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REACTION OF HYDROGEN WITH URANIUM

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W. M. Albrecht and M. W. Mallett

The reaction of hydrogen with uranium was studied in the temperature range 96 to 400 C at pressure levels of $p-p_0$ equal to 430, 150, and 70 mm of mercury (where p is system pressure and p_0 is the plateau dissociation pressure of the uranium hydride product). Reaction rates followed the linear law. At the pressure investigated, the linear rate constant increased with increasing temperature in the range 96 to about 250 C and decreased with increasing temperature from about 250 to 400 C. The variation of temperature and pressure with the linear rate constant in the range 96 to about 250 C is given by the equation:

$$k = 4.11 \times 10^{-3} (p-p_0)^{3/4} \exp(-1820/RT),$$

where k is in units of ml per cm² per sec and $p-p_0$ is in units of mm of mercury.

Two different initial reactions were obtained. One in the range 96 to about 250 at $p-p_0$ of 70 and 150 mm of mercury and 96 to 400 C at $p-p_0$ of 430 mm of mercury showed a gradual increase in the rate of hydrogen consumption until the rate became linear. The other initial reaction followed the parabolic rate law in the range of about 250 to 400 C at $p-p_0$ of 70 and 150 mm of mercury.

Adsorption plays an important role in the over-all reaction mechanism of uranium with hydrogen. In the range 96 to about 250 C, the rate of adsorption is faster than the rate of reaction to form hydride, but it is of the same order of magnitude. Therefore, formation of hydride is the rate-determining step. However, in the range of about 250 to 400 C the rate of adsorption is probably the rate-controlling step, with the exception of the initial parabolic reaction which would be diffusion controlled.

INTRODUCTION

Katz and Rabinowitch^{(1)*} have reviewed most of the investigations of the kinetics of the reaction of uranium with hydrogen carried out before 1944. Another study was made by Straetz and Draley⁽²⁾. Most of this work was performed in systems containing hydrogen at 1-atm pressure. It was generally found that the reaction followed a linear rate law, with a maximum reaction rate occurring at about 225 to 250 C. This could be explained since the plateau dissociation pressure, p_0 , that is the equilibrium hydrogen pressure of a uranium-uranium hydride-hydrogen system, increases very rapidly with temperature at about 250 C. The isothermic plateau dissociation pressure is about 4 mm of mercury at 250 C and 760 mm at 433 C. Therefore, at a fixed system pressure, p , the excess pressure, $p-p_0$, over

*References appear at the end of the report.

the dissociation pressure decreases with increasing temperature, and it would be expected that the reaction rate would decrease. With the system maintained at 1-atm pressure of hydrogen, there would be no reaction to produce hydride at 433 C and above.

There have been other investigations(1, 3) in which the effect of pressure on the kinetics of the reaction was studied. These investigations were carried out in a constant-volume apparatus in which the rate of decrease of pressure with time at constant temperature was determined. Data obtained at Ames(1) followed the equation $-(dp/dt) = K(p_t - p_0)^{5/2}$, where p_t is the residual hydrogen pressure after the reaction has proceeded for time, t . However, there is no ready explanation of the 5/2 power in the equation.

For the present study, the kinetics of the reaction of hydrogen with uranium was studied under the condition that $p - p_0$ is a constant, that is, the hydrogen pressure in excess of the plateau dissociation pressure of the uranium hydride product was constant. The temperature range of 100 to 400 C was chosen.

The values of p_0 used in this study were obtained previously.(4) The variation of p_0 with temperature is given by the equation $\log p_{mm} = -\frac{4590}{T} + 9.39$, which is in good agreement with the data presented by other investigators.(1)

EXPERIMENTAL PROCEDURE

Materials

The uranium used in this study was fabricated(5) into a 3/8-in. - diameter rod. Test specimens were machined from these rods. Analysis of the uranium was obtained by spectrographic, chemical, and vacuum-fusion techniques. The total of all the measured impurities was less than 400 ppm, and each impurity was present in a concentration of less than 100 ppm. The following elements were detected as impurities: aluminum, carbon, chromium, cobalt, copper, iron, magnesium, manganese, nickel, nitrogen, oxygen, silicon, and a few others in very low concentrations.

Pure hydrogen was obtained from the thermal decomposition of uranium hydride. The hydride was prepared by reacting dried tank hydrogen with degreased high-purity uranium chips.

Method

The general method for measuring the rate of reaction between uranium and hydrogen has been previously described for other metal-gas reactions, (6, 7) The apparatus is basically the same as that described in a previous paper (6), but a pressure regulator has been incorporated in the design. A schematic diagram of the apparatus used is shown in Figure 1. The system was evacuated by a two-stage mercury-diffusion pump backed by a mechanical pump.

The modified White gas buret⁽⁸⁾ used to store the hydrogen and to measure the rate of consumption consisted of eight bulbs, each of approximately 50 ml, and an open-end mercury manometer, one arm of which was a graduated 50-ml buret. The pressure regulator (see Figure 1) consisted of an outer Pyrex tube, 40 mm in diameter and 90 cm long, which was connected to the reaction tube. An inner 2-mm Pyrex capillary tube which extended from the top to about 3 cm above the bottom of the outer tube was connected to the gas buret. The pressure, p , to be maintained in the reaction tube was set by lowering the mercury level in the pressure regulator a distance, p mm, below the mercury level when at barometric height. In operation, hydrogen was consumed by a specimen and replacement gas bubbled through the mercury from the capillary tip to maintain the desired pressure (± 1 mm of mercury) in the reaction tube. Both the buret assembly and pressure regulator were water jacketed and maintained at constant temperature (± 0.5 C during the course of a reaction-rate run).

The Vycor reaction tube was sealed to the system with Apiezon W wax, and its dead volume was decreased with a solid Pyrex rod. This dead space also was used to hold a platinum-platinum-10 per cent rhodium thermocouple in contact with the top of a specimen. The thermocouple was used to measure the specimen temperature during the course of a rate experiment.

The reaction tube was heated with a resistance-wound furnace which was controlled by a Foxboro controller, using a Chromel-Alumel thermocouple placed at the resistance windings of the furnace. Temperature of a specimen was maintained to ± 3 C.

Prior to specimen preparation, machined uranium cylinders about 0.8 cm in diameter and ranging from 1 to 4 cm long were abraded with 240-grit silicon carbide paper and vacuum annealed at 600 C for 3 hr. Specimens then were abraded with 240, 400, and 600-grit silicon carbide papers. After the dimensions and weight of the specimens were determined, they were given a final polish with dry 600-grit silicon carbide paper, immediately placed in the reaction tube, and sealed into the system. The system was evacuated for 1 hr at a pressure better than 10^{-5} mm mercury. During this evacuation, the portion of the reaction tube above the specimen was

FIGURE 1. SCHEMATIC DIAGRAM OF MODIFIED SIEVERTS APPARATUS

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flamed periodically to remove adsorbed gases from the walls of the tube. The specimen was then slowly heated to the temperature of the reaction-rate run and held at temperature for a period of about 1-1/2 hr. It was found necessary to take these precautions to keep the induction period of the reaction to a minimum.

While the specimen was being heated at temperature, hydrogen was generated and stored, and the pressure regulator adjusted to the pressure conditions of the run.

With the specimen at the desired temperature, hydrogen was admitted from the gas buret through the pressure regulator which maintained the desired pressure in the reaction tube. By manipulations of the buret leveling bulb and stainless steel needle valve, the buret was continuously balanced to atmospheric pressure. Readings of the buret manometer arms were made at 1/2- to 2-min intervals, depending upon the reaction rate. The quantity of gas consumed by the specimen was the difference between the volume added from the buret and volume remaining in the gas phase in the calibrated dead space. Original geometric dimensions of specimens were used in calculating the quantity of hydrogen reacted per unit area, in units of ml STP hydrogen per cm^2 .

RESULTS

Films

Visual observation of the surface of a uranium specimen during the course of a run showed that at the start of a reaction a blue-black film formed which was considered to be adherent to the metal since it showed no evident cracking or flaking. The same type of protective film formed where the parabolic rate law was followed. No extensive investigation of the adherent films could be made since they could not be preserved upon cooling of the specimen from the temperature of the rate experiment. As soon as the furnace was removed from the reaction tube, the film began flaking off the specimen. At the longer times where the linear rate law was followed there was a continual flaking of the hydride. This would be expected since the flaking off of a film is associated with the linear rate law.

Inspection of the metal surfaces at the end of a reaction experiment showed them to be relatively smooth. The decrease in the surface areas during the experiments averaged about 3 per cent or less, based upon the decrease in the dimensions of the metal specimens. Since the change in surface area was so small, no corrections were made on the original geometric dimensions in calculating the quantity of hydrogen consumed per unit area.

Rate Data

Rates of reaction of pure hydrogen with massive uranium were determined in the range 96 to 394 C at three hydrogen pressure levels of $p-p_0$: 430, 150, and 70 mm of mercury. At all pressure levels, after initial deviations, the rates followed the linear law, $w = kt$, where w is the ml STP hydrogen consumed per cm^2 of surface, t is time, and k is the linear rate constant in units of ml per cm^2 per sec. In each case, the linear rate constant increased with increasing temperature at lower temperatures, but decreased with increasing temperatures above a certain temperature which depended upon the pressure.

For $p-p_0 = 430$ mm of mercury, Figure 2 shows typical plots of w versus t . It is seen that after initial deviations (a gradual increase in rate) the data follow the linear law. Values of the rate constant, calculated from the various plots, are given in Table 1. The rate constants range from 3.5×10^{-2} ml per cm^2 per sec at 102 C to a maximum of 7.6×10^{-2} ml per cm^2 per sec at 264 C, and then decrease to 3.6×10^{-3} ml per cm^2 per sec at 394 C.

In Figure 3 are typical plots of w versus t for $p-p_0 = 150$ mm of mercury pressure. In Table 2 are given the values of the linear rate constants which range from 1.2×10^{-2} ml per cm^2 per sec at 96 C to 2.8×10^{-2} ml per cm^2 per sec at 200 C, and then decrease to 1.9×10^{-3} ml per cm^2 per sec at 356 C. However, at this pressure level two different types of initial deviations were obtained. In the range 96 to 200 C and at 356 C the reaction rate gradually increased until the rate became linear. However, in the range 254 to 326 C the initial reactions followed the parabolic rate law, $w^2 = kt$, where k is the parabolic rate constant $(\text{ml per cm}^2)^2$ per sec. The parabolic behavior can be seen in Figure 4, where the square of w is plotted as a function of t for a number of runs, and it is seen that the data fall on straight lines. The parabolic rate constants which were obtained from these plots and the initial time that the parabolic rate was followed are also given in Table 2. The rate constants ranged from 3.8×10^{-2} $(\text{ml per cm}^2)^2$ per sec at 254 C to 2.2×10^{-2} $(\text{ml per cm}^2)^2$ per sec at 356 C.

For $p-p_0 = 70$ mm of mercury, Figure 5 shows typical plots of w versus t . The linear rate constants obtained from such plots are given in Table 3. The values range from 7.7×10^{-3} ml per cm^2 per sec at 96 C to 1.3×10^{-2} ml per cm^2 per sec at 206 C, and then decrease to 3.0×10^{-3} ml per cm^2 per sec at 253 C. In the range 96 to 206 C the initial deviations showed a gradually increasing rate, and in the range 206 to 303 C they showed a parabolic rate. Parabolic plots are included in Figure 4. The parabolic rate constants and the time that the parabolic rate was followed are given in Table 3. The constants range from 2.1×10^{-2} $(\text{ml per cm}^2)^2$ per sec at 206 C to 1.1×10^{-2} $(\text{ml per cm}^2)^2$ per sec at 303 C.

FIGURE 2. REACTION OF URANIUM WITH HYDROGEN FOR $p-p_0 = 430$ MM MERCURY

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FIGURE 3. REACTION OF URANIUM WITH HYDROGEN AT $p-p_0=150$ MM MERCURY AT 96 TO 356 C

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TABLE 1. RATE CONSTANTS FOR THE REACTION OF URANIUM WITH HYDROGEN AT $p-p_0 = 430$ MM OF MERCURY

Temperature, C	P_0 , mm of mercury	Linear Rate Constant, ml per cm ² per sec
102	0.002	3.5×10^{-2}
150	0.035	4.3×10^{-2}
155	0.050	4.4×10^{-2}
171	0.12	4.9×10^{-2}
206	0.63	5.5×10^{-2}
264	5.5	7.6×10^{-2}
307	30	5.0×10^{-2}
308	30	2.9×10^{-2}
346	93	1.5×10^{-2}
394	316	3.6×10^{-3}

TABLE 2. RATE CONSTANTS FOR THE REACTION OF URANIUM WITH HYDROGEN AT $p-p_0 = 150$ MM OF MERCURY

Temperature, C	P_0 , mm of mercury	Time of Initial Parabolic Reaction, sec	Parabolic Rate Constant, (ml per cm ²) ² per sec	Linear Rate Constant, ml per cm ² per sec
96	0.001	None	--	1.2×10^{-2}
110	0.003	None	--	1.6×10^{-2}
121	0.006	None	--	1.5×10^{-2}
146	0.028	None	--	1.7×10^{-2}
163	0.070	None	--	2.1×10^{-2}
200	0.60	None	--	2.8×10^{-2}
254	4.7	500	3.8×10^{-2}	2.0×10^{-2}
300	25	1200	3.2×10^{-2}	9.1×10^{-3}
326	53	600	2.2×10^{-2}	5.6×10^{-3}
356	123	None	--	1.9×10^{-3}

FIGURE 4. PARABOLIC PLOT OF INITIAL REACTION OF URANIUM WITH HYDROGEN AT $p - p_0 = 150$ AND 70 MM MERCURY

FIGURE 5. REACTION OF URANIUM WITH HYDROGEN AT $p-p_0 = 70$ MM MERCURY AT 96 TO 220 C

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TABLE 3. RATE CONSTANTS FOR THE REACTION OF URANIUM WITH HYDROGEN AT $p-p_0 = 70$ MM OF MERCURY

Temperature, C	p_0 , mm of mercury	Time of Initial Parabolic Reaction, sec	Parabolic Rate Constant, (ml per cm ²) ² per sec	Linear Rate Constant, ml per cm ² per sec
96	0.001	None	--	7.7×10^{-3}
145	0.026	None	--	1.1×10^{-2}
168	0.15	None	--	1.2×10^{-2}
206	0.70	800	2.1×10^{-2}	1.3×10^{-2}
220	1.2	1000	2.2×10^{-2}	8.2×10^{-3}
253	4.6	4000	2.1×10^{-2}	3.0×10^{-3}
303	26.	9000	1.1×10^{-2}	None

It has generally been found that the temperature dependence of rate measurements follows the Arrhenius-type equation, $k = A \exp (-Q/RT)$ where k is the rate constant, A is the frequency factor and Q is the energy of activation. Therefore a plot of logarithms of the rate constants versus the reciprocals of the absolute temperatures should yield a straight line. Such plots are given in Figure 6 for the linear rate constants of the reaction of massive uranium with hydrogen at the three pressure levels of $p-p_0$ equal to 430, 150, and 70 mm of mercury pressure. Equations for the best straight lines through the various sets of points were determined by the method of least squares. It can be seen that the rate constants go through a maximum at each pressure level. The expressions for the linear rate constants are given in Table 4. At the higher temperature where the linear rate decreases with increasing temperature, a negative "energy of activation" is obtained. This is discussed in a later section.

The effect of pressure on the linear reaction rates can be seen in Figure 6. From the equations given in Table 4, linear rate constants were calculated at all three pressures at temperatures in the range 100 to 200 C. The calculated rate constants, k , are given in Table 5. A plot of $\log k$ versus $\log (p-p_0)$ gave straight lines with slopes of about 0.75, which indicates the following relationship between rate constant and pressure ($p-p_0$):

$$k = \frac{dw}{dt} = k_0 (p-p_0)^{3/4}.$$

FIGURE 6. TEMPERATURE DEPENDENCE OF LINEAR RATE CONSTANT FOR URANIUM-HYDROGEN REACTION

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TABLE 4. EXPRESSIONS FOR LINEAR RATE CONSTANTS FOR THE REACTION OF URANIUM WITH HYDROGEN

Pressure, p-p ₀ , mm of mercury	Tempera- ture Range, C	Expression for Linear Rate Constant k	Approximate Error, in a Calculated k, relative per cent
430	102 to 264	$0.421 \exp (-1890/RT)(a)$	3.5
	307 to 394	$6.30 \times 10^{-10} \exp (20,700/RT)$	20
150	96 to 200	$0.399 \exp (-2540/RT)(b)$	5.0
	254 to 356	$2.35 \times 10^{-8} \exp (14,500/RT)$	19
70	96 to 168	$0.118 \exp (-2160/RT)(c)$	1.2
	206 to 253	$8.41 \times 10^{-10} \exp (15,700/RT)$	1.1

(a), (b), and (c): The activation energies for these reactions are 1890 ± 110 , 2540 ± 200 , and 2160 ± 80 cal per mole, respectively.

TABLE 5. VARIATION OF LINEAR RATE CONSTANT WITH PRESSURE FOR REACTION OF URANIUM WITH HYDROGEN

Temperature, C	Linear Rate Constant k, ml per cm ² per sec, at Various p-p ₀		
	70 MM	150 MM	430 MM
100	7.99×10^{-3}	1.30×10^{-2}	3.28×10^{-2}
125	9.59×10^{-3}	1.61×10^{-2}	3.85×10^{-2}
150	1.13×10^{-2}	1.95×10^{-2}	4.43×10^{-2}
175	1.30×10^{-2}	2.30×10^{-2}	5.03×10^{-2}
200	1.48×10^{-2}	2.68×10^{-2}	5.62×10^{-2}

A number of plots of k versus $(p-p_0)^{3/4}$ are given in Figure 7. It is seen that the data fall on straight lines that pass through, or near the origin. A plot of the logarithms of the slopes $(\frac{k}{(p-p_0)^{3/4}})$ of the lines versus $\frac{1}{T}$ is

given in Figure 8. Using these data, and applying the method of least squares the following equation for the linear rate constant, k , in ml per cm^2 per sec, was obtained,

$$k = 4.11 \times 10^{-3} (p-p_0)^{3/4} \exp - \frac{1820}{RT},$$

where $p-p_0$ is in mm of mercury.

Upon consideration of the meager parabolic data obtained in the study, there appeared to be very little change of the parabolic rate constant with temperature and pressure. Therefore, no attempts were made to derive any relationships between these variables for the parabolic data.

DISCUSSION AND CONCLUSIONS

The reaction of uranium with hydrogen was found to follow a linear rate law after initial deviations. From inspection of the Arrhenius plots given in Figure 6, it appears that at least two different rate-controlling processes were found in the temperature and pressure ranges investigated. However, at the higher temperatures where a negative "activation energy" is indicated, an equation more complex than the Arrhenius equation apparently is necessary to define the reaction. Therefore, for a better understanding of the reaction mechanism, the various processes involved in the reaction must be considered.

Essentially, one is concerned with a heterogeneous, gas-solid reaction which follows a linear rate law. The processes involved in such a reaction follow a number of successive steps, the slowest of which determines the rate of the over-all mechanism. These steps are:

- (1) Adsorption of gas on the metal surface
- (2) Reaction at the surface
- (3) Spalling of the product or formation of a very porous product.

However, in the present case, where a porous product is formed, only Steps (1) and (2) need be considered as controlling processes in the over-all mechanism. Usually in gas-metal reactions the rate of adsorption is very rapid compared to rate of reaction. Normal energies of activation for adsorption are of the order of 5 kcal per mole, while those for reaction are of the order of 30 kcal per mole. In the present investigation a low energy of activation of about 2 kcal per mole was obtained, indicating a very fast

FIGURE 7. VARIATION OF LINEAR RATE CONSTANT WITH $p-p_0$ FOR REACTION OF URANIUM WITH HYDROGEN

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FIGURE 8. PLOT OF $\text{LOG } k/(p-p_0)^{3/4}$ VERSUS $1/T$ FOR THE REACTION OF URANIUM WITH HYDROGEN

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reaction in the range 96 to about 250 C. It is believed that the controlling step in this range is the rapid reaction at the surface to form hydride. The rate of adsorption which is part of the mechanism is faster than the rate of reaction to form hydride but is of the same order of magnitude. At the higher temperatures, about 250 to 400 C, the adsorption becomes rate determining. In this range the rate of reaction becomes faster than the rate of adsorption, and, since the fraction of surface covered by the adsorbed gas decreases with increasing temperature, it would be expected that the over-all reaction rate would decrease with increasing temperature. Equations were formulated to determine the relationship between the over-all reaction rate, adsorption equilibrium, reaction equilibrium and temperature for the data. However, no equation was obtained which would give a positive activation energy for the data in the temperature range of about 250 to 400 C.

If it is considered that adsorption plays an important role in the reaction mechanism and that dissociation of the hydrogen occurs at the surface, the pressure dependency should be $(p-p_0)^{1/2}$. From this investigation nothing definite has been concluded concerning the pressure dependency of the reaction. The variation of the reaction rate, k , with the $3/4$ power of $p-p_0$ gives the best fit of the present data (Figure 7). Perhaps, if the study was extended to a wider pressure range the pressure dependency could be established.

The initial reaction (Figures 2, 3, and 5) found in the range 96 to about 250 C at $p-p_0$ of 70 and 150 mm of mercury and 96 to 400 at $p-p_0$ of 430 C, followed a gradual increase in rate of consumption of hydrogen until the rate became linear. It is believed that this period is associated with the formation of the adsorbed layer and the reaction to form hydride increases as the fraction of surface covered with adsorbed gas increases. The reaction reaches a maximum rate and becomes linear when the fraction of surface covered by adsorbed gas becomes a maximum for the experimental temperature and pressure. The parabolic rate law was noted initially in the range of about 250 to 400 C at $p-p_0$ of 70 and 150 mm of mercury (Figure 4). Parabolic behavior is usually considered to result from reactions in which protective films are formed with diffusion being the controlling process. The results of this investigation show that a film is formed during the parabolic reactions, and these films flake off the specimen when the rates become linear.

In general, it is believed that adsorption of hydrogen on the surface of uranium plays a very important role in the over-all reaction mechanism of uranium with hydrogen. In the range 96 to 250 C, the rate of adsorption is faster than the reaction rate at the surface to form hydride, but is of the same order of magnitude. However, in the range of about 250 to 400 C adsorption is probably the rate-controlling step in the reaction, with the exception of the initial parabolic reaction which would be diffusion controlled.

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