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CALCULATIONS OF NONSPALLING ISOTHERMAL
HYDRIDING RATES FOR URANIUM

J. B. Condon

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ABSTRACT

Hydriding rates have been determined for uranium samples under conditions whereby parabolic or nearly parabolic rates prevail. The model used to calculate these rates has no adjustable parameters, is in fair agreement with the literature data, and may be used to predict the hydriding rate for uranium at any temperature, pressure, and sample thickness provided product spalling does not occur.

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SUMMARY

This study demonstrates that, for the hydriding of uranium samples, there are three types of rates possible, provided no spalling from the sample occurs: the parabolic; first-order; and the mixed parabolic, first-order rate laws. The choice of the rate law depends on sample thickness, temperature, and hydrogen pressure. A definitive guide for this choice is given.

For the mixed-rate law, dimensionally reduced equations are derived and some solutions to these equations are given. The dimensionally reduced equations are:

$$\frac{\partial^2 \gamma}{\partial \chi^2} = \frac{\partial \gamma}{\partial \tau} - \frac{\partial \mu}{\partial \tau}, \text{ and}$$

$$\frac{\partial \mu}{\partial \tau} = -\gamma \mu,$$

where:

$$\tau = k C_0 t,$$

$$\gamma = C/C_0,$$

$$\mu = 3 U/C_0, \text{ and}$$

$$\chi = x \sqrt{k C_0 / D}.$$

In these expressions

t represents the real time,

x the real distance into the sample,

k a known first-order rate constant,

C₀ the atomic hydrogen solubility in uranium (by Sieverts' relation),

C the atomic hydrogen concentration,

D the diffusion coefficient of hydrogen in uranium, and

U the local uranium inventory.

The corresponding boundary conditions are:

$$\gamma(\chi, \tau = 0) = 0, \text{ and}$$

$$\gamma (\chi = 0, \tau) = \gamma (\chi = \lambda, \tau) = 1 .$$

$$[\lambda = l \sqrt{k C_0 / D} \text{ (l represents the sample thickness)}]$$

From these equations, a series of generalized curves are derived for the hydriding kinetics.

For the parabolic rate law, comparisons were made to hydriding rates reported in the literature, and fair agreement was obtained.

INTRODUCTION

A method to calculate the hydriding rates of experimental-size uranium samples has been suggested in a previous article.⁽¹⁾ This report presents the results of such calculations for two general cases: (1) the parabolic rate case, and (2) the case for samples too thin to exhibit parabolic rates and too thick to exhibit the first-order rates observed on powders. A third very important case, the linear rate, will be presented in a separate report.

The two cases just enumerated, along with the first-order rate, are all derived from the same set of equations. The assumptions made are merely the absence of spalling and isothermicity in the sample. It would be expected that both assumptions are best for small samples and high temperatures. There are no variable parameters in the model, since all the needed physical parameters have been measured. These parameters include: the first-order rate constant,⁽¹⁾ the diffusion coefficient of hydrogen in uranium,^(2,3) and the solubility of hydrogen in uranium.^(2,3) The set of equations used completely describe the reactant-phase-diffusion mechanism, and the boundary conditions are simple compared to the linear-rate case.

CALCULATIONS OF URANIUM HYDRIDING RATES

It has been demonstrated⁽¹⁾ that the kinetics of the uranium-hydrogen reaction is first order with respect to both uranium and dissolved atomic hydrogen. This law may be utilized, however, only if the thickness of the uranium sample is small enough to neglect the diffusion of hydrogen. On thicker samples, the simultaneous differential equations:

$$D\nabla^2 C = \frac{\partial C}{\partial t} - 3 \frac{\partial U}{\partial t}, \text{ and} \quad (1)$$

$$- \frac{\partial U}{\partial t} = kCU, \quad (2)$$

must be solved to obtain the proper rate. Here, C represents the atomic hydrogen concentration, U the normalized uranium content, D the diffusion coefficient, t the time, and k the first-order rate constant. Calculations will be restricted here to the two-sided plate problem which reduces ∇^2 to $\partial^2/\partial X^2$ and yields the boundary conditions:

$$C(X, 0) = 0, \quad (3)$$

$$C(0, t) = C(l, t) = C_0, \text{ and} \quad (4)$$

$$U(X, 0) = 1, \quad (5)$$

where l again represents the plate thickness and C_0 the interstitial solubility of hydrogen. C_0 is determined by the hydrogen pressure and the absolute temperature. The values for k , C_0 , and D have been determined experimentally and are given by:

$$k = 10.4 \exp(1592/T) \text{ sec}^{-1}, \quad (6)$$

$$C_0 = 5.58 \times 10^{-4} \exp(894/T) P^{1/2} \text{ (mole H/mole U)} \quad (7)$$

(with P in Pa), and

$$D = 1.9 \times 10^{-6} \exp(-5820/T) \text{ m}^2/\text{sec}. \quad (8)$$

The temperature, T , enters into both Equations 1 and 2 by way of D and k . Since the dependence on T of both of these parameters is known, this fact effectively reduces two parameters to one by dimensional arguments. A further reduction in the parameters involves considering only the integral:

$$\int (1-U) dV. \quad (9)$$

This expression provides the integral over the entire sample of the amount of uranium consumed. In the one-dimensional case, this expression is the definition of the penetration of the reaction into the sample. This integral divided by the plate thickness is, therefore, the definition of the extent of the reaction and is usually what is followed experimentally. The reaction behavior can be described by following this integral as a function of the three

parameters: C_0 , T , and t . A further reduction in descriptive parameters will be dealt with later with the use of dimensionally reduced equations.

The only way to solve the equations just given is by numerical methods. There are two extremes, however, for which these equations may be simplified: One is the case where diffusion is very rapid with respect to the first-order rate equation. Under such circumstances, Equation 1 may be ignored and the rate becomes:

$$-\frac{dU}{dt} = k C_0 U; \text{ or, in terms of the penetration rate:} \quad (10)$$

$$\int (1-U) dx = X_I(t) = l (1 - e^{-k C_0 t}). \quad (11)$$

The second extreme case is the parabolic rate law where permeability is the rate-controlling factor. This extreme is not precisely derivable and must be checked by numerical calculations. It has been found that for the two-sided plate problem, the penetration rate, $X_{II}(t)$, is given by:

$$X_{II}(t)^2 \approx 2 D C_0 t. \quad (12)$$

The constant, k , of Equation 2 affects this relationship slightly. For example, calculations made at 350° C indicate that as k approaches infinity, the parabolic rate constant approaches approximately $3DC_0$.

The two preceding rates may be expressed as:

$$\frac{d X_{II}(t)}{dt} = \frac{D C_0}{x} = \left(\frac{D C_0}{2t} \right)^{1/2}, \text{ and} \quad (13)$$

$$\frac{d X_I(t)}{dt} = k C_0 e^{-k C_0 t} = k C_0 (1-x). \quad (14)$$

Since the rate-limiting step is always the lower of the two rates, $X_{II}(t)$ is never rate limiting at either $t = 0$ or $t = \infty$. At $t = \infty$, this limiting is necessary since the parabolic rate law would allow a continuance of the reaction in spite of the limited thickness, l , available. $X_I(t)$ is therefore the rate-controlling law unless there are points at which:

$$\frac{d X_I(t)}{dt} = \frac{d X_{II}(t)}{dt}. \quad (15)$$

Therefore, setting these two equations equal and solving for x , these points are obtained as:

$$x = 1/2 (l \pm \sqrt{l^2 - 4 D/k}). \quad (16)$$

And, it may be concluded that the mechanism may convert to $X_{II}(t)$ if and only if:

$$l > 2 (D/k)^{1/2} . \quad (17)$$

There is, therefore, a critical thickness below which only the first-order rate applies. This critical distance will be designated by l_{CI} and is given by:

$$\begin{aligned} l_{CI} &= 2 (D/k)^{1/2}, \text{ or} \\ l_{CI} &= 8.55 \times 10^{-4} \exp (-3706/T) , \end{aligned} \quad (18)$$

from Equations 6 and 8.

The applicability of only $X_{II}(t)$ depends on how much of the reaction occurs between the two points given by Equation 16. The criterion is somewhat arbitrary, but a conservative view would require 98% of the reaction to occur between these two points. Designating "f" to be the fraction of the reaction before the first crossover point, then:

$$x = fl = 1/2 (l - \sqrt{l^2 - 4D/k}); \text{ and, solving for } l: \quad (19)$$

$$l \geq \frac{1}{\sqrt{f(1-f)}} (D/k)^{1/2} . \quad (20)$$

For the 98% criterion, $f = 0.01$, and there will be a second critical thickness, l_{CII} , above which the pure parabolic rate applies. This thickness is given by:

$$l_{CII} = 10(D/k)^{1/2} = 4.14 \times 10^{-3} \exp (-3706/T). \quad (21)$$

Expression 21 blocks out two regions where the calculation of the rate of hydriding is simply obtained. One of these regions is when the thickness is less than l_{CI} of Equation 18 and is the first-order rate of Equation 10; the second region is for thick samples (ie, with a thickness greater than l_{CII} of Equation 21) for which the parabolic law approximated by Equation 9 should do well. This treatment leaves a range of thicknesses given by:

$$8.55 \times 10^{-4} \exp (-3706/T) < l < 4.4 \times 10^{-3} \exp (-3706/T) , \quad (22)$$

for which calculations are necessary.

Equation 22 suggests that it should be possible to make a calculation at one temperature and thickness and the resulting curves could be applied to other related temperatures and thicknesses. That is, the simultaneous Equations 1 and 2 may be dimensionally reduced with a subsequent disturbance in the boundary conditions.

Letting:

$$\tau = kC_0 t , \quad (23)$$

$$\gamma = C/C_0, \quad (24)$$

$$\mu = 3U/C_0, \text{ and the coordinate change:} \quad (25)$$

$$\bar{\chi} = \sqrt{kC_0/D} \bar{x} \quad (26)$$

(one dimension, $\chi = \sqrt{kC_0/D} x$),

gives:

$$\nabla^2 \gamma = \frac{\partial \gamma}{\partial \tau} - \frac{\partial \mu}{\partial \tau}, \text{ and} \quad (27)$$

$$-\frac{\partial \mu}{\partial \tau} = -\gamma \mu, \quad (28)$$

with the operator, Δ^2 , in terms of the coordinates, $\bar{\chi}$, and is $\partial^2/\partial \chi^2$ in the one-dimensional case. The boundary conditions 3, 4, and 5 become:

$$\gamma(\chi, 0) = 0, \text{ and} \quad (29)$$

$$\gamma(0, \tau) = \gamma(\lambda, \tau) = 1, \quad (30)$$

where:

$$\lambda = \sqrt{kC_0/D} l = l P^{1/4} (55.3 \exp(3259/T)), \text{ and} \quad (31)$$

$$\mu(\chi, 0) = 3/C_0 = 5376 \exp(894/T) P^{-1/2} = \mu_0 \quad (32)$$

(with P in Pa).

A criterion similar to Equation 22 can be given in terms of γ and μ_0 which is:

$$3.439 < \lambda \mu_0^{1/2} < 16.623. \quad (33)$$

The advantage of this method can be seen by the plots of the range and domain of the transformation given in Figures 1 and 2. The transformation reduces the region of concern from a three-dimensional zone of complex shape to a relatively simple two-dimensional zone. Many of the calculations that would be made using the three-dimensional zone would actually be redundant. Furthermore, the calculations also can be broken down into families of curves of common μ_0 and dissimilar calculation cut-off points of differing λ , which allows for relatively easy interpolations for cases not specifically calculated.

It turns out that the literature is devoid of experimental data in the range specified by Equation 33 (and 22). The most convenient experiments in this range would be on thin films at low pressures. Some families of curves are, therefore, given in Figure 3 (a through e). The actual curve of interest may be obtained from these curves by calculations using Equations 23 through 26.

The experimental data available is either linear or parabolic; the latter is of interest here. From numerical calculations it is apparent that, for the extreme parabolic case, the rate constant is approximately $3C_0D$. As an example, the calculation for a 0.15-mm-thick sample at 300°C and 32 kPa yielded a rate of $2.7 C_0D$. The γ and μ corresponding to this calculation are 0.28 and 4.58×10^6 , respectively. According to Figure 2, this result is well within the parabolic realm.

The term $P^{1/2}$ appears in the theoretical rate as a simple multiplicative constant. Therefore, rates that are obtained at different hydrogen pressures may be compared directly with theory by dividing both by $P^{1/2}$. The two sets of data obtained by investigators Alire, et al⁽⁴⁾ and Albrecht and Mallett⁽⁵⁾ are presented this way in Figure 4. Both experimenters' conditions were such that they were in the parabolic realm. The theoretical rate using diffusion data by Mallett⁽³⁾ is also shown. Comparison of the predicted-to-actual rate is not too bad considering the fact that spalling should be quite prevalent under the

Figure 1. THE REGION IN SAMPLE THICKNESS, l , PRESSURE, P , AND TEMPERATURE, T , IN WHICH CALCULATIONS MUST BE DONE TO DETERMINE HYDRIDING RATES.

Figure 2. THE SAME REGION AS IN FIGURE 1 IN WHICH A CALCULATION NEEDS TO BE MADE, ONLY EXPRESSED IN TERMS OF THE DIMENSIONLESS QUANTITIES λ AND μ .

(a) $\mu_0 = 10^3$; $\lambda = 0.5, 0.3, 0.2, 0.1$.

(b) $\mu_0 = 10^4$; $\lambda = 0.16, 0.1, 0.05, 0.03$.

(c) $\mu_0 = 10^5$; $\lambda = 0.05, 0.03, 0.02, 0.01$.

(d) $\mu_0 = 10^6$; $\lambda = 0.016, 0.01, 0.005, 0.003$.

(e) $\mu_0 = 10^7$; $\lambda = 0.005, 0.003, 0.002, 0.001$.

Figure 3. FAMILIES OF CURVES OF VARIOUS λ AND μ_0 QUANTITIES FOR THE CALCULATED $\int (\mu_0 - \mu) dx$, OR "DIMENSIONLESS PENETRATION", AS A FUNCTION OF t , OR "DIMENSIONLESS TIME".

Figure 4. COMPARISON OF PREDICTED VERSUS EXPERIMENTAL RATES IN THE PARABOLIC REALM. (Diffusion Coefficients by both Mallett⁽³⁾ and Davis⁽⁶⁾ are Used)

conditions stated. Thus, the experimental rates should be at least as fast as the predicted rate. Indeed, it is surprising that linear rates were not obtained on the samples used. If thinner samples were used, the agreement might prove better.

CONCLUSIONS

For the hydriding rates of uranium samples, the realms for parabolic, first-order, and mixed rates are presented along with families of curves of the mixed rates. It can be quickly ascertained in what realm the hydriding rate belongs from the particular conditions of temperature, pressure, and sample thickness. If the rate belongs to the mixed realm, a few representative curves are available to back calculate what the hydriding rate should be. To get an exact answer, however, the actual numerical calculation is necessary.

The usefulness of the information in this report is not so much in explaining past literature data but rather in planning future experiments. Prior to running an experiment, a check should first be made to see if the mixed rate would apply (as would be the thin-film case).

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