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HEAT OF FORMATION OF PLUTONIUM HYDRIDES

C. Colmenares and C. Alexander*

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* C. Alexander, Battelle Memorial Institute, Columbus, Ohio

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HEAT OF FORMATION OF PLUTONIUM HYDRIDES

C. Colmenares
Lawrence Livermore Laboratory
Livermore, California

C. Alexander
Battelle Memorial Institute
Columbus, Ohio

The heat of formation of PuH_3 at 298 K was reported by Ivanov and Podol'skaya⁽⁴⁾ to be -46.1 ± 0.1 kcal/mol which was in complete disagreement with the value of -33 ± 3 kcal/mol calculated by Oetting⁽²⁾ based on the data of Johns.⁽⁶⁾ To resolve this discrepancy, Oetting and Harrell⁽⁵⁾ at RFP attempted to determine experimentally the heat of formation of PuH_3 by solution calorimetry, while Alexander,⁽³⁾ sponsored by LLL, undertook the same task using thermogravimetric techniques combined with pressure measurements of the equilibrium partial pressure of hydrogen over the hydride. We are reporting here the results of Alexander.

Thermodynamic Basis for Experimental Method - Results.

In this method, the stoichiometry (H/Pu ratio) of a hydride is determined directly from weight gain measurements. The decomposition pressure of hydrogen, $p(\text{H}_2)$, in equilibrium with the solid hydride at a fixed and constant temperature constitutes the second measurement. Then we may write,

$$\bar{G}(\text{H}_2) = RT \ln p(\text{H}_2) \quad (1)$$

where, $\bar{G}(H_2)$ = partial molal free energy, $\partial G/\partial n$. The standard state is 1 atm and, therefore, $p(H_2)$ is expressed in atmospheres.

Consequently, a series of isotherms are generated from experimental measurements by plotting $\bar{G}(H_2)$ versus H/Pu ratio for various temperatures. As the stoichiometry of the hydrides increases from PuH_2 to PuH_3 , we may write

$$\bar{G}_i \equiv \left(\partial G_i / \partial n_i \right)_{p, T, n_j} \quad (2)$$

where, $\bar{G}_i$ = change in total free energy, G , of a solution when a mole of solute is added to an infinite amount of solution.

Equation (2) may be written as follows by applying partial differentiation,

$$dG = \left(\partial G / \partial n_1 \right)_{n_2, n_3, \dots} dn_1 + \left(\partial G / \partial n_2 \right)_{n_1, n_3, \dots} dn_2 + \dots \quad (3)$$

$$\text{or,} \quad dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \dots \quad (4)$$

For the Pu- H_2 system, if all quantities are expressed in terms of PuH_x , then there is no change in the number of moles of Pu and, hence, n_{Pu} is constant. There,

$$dn_{Pu} = 0 \quad (5)$$

Equation (4) simplifies to

$$dG = \bar{G}_1 dn_1 \quad (6)$$

or for H_2 into

$$dG = \bar{G}(H_2) dn_H \quad (7)$$

At constant temperature, equation (7) may be integrated between $Z = H_2/Pu = 0$ and $Z = 3$

$$\Delta G = - \frac{1}{3} \int_{Z=0}^{Z=3} \bar{G}(H_2) \Delta Z \quad (8)$$

Plotting $\bar{G}$ vs Z the value of ΔG is obtained by graphical integration as shown in Figures 1 and 2.

$$\text{Since,} \quad \Delta G = \Delta H - T\Delta S \quad (9)$$

$$\text{and} \quad \Delta H = \Delta G + T\Delta S \quad (10)$$

where ΔS = change in entropy

ΔH = integral heat of formation.

The value of ΔS is obtained by plotting $\Delta G(H_2)$ versus temperature. The slope of this plot represents ΔS , and ΔH is obtained by setting $T = 0$. Data of this type for PuH_3 and PuD_3 is presented in Figure 3.

From measured hydrogen and deuterium decomposition pressures over their respective hydrides, and from estimated heat capacities, $\Delta H_f^\circ(298 \text{ K})$ has been obtained from plots of $\ln p$ versus $1/T$. A typical plot is shown for $PuD_{1.96}$ in Figure 4. The slope of this plot is $\Delta H/R$ and ΔH may be calculated in the temperature range where the measurements were made. The method is based on the following equations:

$$dp(H_2)/dT = - \Delta H_f p(H_2)/RT^2 \quad (11)$$

$$\text{or} \quad dp(H_2)/P = - (\Delta H_f/RT^2) dT \quad (12)$$

Integrating we have,

$$\ln p(H_2) = - \Delta H_f/RT + \ln A \quad (13)$$

Figure 1. Calculation of ΔG from $\bar{G}$

Figure 2. Partial Molal Free Energy of Deuterium

Figure 3. Gibbs Free Energy for PuD_3

Figure 4. Deuteride Decomposition Pressure

The status of our knowledge on the heat of formation of plutonium hydrides is summarized in Table I.

From the results described, we must conclude that the heat of formation for PuH_3 reported by Ivanov and Podol'skaya is correct.

TABLE 1. Heat of Formation of Plutonium Hydrides

Compound	Temp. Range, °C	ΔH_f , kcal/mol	Ref.
PuH_2	400-800	-37.4 ± 1.2	1
PuD_2	600-800	-35.5 ± 0.7	1
PuH_2	25	-33.3 ± 1.2	2
PuD_2	25	-32.3 ± 0.7	2
PuD_2	25	-38.0	3
	400-600	-35.11	
PuH_3	25	-33 ± 3	2
PuH_3	25	-46.1 ± 0.1	4
PuH_3	25	-46.0	3
PuD_3	25	-44.5	3
PuT_3 (estimate)	25	-43.0	3
PuH_2 (major const.)	25	-45.6 ± 3.6	5
PuH_3 (major const.)	25	-48.0 ± 3.7	5

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