is very similar to that of KrF_4, since the vapor pressure measured at −40°C (assuming no decomposition) is 1.5 to 2 mm. No vapor pressure could be determined at 0°C, beacuse of the rapid rate of decomposition.

The composition KrF_2 was established by decomposing a sample with mercury and analyzing the reaction products. Samples were frozen into a nickel tube containing mercury and the tube was allowed to warm to room temperature. The gas produced was frozen into a Ward, or LeRoy (*5*), low-temperature still and shown to be krypton, and only krypton, by following its vapor pressure as it was transferred by Töpler pump to a gas-measuring burette. Fluorine was determined by treating the mercury fluoride formed with standard NaOH solution and back titrating with HCl.

There is still only a limited amount of experimental evidence on the heats of formation of noble gas fluorides. However, what data there is indicates that XeF_2 is thermodynamically somewhat less stable than XeF_4. The KrF_2-KrF_4 pair apparently follows the same pattern. This has been predicted by Waters and Grey (*6*), among others, who suggested that KrF_4 would "exist," while KrF_2 would be "marginal" (*7*).

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References and Notes

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7. Supported by the U.S. Atomic Energy Commission. I thank A. O. Allen and H. A. Schwartz for the use of their Van de Graaff electron accelerator and for helpful discusssion regarding the irradiation.

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Radar Observations of Mars

During the recent opposition of Earth to Mars, a small group of scientists and engineers at this laboratory succeeded in making a series of radar measurements on the red planet. Observations were made during the several weeks from 31 January 1963 to 2 March 1963, with essentially the same radar as was used to observe Venus during the conjunctions of 1961 and 1962 (*1*). The radar was modified

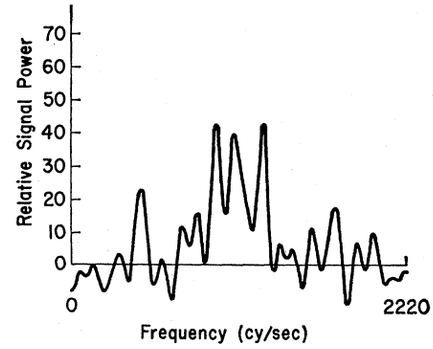

Fig. 1. A spectrogram showing the average echo from Mars obtained over several weeks.