utes, sealed, and heated in an iron container at 500°C for 15 minutes. Sample tubes heated at a lower temperature had no greater chance of surviving the detonation.

Many tubes were broken by the shock of decomposition but from two that remained intact the data in Table 1 were obtained. It can be seen that not all the water was removed even with extensive pumping.

To confirm the quantitative recovery of O_2 from the Toepler pumping system, $KClO_3$ was used as a standard. It gave 2.994 oxygen atoms per mole of $KClO_3$.

The stability of the xenon (VI) oxide seems to be greatly increased with respect to detonation if the oxide is originally prepared from distilled water with a trace of added sulfuric acid, for example, 10 ml of $H_2O + 4\mu l$ of $1M$ H_2SO_4 (*7*).

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14 February 1963

Krypton Tetrafluoride: Preparation and Some Properties

After the discovery of xenon and radon fluorides at Argonne National Laboratory (*1, 2*), the obvious question was: Does krypton, the lower analog of these two inert gases, form similar compounds? The answer is yes.

It was first found that gaseous krypton (Kr) and fluorine (F_2) do not form noticeable amounts of krypton fluorides when they are heated at 400° to 500°C in a nickel vessel. A mixture of Kr (1 part) and F_2 (5 parts) was heated for 1 hour, with negative results. Under the same conditions xenon tetrafluoride is formed from xenon and fluorine, practically quantitatively (*1*). Similarly negative results were obtained (*3*) when a mixture of Kr and F_2 was irradiated with ultraviolet light at −60°C. Furthermore, when Bartlett (*4*) who initiated the recent work on noble-gas compounds by his discovery of $XePtF_6$, tried the same experiment with Kr and PtF_6 or RhF_6, no oxidation took place at temperatures up to 50°C.

However, by taking advantage of the experience of workers at the Research Institute of Temple University in the preparation of the thermally very unstable O_3F_2 (*5*) and O_4F_2 (*6*), we were able to produce krypton fluoride. Recently, we showed that xenon tetrafluoride can be produced quantitatively by electric discharge (see *7*). By using the same method, we have now been successful in producing krypton tetrafluoride (*8*).

The experimental setup (a reaction vessel of volume approximately 650 cm^3, with copper electrodes 2.0 cm in diameter and 7 cm apart) and the experimental conditions (current of 24 to 37 ma, 700 to 2200 volts) were the same as in the earlier investigations (*5*). The mixture of Kr and F_2 (1 and 2 volumes, respectively, to within ±0.1 percent) was admitted, at a pressure of 7 to 12 mm-Hg, into the discharge vessel, which had been cooled to 84° to 86°K by mixtures of liquid O_2 and N_2. In a successful experiment 500 cm^3 of the mixture of Kr and F_2 (at normal temperature and pressure) was *completely* converted to 1.15 g of KrF_4 in 4.0 hours. The rate of conversion depends on the surface condition of the copper-electrodes; in the course of time the electrodes become covered with a white layer of typical CuF_2. With less efficient electrodes the production rate may go down to a tenth of the rate just indicated.

The KrF_4 is deposited on the glass walls of the discharge vessel, primarily in the region between the electrodes, in the form of a white solid. Any unreacted Kr and F_2, as well as SiF_4 or O_2 are pumped, off, as impurities, at a temperature of −78°C. Then the KrF_4 can be sublimed, at −30° to −40° or even 0°C, into a glass storage vessel containing some dry potassium fluoride powder (as a getter for hydrogen fluoride). The composition of the deposit is known from its synthesis and also from analysis on heating (as mentioned below). Like XeF_4, KrF_4 forms beautiful, transparent, colorless crystals, as shown in Fig. 1.

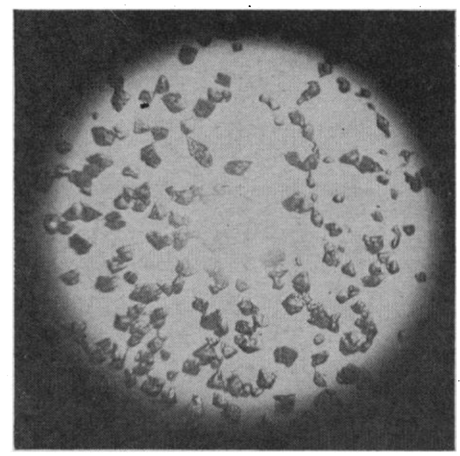

Fig. 1. Crystals of krypton tetrafluoride. [About × 31]

Krypton tetrafluoride is thermally much less stable than XeF_4. However, at −78°C it can be stored for weeks without decomposing. In a polychlorotrifluoroethylene (Kel-F) tube with copper valves, at about 20°C, about one-tenth of the amount present decomposes per hour (*9*). At 60°C the decomposition is rapid; KrF_4 decomposes into its elements—that is

$$KrF_4 \longrightarrow Kr + 2F_2$$

—as determined by analysis (the F_2 is determined by mercury burette; afterwards the krypton gas is determined by volumetric analysis). This rapid decomposition at higher temperatures explains why previous attempts to prepare krypton tetrafluoride had been unsuccessful.

The vapor pressure of the solid KrF_4 was determined (see Fig. 2) by determining and subtracting from the total pressure the amounts attributable to decomposition. For comparison, the

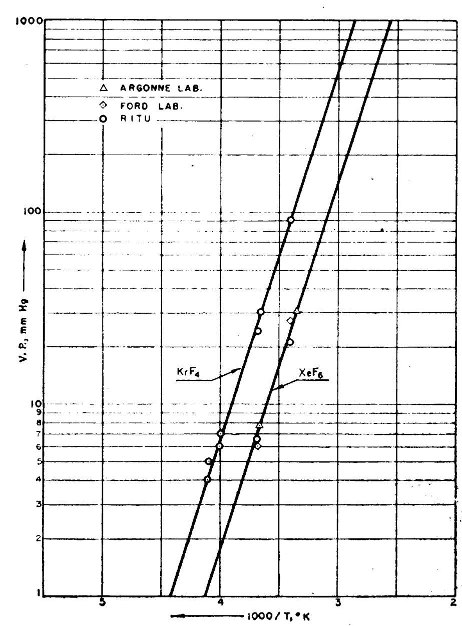

Fig. 2. Vapor pressure of KrF_4 and XeF_6.

data on XeF_6 of the Argonne Laboratory, the Ford Laboratory, G. Cady's laboratory, and our own laboratory (RITU) are included in Fig. 2 (*4*).

The vapor-pressure equation for solid KrF_4 is

$$\log_{10} p_{mm} = 8.531 - 1930/T$$

(T in degrees Kelvin); $\Delta H_{subl.} = 8840$ ($\pm \sim 300$) cal/mole. The curve is practically parallel to the vapor-pressure curve for XeF_6. The extrapolated sublimation temperature (at pressure of 1.00 atm) is approximately 70°C.

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8. This work was supported by the Office of Naval Research [Project Nonr 3085(01)].
9. These figures are given for purposes of orientation only; actually, deposit of CuF_2 on the surface of the vessel is likely to catalyze the decomposition. A study of thermal decomposition in a chemically completely inert vessel will have to be made at some future time.

13 February 1963

Conditioning of a Free Operant Response in Planaria

Abstract. *The response of breaking a photoelectric cell beam was automatically recorded and reinforced. Termination of an intense light was the reinforcement in an escape conditioning situation. The rate of response for the experimental subjects was significantly different from that of controls matched for equivalent changes in light intensity.*

Studies of learning in simple organisms have been concerned with the habituation of a response, classical (Pavlovian) conditioning, and maze behavior. No studies of free operant conditioning (*1*) for species in any phylum from Protozoa to Annelida have been reported. Recent experiments on learning in planaria have dealt with classical conditioning, first studied by Thompson and McConnell (*2*), and maze learning, such as the studies of Best and Rubinstein (*3*).

This report describes experiments in which a free operant response was recorded continuously for periods as long as 165 hours. The response measured was that of the planarian's passage through a narrow beam of light directed at a photoelectric cell, and the reinforcement was the termination of an intense light. The technique is entirely objective since responses are recorded and reinforced automatically.

The apparatus consisted of a small, clear Plexiglas chamber, a light bulb (providing the reinforcing stimulus), a photosensitive diode and light beam, and ordinary control equipment used for operant conditioning experiments. The chamber was designed so that subjects would have a reasonably high operant level without excessively restricting their motion and so that they could be maintained for long periods of time. It was cylindrical, with a depth of 1.27 cm and a diameter of 1.90 cm, and was filled with aged tap water. A narrow beam of light, 3.2 mm in diameter, from a 7-watt clear bulb passed up through the bottom of the chamber, through a small rectangular block of Plexiglas projecting from the chamber wall, and into a fine cylindrical opening leading to the photocell. The subject passed under the projecting block, which was 1.5 mm above the chamber bottom, and interrupted the beam. A 60-watt frosted bulb, 12.7 cm above the chamber, provided the aversive stimulus. The temperature of the water, regulated by a stream of cool air, was between 16° and 18°C.

All subjects were maintained in a large covered jar filled with aged tap water at 18°C and were fed live tubifex worms every 2 to 3 days. A pipette with a large opening was used to transfer the planarians to the chamber. Aged tap water in the chamber was changed every 9 hours for the duration of the experiment. Responses were recorded continuously for periods which averaged about 70 hours. Subjects were removed from the chamber after the procedure of extinction and reconditioning, or because of equipment failure or an accident to the subject. The small light which was trained on the photocell remained on continuously for all procedures, and responses were recorded with the stimulus light on and off.

The subjects were 22 adult *cura foremani*. For the eight experimental subjects, reinforcement was the termination of the light for 15 minutes. Eight subjects (matched controls) were each paired with an experimental animal. Six additional subjects were run with the procedures of light on continuously, light off continuously, and alternating 15-minute periods of light on and light off.

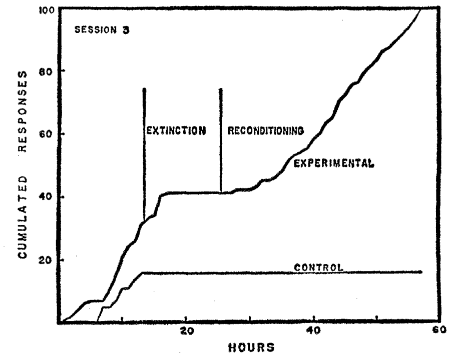

Fig. 1. Cumulated responses as a function of time in hours from the beginning of the experiment. Data for the experimental and matched control subjects are shown. The period for which the extinction procedure was followed is marked on the experimental curve.

The matched control and experimental subjects were placed in adjacent chambers illuminated by the same stimulus light. As indicated by the data for the continuous-light-on and the continuous-light-off subjects, the general activity of *C. foremani* is greatly affected by differences in light intensity apart from any reinforcement contingency. To control for such changes in general activity, the matched control subject was exposed to the same changes in illumination as the experimental subject, but it did not bring about the changes by responding. These subjects

Table 1. Percentage half-hour intervals with response rates of one to two responses per half hour. Results for experimental and matched control subjects are shown. Additional data for subjects with alternating 15 minutes light and 15 minutes dark (ALD), continuous darkness (CD), and continuous light (CL) are listed.

Session	Total time (hr)	Percentage intervals Exptl.	Percentage intervals Control
01	52	64	16
02	79	34	07
03	58	66	05
04	16	46	14
05	107	29	13
06	165	25	09
07	31	26	16
08	68	36	12
ALD	72		19
			12
CD	62		09
			12
CL	73		15
			09