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KINETICS FOR THE REACTION OF HYDROGEN
WITH URANIUM POWDER

J. L. STAKEBAKE

ROCKWELL INTERNATIONAL, ROCKY FLATS DIVISION,
GOLDEN, COLORADO 80401

The reaction of hydrogen with uranium powder was investigated at 13.3 and 26.6 kPa between 50° and 250 °C. The reaction order was independent of temperature but varied from 2/3-order at 13.3 kPa to 1st-order at 26.6 kPa. Increasing temperatures resulted in decreasing reaction rates over the temperature range studied. A reaction mechanism with adsorption as the rate controlling step is proposed to explain the temperature behavior. Decomposition of the hydride was found to follow a zero-order rate process.

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INTRODUCTION

Reaction kinetics for the uranium-hydrogen system have been studied extensively. However, with some exceptions^{1,2} all of the work has been done using bulk uranium samples. Albrecht and Mallet³ studied the reaction at constant pressure using a volumetric technique. They found the reaction rate to be linear following some initial deviations. The reaction velocity passed through a maximum at about 280° and then decreased with further increasing temperatures. This phenomenon is attributed to the decomposition reaction hindering the reaction process. The initial deviations which were observed in the reaction were likely the result of gaseous impurities as well as the oxide film present on the metal. The observed induction time was followed by a nucleation time during which the reaction accelerated to the maximum rate. Subsequent studies by Alire et al.⁴ showed that induction times could be eliminated by using high purity gases. However, the minimum conditions of this study, 175 °C and 100 torr, were probably high enough to override any induction effects caused by surface oxide films.

One means of eliminating the induction effects due to surface oxide films is to prepare the sample in high vacuum. Condon and Larson¹ accomplished this by using uranium powder prepared by the decomposition of uranium hydride. Hydriding conditions varied from about 53 Pa to 2.66×10^3 Pa at 0 to 110 °C. Reaction rates were found to vary inversely with temperature while there was a half-order rate dependence on hydrogen pressure. Volumetric studies conducted by Hashino and Okajima² with powdered uranium showed a temperature dependence similar to that found for coupons. The rate increased with temperature up to 268 °C and then decreased rapidly when the decomposition became predominant.

It was the intent of the present investigation to expand the experimental parameters used by Condon and Larson.¹ Of particular interest were the effects of temperature and surface area on the reaction rate. Measurements were made using a recording electrobalance at two constant pressures, 13.3 kPa (100 torr) and 26.6 kPa (200 torr). Temperatures were varied from 50 to 200 °C. During the study information was also obtained on the dehydriding kinetics of UH_3 in the temperature range 200 to 300 °C.

EXPERIMENTAL

Materials Uranium used for this study was fabricated into a 13 mm diameter rod. Sample coupons were then machined from this master sample. An impurity analysis of this material was obtained using a spark source mass spectrometer. Results from the analysis are shown in Table I. Prior to each experiment, the coupons were cleaned by immersing in 7N nitric acid to remove the oxide film. The samples were then washed in distilled water, dried in alcohol, and placed under vacuum.

Ultra pure hydrogen (99.999%) and argon (99.999%) were used without further purification. Prior to beginning these experiments a mass spectrometer was attached to the system so that the gas atmospheres being used could be analyzed. It was found that surface reactions involving hydrogen within the stainless steel system introduced some contamination into the gas phase. This phenomenon has been described by Beavis.⁶ The result was that hydrogen passed through a heated palladium cell was no purer than the hydrogen direct from the cylinder.

Apparatus All of the kinetic measurements were made gravimetrically. A Cahn Model 100 electromicrobalance was modified for high vacuum use by remounting the weighing mechanism onto an eight inch Conflat* flange. The photocell and light source were located outside the vacuum system. The balance chamber was incorporated into a vacuum system and mounted

* Trademark of Varian Associates.

Table I. Mass Spectrometric Analysis of Uranium

Element	Al	C	Ca	Cr	Cu	Fe
Concentration ppm _w	51	60	1	260	19	70
Element	K	Mg	Mn	N	Na	Ni
Concentration ppm _w	2	2	9	13	3	43
Element	O	S	Si	Other	Total	
Concentration ppm _w	6	2	97	2	640	

with the sample and counterweight tubes inside an inert glovebox. The inert glovebox was used to handle reactive materials. Figure 1 shows schematically the entire experimental system.

The vacuum system included two ion pumps and an oil diffusion pump with a liquid nitrogen cold trap. Minimum pressures attainable were in the 10^{-6} Pa (10^{-8} torr) range and were limited by the low bakeout temperature permitted by the balance. Hydrogen and argon were admitted directly into the system and were not passed through the uranium hydride purifier. Constant pressures were maintained through use of Granville-Phillips automatic pressure controllers. Pressure within the system could be varied from 10^{-4} Pa (10^{-6} torr) to 10^5 Pa (750 torr) and was measured with either an ionization gauge or capacitance manometers. A Veeco gas analyzer was used to analyze both vacuum and gaseous atmospheres.

Sample temperatures were maintained with a resistance heater and a power proportioning programmer. The thermocouple for measuring sample temperature was located next to the sample. Outputs from the thermocouple as well as the pressure meters and the balance were fed into a data acquisition system. All of the data were then processed with a computer.

Procedure All samples were initially cleaned and immediately placed on the microbalance and evacuated. Outgassing was carried out at 22° and 10^{-5} Pa for a minimum of 16 hours. The buoyancy of the coupon was then measured at -196°C in 0 to 3.3 kPa (25 torr) of argon. This measurement was necessary to provide a buoyancy correction factor for argon.

FIGURE 1. Experimental system.

adsorbed during surface area measurements. The uranium coupons were hydrided in 26.6 kPa (200 torr) of hydrogen at 107, 150 and 200 °C. Uranium powder was prepared by dehydriding uranium hydride at 200 to 300 °C.

Both the uranium and uranium hydride powders were characterized by measuring the B.E.T.⁶ surface area. Argon was used as the adsorbate at -196 °C. Following characterization, the uranium powder was hydrided at temperatures ranging from 50 to 200 °C in 13.3 or 26.6 kPa (100 or 200 torr). Using the hydride/dehydride cycling process, a number of experimental runs could be made on each sample. When experiments were completed on any given sample, the hydride was oxidized to U_3O_8 in 26.6 kPa of oxygen.

REACTION KINETICS

Two cases may be considered when dealing with the reaction between a gas and a metal powder to form a single solid product. First, is the case of the "Phase Boundary" reaction where the reaction occurs at the gas-solid interface. In this case, the reaction front moves toward the center of the particle. During the reaction, the total particle size may remain the same, increase, or decrease depending on the molar volume of the product. The core, however, remains unreacted.⁷

The second case to be considered is the Progressive Conversion model where the gas diffusion throughout the particle is very fast and is not rate limiting. Thus, the particle is converted continuously and progressively to the solid product. In both of the cases the steps occurring during the reaction are:

- (i) Adsorption of the gas on the particle surface.

- (ii) Diffusion to reaction sites; either into the bulk or through the product layer to the core surface.
- (iii) Reaction between the gas and solid.

Phase Boundary Model This model can be evaluated by assuming the reaction produces a product layer of thickness y which reduces the radius r_0 of each spherical particle. (Figure 2) The volume of unreacted material at time t becomes:

$$V = \frac{4\pi}{3} (r_0 - y)^3. \quad (1)$$

If α is the fraction of the reaction completed at time t , the volume of material unreacted becomes:

$$V = \frac{4\pi r_0^3}{3} (1-\alpha). \quad (2)$$

By equating (1) and (2) the thickness of the product layer y becomes:

$$y = r_0 [1 - (1-\alpha)^{1/3}]. \quad (3)$$

If the reaction process produces a product whose molar volume is greater than that of the solid reactant, a protective, non-porous layer is formed and the reaction becomes diffusion controlled. This results in the parabolic rate expression for the growth of the product layer given by

$$y^2 = k_p t. \quad (4)$$

Combining Eq. (3) and (4) produces the Jander⁸ equation:

$$y^2 = r_0^2 [1 - (1-\alpha)^{1/3}]^2 = k_p t$$

or

$$[1 - (1-\alpha)^{1/3}]^2 = \frac{k_p}{r_0^2} t = k_j t \quad (5)$$

where k_p is the parabolic rate constant and k_j is the observed Jander rate constant.

FIGURE 2. Phase Boundary model for the reaction of gas with a solid particle.

If the reaction is phase boundary controlled resulting in either a linear reaction rate for the growth of a porous product layer or a reaction directly dependent on the available surface area then

$$y = kt. \quad (6)$$

Combining Eqs. (3) and (6) yields

$$\begin{aligned} y &= r_0 [1 - (1 - \alpha)^{1/3}] = kt \\ \text{or } 1 - (1 - \alpha)^{1/3} &= \frac{kt}{r_0} = K_L t, \end{aligned} \quad (7)$$

where k is the linear rate constant and K_L is the experimentally determined rate. Equation (7) has been used by Muromura and Ouchi⁹ to evaluate the nitrogenation of plutonium hydride.

Progressive Conversion Model In contrast to the phase boundary model this model assumes the reacting gas diffuses rapidly throughout the particle. The reaction converts the particle uniformly to the product as in Fig. 3. The reaction rate is then dependent only on the concentration of the metal available.⁹ Evaluation of the rate for the reaction

using the progressive conversion model involves expressions relating reactant concentrations to time. If M_0 is the initial metal concentration and M_t is the amount hydrided at time t , then the amount of metal unreacted is $M_0 - M_t$. The rate of disappearance of the metal is

$$\frac{-d(M_0 - M_t)}{dt} = \frac{dM_t}{dt} = K(M_0 - M_t)^n \quad (8)$$

If this is integrated with the boundry condition that $M_t = 0$ when $t = 0$, and $n \neq 0$, then

$$K = \frac{1}{t(n-1)} \left[\frac{1}{(M_0 - M_t)^{n-1}} - \frac{1}{M_0^{n-1}} \right] \quad (9)$$

FIGURE 3. Progressive Conversion model for the reaction of a gas with a solid particle.

Since the parameter being measured is W_t , the amount of gas reacted at time t , and W_m is the maximum amount of gas reacted, then

$$M_t = \frac{W_t}{W_m} M_0 \quad (10)$$

the general solution to Eq. 9 becomes

$$K = \frac{1}{t(n-1)} \left[\frac{1}{\left(M_0 - \frac{W_t}{W_m} M_0\right)^{n-1}} - \frac{1}{M_0^{n-1}} \right] \quad (11)$$

Upon rearranging

$$\left(M_0 - \frac{W_t M_0}{W_m}\right)^{1-n} = K(n-1)t + M_0^{1-n}$$

or

$$M_0^{1-n} \left(1 - \frac{W_t}{W_m}\right)^{1-n} = K(n-1)t + M_0^{1-n}$$

or

$$\left(1 - \frac{W_t}{W_m}\right) = \left[K(n-1) M_0^{n-1} t + 1\right]^{1/1-n}$$

The final working equation becomes

$$W_t = W_m \left[1 - (1 + K(n-1) M_0^{n-1} t)^{1/1-n} \right] \quad (12)$$

Equation 12 is valid for $t < \left(\frac{M_0^{1-n}}{K(n-1)}\right)$ and $n \neq 1$.

In the case where $t \geq \left(\frac{M_0^{1-n}}{K(n-1)}\right)$ and $0 < n < 1$ then $W_t = W_m$.

For equation 12: n = order of the reaction.

W_t = weight gain at time t , mg/g.

M_0 = mg atoms of material at start of reaction.

W_m = wt gain at $t = \infty$, mg/g.

K = rate constant.

In the special case where $n = 1$ for a 1st-order reaction Eq. 9 becomes

$$K = \frac{1}{t} \ln \frac{M_0}{M_0 - M_t}, \quad (13)$$

which with the substitution of Eq. 10 becomes

$$W_t = W_m (1 - e^{-kt}). \quad (14)$$

RESULTS

Uranium Coupon Hydriding

Uranium powder samples were initially prepared by hydriding uranium coupons and then decomposing the hydride. Coupon reactions were characterized by an inhibition time caused by the oxide film formed on the coupon after the initial cleaning. The reaction rate accelerated during a nucleation period and then became linear. Table II shows the results from the zero-order reaction. The activation energy for coupon hydriding was calculated, using the Arrhenius equation, to be $4.5 \pm .5$ kcal/mole. This is in general agreement with the activation energies reported by others.^{2,4}

Uranium Powder Hydriding

Successive hydriding runs were made on each sample by decomposing the hydride. This in situ preparation maintained a uniformly clean surface. Figure 4 shows a series of five hydriding runs on the sample in 13.3 kPa (100 torr) at 100 °C. The fourth run of this series reproduced run three and both are shown as a single curve. All of the experimental data were evaluated using Eq. (12). This equation was found to describe the experiments quite accurately. Figure 5 shows both experimental and

Table II. Uranium Coupon Hydriding Rates
in 26.6 kPa Hydrogen

<u>Run</u>	<u>Temperature °C</u>	<u>Rate Constant mg/g·min</u>
1	107	0.080
2	150	0.181
3	200	0.274
4	200	0.265

FIGURE 4. Effects of hydriding-dehydriding cycles on the hydriding of uranium powder in 26.6 kPa (200 Torr) of hydrogen at 200°C.

FIGURE 5. Application of the general rate equation (Eq.) to uranium hydriding.

predicted values for run 2 in Figure 4. Results from the powder hydriding experiments are summarized in Table III.

Data for Series I of Table III were derived from the experimental runs in Figure 4. The rate of reaction increased as the number of hydriding-dehydriding cycles increased. This behavior was also observed in Series II and continued up to about 5 cycles after which the rate was fairly constant for a given set of conditions. The apparent cause of the increased rate is the formation of smaller particles by the cycling process. Surface area measurements showed this to be the case for Series I. Figure 6 illustrates the effect of surface area on the hydriding rate for runs 1-5. The surface area of the uranium powder for run 1 was not measured but was estimated from the surface area of the hydride powder.

Temperature Effect on Powder Hydriding

The effect of temperature on hydriding rates was evaluated in Series II. Six hydride-dehydride cycles were carried out on the sample at 100 °C and in 26.6 kPa of hydrogen. This treatment produced a constant surface area for the sample. Hydriding runs 12-17 were then made. Results of these runs are shown in Fig. 7 and Table II. A uniform surface was verified when run 17 reproduced run 12. It should be noted that the rate of reaction decreased with increasing temperature instead of increasing as normally expected. An Arrhenius plot of these data is shown in Fig. 8. Analysis of the Arrhenius equation,

$$K = Ae^{-A/RT} \quad (15)$$

resulted in a negative activation of -1.59 ± 0.24 kcal/mole.

Table III. Typical Results for the Hydriding of Uranium Powder

Run	Temp. °C	Press. kPa	n	k *	W_m mg/g
<u>Series I</u>					
1-734	100	13.3	0.7	2.02	12.40
2-735	100	13.3	0.6	2.39	12.23
3-736	100	13.3	0.6	2.55	12.25
4-737	100	13.3	0.6	2.62	12.12
5-738	100	13.3	0.6	2.87	12.15
<u>Series II</u>					
6-713	100	26.6	0.6	2.08	12.30
7-714	100	26.6	0.8	2.40	12.02
8-716	91	26.6	0.8	2.94	11.90
9-717	97	26.6	1.0	3.16	12.00
10-719	97	26.6	1.0	3.50	11.99
11-721	102	26.6	1.0	3.62	11.96
12-722	91	26.6	1.0	4.01	11.84
13-724	206	26.6	1.0	2.38	11.87
14-726	150	26.6	1.0	3.41	11.83
15-727	50	26.6	1.0	4.84	11.82
16-728	250	26.6	1.0	1.83	11.69
17-730	104	26.6	1.0	4.08	11.81

* Units for 2/3-order are $\text{mg}^{1/3} \text{g}^{-1/3} \text{min}^{-1}$; 1st-order units are min^{-1} .

FIGURE 6. Effect of surface area on uranium hydriding rates at 100°C in 13.3 kPa (100 Torr) of hydrogen. Solid points are experimental data and the open point was calculated from the hydride surface.

FIGURE 7. Effect of temperature on the hydriding of uranium powder in 26.6 kPa (200 Torr) of hydrogen.

FIGURE 8. Arrhenius plot of the 1st-order rate constants for uranium powder hydriding in 26.6 kPa (200 Torr) of hydrogen. The apparent activation energy was -1.59 kcal/mol.

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The negative activation energy which has been observed has no theoretical meaning. This type of behavior has, however, been observed before for uranium powder,^{1,2} wire,¹¹ and coupons.³ In experiments involving uranium wire and coupons, reaction rates were found to decrease with temperature only when the temperature exceeded about 225 °C.^{3,11} The cause of the unusual behavior at high temperatures is linked to the decomposition of uranium hydride. At temperatures above 225 °C, decomposition of uranium hydride makes the reverse reaction between uranium and hydrogen significant. Thus, the rate of hydriding above 225 °C is a complex function of temperature and hydrogen pressure.

At the low temperatures employed in this work, as well as that of Condon and Larson,¹ another factor must be involved. In both cases the reaction rates continued to increase as the temperature was decreased to as low as 0 °C in case of the Condon and Larson study. Hydrogen pressures were substantially above the decomposition pressure of the hydride so the reverse reaction would have little effect. In order to offer a possible explanation for the observed temperature behavior one can evaluate the temperature dependence of the possible rate controlling steps in the reaction presented in the discussion on reaction kinetics.

In the case of step (iii) the interface reaction rate between hydrogen and uranium will increase with an increase in temperature. The same can be said for step (ii). Furthermore, for the size of uranium particles employed the diffusion of hydrogen is so fast that it plays virtually no role in the reaction rate.¹² This leaves only step (i) to possess an inverse temperature dependence. According to the kinetic

theory of gases the number of molecules striking a surface per second is

$$\frac{dN}{dt} = \frac{P}{(2\pi mkT)^{1/2}} \quad (16)$$

where P is the pressure, m the mass, and T the temperature of the gas molecules. The actual rate of gas adsorption is influenced by the sticking probability, s, which increases with decreasing temperature.

Therefore, the rate of adsorption, r_a , becomes

$$r_a = s \frac{P}{(2\pi mkT)^{1/2}} \quad (17)$$

As the temperature increases the rate of adsorption decreases. If step (i) is rate controlling then the rate of reaction will also decrease with increasing temperature.

Reaction Order and Mechanism

In the case of the "phase boundary" reaction model the highest theoretical reaction order is 2/3. The "progressive conversion" model permits various reaction orders. For the series I experiments, carried out at 100 °C in 13.3 kPa hydrogen, the average reaction order predicted by Eq. 12 was 0.6. When the pressure was increased to 26.6 kPa the reaction order increased to 1.0 with repeated cycling of the sample. Thus, while pressure did affect the reaction order, temperature had no effect.

To compare the various kinetic equations and evaluate the two reaction models, data from two typical runs (2 and 10) were analyzed using Eq. 5, 7, 12, and 14. Applying Eq. 5, the Jander equation, resulted in an unsatisfactory fit to the data. This probably could be predicted since the present reactions were not diffusion controlled as required by the Jander model.

Run 2 was found to be 2/3-order by using the general reaction equation (Eq. 12) with a rate constant of $2.39 \text{ mg}^{1/3} \text{ g}^{-1/3} \text{ min}^{-1}$. When data from this run was fit with the 1st-order exponential equation (Eq. 14) the rate constant was 2.28 min^{-1} . Although the fit for Eq. 14 was good enough to be used to approximate the 2/3-order fit as was done by Condon and Larson,¹ the standard error was about twice as high. Equation 7 was also found to fit the data from run 2. The rate constant for the linear growth of the product layer was 0.652 min^{-1} . It should be noted that "phase boundary" and "progressive conversion" models produce two different 1st-order rate constants.

Run 10 was a 1st-order run as determined by Eq. 12. Both Eq. 12 and 14 fit the data very well over the entire course of the reaction. (Fig. 9) The rate constants were 4.0 min^{-1} using Eq. 12 and 3.98 min^{-1} using Eq. 14. These rates were 1.75 times greater than those for run 2. Results from using Eq. 7 are shown in Fig. 10. Again this equation fit the data well for about 95% of the reaction. The rate for run 10 was 0.827 min^{-1} which was only 1.3 times greater than the rate for run 2.

From the evaluation of the experimental runs one cannot positively select either the phase boundary or progressive conversion models as being the reaction mechanism. Equation 7 for the phase boundary model does not satisfactorily differentiate between the 2/3 and 1st-order reactions. This model does, however, explain the surface area dependence seen in the 2/3-order runs at 100 °C and 13.3 kPa hydrogen. Equation 12 for the progressive conversion model provides the best description of the entire reaction. If hydrogen diffusion throughout the particle is very fast, then this model may provide the best mechanism.

FIGURE 9. Predicted hydriding data from run 10#719 using equations 12 and 14 for a 1st-order reaction.

FIGURE 10. Application of equation 7 to the 1st-order reaction of run 10-719 in 26.6 kPa hydrogen at 97 °C and the 2/3-order reaction of run 2-735 in 13.3 kPa of hydrogen at 100 °C. The straight lines are the computer fits of the data.

Decomposition Kinetics

Compared to the amount of information on the formation of uranium hydride, information on the decomposition is negligible. Early work by Warf¹³ was inconclusive due to temperature and pressure variations. Destrian and Seriot¹⁴ reported an activation energy for UH_3 decomposition of 69.6 kcal/mol which they admitted appeared unusually high. More recently, Condon and Larson¹ found the dehydriding rate to be zero-order with an activation energy of 17.4 kcal/mol in the temperature range 70-200 °C.

Results from the present study were obtained over the temperature range 200 to 300 °C. Dehydriding was found to follow a zero-order rate process. The activation energy calculated from the Arrhenius plot in Figure 11 was $9.5 \pm .6$ kcal/mol. This value was considerably less than the 17.4 kcal/mol reported for the low temperature region 70 to 200 °C.¹ In order to verify the reliability of the present data results at 203 °C were compared with those of Condon and Larson.¹ The rate from this work was 4×10^{-6} gH₂/gU·sec compared to about 2×10^{-6} gH₂/gU·sec. At this one temperature both sets of data appear consistent.

There is no apparent process in the decomposition reaction that would account for two distinctly different activation energies. One possible explanation for the higher value at low temperatures stems from a problem in contamination control. Uranium hydride is extremely reactive. If it is exposed for periods of many hours, which would be required at temperatures of 70° to 100 °C, it will react with residual gases in the system. As the weight gain due to oxidation takes place, the apparent weight loss due to dehydriding decreases. The net result is a rate which is artificially

FIGURE 11. Arrhenius plot of the zero-order rate constants for dehydriding uranium hydride. The activation energy is 9.5 kcal/mol.

low. This entire process becomes less of a factor as temperatures are increased. An Arrhenius plot of data affected in such a manner would yield an activation energy which was erroneously high.

This proposed explanation does not contradict the previously proposed mechanism¹ for the effect of oxygen on hydriding and dehydriding. Hydrides formed in the presence of oxygen were found to have a higher dehydriding rate due to smaller crystallite sizes. Exposure of the hydride to oxygen after formation of the hydride and during dehydriding may be responsible for the apparent slow decomposition rate described above.

CONCLUSION

The hydriding of uranium powder was found to follow a 2/3-order rate in 13.3 kPa of hydrogen but increased to a 1st-order rate as the hydrogen pressure was increased to 26.6 kPa. Comparison of the phase boundary with the progressive conversion reaction models showed little difference between the two. The progressive conversion model did fit all of the data from 0-100% reaction. Increasing the temperature reduced the hydriding rate which can be predicted using a model with adsorption as the rate controlling step. This resulted in an apparent negative activation energy of 1.59 kcal/mol. Repeated hydriding/dehydriding cycles increased the surface area of the sample and also the reaction rate for the first five cycles. Subsequent cycling had little effect on the surface area. Dehydriding was found to be zero-order with an activation energy of 9.5 kcal/mol over the temperature range 200-300 °C.

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