g. carbon per gram cobalt per hour, respectively. The carbon–cobalt ratio for 108B approached asymptotically a value close to the theoretical for Co_2C (0.1015), while for 89K it approached 0.137. The difference between the two experiments may result from free carbon formation during the rapid initial stage of the reaction on catalyst 89K.

Treatment with hydrogen at 208 ± 2° with a flow rate of 0.6 liter per hour rapidly removed the carbidic carbon as methane. X-Ray diffraction patterns proved that the cobalt carbide was converted to the stable α-cobalt. Thus, the metastable β-cobalt can be converted to the stable α-cobalt by way of cobalt carbide at a temperature more than 100° below the transition temperature (340–380°). Other experiments show that the β-cobalt in a reduced 108B catalyst can withstand at least a week of exposure to temperatures as high as 300° without becoming converted to α-cobalt. In the case of the 89K catalyst, not all the carbon deposited during hydrogenation was removed. This supports the conclusion that free carbon was deposited on this catalyst. Moreover, the ratio of the easily removable carbon to the available cobalt corresponds closely to the formula Co_2C.

Figures 1 and 2 both show that the rate of formation of cobalt carbide is much slower than the rate of its hydrogenation. In order to determine whether α-cobalt and β-cobalt as formed react in the same way with carbon monoxide, reduced samples of catalyst 108B were carburized and the carburized samples hydrogenated, these steps being repeated several times. The results are presented in Fig. 3. After the first cycle, the cobalt is in the α-form, but the subsequent cycles were not noticeably different from the first cycle; thus α- and β-cobalt react with carbon monoxide in nearly the same way.

Acknowledgment.—The authors wish to thank Dr. R. B. Anderson, who directed the operation of the catalyst testing, Mrs. Norma Golumbic, who prepared the catalysts, and all the personnel, who operated the catalyst testing units for the catalysts and activity data.

Summary

1. Reduction of the Fischer- and Hall-type Fischer–Tropsch catalysts at 400° leaves the cobalt in the face-centered cubic (β) form which does not convert readily to the hexagonal close-packed (α) form.

2. On carburization of the reduced catalyst, the cobalt is converted to the same carbide previously reported by the authors.[5]

3. The carburization of α-cobalt and β-cobalt as associated with kieselguhr, thoria, and magnesia proceeds at nearly the same rates and results in the same crystalline carbide.

4. Hydrogenation of the carbide forms methane and the stable α-cobalt.

5. The cycle of carbiding the cobalt in the reduced catalyst and hydrogenating the carbide so formed can be repeated apparently indefinitely at 210°.

PITTSBURGH, PA. RECEIVED APRIL 14, 1947

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Formation of Uranium Hydride[1]

BY JOSEPH E. BURKE[2] AND CYRIL STANLEY SMITH[2]

When massive metallic uranium is heated in an atmosphere of hydrogen, uranium hydride is formed and spalls off continuously as an exceedingly fine, gray, highly pyrophoric powder, the maximum particle size of which is 4 to 5 microns. Prior to the war, the compound had been reported only by Driggs,[3] who gave methods for its preparation, and assigned the formula UH_4. During the war several workers[4] studied the compound under the auspices of the Manhattan District. It is the object of this report to describe the effect of reaction temperature and hydrogen purity on the rate of formation of the compound, and to present the results of a new determination of its formula.

Experimental Procedure

For most of the work, 0.5-g. pieces of $^1/_{16}$ inch uranium metal wire of about 99.9% purity were used as starting material. The reaction proceeds in an identical fashion with much larger pieces. The weighed piece of the wire was contained in a Pyrex bulb which was connected to an all-glass gas train. The bulb was evacuated, and then heated to the desired reaction temperature in an accurately controlled electric furnace; hydrogen was then admitted, and both the rate of gas absorption and the total amount of gas absorbed were measured with a gas buret. The total volume of the reaction bulb, gas buret, and connecting lines was about 200 cc. All measurements were made at atmospheric pressure (585 mm. at Los Alamos), and the final measurement of the total amount of gas absorbed was made with the whole apparatus at room temperature.

In the investigations on the effect of hydrogen purity on the reaction, hydrogen was used (1) directly from the

---

(1) This work was carried out under contract between the University of California, and the Manhattan District, Corps of Engineers, War Department. The original report to the Manhattan District is dated November 13, 1943.

(2) Present address: Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois.

(3) U. S. Patents 1,816,830 (1929) and 1,835,024 (1929).

(4) Uranium hydride was first studied on the Manhattan District Project by F. H. Spedding and co-workers at Iowa State College, Ames, Iowa. This work is summarized in reports CC-580 by Spedding, Warf, Newton, Butler, Ayres and Johns, dated April, 1943, and CC-1201, by Spedding, Newton, Warf, Johnson and Nottorf, dated January, 1944. Some of this work has been submitted for declassification and will be submitted to the *Journal of the American Chemical Society* in the near future.

tank, (2) after passing over platinized asbestos at 300° and then over phosphorus pentoxide to remove all oxygen, and finally (3) after passing over uranium turnings at 475°. By the third treatment, all the impurities in the hydrogen which are capable of reacting with uranium are removed. Since the dissociation pressure of uranium hydride is about 760 mm. at 425°, the hydrogen itself does not react with uranium at 475°. Hydrogen purified in the third way is called high-purity hydrogen in the remainder of the report.

Results

Effect of Hydrogen Purity.—When uranium is heated in impure hydrogen taken directly from the tank, an incubation period for the reaction is observed. During this period no apparent reaction occurs, then hydrogen absorption begins and the reaction proceeds to completion. Curve 1, Fig. 1, shows the progress of such a reaction at 250°. One of the objects of this work was to determine the cause of the incubation period. As shown in curves 2, 3 and 4, Fig. 2, the incubation period is shorter at higher temperatures. It was also found to vary with different tanks of hydrogen. Removal of oxygen by passing the hydrogen over platinized asbestos and through phosphorus pentoxide decreased but did not eliminate the incubation period, as is also shown in curve 3, Fig. 2. Purifying the hydrogen by passing it over uranium turnings at 475° eliminated the incubation period at all but the lowest temperatures (curve 4, Fig. 2). This indicates that impurities in the hydrogen, other than oxygen, can be responsible for the incubation period. Nitrogen or hydrocarbons are likely impurities. The fact that oxygen alone can be responsible for the incubation period was demonstrated by adding 0.25% oxygen to the high purity hydrogen; this caused the incubation period to increase from zero to twenty minutes at 250°. The short incubation period found at 150° in high-purity hydrogen was probably due to incomplete outgassing of the vacuum system.

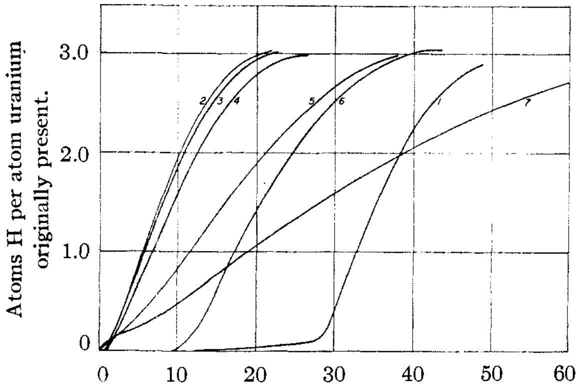

Fig. 1.—Absorption of hydrogen by uranium at various temperatures: curve 1, tank hydrogen at 250°; all other curves in high-purity hydrogen; curve 2, 225°; curve 3, 200° and 250°; curve 4, 175° and 275°; curve 5, 300°; curve 6, 150°; curve 7, 325°.

The results all indicate that the incubation period is caused by the formation of a more or less impermeable film on the surface of the uranium metal, which film must be removed before the reaction can occur at an appreciable rate. At higher temperatures the rate of diffusion of hydrogen through the film is more rapid than at low temperatures. Once the hydride starts to form, the whole surface of the metal spalls off because the density of uranium hydride is only about 10.9, much less than that of uranium. Once the clean underlying surface is exposed the reaction proceeds at the rate characteristic of the temperature.

Since uranium metal is quite active, it tarnishes readily in air. However, films formed either by allowing the metal to tarnish by standing in air at room temperature or by heating the metal in air appeared to have no effect on the incubation period. Films formed in air are apparently more porous and less protective than the films formed in the presence of an excess of hydrogen.

Effect of Temperature.—In Fig. 1, the amount of hydrogen absorbed by the uranium is plotted as a function of time for a number of different reaction temperatures. Except for curve 1, which was determined with tank hydrogen, all the curves were determined using high-purity hydrogen. The curves for 200° and 250°, and for 175° and 275° are not precisely the same, but are so close that for this report they have been drawn as single curves. The slopes of the curves give a measure of the reaction rate. In Fig. 2, curve 1, these values, corrected for the exposed surface area of uranium, are plotted against the reaction temperatures; the open circles refer to rates determined in purified hydrogen, the black circles to less precisely taken data using tank hydrogen. It can be seen that the rate is approximately constant between 200 and 250°, although there is a definite maximum at 225°. The reaction rate is independent of the purity of the hydrogen used.

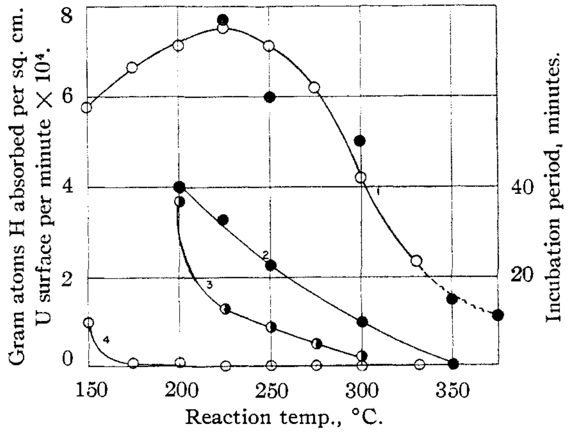

Fig. 2.—Curve 1, effect of temperature on reaction rate; curves 2, 3 and 4, effect of temperature on incubation period: ○, tank hydrogen; ◐, oxygen-free hydrogen; ●, high-purity hydrogen.

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°, 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 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.

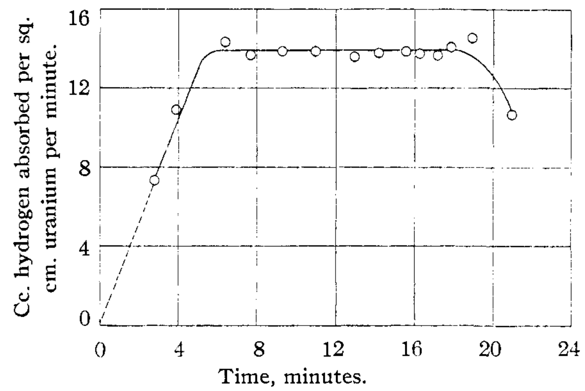

Fig. 3.—Rate of hydrogen absorption corrected for surface area.

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 $UH_{3.0}$.

TABLE I

FORMULA OF URANIUM HYDRIDE AT VARIOUS TEMPERATURES

Temp., °C.	G. atoms H / G. atoms U	Temp., °C.	G. atoms H / G. atoms U	Temp., °C.	G. atoms H / 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, UH_3, can be made readily by heating massive uranium in purified hydrogen at about 225°. 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.

RECEIVED APRIL 9, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Physical Properties and Crystal Structure of C_6F_{12}

BY H. J. CHRISTOFFERS,[1] E. C. LINGAFELTER AND GEORGE H. CADY

A compound having the formula C_6F_{12} was first prepared by Simons and Block,[2] by the reaction of fluorine with finely divided carbon. The same substance was later produced by Fukuhara and Bigelow[3] 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[3] was used to prepare the sample of C_6F_{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 fulfilment 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).