

ENTHALPIES AND TEMPERATURES OF TRANSFORMATION FOR PLUTONIUM USING A DIFFERENTIAL SCANNING CALORIMETER*

C. E. ROLON and G. F. GALLEGOS

*Organic Materials Division, Chemistry and Materials Science Department,
University of California, Livermore, California 94550, USA*

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The enthalpies and temperatures of transformation of high purity plutonium were measured using a differential scanning calorimeter. The results of our study are presented and compared to values obtained by previous methods.

The solid state phase transformations of Pu are of interest both because of the large number of allotropic modifications (5) that occur and their crystallographic complexity [1]. We have re-investigated these transformations using a Perkin-Elmer DSC-2 differential scanning calorimeter (DSC). The advantages of a DSC for this type of work are that hysteresis effects and self-heating problems are minimized because of the small sample size coupled with a high sensitivity. The sample purity was quite high (see Table 1). The technique for the DSC measurements was usual except for the use of oxidized Ta pans. Table 1 lists the results and compares these to previous determinations. The errors are shown in Table 1. The cast Pu samples were kept at 255 K for 315 days before testing to insure as complete a transformation to the α phase as possible.

Calibration standards for both temperatures and enthalpies of transition were high purity In (99.99%) and Pb (99.99%). These standards were dynamically scanned at temperatures near their melting points until the phase changes were complete. Pu samples weighed ~ 30 mg and had a plate-like geometry to insure good thermal contact.

Figure 1 is a plot of dH/dT vs. T that was computer generated from the raw data which was normalized and baseline corrected. The heating rate of the DSC runs was 10 K min^{-1} . Due to the difficulty in resolving the $\delta - \delta'$ and $\delta' - \epsilon$ endotherms, runs were also made at a heating rate of 2.5 K min^{-1} with increased instrument sensitivity. Changes in the heating rates did not affect measured transition temperatures.

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Table 1
Results

Present work*			Literature ⁺	
trans-formation	temp. of transformation, K	ΔH_T , Joules/mole	temp. of transformation, K	ΔH_T , Joules/mole
$\alpha - \beta$	$399.6 \pm 0.6^{**}$	$3503 \pm 140^{**}$	395 ± 4	3420 ± 84
$\beta - \gamma$	489.7 ± 0.9	486 ± 38	480 ± 5	565 ± 63
$\gamma - \delta$	592.6 ± 0.2	655 ± 30	588 ± 7	586 ± 63
$\delta - \delta'$	736.0 ± 2.0	103 ± 41	730 ± 2	84 ± 42
$\delta' - \epsilon$	755.7 ± 1.0	1617 ± 187	752 ± 4	1841 ± 84
$\epsilon - \text{liq.}$	912.1 ± 0.8	2644 ± 175	913 ± 2	2824 ± 105

Chemical composition of sample

^{238}Pu	0.009 wt %	Pu assay 99.96 wt % Sum of spectroscopically determined impurities [2315] ppm.
^{239}Pu	93.64	
^{240}Pu	5.60	
^{241}Pu	0.630	
^{242}Pu	0.03	
^{241}Am	≈ 470 ppm	

* Average of 5 runs.

Heating rates 10 K min^{-1} and 2.5 K min^{-1} .

** 95 percent confidence level.

⁺ Ref. 2. The table on p. 24 of Ref. 2 contains a summary of 15 independent determinations by four traditional methods. The values listed here are those suggested in Ref. 2.

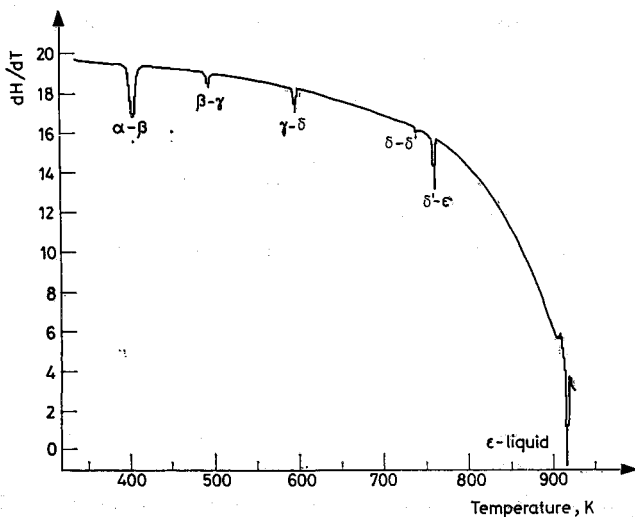


Fig. 1

Our DSC data do not completely agree with the results of previous methods [2]. However, the high accuracy and sensitivity of this method coupled with high purity samples lend added credence to these results and should be considered in determining the recommended values for these transitions.

References

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2. F. L. OETTING, M. H. RAND and R. J. ACKERMANN, "The Chemical Thermodynamics of Actinide Elements and Compounds", Part 1. The Actinide Elements, International Atomic Energy Agency, Vienna, pp 24, 1976.