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THE HALF-LIFE OF PLUTONIUM-239

BY CALORIMETRY *

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The power output from two 1-kilogram samples of pure plutonium metal has been determined by isothermal calorimetry. The major isotopic constituent in both samples was plutonium-239, accounting for 93% in the first sample and 97% in the second sample. After making power corrections for the remaining isotopes, the specific power output of plutonium-239 was found to be $1.931 \pm 0.004 \times 10^{-3}$ watts/gram. The power emitted by the two samples remained essentially constant ($\pm 0.1\%$) for a period of four months.

Using the alpha zero energy for plutonium-239 of 5.1556 Mev and the recoil energy of 0.0863 Mev, the alpha half-life of plutonium-239 was calculated to be $24{,}065 \pm 50$ years. This is compared to the currently accepted value of $24{,}400 \pm 30$ years as determined by absolute alpha (specific activity) low geometry counting techniques.

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DISCLAIMER

INTRODUCTION

Recent calorimetric investigations on the specific powers of the isotopes U-233 (1), Pu-240 (1), and Am-241 (2) have indicated that the half-life of these isotopes as calculated from the specific power is approximately 1% lower than the half-life as determined by the absolute alpha (low geometry) specific activity method. Either method should theoretically give the same half-life value as both methods "count" the alpha particles; the specific activity method by direct counting and the calorimetric method by total or integrated counting. No conclusive evidence evolved from the above investigations to explain the 1% discrepancy between the half-life values as obtained by these two different methods even though each method claims an accuracy of at least ± 0.2%.

Because of the importance of an accurate half-life value for Pu-239, this calorimetric investigation was initiated. In addition, previous calorimetric investigations on Pu-239 (3,4), not as rigorous as this study, indicated a half-life of about 1% below the value recommended by specific activity measurements. In order to obtain a well-defined power measurement on Pu-239, two samples of electrorefined metal were obtained with different isotopic compositions. This approach should partially eliminate any conceivable error due to improper isotopic or chemical analyses.

The results of this investigation did indeed indicate that there is even a greater discrepancy than 1% between the calorimetric and specific activity half-life value for Pu-239.

EXPERIMENTAL

Material

Two samples of plutonium metal were used for this calorimetric investigation. These samples, hereafter referred to as sample A and sample B, were purified by electrorefining. Sample A weighed 717.8 grams while sample B weighed 934.4 grams. Both samples, packaged in identical fashion for the calorimetric measurements, were vacuum sealed under an argon atmosphere in an aluminum container which in turn was sealed in a No. 3 can which fit the calorimeter. This type of encasement was undertaken to insure against oxidation of the metal during the calorimetric measurements.

Analyses

Both samples were chemically analyzed for plutonium after the calorimetric measurements were terminated by the ceric titration method corrected for iron and uranium. These analyses indicated 99.96% plutonium for sample A and 99.91% plutonium for sample B.

Each sample was also subjected to detection of elemental impurities by emission spectroscopy and spark source spectroscopy. Some elements are more reliably detected by emission spectroscopy than by spark source spectroscopy while with other elements the reverse is true. Accordingly the amount of impurity for each individual element was determined by the most reliable method. From these results, sample A contained 344 ppm and sample B contained 410 ppm impurity. These impurities included the metallic elements such as Al, B, Ca, Cr, Fe, Ga, K, Mg, Mn, Ni, Si, Sn, Ta, U, W, and Zn as well as the non-metallic elements C, Cl, N, and O.

Radioassay for americium-241 and plutonium-238 was also performed on the two samples after the calorimetric experiments. These results indicated 32 ppm Pu-238 and 157 ppm Am-241 for sample A and 103 ppm Pu-238 and 459 ppm Am-241 for sample B. Thus the total non-plutonium assay in sample A is 501 ppm (99.95% Pu) which is in good agreement with the chemical assay of 99.96% Pu. For sample B the total non-plutonium assay is 869 ppm (99.91% Pu) which again is in good agreement with the chemical assay of 99.91% Pu.

Americium analyses was also made prior to the calorimetric measurements. These values were 114 ppm Am-241 for sample A and 277 ppm for sample B. These values were used only to determine the growth of Am-241 in the sample during the course of the calorimetric measurements whereas the values determined at the completion of the calorimetric measurements were used in the comparison of the plutonium analysis. It must be noted that the americium content is still comparatively large for electrorefined metal but this was due to the length of time between the electrorefining process and the beginning of the calorimetric measurements.

Both samples were analyzed isotopically on three different occasions, once before the calorimetric measurements and twice after the calorimetric measurements. The weight percent of each isotope is indicated in Table I where the individual value is the average of the three determinations. The limit of error assigned to each isotope was determined by the performance of the mass spectrometer with regard to standard materials at the time that the three isotope analyses were taken. The following limits of error were used: Pu-239 $\pm$ 0.035%, Pu-240 $\pm$ 0.035%, Pu-241 $\pm$ 0.007%, and Pu-242 $\pm$ 0.002%. Plutonium-238 and americium-241 were determined by radioassay as stated previously where the limits of error were Pu-238 $\pm$ 2 ppm and Am-241 $\pm$ 11 ppm.

The samples were also subjected to alpha pulse analysis for detection of foreign isotopes. Only those isotopes listed in Table I were found in either sample.

TABLE I

Isotopic Analysis

	Sample A	Sample B
Pu-238	32 ppm	103 ppm
Pu-239	97.618%	93.847%
Pu-240	2.302%	5.737%
Pu-241	0.073%	0.386%
Pu-242	0.004%	0.021%
Am-241	157 ppm	459 ppm

Calorimetry

The calorimeter used in this investigation is a macro-twin isothermal calorimeter which has been described previously (3). The calorimeter was periodically standardized with a Pu-238 1.6 watt source throughout the course of the calorimetric measurements on the plutonium samples. The 1.6 watt source was available from Mound Laboratory where it had previously been calorimetered on a number of occasions. This is the same calorimeter that was used in the americium work (2) when at that time this calorimeter agreed within 0.1% with the calorimeters at Livermore Radiation Laboratory. Thus with this intralaboratory comparison there was no reason to doubt the results of this calorimeter.

RESULTS

The calorimetric measurements were made on the two samples over a period of about four months. In each case the resulting power was corrected for 100.00% purity and radioactivity decay of Pu-241 to Am-241. Table II gives the day that the specific sample was calorimetered and the resulting power values for the Pu-239 in watts/gram. The total power emitted by sample A was about 1.5 watts while that for sample B was a little over 2 watts. These powers are in the ideal power range for this calorimeter in terms of accuracy of measurement. The error ascribed to the power measurement is $\pm$ 0.1%.

In order to obtain the power value per gram of Pu-239 it was necessary to subtract the power emitted by Pu-238, Pu-240, Pu-241 and Am-241 from the measured power and then normalize to a Pu-239 gram basis. There is such a small amount of Pu-242 present that the power emitted by this isotope is insignificant. A typical example of the above calculation for both samples is given in Table III. Here it is noted that in the case of sample A, the Pu-239 accounted for over 90% of the total power whereas in sample B the Pu-239 accounted for only 78% of the total power.

TABLE II

Calorimetric Results
Power of Pu-239 in Watts/Gram x 10^6

Day	Sample A	Sample B
1	1931.0	
3	1930.8	
7		1930.9
10		1933.2
34	1930.5	
39		1933.0
42		1933.6
74	1929.6	
77	1932.4	
83		1930.3
85		1929.3
134		1929.2
136		1930.3
137	1932.4	
	1931.1 ± 0.9	1931.2 ± 1.3

TABLE III

Sample Calculation for Pu-239 Specific Power

	Sample A Watts	% of Total Watts	Sample B Watts	% of Total Watts
Sample	1.49491		2.17469	
Pu-238	-0.01322	0.9	-0.05453	2.5
Pu-240	-0.11722	7.8	-0.38018	17.5
Pu-241	-0.00187	0.1	-0.01288	0.6
Am-241	-0.01010	0.7	-0.03502	1.6
Pu-239	1.35250	90.5	1.69208	77.8
Pu-239 watts/g	1.9310×10^{-3}		1.9309×10^{-3}	

As Table II indicates the average power per gram of Pu-239 in sample A is $1.9311 \pm 0.0009 \times 10^{-3}$ watts/gram whereas the average power per gram of Pu-239 in sample B is $1.9312 \pm 0.0013 \times 10^{-3}$ watts/gram where the assigned deviation is twice the standard deviation of the mean. The above error only reflects the experimental deviation and not the absolute error. These values may be combined to give $1.93115 \pm 0.0008 \times 10^{-3}$ watts/gram for the specific power of Pu-239.

The absolute error associated with the specific power of Pu-239 is derived from the following values; weight of sample ± 0.1 gram, Pu-238 analyses ± 2 ppm, Pu-238 power 0.567 ± 0.002 watts/gram (5), Pu-239 isotopic ± 0.035%, Pu-240 isotopic ± 0.035%, Pu-240 power $7.097 \pm 0.014 \times 10^{-3}$ watts/gram (1), Pu-241 isotopic ± 0.007%, Pu-241 power $3.62 \pm 0.001 \times 10^{-3}$ watts/gram (6), Am-241 analyses ± 11 ppm

and Am-241 power 0.1145 ± 0.0001 watts/gram (2). Application of statistical analyses to the errors involved indicate that the specific power for Pu-239 is $1.9311_5 \pm 0.0039 \times 10^{-3}$ watts/gram.

Using this specific power, the half-life may be calculated accordingly. The physical constants and conversion factors are taken from Friedlander et al., (7) except for the decay energy.

Since one watt is equivalent to 6.2418×10^{12} Mev, the specific power of Pu-239 is 1.20538×10^{8} Mev $sec^{-1}g^{-1}$.

The alpha decay energy for Pu-239 has been determined by Baranov, et al., (8) to be 5.1556 ± 0.0008 Mev. This value is in good agreement with many other values discussed elsewhere (9). The energy resulting from the recoil of the parent nucleus is 0.0863 Mev so the total energy resulting from a single alpha decay is 5.2419 Mev.

From the specific power value and the energy per alpha particle, the specific decay rate is 2.2995×10^{8} $sec^{-1}g^{-1}$. Using 6.02252×10^{23} atom/mole for Avogadro's number and 239.05216 for the isotopic mass (C^{12} scale), the decay constant is calculated to be 9.12742×10^{-13} sec^{-1}. Dividing this into 0.693147, a half-life of 7.59412×10^{11} sec is calculated. If one defines a year as 365.24 days (3.15567×10^{7} sec/yr), the resulting calculation shows the half-life of Pu-239 to be 24,065 ± 50 where the stated uncertainty is derived from the uncertainty in the specific power given earlier and the uncertainty in the alpha decay energy (±0.005%).

DISCUSSION

Considerable effort has been expended in the determination of the half-life of Pu-239 since the discovery of the element in 1940. The majority of these investigations have relied on the absolute alpha (low geometry) specific activity method. Table IV gives a summary of the reported half-lives of Pu-239. Comparison between the specific activity method and the calorimetric method indicates that the half-life values as determined by the specific activity method are consistently about 1.2-1.3% higher than the half-life value determined by calorimetry. It is surprising that these two sets of values as determined by calorimetry and specific activity should differ as they do, however there appears to be no other interpretation of the data.

If we confine ourselves to the specific activity work of Dokuchaev (14) and Markin (15) and to the calorimetric work reported here, it is evident that the limit of errors reported in these three cases is a little over ± 0.1% yet the differences between the specific activity value and the calorimetric value for the half-life are about 300 years or 1.3%, considerably greater than the error ascribed to either method would indicate.

TABLE IV

Plutonium-239 Half-Life

Investigator	Year	Method	Value
Farwell, et al., (10)	1945	Sp Ac	24,400
Westrum, et al., (11)	1946	Sp Ac	24,400 ±70
Cunningham + Werner (12)	1949	Sp Ac	24,300
Wallmann (13)	1951	Sp Ac	24,360 ±100
Dokuchaev (14)	1959	Sp Ac	24,390 ±30
Markin (15)	1959	Sp Ac	24,412 ±30
Stout + Jones (4)	1945	Cal	24,100 ±240
This Work	1970	Cal	24,065 ±50

One of the complications in the determination of the half-life of Pu-239 by specific activity is the presence of small amounts of Pu-238 and Pu-240 which contribute to the alpha activity. Dokuchaev (14) apparently circumvented the potential trouble by measuring the activity of 12 samples of plutonium with a Pu-239 content ranging from 91.26 to 99.11%. Markin (15), on the other hand, measured the activity of electromagnetically separated Pu-239 with an isotopic purity of 99.92%. Therefore because of the care and caution taken with these measurements, there appears to be no reason to doubt the half-life value as reported by specific activity.

However there is also no apparent reason to doubt the calorimetric value for the half-life of Pu-239. Gross undetected chemical impurities would imply a higher true specific power and a shorter half-life than indicated here. Absence of significant quantities of short-lived high specific power radioactive impurities had been well-established by alpha pulse scanning as well as the lengthy duration of the calorimetric experiments. Oxidation of the sample was prevented by enclosing the sample in an inert atmosphere under a vacuum tight seal. The accuracy of the calorimetric procedure is well-substantiated.

One of the possible complications in the calorimetric determination of the specific power of Pu-239 is the presence of other plutonium isotopes which entails a power correction to the measured power of the sample. This power correction therefore relies not only on the specific power of the other isotopes but also on the amount of the other isotopes which are present. Although the specific powers of the other isotopes are well-known and the amount present is quite reliable (mass spectrometric technique) there is still a remote possibility that the correction calculation may be in error. This work has indicated that there is no apparent gross error in the correction calculation because the amount of correction is significantly different for the two samples and yet the specific power for Pu-239 determined from the two samples is in excellent agreement.

The energy contained in the alpha particle emitted during nuclear disintegration is theoretically transformed to thermal energy when the particle has terminated its travel. It is known that for plutonium some of this energy is transformed into disorientations within the crystal lattice commonly referred to as radiation damage. Radiation damage is quite prevalent at low temperatures, e.g., 4° K, and tends to anneal out of the crystal as the temperature of the sample increases. There is apparently very little radiation damage occurring at room temperature and that which does occur is annealed out so that the net energy effect is zero.

It is believed that radiation damage has no effect on these measurements since the metal was initially taken to the melt for the electrorefining process and then cooled to room temperature before the calorimetric measurements commenced. The temperature of the sample did not go below room temperature at any point. Also if radiation damage were taking place, the measured power would be less than the power expected which would in turn lead to a longer half-life. A remote possibility remains that the sample could be annealing out faster than radiation damage was occurring which would explain a high power emission. This appears to be highly improbable when the thermal history of the sample is considered.

Calorimetry relies upon the energetics of the alpha particle decay process or more specifically the Q value of the nuclear disintegration to determine the number of decays per unit time. Because the Q value is not involved in the specific-activity method of determination of half-life, this raised the possibility that the Q value could be the cause of the discrepancy between the two half-life values. A critical examination of the Q value concept indicates that the Q value is valid. Indeed considerable consequence would develop if the Q value were in error as the mass tables are based on the energetics of the decay scheme, i.e., Q values. A recent mass table by Wapstra, et al., (16) gives the Q value for the Pu-239 alpha decay to U-235 as 5.243 Mev, nearly identical to the Q value used in this calculation. It therefore appears highly doubtful that the energetics of Pu-239 decay are in error by any significant amount.

In light of the discussion it appears that there is no definitive reason to explain the 1% discrepancy in the half-life of Pu-239. This is an unfortunate development as certainly one would expect much better agreement in the half-life value from two well-established experimental techniques such as calorimetry and alpha counting.

It is perhaps enlightening to review two cases of a similar situation which have occurred over the past few years. The Am-241 isotope had a well-established half-life of 458 years by counting techniques reported as late as 1959. However a calorimetric investigation in 1967 (2) reported 432.7 ± 0.7 years which was later substantiated by a counting value of 436.6 ± 3.0 years (17).

The half-life of U-233 up to 1961 was reported by a number of investigators using alpha counting techniques as 1.62×10^5 years. Recent calorimetric studies however indicated a half-life of $1.540 \pm 0.003 \times 10^5$ years for U-233 which is in considerable disagreement with the counting half-life value. However a recent counting value in 1968 (18) reported $1.553 \pm 0.010 \times 10^5$ years which is within the limits of error of the calorimetric value. In both cases, Am-241 and U-233, the recent counting values tend to be higher than the calorimetric value by about 1%, however the limit of error in these counting values is significantly greater than the limit of error in the counting value listed for Pu-239. There is still the implication that the counting values for Am-241 and U-233 tend to run high compared to the calorimetric values.

This value for the half-life of Pu-239 of 24,065 years instead of 24,400 years as previously accepted would effect the physical constants of Pu-239 such as the decay constant, etc. In addition, this value would also alter the half-lives of other plutonium isotopes whose half-life was determined relative to the Pu-239 half-life by the method of isotopic ratios.

Plutonium-240 has been determined to have a half-life of 6580 ± 40 years (19) relative to a Pu-239 half-life of 24,410 years. If 24,065 years is used as the Pu-239 half-life, Pu-240 has a half-life of 6487 ± 40 years in agreement with the calorimetric value for Pu-240 of 6524 ± 10 years (1). This is somewhat fortuitous however as 6580 ± 40 years is also in agreement with the specific activity value of 6600 years for Pu-240.

The half-life of Pu-242 and Pu-244 have been determined to be $3.869 \pm 0.016 \times 10^5$ years and $8.28 \pm 0.10 \times 10^7$ years respectively (20) in reference to a Pu-239 half-life of 24,401 years. Using the calorimetric half-life for Pu-239 the half-lives for Pu-242 and Pu-244 are $3.816 \pm 0.016 \times 10^5$ years and $8.17 \pm 0.10 \times 10^7$ years respectively.

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