HEATS OF FORMATION OF PuO₂ AND U₃O₈

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The heats of formation of PuO₂ and U₃O₈ have been determined by burning pure plutonium and uranium in a bomb calorimeter. The latter substance served for the development of the method. From two series of experiments there was found for PuO₂ the value $\Delta H_{298.15}^\circ = -252.4 \pm 1.1$ kcal/mole, and for U₃O₈ the value found is $\Delta H_{298.15}^\circ = -856.5 \pm 3.1$ kcal/mole, which is in good agreement with the data in the literature.

The heat of formation of PuO₂ has not been determined experimentally. According to an estimate of Brewer, Bromley, and others in 1949 [1], it is equal to 251 kcal/mole, and according to a 1953 estimate of Brewer [2] it is 246 ± 5 kcal/mole.

The heat of formation of U₃O₈ determined by Mixter [3] by burning uranium in a bomb is equal to 845.2 kcal/mole; according to a calculation of the same author [3] based on the heat of reaction of uranium and U₃O₈ with sodium peroxide, it is equal to 895.5 kcal/mole.

According to a determination of Huber and others [4], the heat of formation of U₃O₈ is 854.4 ± 3.0 kcal/mole.

The absence of an experimental value of the heat of formation of PuO₂ leads us to carry out a measurement of this quantity. The development of the method for determining the heat of formation of PuO₂ was worked out with uranium.

Calorimetric Apparatus

In this work two calorimeters of universal type were used, having isothermal cases and differing in the capacity of the calorimetric vessel. The measurement of the temperature in the first calorimeter was carried out with a metastic thermometer and in the second with a calorimetric thermometer. The precision of reading in the first case was ± 0.0005 °, and in the second ± 0.001 °. The temperature in the case of each calorimeter was kept constant to an accuracy of ± 0.01 °. The initial temperature in both experiments was the same (fluctuation ± 0.02 °). The burning was carried out in a Roth bomb (volume 25 ml). Distilled water was the calorimetric fluid. The weighing of the calorimetric vessel with the water and the bomb was carried out to an accuracy of ± 0.0002 %. The weight of the substances to be burned was determined to the accuracy of ± 0.00001 g.

Characteristics of the Uranium and Plutonium

For the burning we used three specimens of uranium (α-modification). The content of impurities in each of them did not exceed a total of 0.1%. Metallographic studies of all the specimens established the absence of inclusions of oxides. Only inclusions of carbides were found.

* Deceased.

** The second series of experiments to determine the heat of formation of PuO₂ was carried out with this calorimeter.
Plutonium. The content of impurities in the plutonium (α-modification) did not exceed a total of 0.07%. The content of plutonium in the specimen, according to the data of a chemical analysis, was 99.88 ± 0.09%. According to the data of a metallographic study inclusions of oxides were absent. Only isolated inclusions of carbide were found.

Method of Burning of the Uranium and Plutonium

The uranium (of weight 0.21-0.29 g) was burned in an open cup of thorium oxide (weight 1-1.2 g; diameter = 10 mm, height = 4 mm, thickness of bottom 0.9 mm), coated on the outside with platinum. This cup was suspended in the center of a platinum crucible placed on the bottom of the bomb and covered with a lid. The ignition of the metal took place after the burning of carbon black (weight about 35 mg), which was contained in another platinum cup fastened directly under the bottom of the cup containing the uranium. The carbon black was burned from the flame of a thread (weight about 1 mg) ignited by an incandescent wire.

The bomb was filled with oxygen at a pressure of 30-37 atm. No deposition of uranium on the walls of the platinum crucible was found. The product of combustion was obtained in the form of a powder.

The same procedures were used in the burning of the plutonium (weight 0.20-0.28 g). In the first series of experiments the plutonium was burned in cups of thorium oxide, in the second series, in cups of beryllium oxide (weight 0.3 g). The product of combustion was obtained in the form of a fused mass. There was no deposition on the walls.

The surface of the metals to be burned was freed from oxides, (for the uranium by mechanical means and for the plutonium by electrolytic etching). To avoid oxidation the plutonium was covered with collodion up to the beginning of the experiment.

By separate experiments it was established that during the time preceding the main interval of the calorimetric experiment, the uranium was not perceptibly oxidized, and no change of weight of the specimen was found. In spite of this, in most of the experiments on burning of uranium it was covered with collodion (weight about 1 mg), since these experiments were intended to imitate closely the experiments on determination of the heat of formation of PuO\(_2\).

Characteristics of the Products of Combustion of Uranium and Plutonium

To determine the completeness of combustion of the metals, the oxides formed were studied both by x-rays and chemically. In the x-ray studies only U\(_4\)O\(_6\) and PuO\(_2\) were found in the products of combustion of the uranium and plutonium.* The findings of the chemical study were: carbon, from the change of electric conductivity of dilute solution of Ba(OH)\(_2\), which absorbed the CO\(_2\) formed by heating the product of combustion in a stream of oxygen; free uranium, by treating the crushed combustion product with hot 20% HCl; free plutonium and lower oxides of the metals, by heating the combustion products at 800 ± 15°C in a stream of oxygen.

In the products of combustion of plutonium no carbon, free metal, nor lower oxides were found.

In the products of combustion of uranium the absence of carbon and free metal was established. Accordingly, the increase of weight when the combustion product of uranium was heated corresponded to the amount of oxygen necessary for the oxidation of the lower oxides of uranium to U\(_3\)O\(_8\).

A calculation from the amount of metal used and the amount of combined oxygen showed that the product of combustion of plutonium immediately after burning in the bomb had the composition PuO\(_{1.05}\) ± 0.04, and the reheated combustion product of uranium had the composition U\(_3\)O\(_8\)0.03 ± 0.01.

Determination of the Heat Capacity of the System

The heat capacity of the system was determined by burning benzoic acid (obtained from the D. I. Mendeleev Institute of Meteorology), with heat of combustion equal to 6329 cal/g. The heat capacity of

* In the burning of plutonium in crucibles of ThO\(_2\), there was found to be formation of a solid solution of Pu\(_2\) in Th\(_2\) with \(a = 5.49\) Å.