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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA o LOS ALAMOS NEW MEXICO

THE HEAT OF COMBUSTION OF PLUTONIUM

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OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

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THE HEAT OF COMBUSTION OF PLUTONIUM

(Title Unclassified)

by

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Los Alamos Report Library	1-20
Aerojet-General Corporation	21
Aerojet-General, San Ramon (IOO-880)	22
AFPR, North American, Canoga Park	23
Albuquerque Operations Office	24
Alco Products, Inc.	25
Argonne National Laboratory	26-29
Armed Forces Special Weapons Project, Washington	30
Army Chemical Center	31
Atomic Energy Commission, Washington	32-34
Atomics International	35-36
Babcock and Wilcox Company (NYOO-1940)	37
Babcock and Wilcox Company (SOO-274)	38
Bettis Plant (WAPD)	39-40
Brookhaven National Laboratory	41
BAR, Aerojet-General Azusa	42
Chicago Operations Office	43
Chicago Patent Group	44
Combustion Engineering, Inc.	45
Division of International Affairs (Pennington)	46
duPont Company, Aiken	47-50
Fluor Corporation	51
General Electric Company (ANPD)	52
General Electric Company, Richland	53-56
Goodyear Atomic Corporation	57
Hanford Operations Office	58
Iowa State College	59
Knolls Atomic Power Laboratory	60
Mallinckrodt Chemical Works	61
Marquardt Aircraft Company	62
Mound Laboratory	63
National Advisory Committee for Aeronautics, Cleveland	64
National Lead Company of Ohio	65
Naval Research Laboratory	66
New York Operations Office	67
Nuclear Metals, Inc.	68
Oak Ridge Operations Office	69
Patent Branch, Washington	70
Phillips Petroleum Company (NRTS)	71-72
Union Carbide Nuclear Company (ORGDP)	73-74
Union Carbide Nuclear Company (ORNL)	75-78
USAF Project RAND	79
U. S. Naval Radiological Defense Laboratory	80
UCLA Medical Research Laboratory	81
University of California Radiation Laboratory, Berkeley	82-83
University of California Radiation Laboratory, Livermore	84-85
University of Rochester	86
Vitro Engineering Division	87
Walter Reed Army Medical Center	88
Technical Information Service Extension (For Official AEC Use)	89-128

[redacted]

[redacted]

ABSTRACT

Precise measurements have been made of the heat of combustion of α-plutonium metal. The heat of combustion of α-plutonium was found to be 4413.4 $\pm$ 4.1 joules/g. at an oxygen pressure of 25 atm. The heat of formation of PuO_2 is calculated to be -1057.7 $\pm$ 1.0 kjoules/mole.

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TABLE OF CONTENTS

TABLE

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Introduction

This report describes the measurements made with an oxygen combustion calorimeter to determine the heat of formation of plutonium dioxide. The only experimentally determined value in the literature for the heat of formation of PuO_2 seems to be that of Popov and Ivanov[1] although some early estimates exist.[2,3]

Method

The method involved the determination of the heat evolved from the burning of a weighed sample of α-plutonium metal in an oxygen bomb calorimeter at a known initial pressure. The calorimeter and its calibration have been described.[4] The energy equivalent of the calorimeter with 25 atm. oxygen was 10,017.8 ± 4.2 joules/°C. as determined with NBS benzoic acid, sample 39f.

The completeness of combustion was determined for each run by grinding the combustion product to a fine powder and igniting at 1000°C. in air. An increase in weight indicated unburned material.

The uncertainties given are twice the standard deviation.

The results are expressed in absolute joules and also in defined calories; 1 defined calorie = 4.1840 absolute joules.

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Because of its toxicity, the plutonium was handled through gloves in an argon atmosphere dry box, where it was cleaned with a file, weighed, and loaded into the bomb. The Parr bomb was screwed into an adapter in the floor of the dry box from the outside so that the outside surface of the bomb remained uncontaminated. Although the top of the bomb was in the dry box, it was protected from serious contamination by means of another adapter which threaded onto the top and shielded it by means of a hood. The bomb was flushed with oxygen prior to a run and exhausted afterwards; operations were carried out in a ventilated hood. In each case the bomb gases were passed through a fiberglass and cotton filter before exhausting to the atmosphere. These precautions were sufficient to prevent contamination of any of the accessory apparatus.

Plutonium Metal

The α-plutonium metal was analyzed at this Laboratory with the following results: Mg, 0.005%; Al, 0.002%; Si, 0.005%; Mn, 0.0025%; Fe, 0.002%; C, 0.004%; O, 0.0035%; and H, 0.0008%. The oxygen was determined by the argon fusion method,[5] the carbon by a microcombustion method, and the hydrogen simply by heating a sample of the metal above its melting point and collecting and analyzing the evolved gas. No other metallic impurities were present in amounts greater than 0.001%. The metal was thus about 99.97% plutonium. The chemical state of the impurities is not known. If it is assumed that the oxygen and carbon

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were combined with the plutonium metal as PuO_2 and PuC, respectively, and not combined with the metallic impurities, then the material was 99.67 mole % plutonium metal.

Density measurements made on the metal revealed a value of 19.56 g./cc., indicating about 8% β-plutonium.

An isotopic analysis of the metal showed 94.55 $\pm$ 0.05 atomic % Pu^{239}, 5.10 $\pm$ 0.05 atomic % Pu^{240}, and 0.35 $\pm$ 0.01 atomic % Pu^{241}. A value of 239.1 is taken as the atomic weight of the plutonium.

Combustion of Plutonium

The plutonium was burned as chunks on sintered discs of plutonium dioxide supported on a platinum platform weighing 29.1 g. New discs, usually three, were used for each run. The discs were made by mixing 2 wt. % Carbowax Pl-400 in CCl_4 with the PuO_2 powder and allowing the CCl_4 to evaporate. Thirty and 60 g. discs were pressed at 10,000 p.s.i. under vacuum for periods of 5 minutes. They were then fired at 1000°C. in air for several hours. Because of its flexibility a 10 mil diameter fuse wire of gallium stabilized δ-plutonium (1 wt. % Ga) was used to ignite the main mass of plutonium. It was threaded through a small hole drilled in the chunk. Since the weight of alloy was only about 2% the weight of the α-plutonium, an accurate value for its heat of combustion was not needed. In all runs 25 atm. oxygen pressure was used. The metal showed no increase in weight when exposed to this pressure for 1 hour. Six runs were made on α-plutonium and two on the alloy. Combustion was complete in all runs. X-ray patterns were taken of each combustion product. The average value for the lattice constant of the cubic unit cell, CaF_2 type, was found to be a = 5.3954 ± 0.0003 Å. This value is slightly smaller than the value of 5.3960 Å which is generally considered correct for stoichiometric PuO_2 and may indicate an oxygen content slightly greater than that needed for stoichiometric PuO_2. The average initial temperature for the runs was 25.3°C. The results are listed in Table I.

Table I

THE HEAT OF COMBUSTION OF PLUTONIUM

Mass α-Pu Burned, g.	Mass δ-Pu Burned, g.	Wt. PuO_2, g.	joules/°, total	ΔT, °K.	Energy from Firing, joules	Energy from Pu, joules/g.	Dev. from Mean
2.9876	0.0622	87.7	10042.5	1.3435	7.2	4420.7	4.3
2.9294	0.0573	106.4	10047.0	1.3126	5.5	4412.6	3.8
3.1487	0.0658	121.3	10050.6	1.4130	6.3	4415.0	1.4
3.2339	0.0618	135.6	10054.0	1.4489	6.8	4417.1	0.7
2.9899	0.0615	135.9	10054.1	1.3404	6.7	4413.3	3.1
3.2311	0.0612	160.6	10060.0	1.4474	6.3	4419.9	3.5
					Av.	4416.4	2.8
					2 x St. Dev.		2.8
	3.2542	129.2	10052.5	1.4441	6.7	4458.9	
	3.2274	128.9	10052.4	1.4355	6.9	4469.0	
					Av.	4464.0	

The specific heat of PuO_2 is estimated at 0.240 joule/g./°. The specific heat of platinum is taken as 0.136 joule/g./°, and the specific heat of O_2 as 0.651 joule/g./°. The amount of Ga_2O_3 formed is so small that its contribution to the energy equivalent of the calorimeter may be neglected. The average value of 4416.4 joules/g. for the α-plutonium must be corrected for the impurities present.

Correction for Impurities

The calculated percentage composition of the α-plutonium by weight is Pu metal, 99.85; PuO_2, 0.03; PuH_2, 0.10; Mg, 0.005; Si, 0.005; Al, 0.002; Mn, 0.0025; Fe, 0.002; C, 0.004. The carbon may be combined with the plutonium as PuC but the amount is small and no serious error is introduced by assuming it to exist in the free state. The heats of combustion of graphite (to CO_2), Mg (to MgO), Si (to SiO_2), Al (to Al_2O_3), Fe (to Fe_2O_3), and Mn (to MnO_2) are taken as 33,000, 24,670, 30,100, 30,970, 7,320, and 9,430 joules/g., respectively. The heat of combustion of the plutonium metal is calculated by equating the sum of the heats of each of the components to the observed heat of combustion and solving for the heat of combustion of the pure plutonium metal. This figure becomes 4413.4 joules/g. or 0.07% lower than the uncorrected value.

Calculation of the Uncertainties

The uncertainties to be attached to the corrected value include

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the uncertainty in the determination of the energy equivalent, which is 0.04%, the uncertainty in the calorimetric measurements which is 2.8 joules/g., or 0.06%, and the uncertainty introduced in the correction for the impurities which is estimated at 0.06%. The combined uncertainty is 4.1 joules/g. The value for the heat of combustion gives, for the reaction in the bomb, a value of $\Delta E_{25.3°} = -1055.2 \pm 1.0$ kjoules/mole (atomic weight of plutonium = 239.1). The correction of this value to 25°C. is less than the uncertainty in the result.

Heat of Formation of PuO_2

To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. Using Rossini and Frandsen's[6] value of $(\partial \Delta E / \partial P)_{301°K.} =$ -6.51 joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$, the value for the heat of formation of PuO_2 becomes -1058.0 ± 1.0 kjoules/mole. Correcting for the 8% β-plutonium present, assuming a heat of 940 calories/mole for the transition,[7] yields a final value, $\Delta H_{25°} =$ -1057.7 ± 1.0 kjoules/mole for the heat of formation of PuO_2. In defined calories this is -252.80 ± 0.24 kcal./mole. The value obtained here for the heat of formation of PuO_2 agrees with that of Popov and Ivanov (-252.4 ± 1.1 kcal./mole) within experimental error. NBS Circular 500[3] gives -251 kcal./mole and Brewer[2] estimates -246 ± 10 kcal./mole.

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Bibliography

(1) Popov, M. M., and Ivanov, M. I., Soviet Jour. Atomic Energy, English Trans., 2, No. 4, 439 (1957).

(2) Brewer, L., Chem. Revs., 52, 1 (1953).

(3) Selected Values of Chemical Thermodynamic Properties, NBS Circular 500, 1952, p. 355.

(4) Holley, C. E., Jr., and Huber, E. J., Jr., "A Precision Calorimeter for the Measurement of Heats of Combustion," LA-2084, November, 1955.

(5) Smiley, W., Anal. Chem., 27, 1098 (1955).

(6) Rossini, F. D., and Frandsen, M., J. Research Natl. Bur. Standards, 9, 733 (1932).

(7) Holley, C. E., Jr., et al., "Thermodynamics and Phase Relationships for Plutonium Oxides," Second International Conference on the Peaceful Uses of Atomic Energy, A/Conf. 15/P/701, USA, June, 1958.

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