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# The heat capacity (8 to 350 K) of $PuH_{1.9}$ , heat capacity (340 to 600 K) of $PuH_{2.0}$ , and recommended thermodynamic properties of $PuH_2$ to 600 K

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The low-temperature heat capacity of  $PuH_{1.9}$ , where the major plutonium isotope was  $^{242}Pu$ , has been determined from 8 to 350 K. The results of this investigation at 298.15 K have been adjusted to correspond to stoichiometric plutonium dihydride:  $PuH_2$ . Standard molar thermodynamic quantities were obtained for  $PuH_2$  at T = 298.15 K:  $C_{p,m}^{\circ}(T) = (43.50 \pm 0.44)$   $J \cdot K^{-1} \cdot mol^{-1}$ ;  $S_m^{\circ}(T) = (72.84 \pm 0.73)$   $J \cdot K^{-1} \cdot mol^{-1}$ ;  $\{H_m^{\circ}(T) - H_m^{\circ}(0)\} = (85.93 \pm 86)$   $J \cdot mol^{-1}$ ; and  $-\{G_m^{\circ}(T) - H_m^{\circ}(0)\}/T = (44.02 \pm 0.44)$   $J \cdot K^{-1} \cdot mol^{-1}$ . These have been combined with experimental high-temperature heat capacities (340 to 600 K) of a sample of  $PuH_{2.0}$ , where the major plutonium isotope as  $^{239}$ Pu, to give the thermodynamic functions of  $PuH_2$  over the temperature range from 298.15 to 600 K.

#### 1. Introduction

Experimental heat capacities for the hydrides of thorium<sup>(1)</sup> and uranium<sup>(2)</sup> have been published. However, the heat capacities of the hydrides of plutonium and the other actinide hydrides have not been reported. A recent review of the actinide hydrides<sup>(3)</sup> presents recommended values for the basic thermodynamic properties derived from experiment. This review also includes some calculated and estimated thermodynamic values for selected actinite hydrides where experimental results are not available.

Part of the reason for the absence of heat capacities for the hydrides of plutonium is the lack of a reliable phase diagram for (plutonium + hydrogen), thus precluding a thorough understanding of the stability, composition limits, and preparative chemistry of the hydrides. Recent studies by Haschke and co-workers<sup>(4, 5)</sup>

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complement the earlier work of Mulford and Sturdy<sup>(6,7)</sup> and greatly help to resolve this problem. It is now possible readily to prepare and analyze (plutonium + hydrogen) compounds, particularly in the lower range of hydrogen composition.

Another reason for the lack of low-temperature heat capacities on (plutonium + hydrogen) compounds is that the most commonly available isotope of plutonium,  $^{239}$ Pu, has a comparatively high self-heating rate associated with its radioactive decay. Recently, however, a sufficient amount of  $^{242}$ Pu, which has a much lower self-heating rate compared with  $^{239}$ Pu, has become available enabling one to make accurate measurements of the low-temperature heat capacity using adiabatic calorimetric techniques. Although the available amount of  $^{242}$ Pu was not sufficient for the preparation of a sample large enough for accurate high-temperature heat-capacity measurements, recent investigations<sup>(8)</sup> indicated that it is possible to measure accurately the heat capacity of plutonium-containing materials above 300 K using  $^{239}$ Pu in spite of the comparatively large self-heating effect.

Thus, with the availability of the  $^{242}$ Pu isotope and a better understanding of the phase diagram and associated physical and chemical properties of (plutonium hydrogen), the opportunity to measure accurately and to interpret the low- and high-temperature heat capacity of PuH<sub>2</sub>(cr) has become a reality.

### 2. Experimental

#### <sup>242</sup>PuH<sub>1.9</sub> LOW-TEMPERATURE HEAT-CAPACITY SAMPLE

Two plutonium hydride samples were used in this research. One sample, made from <sup>242</sup>Pu metal, was used for the low-temperature heat-capacity measurements and the other sample, made from <sup>239</sup>Pu, was used for high-temperature determinations.

The <sup>242</sup>Pu was used for the low-temperature studies because its much lower selfheating rate, compared with <sup>239</sup>Pu, permitted reliable measurements at lower temperatures. The specific power associated with this sample will be discussed in another section of this paper. The chemical purity of the <sup>242</sup>Pu metal was 99.8 mass per cent. The 0.93 cm diameter metal rod was cut into four pieces and cleaned of surface oxide by abrasion. This operation and all subsequent handling of the sample were carried out in a glovebox containing a purified helium atmosphere. The weighed <sup>242</sup>Pu was loaded into a degassed (at 800 K) stainless-steel crucible (4.4 cm long), which in turn was sealed in a cylindrical stainless-steel tube fitted with an O-ring seal and a valve. The sealed assembly was removed from the glovebox and attached to a vacuum and gas-handling system for preparation of the plutoniumhydride sample by reaction with hydrogen obtained by thermal decomposition of  $UH_3$ . After sufficient hydrogen had reacted at room temperature to produce  $PuH_3$ , the hydride was then heated to 670 K for 1 h to promote equilibrium distribution of hydrogen in the sample. The tube was opened in the glovebox and, with the exception of some loose powdered sample near the top of the crucible, most of the hydride was very densely packed and could not readily be removed from the crucible. As a result, only about one-third (7.509 g) of the hydride sample could be recovered for use as the calorimetric sample. The recovered product was loaded into

	10 <sup>6</sup> w		10 <sup>6</sup> w		10 <sup>6</sup> w
Am	123	Cu	2	Mn	2
Be	1	Н,	35	0,	65
С	35	Fe	35	Si	10
Ca	10	Mg	2	Sn	5

TABLE 1. Elemental analysis of plutonium sample: mass fraction w

a small copper capsule, placed in the gold-plated copper calorimeter (laboratory designation 6–GSII), and sealed with  $1.88 \times 10^{-5}$  mol of He. Details of this procedure are described in previous publications.<sup>(9, 10)</sup>

After the heat-capacity measurements had been completed, the sample was analyzed for hydrogen using vacuum-microbalance procedures described in the literature.<sup>(4)</sup> From the measured sample composition n(H)/n(Pu) = 1.75, it was concluded that the sample consisted of  $(92.06 \pm 1.40)$  mass per cent of plutonium hydride with the composition n(H)/n(Pu) = 1.9 and the remainder of the sample was plutonium metal with a trace of dissolved hydrogen in agreement with the results of Mulford and Sturdy.<sup>(6)</sup> X-ray diffraction analysis showed a cubic lattice parameter of  $(0.535 \pm 0.010)$  nm, which agrees with the reported value  $(0.5360 \pm 0.0003)$  nm, for the two-phase  $(Pu + PuH_2)$  region.<sup>(11)</sup> The fact that plutonium metal was not detected is not surprising since its concentration is low and it was quenched from the  $\delta$ -form. The effects of uncertainties in the amounts of  $PuH_{1.9}$  and plutonium in the sample will be discussed after the results have been presented.

#### <sup>239</sup>Pu HIGH-TEMPERATURE HEAT-CAPACITY SAMPLE

The plutonium-hydride sample used for the high-temperature heat-capacity determinations was prepared by the reaction of high-purity  $\alpha$ -Pu (major isotope, <sup>239</sup>Pu) and hydrogen gas obtained from the thermal decomposition of UH<sub>3</sub>. The plutonium metal used in the preparation of the hydride was electrorefined and of the highest purity available. As shown in table 1, chemical analysis of the metal sample indicated 99.99 mass per cent of plutonium. Isotopic analysis, as shown in table 2, indicated that the molar mass of the plutonium metal was 239.113 g·mol<sup>-1</sup>. The high purity of the sample made impurity-corrections unnecessary.

	$M/(g \cdot mol^{-1})^a$	w
<sup>238</sup> Pu	238.049582	0.020
<sup>239</sup> Pu	239.052176	93.77
<sup>240</sup> Pu	240.053827	5.90
<sup>241</sup> Pu	241.056867	0.272
<sup>242</sup> Pu	242.058768	0.036
	$M(\text{sample})/(g \cdot \text{mol}^{-1}) = 239.113$	

TABLE 2. Isotopic analysis of the plutonium sample: molar mass M and mass fraction w

<sup>a</sup> Wapstra, A. H.; Gove, N. B. Atomic Mass Evaluation, Nuclear Data Table 1971, 9, 265.

Three plutonium rods (about 230 g total) were reacted with hydrogen gas at 365 kPa in a closed stainless-steel reaction vessel for approximately 100 h. After that time, the hydrogen overpressure was relieved and the sample was dehydrided at 760 K under a dynamic vacuum of  $4 \times 10^{-4}$  Pa for a period of 16 h. The sample was again hydrided at 365 kPa for 24 h. The hydrogen overpressure was again relieved and the sample was heated to form the desired plutonium dihydride.<sup>(4, 5)</sup> This was accomplished by heating to 533 K under a dynamic vacuum for 24 h. The decomposition isotherms of plutonium hydride have been given previously.<sup>(4, 5)</sup>

The stoichiometry of the hydride was determined by thermogravimetric analysis of a portion of the sample.<sup>(4)</sup> Results for two hydride samples taken from the homogenized product yielded compositions of  $PuH_{1.93}$  and  $PuH_{2.03}$ , respectively. Therefore, the composition of the calorimetric sample was subsequently taken to be  $PuH_{1.98\pm0.05}$  and will be referred to as  $PuH_{2.0}$  in this paper.

The configuration of the adiabatic calorimeter and sample arrangements have been described previously.<sup>(12)</sup> As stated before, the calorimetric sample consisted of four individually encapsulated portions of plutonium hydride. Each one of the four capsules consisted of a heliarc-welded molybdenum capsule (containing plutonium hydride) enclosed within a heliarc-welded capsule (aluminum, type 6061). The double encapsulation was precautionary because of the toxicity and radioactivity of plutonium.

The mass of the plutonium hydride in the calorimetric sample was 129.708 g (= 0.43952 mol), the mass of the molybdenum was 169.691 g, and the mass of the Al 6061 was 39.744 g.

#### CALORIMETRIC MEASUREMENTS FROM 8 to 350 K

A description of the adiabatic calorimetric techniques, cryostat, automatic adiabaticshield control, and semi-automatic method of recording the results used in the heatcapacity measurements are referenced in an earlier paper.<sup>(9)</sup>

The self-heating associated with the radioactivity of the plutonium made the usual discontinuous electrical-heating technique less accurate than usual below 20 K. The temperature drift rate of the calorimeter was  $7 \times 10^{-4} \text{ K} \cdot \text{s}^{-1}$  at 30 K,  $2 \times 10^{-3} \text{ K} \cdot \text{s}^{-1}$  at 20 K, and  $1.4 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$  at 10 K. Since the radioactive power is a constant, we made use of this heat to determine the heat capacity from accurately measured temperature drift rates obtained in the temperature range 8 to 20 K. The discontinuous electrical-heating method was used above 20 K and these heat capacities and the associated temperature drifts were used accurately to evaluate the radioactive power from results obtained between 20 and 38 K. Details of the method are published elsewhere.<sup>(9)</sup>

#### CALORIMETRIC MEASUREMENTS FROM 340 to 600 K

The adiabatic-calorimeter operating procedure for the determination of heat capacities in the temperature range of 300 to 700 K by the discrete-step heating method has been described previously.<sup>(8,12)</sup> Basically, this procedure utilized the

final drift rate of a given heat-capacity measurement as the initial drift rate in the subsequent heat-capacity measurement. The drift rate is defined as the temperature drift of the sample under so-called adiabatic conditions. Since there was a thermal drift of the sample under adiabatic conditions at all times (very rarely was the temperature drift =  $0.000 \text{ K} \cdot \text{h}^{-1}$ ), this drift was always considered in the calculation of the heat capacity.

As described for prior heat-capacity measurements with plutonium materials,<sup>(8)</sup> one major modification had to be made of the method of calculating the heat capacity of the sample because of the self-heating by plutonium. This sample of plutonium hydride, consisting primarily of  $^{239}$ Pu (see table 2), generated about  $2.2 \times 10^{-3}$  W  $\cdot$  g<sup>-1</sup> due to radioactive decay. Since this amounts to 0.28 W for the 129 g sample, it was necessary to cool the sample to compensate for this self-heating so as to reduce the (intrinsic) drift rate. This cooling effect was accomplished by operating the adiabatic shield at a lower temperature than that of the sample and sample adapter; the net effect of this procedure was that the sample was held at a nearly constant temperature. All energy supplied by the calorimetric heater during a discrete heating step was assumed to be reflected in the measured temperature rise of the (adapter + sample), and was thus taken into consideration when calculating the heat capacity.

It was observed, however, that the optimum shield-temperature offset required to maintain an approximately zero temperature drift at all sample temperatures depended on the temperature. This offset was adjusted between each heat-capacity measurement, but kept constant for any single measurement. This meant that one could no longer assume that the final temperature drift of a given heatcapacity determination would be the same as the initial drift of the subsequent measurement. Therefore it was necessary to take the final drift of any given measurement, adjust the temperature of the surrounding adiabatic shield, and then determine the initial drift for the next measurement. Throughout the measurements, the temperature drift was kept as small as possible, and in no case did the temperature-drift correction amount to more than 0.74 per cent of the total heat capacity.

#### 3. Heat-capacity results

#### HEAT CAPACITY OF <sup>242</sup>PuH<sub>1.9</sub> FROM 8 TO 350 K

The experimental molar heat capacities from 20 to 350 K are listed in table 3 in order of ascending temperatures. The temperature rises during the electrical heating periods were approximately  $0.08\langle T \rangle$  from 20 to 38 K,  $0.10\langle T \rangle$  from 38 to 100 K, and 10 K above 100 K. All overlapping results agree well within the experimental precision of  $\pm 0.1$  per cent. The probable error of each value of  $C_{p,m}^{\circ}$  above 50 K is estimated to be 0.5 per cent, including any error arising from correcting for the presence of the plutonium metal in the sample. Between 20 and 40 K the probable error is estimated to be 1.0 per cent and 0.5 per cent at 50 K. The heat capacity of

$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{J \cdot K^{-1} \cdot \mathrm{mol}^{-1}}$	$\frac{T}{\mathbf{K}}$	$\frac{C_{p,m}^{\circ}}{J \cdot K^{-1} \cdot \mathrm{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{J\cdot K^{-1}\cdot \mathrm{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$
19.48	8.27	32.57	23.96	41.16	23.43	104.77	24.57	251.57	40.34
20.77	9.76	32.76	24.20	42.38	22.73	115.21	24.86	261.55	40.97
22.23	11.88	33.75	25.15	43.54	22.14	125.76	25.23	271.61	41.44
23.78	14.14	33.97	25.67	44.70	21.78	136.35	25.83	281.71	42.24
24.93	15.25	34.38	26.08	44.78	22.02	146.77	26.73	291.80	42.65
26.07	16.63	35.18	27.15	48.84	21.88	157.01	28.22	301.88	43.29
26.50	16.68	36.00	27.62	51.40	22.13	167.31	29.36	311.97	44.09
27.79	17.89	36.39	28.19	56.68	22.70	177.62	30.90	322.03	45.41
28.19	18.57	36.44	27.96	62.39	23.13	187.94	32.23	332.04	46.74
29.02	19.22	37.58	27.56	68.81	23.53	198.19	33.68	340.41	47.23
29.47	20.08	38.78	25.78	75.83	23.90	208.35	35.46	347.15	47.84
30.31	20.95	39.70	25.06	83.43	24.29	218.45	37.07		
31.03	21.96	39.80	24.90	86.21	24.53	228.59	39.06		
31.39	22.40	39.97	24.37	91.72	24.69	238.73	40.41		
31.55	22.59	41.11	23.81	95.19	24.82	242.26	40.46		

TABLE 3. Standard molar heat capacity of <sup>242</sup>PuH<sub>1.9</sub> at constant pressure from 20 to 350 K.  $M(PuH_{1.9}) = 243.928 \text{ g} \cdot \text{mol}^{-1}; p^\circ = 101325 \text{ Pa}$ 

 $PuH_{1.9}$  was calculated from the equation:

$$C_{p,m}^{\circ}(\operatorname{PuH}_{1,9}) = \{C_{p,m}^{\circ}(\operatorname{sample}) - 0.080C_{p,m}^{\circ}(\operatorname{Pu})\}/0.920,$$
(1)

where  $C_{p,m}^{\circ}(\text{sample})$  was calculated using a molar mass appropriate for the amounts of  $^{242}\text{PuH}_{1.9}$  and  $^{242}\text{Pu}$  in the sample, and using  $C_{p,m}^{\circ}(\text{Pu})$  values reported by Sandenaw and Gibney.<sup>(13)</sup> Because the molar mass of plutonium dominates the value of the molar mass of the hydride, the amount of Pu used for  $C_{p,m}^{\circ}(\text{sample})$  is only 0.06 per cent higher than if the sample were entirely PuH<sub>1.9</sub>. The actual values of  $C_{p,m}^{\circ}(\text{PuH}_{1.9})$  were higher than those of  $C_{p,m}^{\circ}(\text{sample})$  by about 1.8, 4.7, 2.0, 0.0, 1.2, 1.9, and 2.1 per cent at 8, 20, 50, 100, 200, 250, and 350 K, respectively.

The values of  $C_{p,m}^{\circ}$  listed in table 4 were derived from temperature drifts as stated earlier. The radioactive self-heating power was evaluated from 24 points between 19.48 and 36.44 K, given in table 3. The observed value was  $(0.1522 \pm 0.0003) \text{ mW} \cdot \text{g}^{-1}$  which agrees with the value  $(0.1529 \pm 0.0006) \text{ mW} \cdot \text{g}^{-1}$ , calculated from a plutonium isotopic analysis and the specific power of each isotope.<sup>(14)</sup>

TABLE 4. Standard molar heat capacity of  $^{242}$ PuH<sub>1.9</sub> at constant pressure from 8 to 20 K, derived from temperaturedrift measurements as described in the text.  $p^{\circ} = 101325$  Pa

$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,m}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_{p,\mathfrak{m}}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$
8	0.73	11	1.62	14	3.26	17	5.77	19.48 <i>°</i>	8.27 ª
9	0.97	12	2.06	15	4.01	18	6.76	20	8.94
10	1.26	13	2.61	16	4.86	19	7.82		

" Usual electrical-heating method used.



FIGURE 1. Experimental heat capacity of  $PuH_{1.9}$ .  $\Box$ , From temperature-drift measurements;  $\bigcirc$ , from usual adiabatic-calorimetric measurements.

Several hundred temperature-drift measurements were made, including several runs through the  $\lambda$ -peak (see figure 1). All heat-capacity values were reproducible and no effect associated with radiation damage was detected, as had been found for  $^{242}PuF_3$ .<sup>(9)</sup> We estimate that the probable error of the values of  $C_{p,m}^{\circ}$  in table 4 is 5 per cent at 8 K, 2 per cent at 15 K, and 1 per cent at 20 K.

The molar heat capacity at constant pressure can be represented by

$$C_{p,m}^{\circ}(\operatorname{PuH}_{1.9}) = C_{\operatorname{acoustic, m}} + C_{\operatorname{optical, m}} + C_{\operatorname{cond, m}} + C_{\operatorname{antif, m}} + C_{\operatorname{el, m}} + C_{\operatorname{excess, m}}, \quad (2)$$

where  $C_{\text{acoustic, m}}$  is the molar heat-capacity contribution of the acoustic modes,  $C_{\text{optical, m}}$  is the contribution of the optical modes (hydrogen vibrating out of phase with the plutonium),  $C_{\text{cond, m}}$  arises from the conduction electrons,  $C_{\text{el, m}}$  is associated with the electronic energy levels of  $\text{Pu}^{3+}$  in the  $\text{PuH}_{1.9}$  (see discussion below), and  $C_{\text{excess, m}}$  is a possible heat-capacity contribution resulting from a change in hydrogen sites as self-diffusion of hydrogen becomes significant above about 200 K as discussed below.

The complexities associated with the evaluation of the individual contributions to  $C_{p,m}^{\circ}(\operatorname{PuH}_{1.9})$  are such that a satisfactory quantitative interpretation of  $C_{p,m}^{\circ}(\operatorname{PuH}_{1.9})$  are such that a satisfactory quantitative interpretation of  $C_{p,m}^{\circ}(\operatorname{PuH}_{1.9})$  against temperature is not possible. However, it is possible to interpret qualitatively the general features of the heat-capacity curve shown in figure 1. The  $\lambda$ -type peak near 36 K is associated with antiferromagnetic ordering reported by Aldred *et al.*<sup>(15)</sup> near 30 K. Below 36 K,  $C_{\text{antif,m}}$  falls off rapidly with  $T^3$  at low temperatures.<sup>(16)</sup> There is another large contribution to  $C_{p,m}^{\circ}$  in the region of the  $\lambda$ -peak, namely  $C_{el,m}$ . This heat capacity is associated with electronic energy levels occasioned by the splitting

of the ground state of the  $Pu^{3+}$  ion by the crystal electric field. Aldred et al.<sup>(15)</sup> have reported that the crystal-field ground state is a doublet  $\Gamma_7$  with a quartet  $\Gamma_8$  excited state 70 cm<sup>-1</sup> above it. They also point out that because of this small wavenumber separation, the  $\Gamma_{\gamma}$  ground state and the  $\Gamma_{8}$  excited state will be mixed by the exchange field in the antiferromagnetic regime. Therefore, the calculation of  $C_{el,m}$ against temperature, assuming no mixing, would be considerably in error; however, we have calculated  $C_{\rm el,\,m}$ , with no allowance for mixing, and found  $C_{\rm el,\,m}/(J \cdot K^{-1} \cdot mol^{-1})$  to be 0.9 at 15 K, 2.7 at 20 K, 5.7 at 30 K, 6.3 at 38 K, slowly decreasing to  $2 J \cdot K^{-1} \cdot mol^{-1}$  at 100 K. This approximate calculation of  $C_{el,m}$ indicates that both  $C_{\text{antif, m}}$  and  $C_{\text{el, m}}$  reach maximum values in the region of 35 to 40 K, as expected, and neither can be evaluated as a function of temperature. The decrease in slope of  $C_{n,m}^{\circ}$  against T (figure 1) near 100 K is at least partially due to the decrease in  $C_{el,m}$  and possibly due to  $C_{antif,m}$  tending to negligible values. The increase in slope above 130 K is undoubtedly associated with increasing values of  $C_{\text{optical, m}}$  This heat-capacity contribution could be readily calculated if the hydrogen vibrational wavenumbers and degeneracies were known. Hydrogen atoms are believed to occupy tetrahedral sites,<sup>(17)</sup> and, therefore, wavenumbers of (1000+100) cm<sup>-1</sup> would be expected.<sup>(18)</sup> As can be seen in figure 1, there is an increase in the slope of  $C_{p,m}^{\circ}$  against T between 200 and 240 K, followed by a flattening of the curve between 240 and 250 K, and then a more modest slope above 250 K. Although we have no direct information to account for this feature, it is possibly due to a small net change in the distribution of the hydrogen atoms among the available interstitial sites made possible by the onset of self-diffusion above 200 K. LaH<sub>2.00</sub> and LaH<sub>2.03</sub> show<sup>(19)</sup> an enhanced heat-capacity feature similar to that for PuH<sub>1.9</sub> in the same temperature region. N.m.r. experiments reported by Schreiber and  $Cotts^{(20)}$  on LaH<sub>x</sub> showed that there is a sharp dependence on x of the activation energy for self-diffusion of hydrogen. They found that varying x from 2.00 to 2.03 caused a shift of the beginning of the narrowing of the resonance line by about 50 K, an effect which is consistent with the heat-capacity results reported by Bieganski.<sup>(19)</sup> A similar, but smaller effect has been noted by Ohlendorf and Flotow<sup>(18)</sup> for LaNi<sub>5</sub>H<sub>6.39</sub> in the temperature region 120 to 160 K. Cinader et al.<sup>(17)</sup> report an n.m.r. investigation of  $PuH_x$  for x = 1.78, 2.35, 2.65, and 2.78. Their results for PuH<sub>1.78</sub> show no motional narrowing up to room temperature, and this suggested to them that the activation energy for diffusion was higher for PuH<sub>1.78</sub> than for higher values of x. With the present information, we believe that the most probable explanation of the enhanced heat capacity of  $PuH_{1,9}$  is a small change in the hydrogen-site occupancies above about 200 K; below this temperature it is presumed that the hydrogen is "frozen" in the most stable sites.

At low temperatures (T < 15 K), as  $T \rightarrow 0$ , the heat capacity of PuH<sub>1.9</sub> is represented by the equation:

$$C_{p,m}^{\circ} = \gamma T + \beta T^{3} + C_{el,m}, \qquad (3)$$

where  $\gamma T = C_{\text{cond}, m}$  and  $\beta T^3 = (C_{\text{acoustic}, m} + C_{\text{antif}, m})$ .  $C_{\text{el}, m}$  was calculated as discussed above (assuming no mixing) and found to be 0.90  $\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \text{mol}^{-1}$  at 15 K, falling to 0.009  $\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \text{mol}^{-1}$  at 8 K. A plot of  $(C_{p,m}^{\circ} - C_{\text{el},m})/T$  against  $T^2$ 



FIGURE 2.  $(C_{p,m} - C_{el})/T$  against  $T^2$ . The dashed line is an extrapolation to  $T \to 0$ . See the text for an explanation of the significance of the plot.

(figure 2) from  $T^2 = 64$  to  $T^2 = 225 \text{ K}^2$  indicates that  $(C_{p,m}^{\circ} - C_{el,m})$  can be adequately represented by the sum of terms in T and  $T^3$  as  $T \to 0$ . The value of  $(C_{p,m}^{\circ} - C_{el,m})/T$  at  $T^2 \to 0$  is 0.040 J·K<sup>-1</sup>·mol<sup>-1</sup> and this is the value of  $\gamma$ . This value could be in error by 25 per cent and heat capacities at lower temperatures are necessary to obtain  $\gamma$  more precisely. The value of  $\gamma$  above the antiferromagnetic transition might be considerably different from that reported here.

## HEAT CAPACITY OF <sup>239</sup>Pu<sub>2.0</sub> FROM 340 TO 600 K

The high-temperature heat capacities obtained in this investigation, and listed in table 5, are based on two sets of observations taken on the same sample of

<u></u>	C <sup>°</sup> <sub>p, m</sub>	T	<i>C</i> <sup>°</sup> <sub><i>p</i>, m</sub>	T	$C_{p,\mathrm{m}}^{\circ}$	T	$C_{p, m}^{\circ}$	T	<i>C</i> ° <sub><i>p</i>, m</sub>
К	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	<sup>1</sup> K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
	Set I	453.862	62.1672	554.400	71.1501	400.034	55.2466	511.832	69.0970
346.913	49,3674	462.535	62.1325	566.064	71.2764	410.465	56.3148	524.063	70.3847
356.563	49,4522	471.022	63.1547	573.515	72.5325	419.160	57.2591	532.956	70.7346
366.150	) 51.4935	479.422	64.3309	580.826	5 74.4693	429.230	58.7062	541.297	70.8582
375.679	52,1444	487.786	65.1491	588.219	73.6702	438.615	59,3883	549.390	72.5145
387.091	53,2705	495.832	66.3370	595.340	75.6057	447.895	60.0518	557.179	73.4115
396 816	541111	507.283	67.9854	602.825	72.2788	458.892	62.6594	565.061	73.2072
406.257	55.4407	515.014	68.8502		Set II	467.970	64.2892	572.468	73,9413
415.650	) 56.3308	522.678	68.7790	260.061	51 1/22	476.500	64.4509	579.487	75.0288
424.604	57,4845	530.398	69.2540	270 250	50.0040	485,044	66.2448		
436.635	5 58.7786	538.345	69.6311	370.233	53 3705	493.610	66.8574		
445.277	60.8353	546.396	70.3330	389.017	53.7839	502.148	68.2591		

TABLE 5. Standard molar heat capacity of PuH<sub>2</sub> from 340 to 600 K.  $p^{\circ} = 101325$  Pa



FIGURE 3. Experimental high-temperature heat capacities of  $PuH_2$ .  $\Box$ , Actual experimental results;  $\bigcirc$ , smoothed low-temperature results for  $PuH_2$ .

plutonium hydride. The experimental heat capacities are normalized to 1 mol of  $PuH_2$  and corrected for the heat capacity of molybdenum, Al 6061, and the sample holder reported previously.<sup>(12)</sup>

These experimental molar heat capacities are presented in figure 3, along with the smoothed low-temperature heat capacities of  $PuH_2$ . The curve shown in this figure was determined by regression analysis and is given by the equation:

$$C_{p,m}^{\circ}(T)/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}) = 47.307 - 0.1763(T/\mathbf{K}) + + 7.231 \times 10^{-1}(T/\mathbf{K})^2 - 5.845 \times 10^{-7}(T/\mathbf{K})^3,$$
(4)

where the standard deviation is 0.70 (1.2 per cent).

The assigned error for the molar heat capacity of  $PuH_2$  in the temperature range of 340 to 600 K is  $\pm 2.5$  per cent, which takes into account the standard error of the fit of the equation, the possible bias in the calorimetric measurements, and the chemical analysis of the sample.

#### 4. Derived thermodynamic results

#### THERMODYNAMIC FUNCTIONS OF PuH1.9 TO 350 K

To obtain thermodynamic functions relative to  $T \to 0$ , it was necessary to extrapolate  $C_{p,m}^{\circ}$  from 8 K to  $T \to 0$ . The extrapolation is represented by the dashed section of the curve in figure 2. Below 8 K,  $C_{el,m}$  is negligible and the dashed line can be represented by the equation:

$$(C_{p,m}^{\circ}/T)/(J \cdot K^{-2} \cdot mol^{-1}) = 0.040 + 0.00080(T/K)^{2},$$
(5)

and this equation was used to calculate the values of  $S_m^{\circ}$ ,  $\{H_m^{\circ}(T) - H_m^{\circ}(0)\}$ , and

Т	$C_{p,m}^{\circ}$	$S^{\circ}_{\mathbf{m}}(T)$	$H^{\circ}_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(0)$	$-\left\{G_{\mathbf{m}}^{\circ}(T)-H_{\mathbf{m}}^{\circ}(0)\right\}/T$
ĸ	$J \cdot K^{-1} \cdot mol^{-1}$	$\overline{J \cdot K^{-1} \cdot mol^{-1}}$	$J \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
8	0.73	(0.457)	(2.10)	(0.195)
10	1.26	0.673	4.06	0.267
15	4.01	1.621	16.21	0.540
20	8.93	3.406	47.82	1.015
25	15.39	6.099	108.8	1.747
30	20.60	9.335	197.9	2.738
35	26.86	12.987	316.8	3,936
36.38 <sup>b</sup>	28.20	14.818	383.0	4.290
40	24.67	16.587	451.4	5.302
45	21.94	19.288	566.0	6.710
50	22.01	21.59	675.3	8.084
60	22.92	25.69	900.4	10.68
70	23.62	29.27	1133.2	13.08
80	24.30	32.47	1372.4	15.32
90	24.58	35.35	1616.5	17.39
100	24.74	37.95	1863.2	19.32
110	24.80	40.31	2111	21.12
120	24.95	42.47	2359	22.81
130	25.37	44.48	2611	24.40
140	26.13	46.38	2868	25.89
150	27.20	48.22	3134	27.33
160	28.48	50.02	3413	28.69
170	29.83	51.79	3704	30.00
180	31.18	53.53	4009	31.26
190	32 54	55.25	4328	32 47
200	33.98	56.96	4660	33.66
210	35.62	58.65	5008	34.80
220	37 47	60.35	5373	35.93
230	39.28	62.06	5757	37.03
240	40.41	63.76	6157	38.11
250	40.33	65.40	6560	39.16
260	40.87	67.00	6965	40.21
270	41.46	68.55	7377	41.23
280	41 97	70.07	7794	42.23
290	42.50	71.55	8217	43.22
300	43.18	73.00	8645	44 18
310	44.07	74 43	9081	45 14
320	45 14	75.85	9527	46.08
330	46.27	77.05	9084	47.00
340	47 30	78.65	10452	47.00
350	48.01	80.03	10930	48.80
200 15	42 DA	77 72	8565	
270.1J	+J.0+ ↓0.22	+036	43	++.00 +0.22
	I. 0.22	10.50	<u>_</u> 45	10.22

TABLE 6. Standard molar thermodynamic functions of  $PuH_{1.9}$ .<sup>*a*</sup>  $p^{\circ} = 101325$  Pa

<sup>a</sup> We assume that thermodynamic functions of  ${}^{242}PuH_{1,91}$  are equal to those of  ${}^{239}PuH_{1,9}$ . <sup>b</sup> Temperature of maximum heat capacity of  $\lambda$ -peak. <sup>c</sup> The values of the functions in this line are adjusted to the composition PuH<sub>2</sub>. The details of this adjustment are delineated in the text.

 $-\{G_{m}^{\circ}(T)-H_{m}^{\circ}(0)\}/T$  at 8 K, as given in table 6. The irregular shape of the heatcapacity curve (see figure 1) necessitated the division of the  $C_{p,m}^{\circ}$  values into five sections to evaluate the thermodynamic functions. Each of the four sections, from 8 to 24 K, 24 to 35 K, 50 to 242 K, and 242 to 350 K, was fitted to a polynomial in *T*, and the heat capacities and thermodynamic functions were calculated using these polynomials. A plot of  $C_{p,m}^{\circ}$  against *T* in the region 35 to 50 K was used to obtain the values of  $C_{p,m}^{\circ}$  in table 6, and the thermodynamic functions were calculated from appropriate integrations of  $C_{p,m}^{\circ}$  read from this plot at close temperature intervals. We estimate that each entry above 50 K in table 6 has a probable error of 0.5 per cent.

The standard molar entropy of PuH<sub>1.9</sub> at 298.15 K is  $(72.73 \pm 0.6)$  J·K<sup>-1</sup>·mol<sup>-1</sup> and is believed to be the practical entropy appropriate for thermodynamic calculations. This, of course, assumes that there are no unusual heat-capacity contributions below 8 K where the extrapolation to  $T \rightarrow 0$  begins. A comparison of the entropy of PuH<sub>1.9</sub> with that of ThH<sub>2</sub> at 298.15 K supports this assumption. The standard molar entropy of ThH<sub>2</sub> at 298.15 K is  $(50.73 \pm 0.10)$  J·K<sup>-1</sup>·mol<sup>-1</sup>,<sup>(2)</sup> and thus that of PuH<sub>1,0</sub> is larger by 22.0 J·K<sup>-1</sup>·mol<sup>-1</sup>. The standard molar entropy of ThH<sub>2</sub> has no contributions from  $C_{\text{antif, m}}$ ,  $C_{\text{el, m}}$ , or  $C_{\text{excess, m}}$ . If we take the magnetic ground-state wavefunction of  $PuH_{1,9}$  to consist of a J = 5/2 manifold,<sup>(15)</sup> then  $(S_{\text{antif}, m} + S_{\text{el}, m}) = R \ln 6 = 14.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for PuH<sub>1.9</sub>; this still leaves a residual entropy of 7.1  $J \cdot K^{-1} \cdot mol^{-1}$  compared with that of ThH<sub>2</sub>. A rough estimate of  $S_{\text{excess, m}}$  arising from  $C_{\text{excess, m}}$  is 0.8 J·K<sup>-1</sup>·mol<sup>-1</sup> and this reduces the entropy difference to 6.3  $J \cdot K^{-1} \cdot mol^{-1}$ , which is due to the higher average value of y for PuH<sub>1.9</sub>, compared with that for ThH<sub>2</sub> which is  $2.75 \times 10^{-3} \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$  (2) As discussed above, the low-temperature (T < 36 K) value of  $\gamma(\text{PuH}_{1.9})$  is 0.040 J·K<sup>-2</sup>·mol<sup>-1</sup>, but the value of  $\gamma$  above the antiferromagnetic transition is unknown. The 6.3  $J \cdot K^{-1} \cdot mol^{-1}$  entropy difference, if exact, would require that the average value of  $\gamma$  for PuH<sub>1.9</sub> be 0.024 J·K<sup>-2</sup>·mol<sup>-1</sup> between  $T \rightarrow 0$  and 298.15 K. We believe that the available evidence indicates that  $S_m^{\circ}(PuH_{1.9}, cr, 298.15 \text{ K}) =$  $(72.73 \pm 0.36)$  J·K<sup>-1</sup>·mol<sup>-1</sup> is the practical entropy.

#### THERMODYNAMIC FUNCTIONS OF PuH<sub>2</sub> AT 298.15 K

In order to have thermodynamic functions of  $PuH_2$  at 298.15 K to use with the functions for  $PuH_2$  at higher temperatures, it is necessary to adjust  $C_{p,m}^{\circ}$ ,  $S_m^{\circ}$ , and  $\{H_m^{\circ}(T) - H_m^{\circ}(0)\}$  for a composition corresponding to  $PuH_{1.9}$ . It is reasonable to expect the contributions to these functions due to antiferromagnetism, electronic levels, and the acoustic modes to be essentially equal to  $PuH_{1.9}$  and  $PuH_2$  at 298.15 K. The contribution from the conduction electrons and the excess effect noted just below 250 K may be slightly higher or lower, but there is no way to know and, therefore, we assume they are the same for both hydrides. The change from n(H)/n(Pu) = 1.9 to 2.0 will increase the values of the functions and the change can easily be calculated using appropriate harmonic-oscillator functions.<sup>(21)</sup> As mentioned earlier, the average optical-mode wavenumber for hydrogen in tetrahedral sites is 1000 cm<sup>-1</sup>, and this is the only variable needed to adjust

the thermodynamic functions of  $\operatorname{PuH}_{1.9}$ . The results for  $\operatorname{PuH}_2$  at 298.15 K are:  $C_{p,m}^{\circ} = 43.50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $S_{m}^{\circ} = 72.84 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ,  $\{H_{m}^{\circ}(T) - H_{m}^{\circ}(0)\} = 8593 \text{ J} \cdot \text{mol}^{-1}$ , and  $-\{G_{m}^{\circ}(T) - H_{m}^{\circ}(0)\}/T = 44.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . We believe that these values have a probable error of 1 per cent. At 350 K, where the low-temperature and high-temperature heat capacities overlap,  $C_{p,m}^{\circ}(\text{PuH}_2, \text{ cr}, 350 \text{ K}) = (48.9 \pm 0.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  from the low-temperature results may be compared with  $(49.1 \pm 1.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  from the high-temperature results.

#### THERMODYNAMIC FUNCTIONS OF PuH<sub>2</sub> TO 600 K

The thermodynamic functions for  $PuH_2$  are given in table 7. These results are based on the heat capacity and entropy of  $PuH_2$  derived from the low-temperature results at 298.15 K and the heat capacity of  $PuH_{2.0}$  obtained from the high-temperature results, where the heat-capacity values in the temperature range 298.15 to 600 K are

T	$C_{p,m}^{\circ}$	$S_m^{\circ}(T)$	$H_{\rm m}^{\circ}(T) - H_{\rm m}^{\circ}(298.15 {\rm K})$	$-\{G_{\rm m}^{\circ}(T)-H_{\rm m}^{\circ}(298.15 {\rm K})\}/T$
ĸ	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	J · mol <sup>−1</sup>	$J \cdot K^{-1} \cdot mol^{-1}$
298.15	43.50	72.84	0.00	72.84
300.00	43.71	73.11	80.70	72.84
310.00	44.73	74.56	522.88	72.87
320.00	45.78	75.99	975.40	72.95
330.00	46.87	77.42	1438.61	73.06
340.00	47.98	78.84	1912.82	73.21
350.00	49.12	80.24	2398.30	73.39
360.00	50.28	81.64	2895.27	73.60
370.00	51.46	83.04	3403.95	73.84
380.00	52.65	84.45	3924.49	74.10
390.00	53.86	85.81	4457.04	74.38
400.00	55.07	87.19	5001.68	74.68
410.00	56.29	88.56	5558.48	75.01
420.00	57.51	89.93	6127.46	75.34
430.00	58.72	91.30	6708.62	75.70
440.00	59.93	92.67	7301.90	76.07
450.00	61.13	94.03	7907.23	76.45
460.00	62.32	95.38	8524.50	76.85
470.00	63.49	96.74	-153.55	77.26
480.00	64.64	98.08	9794.21	77.68
490.00	65.76	99.43	10446.24	78.11
500.00	66.86	100.77	11109.40	78.55
510.00	67.93	102.10	11783.39	78.99
520.00	68.96	103.43	12467.90	79.45
530.00	69.96	104.75	13162.56	79.92
540.00	70.91	106.07	13866.97	80.39
550.00	71.82	107.38	14580.71	80.87
560.00	72.69	108.68	15303.31	81.36
570.00	73.50	109.98	16034.27	81.85
580.00	74.25	111.26	16773.05	82.34
590.00	74.95	112.54	17519.09	82.84
600.00	75.58	113.80	18271.77	83.35

TABLE 7. Standard molar thermodynamic functions for  $PuH_2(cr)$ .  $p^\circ = 101325$  Pa

represented by the equation:

$$C_{p,m}^{\circ}(\operatorname{PuH}_{2.0}, \operatorname{cr})/(J \cdot K^{-1} \cdot \operatorname{mol}^{-1}) = 47.307 - 0.1763(T/K) + 7.231 \times 10^{-4}(T/K)^2 - 5.845 \times 10^{-7}(T/K)^3.$$
 (6)

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