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DECOMPOSITION KINETICS OF PLUTONIUM HYDRIDE

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INTRODUCTION

Actinide hydrides are frequently employed as intermediates for preparing the nitrides or the powdered metals and, therefore, are particularly important compounds of elements employed as nuclear fuels. Of the three actinides (Th, U, Pu) of interest to the nuclear-reactor industry, the least is known about the properties of the plutonium-hydrogen systems.

Earlier studies have shown that the complex behavior of plutonium closely resembles that of the lanthanides in that it reacts with hydrogen to form a CaF_2-type dihydride, a cubic hydride of variable composition between PuH_2 and PuH_3, and a LaF_3-type trihydride.(1-3) Thermodynamic data based on PTX equilibrium measurements have been included in these reports, but kinetic data for plutonium hydride, PuH_x, are quite limited. Rate data have been reported for the reaction of massive and powdered Pu.(4-6) The absence of kinetic data for the decomposition process is somewhat surprising, since the only practical method for preparing powdered plutonium is based on thermal decomposition of the hydride.(7,8) The present study was undertaken to investigate the dissociation kinetics of PuH_x both in the two-phase region ($0<X<1.95$) and in the nonstoichiometric region ($1.95<X<3.0$).

EXPERIMENTAL

Electrorefined α-phase plutonium (461 wppm impurity) and δ-stabilized plutonium with 1.0 wt % Ga were used in these tests. The Ga alloy, which contained 0.13 wt % impurities, was used exclusively

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after initial tests demonstrated that the hydrides from alloyed and unalloyed samples behaved identically. Ultra-pure hydrogen used in the experiments was purified with UH_3. PuH_x was prepared and dehydrided in Al or quartz buckets on two vacuum microbalance systems, a Cahn Model RG and a Cahn Model 100. H_2 was admitted to the systems at controlled temperatures and pressures to form PuH_x samples in the range $2.7<X<3.0$. The mass of H_2 evolved during thermal decomposition was measured as a function of time, temperature and H_2 pressure.

RESULTS AND DISCUSSION

The Pu-$PuH_{1.95}$ Region

Equilibrium Measurements. Static equilibrium pressure data were measured in a temperature range (349-498 °C) which was below the 600-800 °C range of the previous study.(2) Results show that the equilibrium hydride composition is approximately $PuH_{1.95}$ and that the vaporization reaction is best described by Eqn. 1.

$$1.026\ PuH_{1.95}(s) \rightarrow 1.026\ Pu(s) + H_2(g). \qquad (1)$$

The least squares refinement of the ℓnP (H_2, torr) vs $1/T$ data yields a slope of (-19150 ± 850) and an intercept of (22.9 ± 1.21). For Eqn. 1, $\Delta H^\circ_{697} = 38.1 \pm 1.7$ kcal/mol and $\Delta S^\circ_{697} = 32.3 \pm 1.7$ cal/deg mol. The enthalpy of formation calculated for $PuH_{1.95}$ at 697K, -37.1 ± 1.7 kcal/mol, is in excellent agreement with the results reported by Mulford and Sturdy(2) for the hydride prepared from α-plutonium.

Kinetic Measurements. Decomposition rates for $PuH_{1.95}$ were obtained from linear mass-loss isotherms. Since the decomposition rates defined by their slopes are independent of the $PuH_{1.95}$ to Pu ratio, the kinetics of the reaction are best described as zero order. An evaluation of the data obtained with both balance systems show that the absolute decomposition rate, K, is influenced by vacuum system conductance, sample container material, and sample configuration. For a given set of conditions, the rates measured for hydride prepared from α-Pu were in excellent agreement with those of samples prepared from the δ-stabilized alloy. K is apparently independent of the hydride surface area, which varied from 0.10 to 0.30 m^2/g. The effects of temperature and vacuum system conductance are shown by the Arrhenius results in Fig. 1. The data points indicated by open circles were obtained with the vacuum system at maximum conductance; those marked by solid symbols were obtained with the system at a reduced conductance. Although the absolute rate is reduced by decreasing the pumping speed, the energies of activation are identical. The average E_a obtained from the data sets in Fig. 1

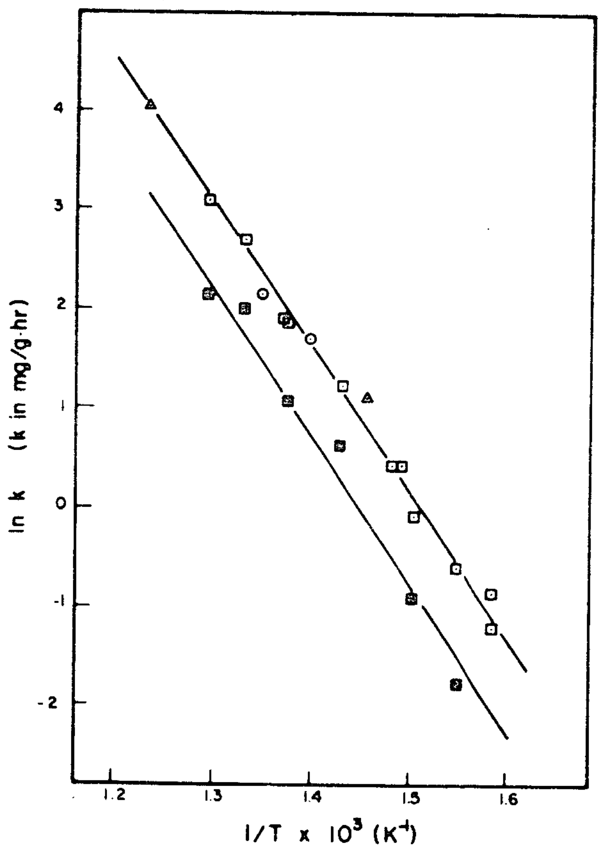

Figure 1. Arrhenius results for the decomposition of $PuH_{1.95}$.

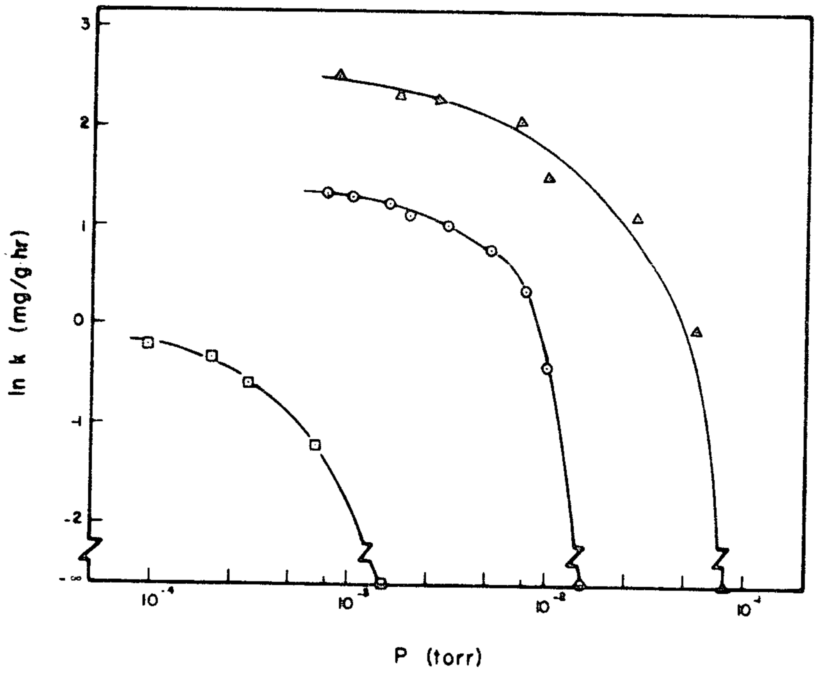

Figure 2. The dependence of the decomposition of $PuH_{1.95}$ on the H_2 pressure.

and from a third set obtained with the second balance system is 27.3 ± 1.4 kcal/mol.

Since the hydrogen pressure in a system with fixed conductance inherently increases with decomposition temperature or decomposition rate, the data in Fig. 1 were not measured at the same pressure. The results of tests to determine the effects of residual hydrogen pressure on the rate are shown in Fig. 2 for three temperatures within the test range. As the residual hydrogen pressure, P, approaches the equilibrium value, P_o, at $\ell nk = -\infty$, the rate is sharply reduced. Since all the data were measured in pressure insensitive ranges where $P \leq 0.1P_o$, we believe that the reported E_a is in good agreement with the hypothetical isobaric value.

The data in Fig. 2 have been employed to determine the pressure dependence of the decomposition rate for the relative pressure range $0.2 < P/P_0 < 0.6$. Linear least-squares refinements of the isothermal rate data using the logarithmic form of the equation $K = AP^n$ follow. At 366, 414 and 460 °C, the observed values of n are (-0.48 ± 0.13), (-0.49 ± 0.07) and (-0.55 ± 0.10), respectively; the corresponding ℓnA values are (-4.49 ± 1.16), (-2.02 ± 0.43) and (-1.03 ± 0.50). It is obvious that K is inversely proportional to the square root of the hydrogen pressure. If the temperature dependence of A is included, the general equation for decomposition is given by Eqn. 2 for T in the range 366-460°, P in torr and K in mg/g hr.

$$K = (0.00367\ ^\circ C - 1.349)P^{-1/2} \qquad (2)$$

The Nonstoichiometric Hydride

Kinetic Measurements. The time dependence of composition isotherms for the nonstoichiometric range $(X>1.95)$ are shown in Fig. 3. Zero time for each isotherm (cf. the temperature listed above each curve in Fig. 3) was marked by attainment of a dynamic hydrogen pressure less than 10^{-3} torr. The assymptotic approach of the lower temperature isotherms to essentially constant values coincides with attainment of a constant residual pressure. The 305° isotherm shows that the composition changes rapidly until a constant X-value of 1.95 is reached. At temperatures ≥389°, X changes so rapidly that only linear rates of the two-phase region can be accurately measured.

The temperature dependence of the decomposition rate in the non-stoichiometric range has been quantified using graphically determined slopes of the isotherms along constant-composition sections of Fig. 3. The decomposition reaction for the hydride in the solid solution region $(X>1.95)$ is described in Eqn. 3.

$$PuH_X(s.\ soln.) \rightarrow Pu\ (s.\ soln.) + X/2\ H_2(g). \qquad (3)$$

Use of the formulation "Pu (s. soln.)" implies that the condensed product is a hydride that is more metal-rich than the reactant. Values of E_a (in kcal/mol) obtained by Arrhenius analysis of the rate data at constant X-values are: 26.0 at 2.10; 20.5 at 2.20; 17.5 at 2.30; 11.2 at 2.40; 8.3 at 2.50; and 7.8 at 2.60. These results show that E_a is inversely proportional to X over the accessible composition range.

Preparative Methods. Another result derived from the decomposition isotherms in Fig. 3 is important to the preparative chemistry of the nonstoichiometric hydride. For the 25-250 °C range, a graph of the terminal composition vs. isotherm temperature is linear with a slope of ($-3.300 \pm 0.007 \times 10^{-3}$ X-units/°C) and an intercept of (2.78 ± 0.01). Compositions are accurately predicted by this relationship only if the PuH_x is freshly prepared.

CONCLUSIONS

A closer examination of the kinetic data for decomposition of $PuH_{1.95}$ provides insight into a possible mechanism for the hydriding and dehydriding reactions of plutonium. The fact that the rate of the hydriding reaction, K_H, is proportional to $P^{1/2}$(5,6) and the rate of the dehydriding process, K_D, is inversely proportional to $P^{1/2}$ suggests that the forward and reverse reactions proceed by opposite paths of the same mechanism. The $P^{1/2}$ dependence of hydrogen solubility in metals is characterestic of the dissociative absorption of hydrogen;(9) i.e., the reactive species is atomic hydrogen. It is reasonable to assume that the rates of the forward and reverse reactions are controlled by the surface concentration of atomic hydrogen, $[H_s]$, that $K_H = c'[H_s]$, and that $K_D = c/[H_s]$, where c' and c are proportionality constants. For this surface model, the pressure dependence of K_D is related to $[H_s]$ by the reaction $[H_s] \rightleftarrows 1/2\ H_2(g)$ and by its equilibrium constant $K_e = [H_2]^{1/2}/[H_s]$. In the pressure range of ideal gas behavior, $[H_s] = K_e^{-1}(RT)^{-1/2}$ and the decomposition rate is given by $K_D = cK_e(RT)^{-1/2}P^{1/2}$. For an analogous treatment of the hydriding process with this model, it can be readily shown that $K_H = c'K_e^{-1}(RT)^{-1/2}P^{1/2}$. The inverse pressure dependence and direct temperature dependence of the decomposition rate given by Eqn. 2 are correctly predicted by this mechanism which we believe is most consistent with the observed behavior of the Pu-H system.(10)

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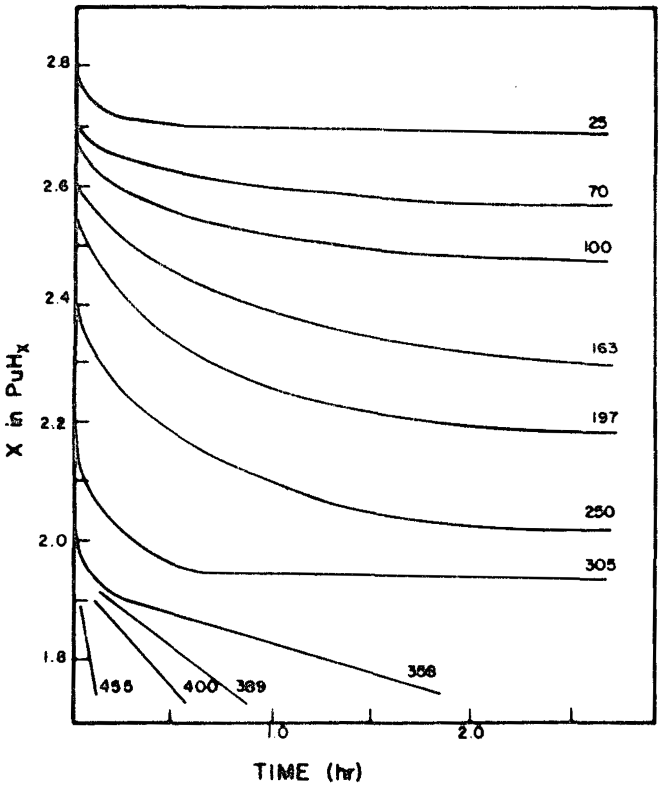

Figure 3. Decomposition isotherms of nonstoichiometric PuH$_X$.

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