

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Plutonium-Hydrogen System. I. Plutonium Dihydride and Dideuteride¹

BY ROBERT N. R. MULFORD AND GLADYS E. STURDY

RECEIVED DECEMBER 30, 1954

Pressure-temperature-composition data are presented for the plutonium-hydrogen and plutonium-deuterium systems in the composition ranges Pu-PuH₂ and Pu-PuD₂. The heats of formation of PuH₂ and PuD₂ are calculated from the pressure-temperature data and are given as: Pu + H₂(g) → PuH₂(s)², Δ*H* = -37.4 ± 1.2 kcal.; Pu + D₂(g) → PuD₂(s)², Δ*H* = -35.5 ± 0.7 kcal. Equations for the decomposition pressure-temperature relationships are given as: for PuH₂, log₁₀ *P* (mm.) = 10.01 ± 0.32 - (8165 ± 263)/*T*(°K.); for PuD₂, log₁₀ *P* (mm.) = 9.71 ± 0.19 - (7761 ± 151)/*T*(°K.). The data and equations cover the temperature ranges 400-800° for PuH₂ and 600-800° for PuD₂.

Introduction

Work on the plutonium-hydrogen system by Johns³ showed the existence of a two-solid phase composition range between Pu and PuH₂. For compositions between PuH₂ and PuH₃, a solid-solubility range was found where a single solid phase existed.

It seemed desirable to repeat some of Johns' work using purer plutonium than was available to him, and to obtain more data in order to calculate the heats of formation of the hydride and deuteride more accurately. The present paper confirms Johns' results as regards the formation of PuH₂ and PuD₂, extends the temperature range of his results considerably, and provides what are believed to be more accurate values for the heats of formation.

Experimental

The measurements were made in a glass vacuum system consisting of a gas buret, sample bulb, combined mercury manometer and McLeod gage, and a bulb containing uranium hydride or deuteride to serve as a source of pure hydrogen or deuterium. The system was so designed as to avoid the presence of stopcocks wherever possible. In particular, there were no stopcocks in the gas buret, sample bulb and manometer part of the system, so that during the experiments there was no possibility of leakage or contamination of the gas phase.

A sample of plutonium metal was contained in a crucible in the silica sample bulb surrounded by a controlled furnace. Sample temperature was measured with a calibrated Pt/Pt-13-Rh thermocouple in a thermocouple well on the silica bulb. Because of the tendency for hydrogen to diffuse through silica at high temperatures, the temperature of the sample bulb was never raised above 800° with hydrogen inside. Tests showed that hydrogen loss at 800° under the conditions of the experiment was negligible. The quantity of hydrogen admitted to the sample bulb was measured in the gas buret which was water jacketed for constant temperature. A cathetometer was used to read mercury levels. The accuracy of measurement of a quantity of hydrogen with this buret was about ±0.2%. Pressure of hydrogen over the sample was measured with the combined manometer and McLeod gage, the manometer being used for pressures of 3 mm. or more, and the McLeod gage for lower pressures. Pressures on the manometer were read to ±0.1 mm., and to about ±1% on the McLeod. Composition values are estimated to have a maximum error of ±0.01 atom-ratio unit for the data in Figs. 1 and 2. Temperatures are within ±1°, which produces a ±2% uncertainty in the plateau pressure values. A suitably large sample of metal was used so that the quantity of hydrogen in the gas phase was only a small fraction of the total hydrogen in the system. An experimental error in the calculated quantity of gaseous hydrogen thus had a small effect on the calculated solid composition, so that most of the error in the solid composition

figures was due to error in measurement of the total quantity of hydrogen put into the bulb from the gas buret.

Hydrogen or deuterium was obtained from the thermal decomposition of UH₃ or UD₃. Mass spectrometer analysis of such hydrogen has shown the major impurity to be 0.02% nitrogen.

The plutonium had a nominal purity of 99.60 atomic percent., obtained by subtracting from 100% the total of amounts of elements other than plutonium found in analyses for each element. It is not possible to predict accurately the effect of metal purity on the compositions given in Figs. 1 and 2, since it is not known how the impurities are involved in the reaction of the plutonium with hydrogen. A rough estimate may be made, however, that the error introduced into the composition calculations by impurities in the metal is of the order of 0.5%, which is about the same as the experimental error in measuring composition.

A large part of the data is at temperatures above the melting point of plutonium, and it was necessary to contain the sample in a crucible of some refractory inert to molten plutonium, hydrogen and PuH₂. Calcium oxide crucibles were found to be satisfactory. The sample bulb was arranged so as to enable the crucible to be outgassed in place, after which the vacuum was broken with dried, CO₂-free air and the top of the bulb blown open. A cleaned piece of plutonium was then dropped into the crucible and the top of the bulb sealed off with little chance for gas pickup by the crucible. After insertion into the system, the metal samples were outgassed in place by slow heating to 850° while maintaining a vacuum of 10⁻⁶ mm.

Some test of whether the data represented equilibrium was necessary. The test used was to approach the pressure value of a particular *P-T-C* point from both higher and lower pressures at constant temperature and composition. This was done by starting the test at a higher or lower temperature (and hence higher or lower pressure), setting the furnace to control at the temperature desired, and observing the changes of pressure and temperature with time. When achievement of equilibrium was slow, the sample reached constant temperature before a constant pressure was reached, and it was then possible to follow change of pressure with time at constant temperature. As the pressure changed, the composition of the condensed phases also changed slightly so that the test was not entirely ideal. But it did provide some assurance that equilibrium conditions were being realized, and also provided information as to the times required to reach equilibrium at various temperatures. Several of the points on each of the plateaus in Fig. 1 were checked in this manner, and the pressures were found to be reproducible from both above and below.

The pressure-temperature-composition data were obtained by holding the sample at constant temperature long enough for the system to come to equilibrium, using the test described above to ensure that equilibrium conditions were being attained.

It was not possible to pre-set the furnace controller to the exact isotherm temperatures, so that the actual data were obtained at temperatures slightly higher or lower than desired. This necessitated small interpolations on a pressure-temperature plot to correct the pressures to the isotherm temperatures. The observed pressure values were plotted as log *p* vs. reciprocal absolute temperature to permit straight line interpolation of the pressures to the desired isotherm temperatures. The extent of such interpolation was seldom greater than 5°. Compositions of the condensed phase of the system were calculated for each temperature and pressure by assuming that the quantity of hydrogen in

(1) Work done under the auspices of the AEC.

(2) The plutonium and plutonium hydride or deuteride indicated in the equations are actually saturated solutions of hydrogen or deuterium in plutonium and plutonium in PuH₂ or PuD₂, respectively. The saturation solubilities vary with temperature.

(3) I. B. Johns, MDDC 717, September 14, 1944.

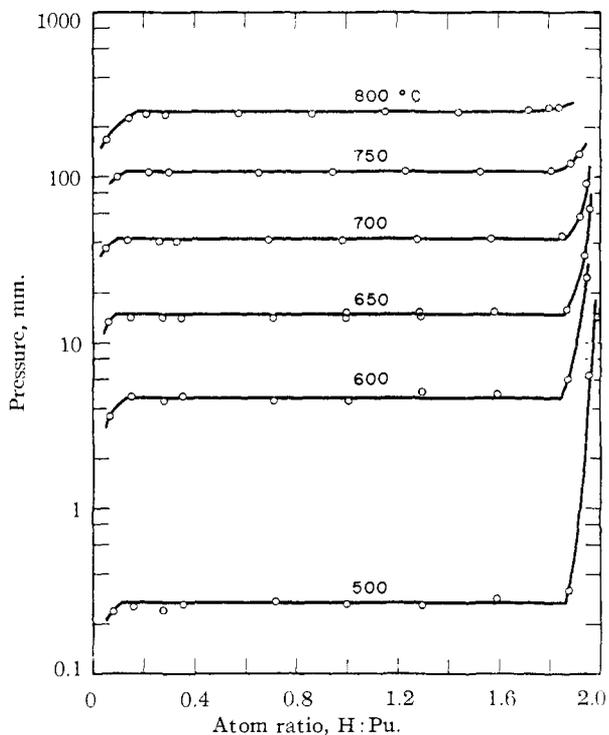


Fig. 1.—Hydride isotherms.

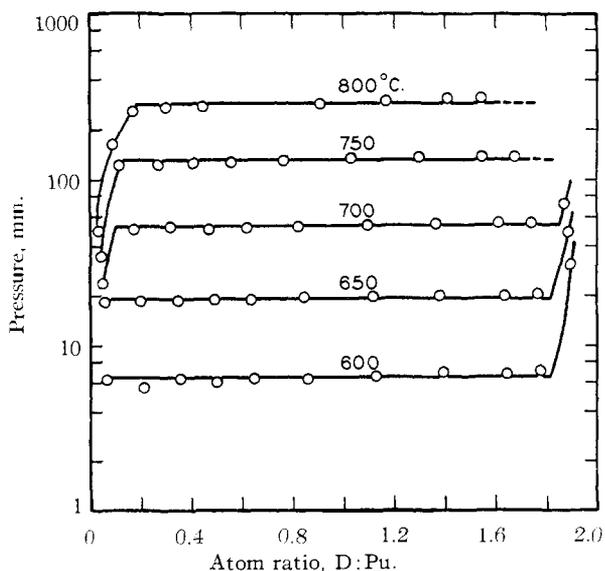


Fig. 2.—Deuteride isotherms.

the condensed phases was the difference between the total quantity of hydrogen put into the bulb and the amount present as gas phase at equilibrium, the latter being calculated from the appropriate volumes, temperatures and pressures.

As an indication of the orders of magnitude involved in the calculations, in one experiment, 2.197 g. of Pu was used, the total gas volume was 58.84 cc., of which 10.2 cc. was at room temperature. The latter volume was measured by filling the sample bulb with water before use; the total volume was measured by expanding helium from the gas buret into the sample volume.

Results and Discussion

The equilibrium pressure-temperature-composition values for plutonium-hydrogen and pluto-

niun-deuterium are shown plotted as isotherms on pressure-composition coordinates in Figs. 1 and 2. The horizontal portions of the isotherms represent composition ranges where two condensed phases coexist, one being Pu metal, the other PuH_2 or PuD_2 . The right-hand ends of the isotherms bend upward at compositions slightly lower than the stoichiometric composition PuH_2 , indicating that some solubility of Pu in PuH_2 exists, or that PuH_2 is non-stoichiometric, existing over a homogeneity range. The left hand, non-horizontal, ends of the isotherms indicate ranges of composition where solubility of hydrogen or deuterium in plutonium exists.

Estimates may be made of the lower limits of composition of PuH_2 from Fig. 1 and these limits are listed in Table I.

TABLE I
LOWER COMPOSITION LIMITS FOR PuH_2

Temp., °C.	Atom ratio (H/Pu)	Temp., °C.	Atom ratio (H/Pu)
500	1.88	700	1.85
600	1.86	750	1.80
650	1.86	800	1.75

The composition range between stoichiometric PuH_2 and the values in Table I obviously represents a PuH_2 lattice which is either hydrogen deficient or plutonium rich. Three explanations appear possible: some of the hydrogen positions are vacant, some of the hydrogen positions contain plutonium atoms, or plutonium is present interstitially with all of the hydrogen positions occupied by hydrogen atoms. No choice between these three is possible from the present data.

At the low composition end of the isotherm plot, solubility limits for hydrogen in plutonium at the various temperatures likewise may be obtained, but the present data are not adequate to make any reliable estimates, especially since any description of the solubility behavior must take into consideration the phase transformations in pure plutonium. It is expected that an account of this aspect of the plutonium-hydrogen system will be presented subsequently.

The plateau pressures of Figs. 1 and 2 actually represent the equilibrium decomposition pressures for PuH_2 or PuD_2 at the various temperatures. If the plateau pressures are plotted on a logarithmic scale vs. reciprocal absolute temperature, a straight line may be drawn through the points. This is shown in Fig. 3 for both PuH_2 and PuD_2 . Below 500° , approach of the system to equilibrium was found to be very slow, and isotherm data were not obtained. Enough pressure measurements to establish decomposition pressure values were made, however, for PuH_2 at 400 and 450° , testing each pressure for equilibrium. The points obtained are plotted on Fig. 3.

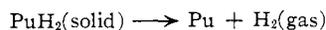
The times required for the system to reach equilibrium varied somewhat with composition as well as with temperature. At 700° , for example, equilibrium generally was reached in an hour or less when two solid phases were present, and in shorter times when only a single solid phase was present. At 450° about 20 hours were required when two solid phases

were present. No true hysteresis was observed (such as has been reported for the uranium-hydrogen system by Spedding, *et al.*⁴), but it should be noted in this connection that the present studies were conducted only by adding hydrogen to the system and no isotherms were obtained for removal of hydrogen. Where hysteresis has been reported for metal-hydrogen systems, it has generally taken the form of the isotherms for addition and removal of hydrogen failing to coincide.

From the slopes of the lines in Fig. 3, the heats of evolution of hydrogen and deuterium may be found by application of a form of the van't Hoff equation

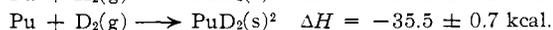
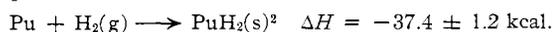
$$\ln P = -\Delta H/RT + \text{constant}$$

where P is the decomposition pressure, T is the absolute temperature, R is the gas constant, and ΔH is a heat of evolution. The ΔH values obtained will be for the removal of one mole of gas from the condensed portion of the system or, in this case, for the decomposition of one mole of PuH_2 according to the equation



Reversing the signs of the ΔH 's will give the heats of formation for PuH_2 and PuD_2 . The Pu metal in the above equation will be saturated with hydrogen and the PuH_2 will be saturated with Pu, according to the solubility limits on the isotherms of Figs. 1 and 2. The effect of dissolved hydrogen on the melting point of plutonium is not known, and consequently it is not known whether the PuH_2 was in equilibrium with solid or liquid Pu at the temperatures studied. For this reason, the state of the Pu in the equation is unspecified. The melting point of pure plutonium is about 639.5° ,⁵ and it will be seen that the temperatures for which data were obtained lie both above and below 639.5° . One might expect break points at the melting temperature in Fig. 3, where the slopes would change by an amount equivalent to the heat of fusion for the hydrogen-saturated plutonium phase. The estimated heat of fusion for pure plutonium is of the order of 0.5 kcal. per g. atom,⁶ which is smaller than the uncertainty in the $\Delta H_{\text{formation}}$ values, so that the explanation for the lack of break points appears to be that the effect is too small to observe. In addition, two allotropic transformations exist in pure plutonium between 400 and 500° ($\delta \rightarrow \delta'$ at 451° and $\delta' \rightarrow \epsilon$ at 476°).⁵ The heats of transformation should also affect the slopes of the lines in Fig. 3. Again, however, the estimated values for the heats of transformation are very small (<0.1 kcal. for $\delta \rightarrow \delta'$ and about 0.1 kcal. for $\delta' \rightarrow \epsilon$)⁶ and the effects on Fig. 3 are apparently too small to observe.

The values for the heats of formation of PuH_2 and PuD_2 were obtained from the slope of the least-square line through the points shown in Fig. 3. The limits given are the errors as estimated from experimental accuracy. The heats so obtained are



(4) F. H. Spedding, *et al.*, *Nucleonics*, **4**, 4 (1949).

(5) E. R. Jette, *J. Chem. Phys.*, **23**, 365 (1955).

(6) E. M. Cramer, Los Alamos Scientific Laboratory, unpublished results of thermal analysis measurements.

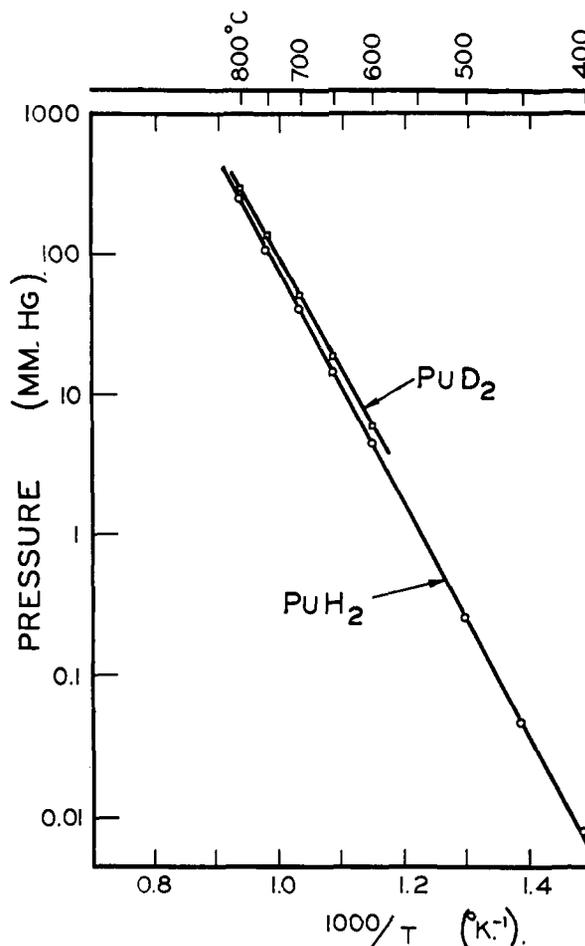


Fig. 3.—Decomposition pressures.

Empirical equations for the relationship between decomposition pressure and temperature may also be obtained by least-square methods. The equations are

$$\text{for PuH}_2: \log_{10} P = 10.01 \pm 0.32 - (8165 \pm 263)/T$$

$$\text{for PuD}_2: \log_{10} P = 9.71 \pm 0.19 - (7761 \pm 151)/T$$

where P is in mm. of mercury and T in degrees Kelvin. Table II shows the smoothed values for the decomposition pressures calculated from the above equations.

TABLE II

SMOOTHED VALUES FOR DECOMPOSITION PRESSURES					
Temp., °C.	Decom. pressure (mm.) PuH ₂	PuD ₂	Temp., °C.	Decom. pressure (mm.) PuH ₂	PuD ₂
400	0.008	..	650	14.7	20.0
450	0.052	..	700	41.3	53.6
500	0.278	..	750	105.9	131.0
550	1.23	..	800	251.2	297.0
600	4.58	6.61			

The plutonium dihydride produced in the course of the experiments was in the form of gray, metallic-looking flakes. Because of the volume increase when Pu is converted to PuH_2 the product usually breaks up, although under some conditions a fairly coherent shell of PuH_2 was obtained surrounding the original piece of Pu. The flakes were quite brittle and could be easily powdered by grinding in a mortar.

As described by Johns,³ PuH₂ will take considerable hydrogen into solid solution to form a solid of composition approaching PuH₃. We have also observed this behavior and, in addition, it appears that as the composition of the solid solution of hydrogen in PuH₂ approaches PuH₃, the cubic PuH₂ lattice transforms to a hexagonal structure. This will be treated in detail in a subsequent report.

Debye powder patterns of many samples of PuH₂ have been examined by F. H. Ellinger of this Laboratory, and the authors are indebted to him for permission to include the following unpublished information for reference purposes: The structure of PuH₂ is face-centered cubic (fluorite type) with cell dimension 5.359 ± 0.002 Å. The calculated X-ray density is 10.40 g./cc.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Acid Hydrolysis of Ethyl Dichloroacetate in Acetone-Water Solvent¹

BY P. MADHAVAN NAIR AND EDWARD S. AMIS

RECEIVED JANUARY 28, 1955

The acid hydrolyses of ethyl dichloroacetate were investigated in acetone-water media at 25, 35 and 45°. The neutral hydrolyses of the ester in the same solvent media were studied at 35 and 45°.

Introduction

An investigation of the rates of hydrolysis of substituted halogen esters in mixed solvents might be expected to throw light on the influence of substitution on the various factors involved in the solvent effect upon reactions in solution. The results of a study of the acid-catalyzed and neutral hydrolysis of ethyl dichloroacetate are reported in this communication.

Experimental

Acetone was purified as described previously.² Ethyl dichloroacetate was shaken up with 3% sodium bicarbonate solution to remove free acid, washed with distilled water, dried over anhydrous CaSO₄ for three days and distilled under reduced pressure. The fraction boiling between 131.0 and 131.5° under 401 mm. pressure was collected for use.

All water was double distilled, a little potassium permanganate being added before the second distillation.

Procedure.—Stock solutions of Ba(OH)₂ and HCl of strengths 0.0250 and 0.6000 *N*, respectively, were prepared from analytical reagent grade materials and these were standardized using potassium acid phthalate, phenolphthalein serving as indicator. The strengths of the stock solutions were checked periodically.

All glassware was standardized. The thermostats employed controlled temperature within $\pm 0.02^\circ$ at 25° and 35° and within $\pm 0.03^\circ$ at 65°.

The procedure for preparing solutions for kinetic runs was the same as reported in previous studies on ester hydrolysis.^{2,3} The required volume of acetone, kept at the temperature of the experiment, was pipetted into a 100-ml. volumetric flask, the required amount of the standard acid to make a 0.0500 *N* solution was added and the contents made up approximately to the neck of the flask with water. The solution was then left in the bath for 1.5 to 2 hours to attain temperature equilibrium. Each run was started by adding the required volume of the ester from a micropipet to make a 0.0500 *N* solution and making up with water at the temperature of the bath. The flask was withdrawn, well shaken and quickly returned to the bath. The time of shaking was taken as starting time since in most cases the ester does not go into solution until it is shaken; 10-ml. samples were withdrawn at convenient intervals and run

into crushed ice prepared from the purified water and titrated against standard calcium hydroxide (approximately 0.025 *N*, actual standardization being to four significant figures) using brom phenol blue as indicator.

The procedure for neutral hydrolysis was the same except no acid was added to the run.

The unimolecular rate constants k' for the acid catalyzed and k_n for neutral runs were obtained from plots of $\log(a-x)$ against t , where $(a-x)$ is the concentration of unreacted ester at time t . The true rate constant k_a for the acid-catalyzed reaction was calculated from the expression

$$k' = k_a(H) + k_n$$

Activation energies in the case of acid hydrolyses were calculated from plots of $\log k'$ vs. $1/T$. Since neutral hydrolysis was done at two temperatures only, the values were calculated straight from the velocity constants.

The low solubility of Cl₂CHCOOEt in water-rich solvent mixtures limited the range of investigation. An ester concentration of 0.05 *M* was desirable for reasonable accuracy in the measurements by the procedure employed and it is impossible to prepare a solution of that strength even in 40% acetone. The solvent compositions employed in the study were 50, 60, 70 and 80% by volumes of acetone.

The specific reaction rate constants were in general reproducible to within $\pm 3-5\%$. The greatest variation (5%) was found in the solutions containing the larger percentages of acetone.

Discussion

The velocity constants for both acid and neutral hydrolysis in the various media are given in Tables I and II and indicate that the changes of the rate constants with solvent composition are roughly the same as obtained by Nair and Anantakrishnan³ and Hockersmith and Amis² for acid hydrolysis of ethyl acetate and methyl propionate, respectively, in acetone-water systems. The activation energies and frequency factors for acid-catalyzed and neutral hydrolysis are shown in Tables III and IV. There was no noticeable drift of the constants for the neutral hydrolyses since the acid formed was weak and at low concentrations.

The changes in activation energy and PZ factor are in the expected direction for halogen substitution at the α -position. The decrease in activation energy is more than compensated by the decrease in the PZ factor and hence the hydrolysis is very slow compared to that of ethyl acetate.

The specific velocity constant for the neutral hy-

(1) This work was done on a contract made by the Institute of Science and Technology of the University of Arkansas with the Office of Naval Research.

(2) J. L. Hockersmith and E. S. Amis, *Anal. Chim. Acta*, **9**, 101 (1953).

(3) P. M. Nair and S. V. Anantakrishnan, *Proc. Ind. Acad. Sci.*, **32**, 85 (1950).