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Abstract

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STANDARD HEATS OF FORMATION OF $ZrCl_4$ AND $HfCl_4$

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Accurate thermodynamic data for zirconium and hafnium tetrachlorides are of not only theoretical but also practical interest, in connection with the use of $ZrCl_4$ and $HfCl_4$ for obtaining metallic zirconium and hafnium of a high degree of purity and for separating these metals from one another.

The present work is devoted to the determination of the heats of formation of $ZrCl_4$ and $HfCl_4$. The determinations were carried out by a direct method—by direct chlorination of metallic Zr and Hf at a temperature of about 400°; carefully analyzed samples of high-purity metals obtained by the iodide method were used.

Experimental Part

Method of determinations. The heat of chlorination was measured in a precision combustion-heat calorimeter with a water isothermal jacket. The reaction was carried out in an all-nickel calorimetric bomb equipped with an electric microfurnace for heating the metal samples in an atmosphere of chlorine. The heating element of the microfurnace was nichrome ($R_{20^\circ} \simeq 38\ \Omega$), insulated with quartz glass. The design of the bomb and microfurnace was analogous to that described in our work (^{1}). The capacity of the bomb was 245 cm^3.

Before an experiment, the weighed portion of metal (0.7-1.2 g Zr or 1.5-2.2 g Hf —one or several pieces) was weighed to $2 \cdot 10^{-5}$ g and placed in the microfurnace of the bomb in a thin-walled quartz cup. The bomb was flushed with argon to remove air, evacuated to a pressure of $3 \cdot 10^{-3}$ mm Hg, and filled with dry gaseous chlorine (weight of chlorine $\simeq$ 5.6 g). At the beginning of the main period of the experiment, current ($\simeq$ 1 A) from a storage battery was switched on to the microfurnace. After 1.5 min from the start of heating, an almost constant temperature, close to 400°, was reached in the microfurnace. Heating by current continued for 8.5-11 min; the duration of the main period of the experiment was 30-35 min.

The temperature rise of the calorimetric system ($\simeq 3^\circ$) was measured with a 50-ohm Pt resistance thermometer connected in a bridge circuit (^{2}). Three arms of the bridge were located in the calorimeter jacket at a constant temperature (within 0.002°). The bridge was balanced by a precision, preliminarily calibrated resistance box connected in parallel to one of the bridge arms. The null instrument in the bridge circuit was an F 116/1 photocompensation microvolt-microammeter with a sensitivity of $2 \cdot 10^{-8}$ V, which provided a temperature sensitivity of $4 \cdot 10^{-5}$°. Measurements of the temperature of the calorimetric system during the experiment were made at intervals of 0.5 min.

To determine the work of the current in the microfurnace of the bomb, a potentiometric method was used; the time during which the current was passed was measured with a printing chronograph to an accuracy of 0.01 sec. During the first 2 min of heating, the voltage both across the heater and across the standard resistance coil—

Table 1

Impurities (in wt. percent)

Sample	H	O	N	C	Fe	Mg	Ti	Al	Cu	Ni	Mn	Si	Mo	Ca
Zirconium	$8 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$2.3 \cdot 10^{-2}$	$5.7 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	—	$5 \cdot 10^{-3}$
Hafnium, sample 1	$4 \cdot 10^{-3}$	$3 \cdot 10^{-2}$	$< 5 \cdot 10^{-3}$	$< 5 \cdot 10^{-2}$	$6 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	—	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	$7.8 \cdot 10^{-3}$	—
Hafnium, sample 2	$9 \cdot 10^{-4}$	$2.2 \cdot 10^{-2}$	$< 5 \cdot 10^{-3}$	$< 5 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	—	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	—	$4 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$8.6 \cdot 10^{-3}$	—

···included in series in the microwave-oven circuit, was measured continuously, using to compensate each of the voltages a five-decade potentiometer KL-48 (accuracy class 0.015) and a self-recording potentiometer EPP-09 (with a 10 mV scale, a chart speed of 1 sec, and accuracy class 0.5). Subsequently, the nearly constant voltages established on the heater and the coil were measured with KL-48 potentiometers at intervals of 0.5 min.

In determining the heat equivalent of the calorimetric system, heat was introduced by means of the microwave-oven bomb, the current strength being the same as in the experiments on chlorination of the metals, while the bomb was filled with argon to a pressure of 7 atm.

All instruments used for measuring the electrical energy had first been checked at the Institute of Measures and Measuring Instruments.

The heat equivalent of the calorimetric system was (calculated on the assumption that the bomb contained no reacting substances or reaction products)

14028.2 ± 1.0* cal/ohm (from 10 determinations). It was assumed that 1 cal = 4.1840 joules.

The temperature at the beginning of the main period in all experiments on chlorination of the metals and on determination of the heat equivalent of the calorimetric system was 25.0°.

Starting substances. The zirconium and hafnium samples were analyzed for impurities of metals and silicon, for hydrogen and oxygen (by the vacuum-fusion method), and also for carbon and nitrogen. The largest impurities in the metal samples investigated were: hafnium in zirconium, 0.057 wt.%, and zirconium in hafnium, 0.78 wt.% in the first sample and 0.78 wt.% in the second hafnium sample. The contents of the remaining impurities are given in Table 1.

Before the experiments the chlorine was dried and then purified from traces of air by freezing and evacuation (repeated four times).

Results of the calorimetric experiments and their discussion. In all experiments the metal samples reacted readily with chlorine. The reaction products deposited on the lid and walls of the bomb; in the quartz cup in which the metal was placed there remained only a little unvolatilized chloride. With an excess of chlorine under the experimental conditions, the reaction products could only be the higher chlorides of Zr, Hf, and most of the elements present as impurities in the metal samples.

The results of the calorimetric determinations are presented in Table 2.

* The error here and below is twice the quadratic error of the mean result.

In calculating the values of ΔU_B (Table 2) for the heats of reaction between metal samples and gaseous chlorine under the conditions of their occurrence in the calorimetric bomb, a small correction was taken into account for the heat capacity of the substances contained in the bomb after the reaction had been carried out. The corrections for impurities (Table 2) were calculated on the basis of the following assumptions: a) the impurities O, H, N, and C are chemically combined with zirconium or, respectively, with hafnium; b) the remaining impurities are dissolved in the metal samples with a heat of dissolution equal to zero. This latter assumption cannot lead to an appreciable error in the values of the heats

Table 2

	Heat of chlorination of the metal preparation under the conditions of the reaction, ΔU_B (25°), cal per 1 g of preparation	Correction for impurities, cal per 1 g of preparation	Standard heats of formation ΔH_f^0, $ZrCl_4$ and $HfCl_4$, kcal/mol
Zirconium	-2547.2 ± 0.8(from 8 experiments)	-5.7 ± 2.1	-234.35 ± 2.1
Hafniumsample 1	-1324.6 ± 0.6(from 7 experiments)	$+6.8 \pm 2.4$	-236.70 ± 0.45
sample 2	-1326.2 ± 0.5(from 7 experiments)	$+6.2 \pm 1.6$	-237.10 ± 0.31

of formation of $ZrCl_4$ and $HfCl_4$, owing to the low content of these impurities in the initial metal samples. The comparatively large errors of the corrections for impurities are due mainly to the accuracy of the quantitative determinations of hydrogen, oxygen, carbon, and nitrogen in the zirconium and hafnium preparations. In calculating the values of the standard heats of formation of $ZrCl_4$ and $HfCl_4$, Woshburn corrections for conversion to the standard states of the reacting substances and reaction products were taken into account; it was assumed that $ZrCl_4$ and $HfCl_4$ do not react with chlorine (^{3,4}).

The values of the heats of formation of the hydrides, nitrides, and carbides of zirconium and hafnium, as well as of some chlorides, were taken from handbooks (^{5,6}) and from papers ($^{7-11}$). In the calculations it was assumed that the impurities ZrO_2 and HfO_2 are not chlorinated, while the carbides and nitrides of Zr and Hf give, in addition to the corresponding metal tetrachlorides, graphite and nitrogen. The molecular weights of all compounds were calculated using the table of atomic weights adopted in 1961 (^{12}).

Experiments with two hafnium samples gave mutually well-agreeing values of the heat of formation of $HfCl_4$ (Table 2); the average weighted value of these two values is ΔH_f^0 ($HfCl_4$, cryst.) $= -236.97 \pm 0.25$ kcal/mol (from Hf, metal, and Cl_2, gas).

At the time the present work was begun, the heat of formation of $HfCl_4$ had not been determined. A paper has recently been published (^{4}) in which, for the heat of formation of $HfCl_4$, the value $\Delta H_f^0 = -236.7 \pm 0.5$ kcal/mol was obtained. The results of the present work and of work (^{4}) agree well with one another. Both values were obtained by a direct method, starting from preparations of substances of a high degree of purity and using two different experimental techniques. This makes it possible to regard the value of the heat of formation of $HfCl_4$ as reliably established.

For the heat of formation of $ZrCl_4$, the following values had previously been obtained (experimentally): −272 kcal/mol (13) from determinations of the heat of hydrolysis of $ZrCl_4$, -231.9 ± 0.5 (14) and -234.7 ± 0.4 kcal/mol (3) by chlorination of zirconium. The value −272 kcal/mol may be considered overestimated because of the difficulty of identifying the hydrolysis products. In work (14) the zirconium samples were not chlorinated completely. In addition, the purity of the initial substances was characterized insufficiently: in particular, analyses for gaseous impu-

···mixtures, failure to take account of which can have a very substantial effect on the final result (see Table 2). Work (3) is not only free of these shortcomings, but was also carried out with more advanced calorimetric apparatus.

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Note: Figure translations are in progress. See original paper for figures.