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Author(s): Roberta N. Mulford and
Damian C. Swift

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Los Alamos
NATIONAL LABORATORY

Formation of Plutonium Hydride PuH_2: Description of the Reaction Rate Surface as a Function of Pressure and Temperature

Roberta N. Mulford, *NMT-15 Los Alamos National Laboratory*
Damian C. Swift, P-24 *Los Alamos National Laboratory*

The hydriding reaction of plutonium metal is used increasingly in the recovery and processing of plutonium. There is thus an increased need for an understanding not only of the thermodynamic parameters governing the reaction, but also of the kinetic behavior to be expected with variations in process parameters such as pressure and temperature. A mathematical description of the behavior of the hydriding process in the entire reaction space in P, T, and rate provides a predictive capability, and enables the reaction rate to be optimized. In addition, given a well-defined description of this rate surface as a function of pressure and temperature, process parameters may be selected to optimize other important parameters such as particle size. These parameters may in some cases be mapped as regions or separate functions onto the surface described here.

We examined published data on the hydriding rate for Pu, and developed a functional form for the rate in terms of the pressure and temperature state of the system. A function describing the rate as a function of both pressure and temperature simultaneously was required to fit all the available data. Treatment of data as a function of temperature alone, i.e. a projection of the data on an isobaric surface, indicates a dependence on temperature that exhibits a large amount of scatter, and does not indicate any particular functional dependence.

see Figure 1

The function used to describe the data is :

$$k_{hyd}(p,T) = \alpha \frac{\alpha}{\beta p^{-1/2} + \gamma} \left(1 - \frac{T}{T_{eqm}} \right)^{1/m}$$

where

$$T_{eqm} = \frac{8165}{10 - \log_{10} p} - 273, {}^{o}C$$

and $\alpha = 1.1$, $\beta = 1/k_2 K_{1/2} = 0.7608476$ ($\text{min.torr}^{1/2}$), $\gamma = 1/k_2 = 1/2.69$ (min), $m = 2.5$.

The function selected was provided with an adjustable curvature in temperature by choosing an algebraic form with a fitting parameter $1/m$. This approach provides a practical empirical fit to the data: no information on the activation energy of the reaction was inferred from this functional form. The function was bounded in the P vs. T plane and in the rate vs. P plane by known functions published previously. [1,2] The function describing rate as a function of pressure given in reference 2 is seen to require a slight correction, about 10%, as it was determined from data at various temperatures projected onto an isothermal plane.

see Figure 2

The actual dependence of rate on temperature is expected to have an Arrhenius-like form, $\exp(-E_a/RT)$ rather than the power-law function chosen. The feasibility of this form is discussed, and the quality of fit to known data described. Participation of a second species, PuH_3, in the reaction was examined and determined to require a minor extension to the model presented.

The reaction is seen to exhibit a rather weak ($1/m = \sim 1/2$) dependence on temperature. Near the equilibrium line where k [forward] = ~ k [reverse], the rate obviously decreases rapidly toward zero. The variation of rate with pressure is seen to be very strong in the low pressure region where surface coverage by hydrogen dominates the reaction rate, a behavior well-described in the literature.[2] The thermal behavior probably indicates a mechanism in which transport plays a major role.

The application of this function to a hydride-dehydride recovery process provides a useful description of the behavior of the system during the onset of hydriding, a transient period during which the reaction heats the system and temperature may fluctuate. This portion of any process is difficult to control or monitor, due to the relatively rapid changes occurring in the system.

The function described provides a useful tool for practical application and manipulation of the hydriding reaction. Description of the system in terms of Arrhenius rates yields some information on the activation energies of the system.

[1] R.N.R. Mulford and G.E. Sturdy, J. Am. Chem. Soc., **77,** 3449 (1954).

[2] J.L. Stakebake, J. Electrochem. Soc. **128,** 2383 (1981).

Figure 1. Dependence of rate k on temperature in degrees C.

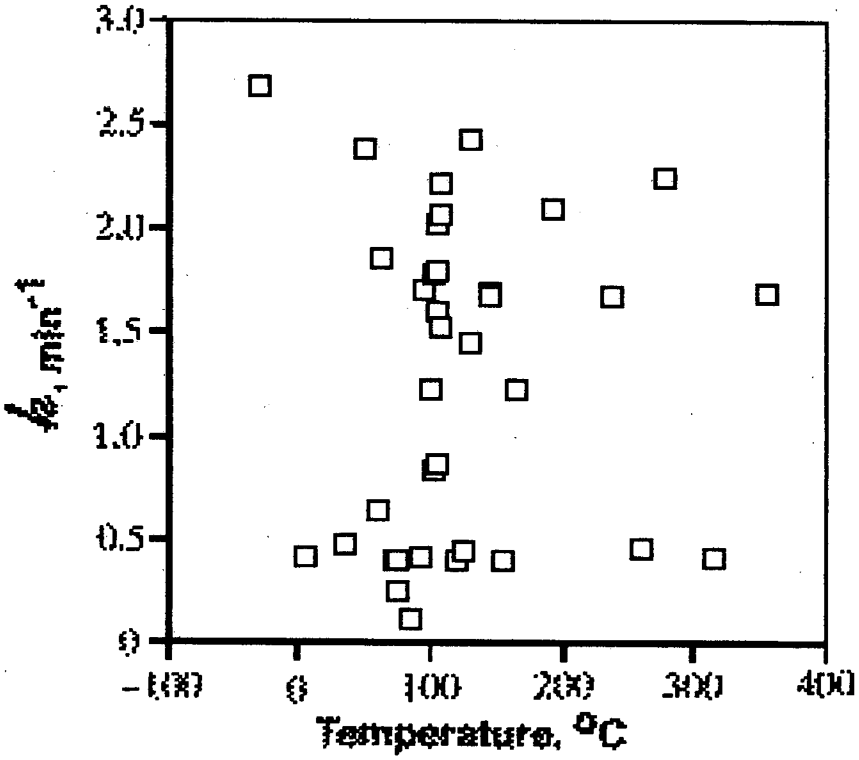

Figure 2. A view of the surface described by Equation 1 in P, T, and rate (k) space.