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THE FORMATION OF URANIUM HYDRIDE

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Chemistry - Uranium

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ABSTRACT

The effect of temperature on the rate of the reaction $2U + 3H_2 \rightarrow 2UH_3$ has been investigated between 150 and 375° C. The hydride forms most rapidly at 225° C. With unpurified tank hydrogen, an incubation period is found during which no apparent reaction occurs. The incubation period can be eliminated by suitably purifying the hydrogen. In eleven runs in highly purified hydrogen, the formula of the product averaged $UH_{3.00}$.

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INTRODUCTION

The work described in this report was started by C. S. Smith and was completed by J. E. Burke. The main objects were to study the effect of reaction temperature and of hydrogen purity on the reaction of hydrogen with massive uranium metal. A few incidental observations are also reported.

EXPERIMENTAL PROCEDURE

For most of the work, a half-inch length of 0.0625 uranium wire made by Westinghouse in 1942 from electrolytic metal was contained in a small closed-end pyrex tube which was heated in an electric tube furnace equipped with automatic temperature control. Hydrogen was admitted to the evacuated tube after it had reached the desired reaction temperature and the rate at which it was absorbed was measured with a gas burette. The pressure was maintained at atmospheric, which at this location is 580-590 mm.

For most of the work an all-glass gas train was used, but for the early work a less elaborate apparatus, with rubber connections, was used. Hydrogen directly from the tank was used for the early experiments. At an intermediate stage of operations the oxygen was removed by passing it over platinized asbestos at 300° C and through P_2O_5. For the final work, all impurities capable of reacting with uranium were removed by passing the hydrogen over uranium metal turnings at 475° C, at which temperature the hydride does not form at atmospheric pressure.

EFFECT OF TEMPERATURE ON RATE OF REACTION

The data on the absorption of hydrogen by uranium are given by the curves in Fig. 1. Except for the one run in tank hydrogen at 250° C, all these tests were made with hydrogen purified over uranium turnings. The

curves for 200 and 250°, and for 175 and 275° are not precisely the same, but are so close to each other that in this report they are given as single curves.

The slopes of the curves give a measure of the rate of reaction. The slopes of the approximately straight-line portions of the curves have been measured and corrected for surface area of the uranium wire. These data are listed in Table I and are platted as circles in Fig. 3.

TABLE I

Effect of Temperature on Reaction Rate
Hydrogen Purified Over Uranium Turnings

Reaction Temp. °C	Spec. wt. gms.	Ratio atoms H : atoms U	(Gm. atoms H absorbed/min /cm^2 sur. area U) x 10^4
150	0.4240	3.03	5.80
175	0.4281	2.99	6.70
200	0.4183	2.96	7.10
225	0.4240	3.04	7.55
250	0.4300	3.03	7.10
275	0.4345	3.03	6.20
300	0.4384	2.99	4.12
330	0.4125	2.92	2.30

Average Formula $UH_{3.00}$

The hydride forms most rapidly at 225°C but there is no great difference in the rate of formation between 175° and 250° C. At higher temperatures the rate falls off rapidly as might be expected from earlier data on temperature-pressure relationships in this system.

The values of the hydrogen-uranium atomic ratio in the hydride formed,

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calculated from the weight of the specimen and the volume of hydrogen formed, are given in column 3 of Table I. The error in this ratio would be $\pm$ 0.03 if one assumes room temperature to be off by 1° C, gas volume by 1 cm^3 and barometric pressure by 1 mm, with all errors in the same direction. Thus there is probably no significant difference between the formulas of the hydride produced between the temperature of 150 and 300° C, but the hydride formed at 330° C has a significantly lower hydrogen content.

To determine whether the rate of hydrogen absorption is a function of surface area, the volume of hydrogen absorbed per minute per square centimeter of surface area of uranium present was calculated for the 225° curve. The surface area was corrected for the amount of uranium that had reacted, with the assumption that the reaction progressed uniformly in from the surface. The results are listed in Table II. These data are plotted in Fig. 2.

The rate of reaction thus appears to be practically constant for a given surface area, except at the beginning and end of the reaction. It is realized that the true surface area of the specimen may differ tremendously from the simple geometrical surface area. However, it is likely that once the hydride is forming freely, the ratio between true and apparent surface area will be constant. At the beginning and especially at the end of the reaction, the ratio will certainly not be constant and this undoubtedly accounts for part of the dip at the ends of the curve. A slight incubation period before the reaction starts accounts for most of the dip at the beginning of the curve.

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TABLE II

Rate of Hydrogen Absorption corrected for Surface Area of Uranium Specimen.

Percent Total Vol. H_2 used	Time - minutes	Cm^3 H_2 Absorbed per min per cm^2 area of U.
10	2.8	0.730
20	3.9	1.09
30	5.2	1.34
40	6.4	1.43
50	7.8	1.36
60	9.3	1.38
70	11.0	1.38
80	13.0	1.35
85	14.2	1.37
90	15.6	1.38
92	16.3	1.37
94	17.2	1.36
96	17.9	1.40
98	19.0	1.45
100	21.0	1.06

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EFFECT OF HYDROGEN PURITY

The effect of hydrogen purity was investigated quite extensively. The most striking effect of impurity in the hydrogen is an incubation period for the reaction, during which time no apparent reaction occurs.

A sample curve obtained with unpurified electrolytic tank hydrogen at 250° C is given in Fig. 1. In this case practically no absorption of hydrogen occurred for 28 minutes; then the reaction started suddenly and proceeded at the normal rate.

Removal of oxygen from the hydrogen by passing it over platinized asbestos and drying reduces the incubation period but does not eliminate it. Passing the hydrogen over heated uranium turnings practically eliminates the incubation period. This indicates that impurities in the hydrogen other than oxygen can also be responsible for the incubation period. Nitrogen is the most likely impurity. The effect of oxygen on incubation period was confirmed by introducing about 0.25 percent O_2 into purified hydrogen; this caused the incubation period to increase to about 20 minutes at 250° C.

The effect of hydrogen purity and of reaction temperature on hydrogen purity on the duration of the incubation period is shown in Table III.

Even with the purest hydrogen used, an incubation period was found at 150° C. This may be due to traces of adsorbed moisture in the specimen tube and in the rest of the system.

The results all seem to indicate that the incubation period is caused by the formation of a more or less impermeable oxide film on the surface of the uranium, which film must be removed before the hydride reaction can occur. A higher temperature would permit more rapid diffusion of hydrogen through the film, so that the surface layer would spall off more rapidly, and permit the reaction to proceed.

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TABLE III

Effect of Reaction Temperature and Hydrogen Purity on Incubation Period.

Reaction Temperature °C	Incubation Period Minutes for		
	unpurified tank H_2	H_2 passed over hot Pt + asbestos and P_2O_5	H_2 passed over U turnings
150	--	--	10
175	--	--	1
200	40	37	1
225	33	13	0
250	23	9	0
275	--	5	0
300	10	2	0
330	--	--	0
350	0	--	--
375	0	--	--

The film responsible for incubation must form in hydrogen, because neither an oxide-nitride film formed previously at room temperature in air, nor a similar film formed by holding at 260° C for 2 minutes had a measurable effect on incubation period.

Hydrogen purity has no large effect on the rate of reaction. In Fig. 1 it can be seen that the slope of the 250° curve in tank hydrogen is approximately the same as the slope of the 250° C curve in purified hydrogen. In Fig. 3 the reaction rates from a number of runs made in tank hydrogen have been plotted (the x-points). They correspond very closely to the rates in purified hydrogen.

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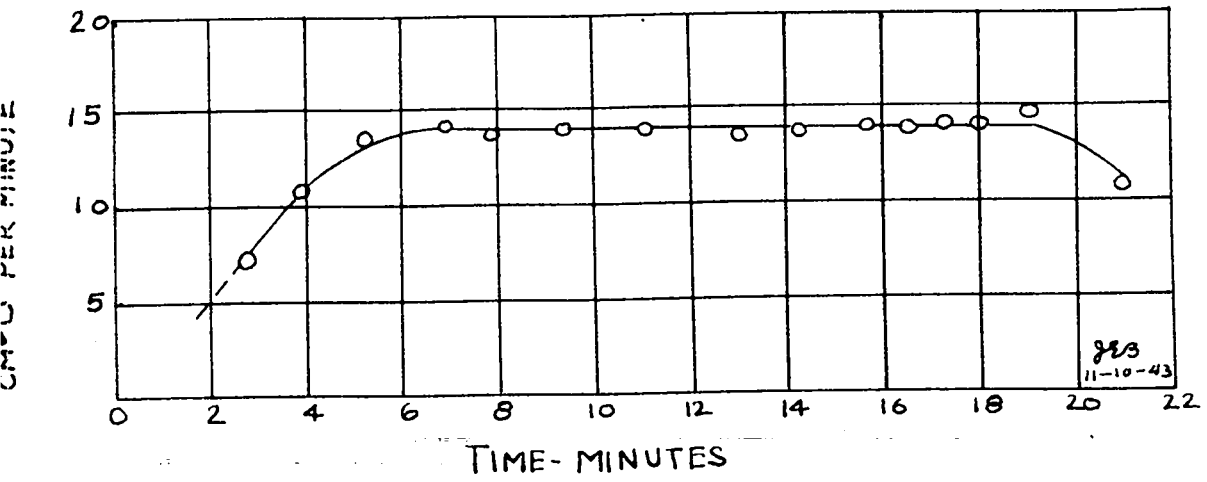
One run was made in a continuous stream of tank hydrogen, to determine the effect of continuously replenishing the supply of impurity. The reaction occurred, only slightly more slowly than in stagnant hydrogen, the total time required being slightly over an hour as compared with about 50 minutes with the still gas. The product was blacker than that obtained in still hydrogen. Apparently, once the reaction starts, the hydride itself can act as a getter to purify the hydrogen, allowing the reaction to proceed.

EFFECT OF THE METAL

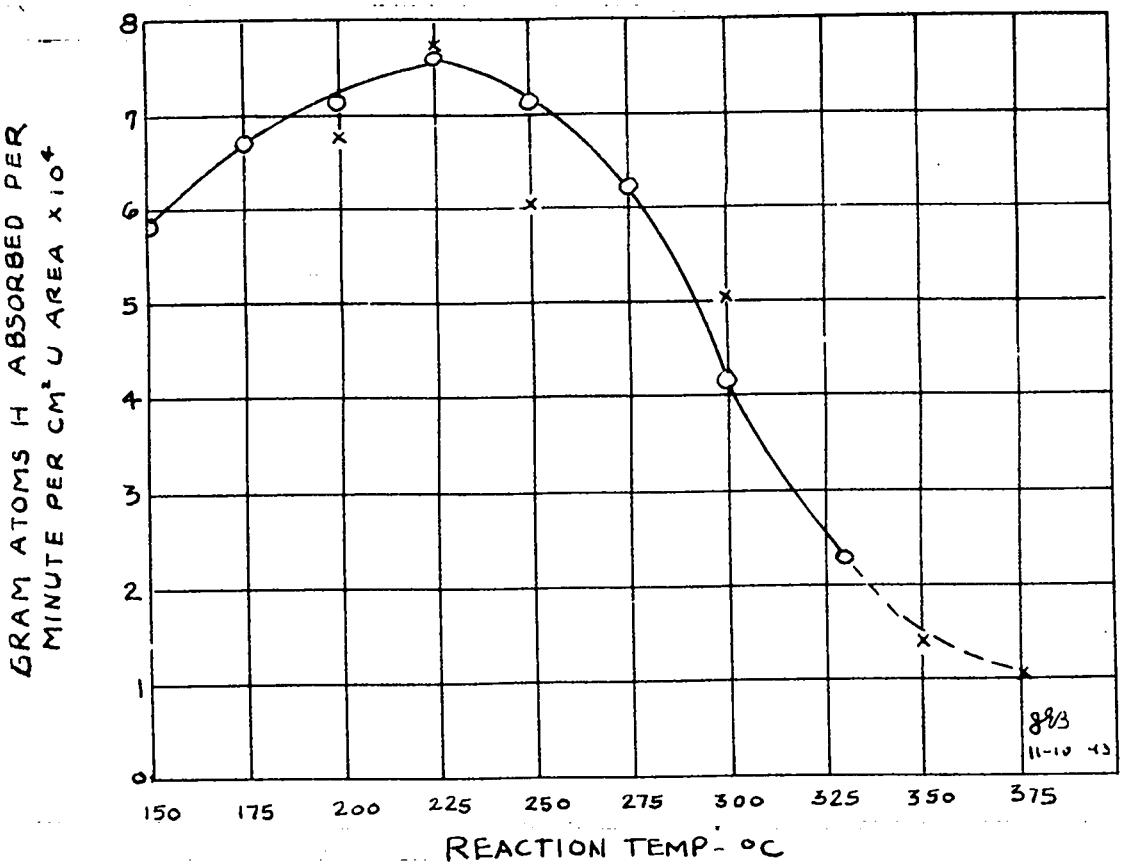
Practically all of the tests reported here were made on samples of 0.0625" uranium wire. However, to determine the effect of metal variables, a piece of biscuit # 2032 reduced by calcium in a bomb with a fired magnesia liner, was converted to hydride at 250° C. The hydrogen-uranium ratio in the product was 3.01 and the hydrogenation appeared to proceed in normal fashion.

Several runs were made at 250° C with wire which had been reduced about one quarter in thickness by cold rolling. The rate of hydrogen absorption by these specimens was only about 80 percent of the rate for the unworked specimens, on the assumption that rolling caused no change in surface area. After correcting the result for the larger surface area of the worked specimen, the rate is found to be only about 57 percent of that for the unworked specimen. No explanation is offered for this at present.



RATE OF HYDROGEN ABSORPTION CORRECTED FOR SURFACE AREA OF URANIUM SPECIMEN. REACTION TEMPERATURE- 225°C.

FIG 2



EFFECT OF TEMPERATURE ON REACTION RATE
O - PURIFIED HYDROGEN X - TANK HYDROGEN

FIG 3