Enthalpy of Formation of Zirconium Carbide

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Zirconium carbides with carbon-zirconium ratios varying from 0.63 to 0.98 were burned in an oxygen bomb calorimeter. The enthalpy of formation of $ZrC_{1.0}$ was found by extrapolation to be $\Delta H^\circ_{f\ 298^\circ K.} = -49.5 \pm 0.6$ kcal. per mole from the equation $-\Delta H^\circ_{f\ 298^\circ K.} = -7.4 \pm 1.3 + (84.1 \pm 3.3)x - (27.2 \pm 2.0)x^2$, where x is the carbon-zirconium ratio.

THE ENTHALPY of combustion of ZrC has been determined by Mah and Boyle (*6*) and by Mah (*5*). In the earlier investigation the sample was not well characterized as to impurities. In the more recent determination by Mah, $\Delta H^\circ_{298} = -308.60 \pm 0.55$ kcal. per mole was found for the combustion of two samples, $ZrC_{0.93}$ (0.11% free carbon, 0.18% N, and 0.17% O) and $ZrC_{0.99}$ (0.12% Ti, 0.07% N, 0.05% O, and an unknown amount of free carbon). For a third sample $ZrC_{0.71}$ (0.5% O, 0.22% N, and 0.12% Ti) the enthalpy of combustion was found to be $\Delta H^\circ_{298} = -295.17 \pm 0.70$ kcal. per mole. Because of the large uncertainty introduced by impurities in these determinations, the enthalpy of combustion of a series of carbides was measured in order to obtain a more reliable value for the enthalpy of formation of ZrC_x.

EXPERIMENTAL

The carbide samples were made by arc-melting Zr metal and spectroscopic graphite rods together. These master alloys were then reduced to −80-mesh in a steel impact mortar, cleaned of Fe with 6*N* HCl, dried in vacuum, and mixed to give the desired composition. The mixtures were heated in vacuum, first in a graphite crucible and then as sintered plugs on a tungsten tripod using an eddy current concentrator. The heating schedule for each sample is listed in Table I. The plugs were then reduced to −80-mesh.

Table I. Heating Schedule for Zirconium Carbides

Composition, C/Zr	Temp., °C.	Time, Hr.	Final Vacuum, Torr	*a*, A.
$ZrC_{0.98}$[a]	2100	91	8×10^{-8}	4.6990 ± 0.0003
$ZrC_{0.84}$	2550	35	3×10^{-7}	4.7020 ± 0.0001
$ZrC_{0.77}$	1900	12	1×10^{-7}	4.6999 ± 0.0002
$ZrC_{0.63}$(I)	1950	24	5×10^{-8}	4.6931 ± 0.0002
$ZrC_{0.63}$(II)	1800	4	5×10^{-8}	4.6935 ± 0.0002
$ZrC_{0.63}$(III)	1850	24	5×10^{-8}	4.6942 ± 0.0002

[a] Heated in graphite crucible for total time.

X-ray patterns of the carbides showed only face-centered cubic material. The lattice parameters are given in Table I and carbide analyses in Table II. The Zr, C, H, N, and O were determined chemically and the other metallic impurities by emission spectroscopy. The uncertainty on the Zr and C analysis is estimated to be 0.5%. On the other chemical analysis the uncertainty is 10%, and on the spectrographic analysis the uncertainty is 50%. The uncertainty in the coefficient for the carbon is estimated to be ±0.01.

A Lund rotating bomb calorimeter (*7*), modified to use a standard Parr bomb No. 1105 without rotation, was used for all of the energy of combustion measurements. Samples were burned in the bomb on sintered ZrO_2 disks in oxygen at 25-atm. pressure, and at an average initial temperature of 25.0° C. Ignition was brought about by passing a current through zirconium fuse wire. The calorimeter temperatures were measured to 0.0001° C. with a Hewlett Packard quartz thermometer No. 2801A. Times were measured to the nearest second. The corrected temperature rise was determined by the method of Dickinson (*1*) and is believed to be accurate to ±0.001° C.

The 6 kg. of water in the calorimeter can were weighed to 0.05 gram. The combustion samples were weighed to 0.0001 gram and the fuse wire to 0.00001 gram. The ZrO_2 disks were weighed to 0.1 gram. The precision of the calorimeter as measured (all uncertainty intervals are expressed as twice the standard deviation of the mean except as otherwise noted) on combustions of benzoic acid is 19 parts in 67,000 or about 0.013%.

The energy equivalent of the calorimeter as determined by combustion of standard benzoic acid (NBS sample 39i) was 6706.9 ± 1.9 cal. per degree, the calorie being the defined thermochemical calorie, equal to 4.184 absolute joules.

Each combustion product was heated to 1000° C. in an atmosphere of oxygen and any carbon dioxide formed was collected and weighed to determine if any unburned material remained. The combustion in the bomb was 99.9 to 100% complete, and a small correction was applied when neces-

Table II. Analysis of Zirconium Carbides

	Weight %					
	$ZrC_{0.63 \pm 0.01}$ (I)	$ZrC_{0.63 \pm 0.01}$ (II)	$ZrC_{0.63 \pm 0.01}$ (III)	$ZrC_{0.77 \pm 0.01}$	$ZrC_{0.84 \pm 0.01}$	$ZrC_{0.98 \pm 0.01}$
Zr	92.0	92.0	92.0	90.6	90.0	88.1
Carbon combined	7.65	7.63	7.67	9.18	9.93	11.38
Carbon free	...	...	...	...	...	0.50
H	0.003	...	0.002	0.002	0.005	0.002
N	0.014	0.008	0.011	0.005	0.006	0.003
O	0.32	0.35	0.26	0.18	0.052	0.044
Si	0.03	0.003	0.01	0.001	...	...
Fe	0.005	0.001	0.02	0.01	0.005	0.003
Cu	0.001	...	...	...	0.001	...

Table III. Energy of Combustion of ZrC_x at 25° C.

(Uncorrected for impurities)

Mass Burned, G.	Wt. of Fuse, Mg.	Wt. of ZrO_2, G.	Energy Equiv., Cal./Deg.	ΔT, ° C.	Firing Energy, Cal.	Energy ZrC_x, Cal./G.	Dev. from Mean, Cal./G.
			$x = 0.63$ (I)				
2.1893	13.60	22.7	6712.6	0.9468	1.4	−2884.5	1.7
2.4618	13.13	22.7	6712.7	1.0626	1.3	−2881.6	1.2
2.7370	13.76	22.7	6713.0	1.1823	1.6	−2884.8	2.0
1.9440	13.84	24.8	6712.9	0.8408	1.3	−2882.2	0.6
2.2522	13.64	24.8	6712.9	0.9733	1.4	−2883.0	0.2
2.5678	14.03	24.8	6713.0	1.1078	1.6	−2879.8	3.0
2.7214	13.89	24.8	6713.0	1.1750	1.4	−2883.2	0.4
1.9135	15.24	24.8	6712.9	0.8287	1.5	−2883.6	0.8
					Av.	−2882.8	
					Std. dev. of mean	0.6	
			$x = 0.63$ (II)				
2.5004	13.66	24.8	6713.0	1.0802	1.6	−2883.7	2.3
1.9671	13.57	25.7	6713.0	0.8507	1.4	−2882.6	1.2
2.7443	13.89	25.7	6713.1	1.1841	1.5	−2881.4	0.0
2.4651	14.32	25.7	6713.0	1.0653	1.5	−2883.7	2.3
2.1092	14.09	25.7	6713.0	0.9111	1.2	−2880.0	1.4
2.6177	16.09	25.7	6713.1	1.1297	1.3	−2878.9	2.5
2.3029	13.64	26.0	6713.1	0.9941	1.1	−2880.2	1.2
2.9293	16.44	26.0	6713.2	1.2642	1.5	−2880.6	0.8
					Av.	−2881.4	
					Std. dev. of mean	0.6	
			$x = 0.63$ (III)				
2.5408	13.53	25.5	6713.1	1.0981	1.4	−2885.5	0.2
2.8536	13.95	25.5	6713.1	1.2327	1.6	−2885.3	0.4
2.1098	13.86	25.6	6713.0	0.9127	1.3	−2884.5	1.2
2.2531	13.06	25.6	6713.0	0.9748	1.4	−2887.0	1.3
2.6130	13.38	25.6	6713.1	1.1295	1.4	−2886.5	0.8
2.0378	13.33	25.6	6713.0	0.8821	1.4	−2886.3	0.6
2.7298	13.01	17.5	6712.0	1.1789	1.2	−2884.5	1.2
2.3001	12.98	17.5	6711.9	0.9947	1.4	−2885.8	0.1
					Av.	−2885.7	
					Std. dev. of mean	0.3	
			$x = 0.77$				
2.7146	14.76	25.8	6713.1	1.1816	1.5	−2905.9	1.1
2.2446	14.32	25.8	6713.1	0.9787	1.1	−2908.2	1.2
2.4917	13.40	22.9	6712.7	1.0854	1.4	−2908.1	1.1
2.3989	13.53	22.9	6712.7	1.0452	1.5	−2907.9	0.9
2.0371	13.38	26.0	6712.9	0.8874	1.6	−2904.6	2.4
2.8064	13.48	26.0	6713.2	1.2219	1.5	−2908.4	1.4
2.6159	14.00	26.0	6713.2	1.1398	1.5	−2909.1	2.1
2.3060	12.94	25.5	6713.0	1.0033	1.3	−2904.0	3.0
					Av.	−2907.0	
					Std. dev. of mean	0.7	
			$x = 0.84$				
2.2958	15.59	51.7	6716.7	1.0098	1.6	−2934.1	1.1
2.3237	15.88	25.8	6713.1	1.0222	1.4	−2932.9	0.1
2.3532	15.72	25.8	6713.1	1.0350	1.6	−2932.8	0.2
2.3447	15.14	25.8	6713.1	1.0320	1.6	−2935.5	2.5
2.3303	15.08	26.1	6713.1	1.0246	1.1	−2932.6	0.4
2.3141	14.53	26.1	6713.1	1.0184	1.5	−2935.7	2.7
2.3373	14.71	26.1	6713.1	1.0264	1.6	−2929.2	3.8
2.3352	15.42	26.1	6713.1	1.0277	1.5	−2934.7	1.7
2.3382	13.76	26.3	6713.1	1.0267	1.4	−2930.2	2.8
2.3107	13.31	26.3	6713.1	1.0153	1.4	−2932.5	0.5
					Av.	−2933.0	
					Std. dev. of mean	0.7	
			$x = 0.98$				
2.0429	12.80	26.0	6713.0	0.9148	1.4	−2987.3	1.9
2.6486	13.75	26.0	6713.2	1.1860	1.4	−2990.6	1.4
2.8186	13.61	25.8	6713.1	1.2612	1.3	−2989.5	0.3
2.3143	13.46	25.8	6713.0	1.0363	1.4	−2988.6	0.6
2.0102	13.65	25.8	6713.0	0.9019	1.3	−2991.6	2.4
2.5362	13.94	25.8	6713.1	1.1368	1.4	−2992.6	3.4
2.7119	13.43	25.8	6713.1	1.2119	1.5	−2985.2	4.0
2.5028	14.35	25.8	6713.1	1.1203	1.4	−2987.8	1.4
					Av.	−2989.2	
					Std. dev. of mean	0.9	

sary. Samples of the carbides exposed to 25 atm. of oxygen for 1 hour showed no detectable weight gain. Only the monoclinic form of ZrO_2 was found in the combustion products by x-ray analysis. A mass spectrographic analysis was made on the combustion product gas from one sample of $ZrC_{0.77}$. No CO was observed within a limit of detection of 0.01%.

RESULTS

The energies of combustion for six different zirconium carbide samples are given in Table III.

The measured energies of combustion were corrected for impurities, assuming that the impurities were present as H_2O, ZrN, SiC, Fe, and CuO. The enthalpies of formation in kilocalories per mole used for the corrections are: ZrN, −87.3 (*4*); CO_2, −94.05 (*8*); SiC, −12.4 (*4*). The 1961 atomic weights were used. The total correction for impurities other than oxygen and free carbon was about 0.02 ± 0.01%. The correction for free carbon in $ZrC_{0.98}$ was 1.30 ± 0.02%.

The energies of combustion could be corrected for the oxygen impurity by assuming the oxygen to be in the form of ZrO_2 or ZrO. However, neither of these assumptions is satisfactory because the oxygen is probably dissolved in the ZrC lattice. Therefore the data from these series of $ZrC_{0.63}$ combustions were plotted against the oxygen contents, giving a good straight line which was extrapolated to zero oxygen content, yielding a value of 4.8 ± 1 cal. per gram per 0.1% oxygen as the effect of the oxygen. The extrapolated value was used for the energy of combustion of oxygen-free $ZrC_{0.63}$. This same oxygen effect correction was also used to correct for the oxygen impurity in the carbides with larger carbon-zirconium ratios. If the oxygen had been assumed to be present as ZrO_2 in the samples of $ZrC_{0.63}$, the correction for the oxygen impurity would have been 15 cal. per gram larger for the sample with the largest oxygen content.

The enthalpies of combustion and formation for ZrC_x corrected for impurities, reduced to unit fugacity of oxygen, and converted to a constant pressure process are given below.

x	0.63	0.77	0.84	0.98
$-\Delta H^\circ_{298^\circ \text{K.}}$	287.4 ± 1	294.2 ± 0.2	298.1 ± 0.2	306.5 ± 0.2
$-\Delta H^\circ_{f\,298^\circ \text{K.}}$	34.9 ± 1.1	41.3 ± 0.6	44.0 ± 0.6	48.8 ± 0.6

The enthalpies of combustion for the series of compositions from $ZrC_{0.63}$ to $ZrC_{0.98}$ were fitted by weighted least squares with the equation $-\Delta H^\circ_{298^\circ \text{K.}} = 271.1 \pm 0.8 + (8.2 \pm 1.9)x + (28.3 \pm 1.2)x^2$, where x is the carbon coefficient. Using this equation the enthalpy change for the reaction

$$ZrC_{1.00} + 2\,O_2 = ZrO_2 + CO_2$$

is $\Delta H^\circ_{298^\circ \text{K.}}$ −307.7 ± 0.4 kcal. Combining the enthalpies of combustion for ZrC_x with the enthalpy of formation for ZrO_2, $\Delta H^\circ_{f\,298^\circ \text{K.}} = -263.1 \pm 0.5$ (*2, 3*) and CO_2 (*8*), one obtains for the enthalpy of formation of ZrC_x by least squares, the equation

$$-\Delta H^\circ_{f\,298^\circ \text{K.}} = -7.4 \pm 1.3 + (84.1 \pm 3.3)x - (27.2 \pm 2.0)x^2$$

Using this equation the enthalpy of formation of $ZrC_{1.00}$ is $\Delta H^\circ_{f\,298^\circ \text{K.}} = -49.5 \pm 0.6$ kcal. per mole.

In comparing the enthalpy of combustion of $ZrC_{1.00}$ reported in our work with that of Mah (*5*) the difference of 0.9 kcal. per mole could easily be explained by the impurities in Mah's samples. In the sample $ZrC_{0.99}$ no free carbon was reported, whereas at this composition free carbon would be expected. The presence of a small amount of free carbon would bring her value for this sample into agreement with the author's results. If the energy of combustion for the sample $ZrC_{0.93}$ is corrected for impurities using the actual composition instead of $ZrC_{1.00}$ plus free zirconium as she assumed, Mah's value is in reasonable agreement with the values reported in this paper.

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