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

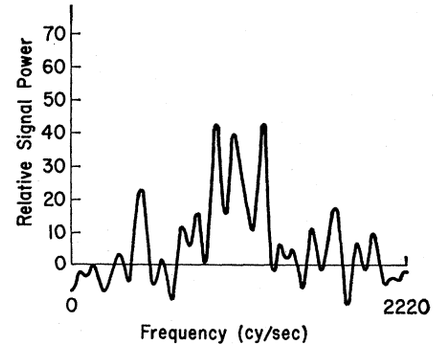

Fig. 1. A spectrogram showing the average echo from Mars obtained over several weeks.

to transmit 100-kw signals, and the total temperature of the noise within the system was lowered to 37°K.

Two types of experiments were performed. In one, the total power of the echo was measured by means of radiometer techniques. In the other, the autocorrelation approach was used to analyze this power into its frequency spectrum (*2*).

Over 65 hours of signal integration is represented in Fig. 1, covering a full 360 degrees of Martian longitude. A pure sine wave was transmitted, but because of the Doppler effect that results from the planet's rotation, the echo spans a frequency interval of 7.6 kc. Most of the power is contained in a band of only 450 cy/sec; this corresponds to reflections from a disk about 250 miles wide on the surface of Mars. Thus, the sub-earth points stand out as small areas of highlight—that is, areas showing more light than the surroundings. Venus shows a similar area of highlight, but it is larger in proportion to its size and speed of rotation. Mars is somewhat smoother than Venus in this sense.

Each transmission cycle lasted about 11 minutes, the time required for a radar signal to get to Mars and back. This was followed by a receiving cycle of the same length. In this way, each successive transmission cycle illuminated an area about 200 miles farther westward at about 13 degrees north latitude on Mars. Throughout the nights of the experiment, each 250-mile disk was illuminated about 12 times. The average power of the signal from each of these areas defines a map of radar "brightness" (Fig. 2) for the 13-degree parallel. Since echo power was measured through a pre-

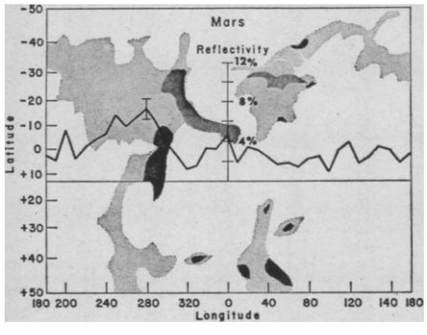

Fig. 2. A radar map of Mars, with some of the visible features of the planet shown in the background. Syrtis Major is the area at 290° longitude, in the equatorial region.

detection filter with a bandwidth of 400 cy/sec, dark areas may be due either to lower reflectivity, or to rougher areas which spread the signal beyond the filter passband. It is interesting to note that the region of Syrtis Major appears light to radar but dark to visual observations. The experimentally determined standard deviation of the observations is marked on the curve. It was measured without signal input to the receiver. An average reflectance of 3.2 percent is obtained by averaging all of these data together.

Mars is a very difficult radar target because of its great distance from Earth and rapid rate of rotation. During future oppositions, when radar technology is more advanced and Mars comes much closer to us than the 100,000,000 km (62,400,000 miles) this year, it will be possible to obtain data for much more detailed maps.

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1. R. M. Goldstein and R. L. Carpenter, *Science* **139**, 910 (1963).
2. The equipment which was used to accomplish this will be described in detail in a Jet Propulsion Laboratory report, now in preparation.

1 July 1963

Relative Dating of Arlington Springs Man

Abstract. *Relative dating tests confirm the antiquity of the Arlington Springs human femur.*

In 1959 P. C. Orr discovered two human femurs at a depth of 11 m (37 ft) in Quarternary sediment exposed at Arlington Canyon, Santa Barbara, California. The discovery was investigated by a team of geologists and archeologists in 1960 (*1*), and further work at the site resulted in datable carbonaceous material being found adjacent to the human bones. A sample collected by Orr, W. Farrand, and W. S. Broecker was dated by Broecker at the Lamont Geological Laboratory as 10,000 ± 200 years old (*2*).

If it is assumed that the human bones are not part of a burial from a higher surface, they represent one of the very few Pleistocene men of the Americas. At the suggestion of W. F. Libby, a sample of one of the femurs was sent to us in London for tests of relative datings. My assistant, Mrs. E. Gardiner, made a radiometric assay of the sample as means of assessing its uranium content. The sample was then submitted to the Government Chemist's Laboratory, where R. G. Cooper determined the fluorine and phosphate contents, and E. J. Johnson the nitrogen content (Table 1).

Table 1. Analyses of early human bones from North and Central America. The italic lines indicate bone source.

F (%)	$\frac{\%F}{\%P_2O_5}\times 100$	e.U_3O_8 (ppm)	N (%)
	Arlington Springs, Calif.		
1.2	3.6	28	0.23
	Tepexpan, Mexico		
2.0	6.8	1	0.06
	Midland, Texas		
0.8	10.4	13	0.03
	Lagow, Texas		
0.2	0.6	3	1.2
	Natchez, Mississippi		
0.9	3.4		1.4
	Compare: Modern bones		
<0.1	0.1	<1	~4.0
	Camelops, *Lagow*		
~1.5		36	0.5
	Mylodon, *Natchez*		
1.0	4.9		1.6

Although no other bones from the same, or from earlier and later, levels have yet been sent for analysis as controls, the ratio of fluoride to phosphate and the uranium content are both high enough, and the nitrogen content low enough, to be reassuring in regard to the high antiquity of the bone in question. Series of bone samples from comparable sites in North and Central America have already been assayed for F, U, and N (*3*), and when the composition of the Arlington Springs bone is considered in the light of these results, there is no reasonable doubt that it is "fossil" rather than subfossil, and unquestionably it is not a recent intrusive burial. For present purposes the results summarized in Table 1 are sufficiently significant.

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References and Notes

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1 August 1963