

It is of interest to know the rate controlling factor for the reaction. It was observed that the reaction progresses uniformly in from the surface of the wire. Even when starting with a  $1/16$  inch wire, a very thin wire could be recovered when the reaction was almost completed. For one run at  $225^\circ$ , the exposed area of the unreacted uranium wire was computed for various stages in the reaction, assuming that the wire remained perfectly cylindrical in shape. The reaction rate per unit of exposed area, computed from these values and from the slope of the curve in Fig. 1 at the same time, has been plotted as a function of time in Fig. 3. It can be seen that the rate of hydrogen absorption is constant for constant surface area, except at the beginning and end of the reaction. It is realized that the true surface area may differ tremendously from the apparent geometric surface area, but it seems proper to assume that once the

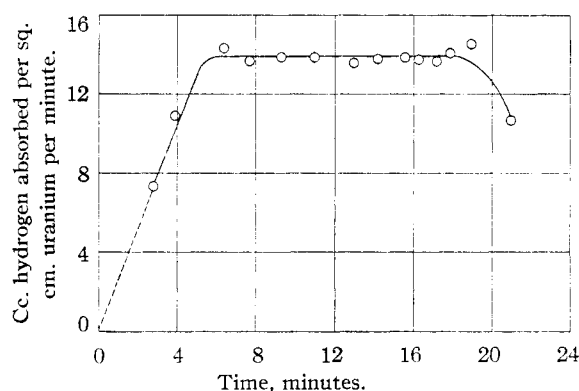


Fig. 3.—Rate of hydrogen absorption corrected for surface area.

hydride is forming freely, the ratio between the two surface areas will be constant. At the beginning and end of the reaction this ratio will certainly not be constant, and this probably accounts for the dip at the ends of the curve.

**Formula of the Hydride.**—The values of the hydrogen-uranium atomic ratio in the hydride formed are given in Table I. These values were calculated from the weight of the uranium sample taken and the corrected volume of the hydrogen consumed. A consideration of the possible errors in the measurement indicates that the values are accurate to at least 1%. Differences in the listed values are probably not significant. The average of all the determinations made gives a formula of  $\text{UH}_{3.0}$ .

TABLE I  
FORMULA OF URANIUM HYDRIDE AT VARIOUS TEMPERATURES

| Temp.,<br>°C. | G. atoms H<br>G. atoms U | Temp.,<br>°C. | G. atoms H<br>G. atoms U | Temp.,<br>°C. | G. atoms H<br>G. atoms U |
|---------------|--------------------------|---------------|--------------------------|---------------|--------------------------|
| 150           | 3.03                     | 225           | 3.04                     | 300           | 2.99                     |
| 175           | 2.99                     | 250           | 3.03                     | 330           | 2.92                     |
| 200           | 2.96                     | 275           | 3.03                     |               |                          |

### Summary

Uranium hydride,  $\text{UH}_3$ , can be made readily by heating massive uranium in purified hydrogen at about  $225^\circ$ . The reaction is slower at lower and higher temperatures. In impure hydrogen there is an incubation period before the reaction starts but it can be eliminated by purifying the hydrogen. Once the reaction starts, the reaction rate is controlled only by the exposed surface area of the uranium metal.

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## Physical Properties and Crystal Structure of $\text{C}_6\text{F}_{12}$

BY H. J. CHRISTOFFERS,<sup>1</sup> E. C. LINGAFELTER AND GEORGE H. CADY

A compound having the formula  $\text{C}_6\text{F}_{12}$  was first prepared by Simons and Block,<sup>2</sup> by the reaction of fluorine with finely divided carbon. The same substance was later produced by Fukuhara and Bigelow<sup>3</sup> who caused fluorine to react with benzene vapor in the presence of a copper catalyst. Each of these groups has held the opinion that the compound is dodecafluorocyclohexane.

We undertook the investigation of the crystal structure of this compound by X-ray methods hoping that the structure of the molecule might

be definitely established. This hope was not realized, however, for the molecules appeared to be rotating and the X-ray photographs gave information only about the arrangement of the molecules in the crystal but not about their structure.

### Experimental

**Preparation.**—A modification of the procedure of Fukuhara and Bigelow<sup>3</sup> was used to prepare the sample of  $\text{C}_6\text{F}_{12}$  used in this work. Benzene vapor, diluted by nitrogen, was allowed to react with an excess of gaseous fluorine in the presence of a catalyst composed of copper screening. The product of the reaction was condensed in a vessel cooled by solid carbon dioxide and was later brought into contact with ice and water to remove hydrogen fluoride. The resulting mixture was then stored for two weeks in contact with pellets of sodium hydroxide. At the end of this time the product was removed from the solid and was refined by fractional distillation through a column packed with glass helices and having a length of 65 cm. and a

(1) This paper is abstracted from a thesis submitted by H. J. Christoffers in partial fulfillment of the requirements for the degree of Master of Science to the University of Washington in 1945. The subject matter was presented at the Northwest Regional Meeting of the American Chemical Society in Seattle, Washington, on October 20, 1945.

(2) Simons and Block, *THIS JOURNAL*, **61**, 2962–2966 (1939).

(3) Fukuhara and Bigelow, *ibid.*, **63**, 2792–2795 (1941).

diameter of 1 cm. A high reflux ratio was used throughout the distillation and several cuts were collected. One of these distilling between  $50.3^\circ$  and  $52.3^\circ$  (average about  $51.0^\circ$ ) at a pressure of 760 mm. had a volume of 11.1 ml. This cut had the characteristics of a nearly pure sample of  $C_6F_{12}$  and was used for most of the work described below. Considerable difficulty was experienced while collecting the material because the distillate froze in the condenser and the outlet tube at the head of the column. The sample was more highly refined by a simple distillation under pressure of about 120 cm. of mercury. A small middle cut obtained in this way was used for X-ray diffraction studies and for melting point determinations.

**Physical Constants.**—The melting point of the solid was determined using a thin-walled melting point tube sealed at both ends and immersed in oil circulating in an apparatus like that of Hershberg.<sup>4</sup> A thermometer tested by the U. S. Bureau of Standards was used and temperatures were read correctly to the nearest  $0.1^\circ$ . Upon being warmed slowly, the solid started to melt at  $55.2^\circ$  and the last crystal disappeared at  $58.2^\circ$ . This means that the true melting point of the compound is somewhat above  $58.2^\circ$  and is not as low as the  $49^\circ$  value reported by Fukuhara and Bigelow.<sup>3</sup> The frozen solid is transparent, but it is not a glass as described by Simons and Block.<sup>1</sup> Liquid  $C_6F_{12}$  supercools to about  $52^\circ$  before it starts to freeze.

A transition from one solid form to another was detected by thermal analysis using the less highly refined sample of  $C_6F_{12}$ . As heat was slowly removed from the sample, starting at room temperature, the rate of cooling decreased at about  $-110^\circ$  and again increased at about  $-114^\circ$ . As the sample warmed from  $-183^\circ$  the rate of temperature rise decreased at about  $-104^\circ$  and again increased at about  $-100^\circ$ . No sharp breaks in the cooling and warming curves were observed, and evidence for only the one transition at about  $-105^\circ$  was obtained. This value should not be regarded as highly accurate, but there is no doubt about the occurrence of a transition of some sort at approximately this temperature.

The density of the solid was determined by adjusting the concentration of a mixture of carbon tetrachloride and methyl iodide until a crystal of  $C_6F_{12}$  would float without rising or sinking except by movement of the liquid. At  $23^\circ$  the density of the solid was found to be  $1.93 \pm 0.01$  g. per ml.

Molecular weight determinations were made using a bulb filled with the gas at a pressure of about 150 mm. and at room temperature. The individual values 302, 302 and 303 compare favorably with the theoretical value, 300, and with the experimental values of Simons and Block<sup>1</sup> and of Fukuhara and Bigelow.<sup>3</sup> These measurements were made primarily as a confirmation of the purity of the sample.

**X-Ray Crystallographic Analysis.**—Since the very high volatility of the solid  $C_6F_{12}$  precluded the possibility of obtaining X-ray data from unconfined crystals, all of the samples subjected to X-ray analysis were contained in sealed 0.5-mm. diameter "powder tubes." We were unable to grind the plastic solid to a fine powder which could be poured into the tube. Instead of using the usual technique for packing a "powder tube," the soft solid was pushed into place with a wire. This procedure thoroughly smashed the original crystals, but it left a transparent mass of solid which failed to give a typical powder pattern picture when studied by X-rays. Packing the broken material together seemed to cause it to change into a rather small number of moderate sized crystals.

Two procedures were used to obtain single crystals. In each case a sample of the compound was sealed into a powder tube. One tube was heated in water to  $65^\circ$  and was then allowed to cool very slowly. The other tube was warmed in the melting point apparatus until nearly all of the solid had melted and was then allowed to cool slowly. When the second tube was used, a part of the solid which crystallized at  $58.1^\circ$  was held in the X-ray beam. The X-ray photographs revealed no differences between the types of crystals in the two tubes.

Rotation and oscillation photographs were taken with each of these crystals, using unfiltered CuK radiation. The most useful series of pictures was a group of 21° oscillation patterns taken over a range of  $66^\circ$  about one axis. The identity period along the axis of rotation was measured to be 10.00 kx. All spots appearing on all photographs were indexed satisfactorily by means of a cubic-reciprocal lattice corresponding to  $a = 10.00$  kx. All spots were extinguished except those for which  $h, k, l$  were all odd or all even. This classifies the crystal as being face-centered cubic.

The density indicates four molecules per unit cell, in agreement with the requirements of a simple face-centered arrangement. The densities are: calculated, 1.98; observed, 1.93 g. per ml.

The intensity of the spots was found to drop off very rapidly with increasing angle of diffraction. On one picture in particular, taken with a very long exposure, the intensity of (111) was well above the sensitivity limit of the film, yet no spots could be found beyond (440) ( $\frac{\sin \theta}{\lambda} = 0.278$ ).

The visually estimated relative intensities, corrected for the Lorentz and polarization factors are: (111), 100; (200), 30; (220), 20; (311), 30; (222), 60; (400), 15; (331), 2; (420), 4; (422), 0; (333), 10; (440), 3.

### Discussion

The properties of  $C_6F_{12}$  are those of a solid in which the molecules may be rotating. The solid is soft and highly volatile. It has a high coefficient of expansion, as indicated by the appearance of cracks when the material cools. At about  $-105^\circ$  it undergoes transition which probably results from the cessation of rotation of the molecules. The molecules are arranged in a cubic close-packed array, indicating that they are effectively spherical. The intensity drops off rapidly with increasing angle of diffraction. All of these characteristics are recognized as those of a solid containing rotating molecules.<sup>5,6</sup> It is known that molecules of derivatives of cyclohexane are likely to rotate in the solid state<sup>7</sup> and that the van der Waals forces between molecules of fluorocarbons are low.<sup>2</sup>

The intensities of the spots should perhaps be discussed further. In a cubic close-packed crystal consisting of atoms, a type found for many metals, the intensity is observed to fall off regularly with increasing angle of diffraction. The intensity of diffraction of  $C_6F_{12}$  does not fall off regularly, but shows several maxima and minima. This may be considered as evidence for lack of completely free rotation, or it may be regarded as due to the nature of the "atomic" scattering factor of the freely rotating  $C_6F_{12}$  molecule, whose electron density does not decrease regularly from the center out, but is better represented by a spherical shell of electron density. Rough calculations of the scattering factor of a shell of electron density show maxima and minima when plotted against  $\sin \theta/\lambda$ .

The datum concerning the effective "diameter" of the  $C_6F_{12}$  molecule deserves comment. This is given by one half of the diagonal of a face of the unit cell, which is 7.07 kx. A calculation of the

(5) Finbak, *Arch. Math. Naturvidenskab*, **B42**, No. 1 (1938).

(6) Backer and Perdok, *Rec. trav. chim.*, **62**, 533 (1943).

(7) White, *Bell Labs. Record*, **15**, 11 (1936).

(4) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

internuclear distance between fluorine atoms on opposite sides of the molecule was made using the tetrahedral angle for carbon valence bonds and the values of the carbon-carbon and carbon-fluorine distances of 1.50<sup>8</sup> and 1.35 Å., respectively.<sup>9</sup> This calculated distance is 5.38 Å. for the boat form of the molecule. The difference between this and the observed "diameter" leaves the fluorine atom a van der Waals radius of only 0.85 Å, a value to be compared with 1.35 Å given by Pauling.<sup>10</sup> Other instances in which a lack of space for rotation of molecules has been noted have been explained as due to interpenetration<sup>5</sup> or oscillation rather than complete rotation.<sup>6</sup> It may very well be that the van der Waals radius of a fluorine atom in a fluorocarbon molecule is less

(8) Karle and Brockway, *THIS JOURNAL*, **66**, 574-584 (1944). These authors give the value for the carbon-carbon distance in the dimer of trifluoroacetic acid as 1.47 ± 0.03 Å.

(9) Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(10) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 176.

than 1.35 Å. This would be in accord with the known variability of the van der Waals radius and the abnormally small values for carbon-carbon and carbon-fluorine bond distances in molecules in which two or more fluorine atoms are bonded to a single atom of carbon.<sup>8,9</sup>

### Summary

The compound C<sub>6</sub>F<sub>12</sub> (probably dodecafluorocyclohexane) forms face-centered cubic crystals with  $a = 10.00$  kx. in which the molecule has an apparent diameter of 7.07 kx. Properties of the solid form of the substance indicate that its molecules probably rotate down to a temperature of about -105°. At this point a transition occurs which may be due to the cessation of the rotation. The crystals sublime at 51° under 760 mm. pressure and melt when confined at about 58.2°. The solid has a density of 1.93 g. per ml. at 23°.

SEATTLE, WASHINGTON

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## The Quantitative Measurement of Tritium: Hydrogen-Alcohol-Argon Mixtures

BY MAXWELL LEIGH EIDINOFF

### Introduction

The development of methods for the quantitative determination of tritium is of value inasmuch as its thirty-one year half life<sup>1</sup> and availability render its use as a tracer element very advantageous. Tritium activity has been measured by introducing into a Geiger-Müller counter tube active butane,<sup>2</sup> active water vapor plus propane,<sup>3</sup> active hydrogen plus ethanol vapor.<sup>4,5</sup> Black and Taylor,<sup>6</sup> in a careful study of the hydrogen-water isotope equilibrium, used a counting gas mixture containing hydrogen, water vapor, argon and ethanol. The plateau characteristics and convenience of measurement are influenced by the composition and partial pressures of the counting mixture constituents and the dimensions of the counter. Recently a procedure for tritium determination using a quartz ionization chamber attached to a Lauritsen electroscope has been described by Henriques and Margnetti.<sup>7</sup> Since the argon plus ethyl alcohol counting mixture has been used extensively in counter research, it was decided to study the hydrogen-argon-ethyl alcohol system as a quantitative procedure for the

measurement of tritium.<sup>8</sup> This paper describes apparatus and procedures developed and results obtained.

### Experimental

**Geiger-Müller-Counter Tubes.**—Several counter tubes having the dimensions shown in Fig. 1 were used in this investigation. The glass envelope and tungsten-glass seals permit ready degassing and vacuum tightness over extended periods of use. A useful improvement in design has been provision for a capillary tube and stopcock and a large bore stopcock. The former minimizes diffusion of gases from the tube during the filling operation while the latter, leading directly to the high vacuum line, permits more rapid evacuation of the tube between successive fillings. The effective counting volume is about 200 cc. Although ceiling illumination did not significantly affect the measured counting rates, the counters were shielded from light by a dark cloth during the measurements. One tube was permanently surrounded by a 3/8 inch lead shield to reduce laboratory background variations.

**Filling Line and Bank of Counters.**—The gas mixing lines are illustrated in Fig. 2 with the exception of the high vacuum system. The manometer and McLeod gage (H) permit convenient control over the quantity of gas admitted up to the beginning of the capillary tubing manifold (K). The latter minimizes gas dead space above the counter tubes and back diffusion of the gases in the counter tube during the filling operation. As a result of a pressure differential, gas flows into the counter tubes through the capillary (M). A Zimmerli gage<sup>9</sup> (not shown in Fig. 2) was found accurate to 0.1 mm. pressure and was used in many fillings in place of the vacuum end manometer (L).

(8) A hydrogen-helium-ethyl alcohol counting mixture is briefly described by A. F. Reid in the monograph "Preparation and Measurement of Isotopic Tracers," J. W. Edwards Co., Ann Arbor, Mich. (1946).

(9) Made by Scientific Glass Apparatus Co., Bloomfield, N. J.

- (1) R. D. O'Neal and M. Goldhaber, *Phys. Rev.*, **58**, 574 (1940).
- (2) T. M. Powell and E. B. Reid, *THIS JOURNAL*, **67**, 1020 (1945).
- (3) B. J. Fontana, *ibid.*, **64**, 2503 (1942).
- (4) M. B. Allen and S. Ruben, *ibid.*, **64**, 948 (1942).
- (5) W. F. Libby and C. A. Barter, *J. Chem. Phys.*, **10**, 184 (1942).
- (6) J. F. Black and H. S. Taylor, *ibid.*, **11**, 395 (1943).
- (7) F. C. Henriques, Jr., and C. Margnetti, *J. Ind. Eng. Chem., Anal. Ed.*, **18**, 420 (1946).