known sources of errors, gave an over-all uncertainty of 0.12%. The enthalpy of combustion of hafnium metal under bomb conditions was −272.98 ± 0.32 kcal. per mole. Correction to unit fugacity of oxygen and to constant pressure leads to $\Delta Hf^\circ_{298.15^\circ K.}(HfO_2) = -273.6 \pm 0.3$ kcal. per mole as the enthalpy of formation of hafnium dioxide: $Hf(c) + O_2(g) = HfO_2(c)$. The uncertainty attached to the value is twice the standard deviation of the mean. This value is 7.5 kcal. more negative than Humphrey's value (*3*) and 2.1 kcal. more negative than Roth's and Becker's value (*5*).

ACKNOWLEDGMENT

The authors appreciate the efforts of Helen Cowan, certain chemical analyses; Group CMB-1 of this laboratory for chemical and spectrochemical analysis, Finley Ellinger, x-ray analysis; Virginia Shadden and Cletis Land, metallographic analysis.

LITERATURE CITED

(1) Holley, C.E., Jr., Huber, E.J., Jr., *J. Am. Chem. Soc.* **73**, 5577 (1951).
(2) Huber, E. J., Jr., Matthews, C. O., Holley, C. E., Jr., *Ibid.*, **77**, 6493 (1955).
(3) Humphrey, G. L., *Ibid.*, **75**, 2806 (1953).
(4) Mah, A. D., *U.S. Bur. Mines Rept. Invest.* **6518** (1964).
(5) Roth, W. A., Becker, G., *Z. Physik. Chem.* **A159**, 1 (1932).
(6) Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., Schumm, R. H., *Natl. Bur. Std. Tech. Note* **270-1** (1965).

RECEIVED for review August 21, 1967. Accepted October 23, 1967. Work done under the auspices of the U. S. Atomic Energy Commission.

Enthalpies of Formation of Thorium Mono- and Dicarbides

ELMER J. HUBER, Jr., CHARLES E. HOLLEY, Jr., and N. H. KRIKORIAN
University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M. 87544

A series of analyzed thorium carbides has been burned in an oxygen bomb calorimeter. The enthalpies of formation of $ThC_{1.00 \pm 0.01}$ and $ThC_{1.91 \pm 0.01}$ were −29.6 ± 1.1 and −29.9 ± 1.1 kcal. per mole, respectively, at 298.15° K.

THE refractory nature of the thorium carbides with melting points above 2600° C. is an important consideration for their use in nuclear reactors. Recent reviews on the thorium–thorium carbide system (*3, 10*) describe the methods of preparation of the mono- and dicarbides (no sesquicarbide has been synthesized), phase relationships, structures, and some thermochemical properties. Heats of formation values in the literature are in wide disagreement. They rely mostly on vapor pressure measurements with estimated free energy functions or e.m.f. measurements on cells at elevated temperatures combined with estimated heat capacities.

This paper describes the results obtained from the combustion of four samples of the monocarbide phase and two samples of the dicarbide phase of thorium. The combustions were carried out in an oxygen bomb calorimeter at a known initial pressure of oxygen (*5*). The energy equivalent of the calorimeter as determined by the combustion of standard benzoic acid was 2384.3 ± 0.6 cal. per degree.

PREPARATION OF THORIUM CARBIDES

The thorium carbides were prepared by a fusion reaction in an arc furnace (*3, 10*). Thorium metal rods from Oak Ridge National Laboratory were used. The surface was cleaned using anodic electropolishing in a bath of 75% H_2SO_4 containing chromic acid (10 grams per liter). The metal was then washed with distilled water and dried. Chemical analysis gave the following results: Th, 99.7%; O_2, 0.13%; and in parts per million, the following: Li, < 0.1; Be, 3; B, 0.8; Na, 2; Mg, 20; Al, 3; Si, 30; Ca, 3; V, < 40; Cr, 30; Mn, 1; Fe, 80; Co, < 2; Ni, 70; Cu, 30; Pb, 2. Spectrographic quality graphite rods were used as the source of carbon for the preparation.

The arc furnace was of water-cooled copper construction. It had a movable cathode with a 1-inch diameter Type AUC graphite tip (Carbon Products Division of the Union Carbide Corp.). The furnace could be evacuated by an oil diffusion pump backed by a mechanical pump to approximately 10^{-6} mm. The power for melting of samples came from a 34.5-kw. welding generator of the rectifier type. A high frequency unit was used to initiate the arc.

The thorium carbides were prepared by placing the thorium metal rods and spectrographic quality graphite rods side by side on the copper hearth and closing the furnace. Each batch totaled approximately 60 grams. After evacuation of the system, helium was admitted to a pressure approximately 8 to 10 cm. below the ambient atmospheric pressure. Next, a button of zirconium metal was melted in the arc furnace as a "getter" for the impurities in the helium. The thorium was then melted in contact with the graphite to form the carbide. After the carbide piece had cooled, it was turned over in the hearth by means of the movable cathode without opening the furnace to the atmosphere. What was previously the bottom side of the sample could now be melted. This procedure was repeated three times for each of the compositions. The carbides have a gold cast, and are shiny, metallic, and brittle. Their analyses are summarized in Table I.

There was a small amount of hydrogen, 0.004%, in the second dicarbide sample, and the higher carbides had some free carbon present. X-ray patterns of the monocarbides gave a = 5.3137, 5.3268, 5.3387, and 5.3438 A., respectively, for these face centered cubic materials. The patterns of the two dicarbides showed only the monoclinic (α) form.

Metallography was conducted on each of the samples using polarized light. Polishing and etching was attempted on each sample. Photomicrographs showed some grain boundary precipitate and some contamination.

The oxygen impurity was assumed to be combined with the metallic impurities and the nitrogen and any excess oxygen with the thorium. The calculated compositions are shown in Table II. There is an estimated uncertainty of ± 0.01 in the coefficient of the carbon in the formula of each carbide.

Table I. Analyses of Thorium Carbides, Wt. %

	$ThC_{0.75}$	$ThC_{0.81}$	$ThC_{0.91}$	$ThC_{1.00}$	$ThC_{1.91}$	$ThC_{1.91}$
Th	96.0	95.8	95.3	94.9	90.8	90.9
C_c	3.61	3.99	4.38	4.86	8.93	8.97
C_f	...	...	...	0.055	0.14	0.04
O	0.37	0.18	0.24	0.161	0.066	0.016
N	0.012	0.013	0.018	0.009	0.008	0.012
Si	0.004	0.004	0.005	0.005	0.002	0.005
Fe	0.0015	0.001	0.002	0.002	0.001	0.015
Ni	0.003	0.003	0.005	0.004	0.005	0.003
Cu	0.002	0.003	0.004	0.004	0.012	0.0075

Table II. Calculated Composition of Thorium Carbides, Wt. %

	$x = 0.75$	0.81	0.91	1.00	1.91	1.91
ThC_x	96.83	98.37	97.82	98.54	99.22	99.77
ThO_2	2.99	1.43	1.91	1.26	0.49	...
Th_3N_4	0.16	0.19	0.25	0.12	0.12	0.15
SiO_2	0.01	0.01	0.01	0.01	0.00	0.01
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.02
NiO	0.00	0.00	0.01	0.01	0.01	0.00
CuO	0.00	0.00	0.00	0.00	0.02	0.01
C_f	...	...	...	0.05_5	0.14	0.04

METHOD AND RESULTS

The method has been described (*5*). Each sample was burned in oxygen at 25 atm. pressure on sintered disks of ThO_2. Ignition was made by passing an electrical current through a 10-mil diameter thorium fuse wire. The average initial temperature was 25.08° C. with an average temperature rise of 1.20° C.

Preliminary runs indicated that the material could not be burned as massive chunks. Even with powdered samples, the completeness of combustion was variable and usually low. A coating of thorium oxide seemed to prevent further combustion. With the addition of an equal weight of thorium dioxide to the powdered carbide, using a glass-window bomb (*9*), combustion was smoother and more nearly complete. Evidently, the presence of the thoria reduces the burning temperature and prevents newly formed thoria from covering unburned carbide and smothering the combustion.

Table III. Heats of Combustion

Mass Burned, Grams	Wt. Fuse, Mg,	Wt. ThO_2, Grams	Energy Equiv., Cal./Deg., Total	ΔT, ° C.	Energy from		Dev. from Mean, Cal./Gram
					Firing, cal.	ThC_x, cal./gram	
$x = 0.75$							
1.7847	47.22	78.9	2393.4	1.0651	1.9	−1397.0	3.3
1.8938	48.93	39.1	2391.2	1.1251	1.9	−1387.3	6.4
1.8442	49.05	41.7	2391.4	1.1125	2.2	−1408.1	14.4
2.1293	47.16	42.5	2391.4	1.2794	2.2	−1408.2	14.5
2.0056	47.08	44.0	2391.5	1.1933	2.2	−1392.5	1.2
1.8830	47.94	43.8	2391.5	1.1143	2.2	−1382.2	11.5
2.0905	47.32	41.9	2391.4	1.2396	2.2	−1388.7	5.0
2.2001	48.45	43.0	2391.4	1.3077	3.2	−1392.4	1.3
2.1928	46.18	43.2	2391.4	1.3040	2.1	−1394.8	1.1
2.2495	48.14	44.2	2391.5	1.3293	1.9	−1385.6	8.1
					Av.	−1393.7	6.7
					Std. dev. of the mean		2.8
$x = 0.81$							
2.1291	47.08	43.2	2391.4	1.2768	1.7	−1405.6	0.1
2.1023	51.45	31.8	2390.8	1.2656	1.9	−1407.8	2.1
1.9500	47.77	31.5	2390.8	1.1755	2.0	−1409.6	3.9
2.0320	48.50	33.2	2390.9	1.2201	1.8	−1404.9	0.8
2.1424	48.17	32.2	2390.8	1.2842	2.0	−1404.1	1.6
2.1012	49.77	31.8	2390.8	1.2574	2.7	−1399.8	5.9
2.1243	62.06	32.1	2390.8	1.2848	2.2	−1408.4	2.7
1.8565	50.43	32.3	2390.8	1.1187	2.3	−1405.5	0.2
					Av.	−1405.7	2.2
					Std. dev. of the mean		1.1
$x = 0.91$							
1.9473	47.85	31.3	2390.8	1.1635	1.7	−1396.9	12.1
1.9187	48.75	32.5	2390.8	1.1489	1.9	−1398.9	10.1
1.9920	48.52	32.7	2390.9	1.1929	2.2	−1400.2	8.8
1.9299	48.57	32.6	2390.8	1.1743	2.2	−1422.1	13.1
2.0430	48.94	33.0	2391.0	1.2346	2.4	−1413.8	4.8
1.9388	47.64	32.5	2390.9	1.1624	2.8	−1401.3	7.7
2.1757	49.22	31.7	2390.9	1.3197	3.8	−1420.2	11.2
2.0750	47.56	32.9	2391.0	1.2560	1.9	−1417.7	8.7
2.0861	28.45	31.2	2390.9	1.2577	1.8	−1423.5	14.5
1.9071	48.01	43.5	2391.5	1.1386	1.8	−1395.4	13.6
					Av.	−1409.0	10.5
					Std. dev. of the mean		3.6

A further complication was present because of reactivity with atmospheric moisture. It was necessary to handle these materials in an inert atmosphere box (dew point maintained at −55° C.). The gain in weight of samples exposed to the dry bomb atmosphere (25 atm. of oxygen) for an hour was, however, negligible.

The amount of unburned material was determined by heating each combustion product in an atmosphere of oxygen at 1000° C. Any carbon dioxide and water evolved was collected and weighed. A loss in weight of the sample could be due to three factors: adsorbed carbon dioxide; adsorbed water; and combustion of free carbon. A gain in weight of the sample could be due to the combustion of unburned carbide and nitride to thoria. The difference (gain or loss) as measured is equated to the sum of the other factors. Thus, it is possible to solve for the amount of unburned carbide. The method is not entirely satisfactory because it ignores adsorption of oxygen and assumes that both elements of the carbide burn equally completely which may not be the case (*7*). Where the completeness of combustion is high this method, however, is probably a good approximation. From eight to 10 runs were made on each sample. The completeness of combustion averaged 97.8%. X-ray patterns of the combustion products showed only ThO_2 with $a = 5.5975 \pm 0.0002$ A. The specific heat of ThO_2 was taken as 0.0564 cal. per gram per degree. The runs are listed in Table III.

The measured enthalpies of combustion were corrected for the impurities by using the following enthalpies of formation: Th_3N_4, −310 (*8*); ThO_2, −293.2 (*4*); NO_2, +7.9 (*6*); CO_2, −94.05 (*11*) kcal. per mole. The nitride may have been in the form of ThN, but the amounts are too small to introduce any significant error. The 1961 atomic weights were used (*2*).

After reduction to unit fugacity of oxygen and conversion to a constant pressure process, the resultant values were combined with the necessary auxiliary equations to give the values for the enthalpies of formation of the individual carbides. An example illustrates the method used:

$$\begin{array}{ll}
ThO_2(c) + CO_2(g) \rightarrow ThC(c) + 2O_2(g) & \Delta H_1 \\
Th(c) + O_2(g) \rightarrow ThO_2(c) & \Delta H_2 \\
C(grap.) + O_2(g) \rightarrow CO_2(g) & \Delta H_3 \\
\hline
Th(c) + C(grap.) \rightarrow ThC(c) & \Delta H_f^\circ = \Delta H_1 + \Delta H_2 + \Delta H_3
\end{array}$$

In this manner, the enthalpies of formation listed below were found for ThC_x, in kcal. per mole for the series:

x	0.75	0.81	0.91	1.00	1.91	1.91
$-\Delta H_f^\circ$	16.6 ± 1.6	23.5 ± 0.9	28.4 ± 1.9	29.6 ± 1.1	29.7 ± 1.8	29.9 ± 1.3

The uncertainties attached to the ΔH_f° values include the uncertainties in the determination of the energy equivalent of the calorimeter, the calorimetric measure-

of Thorium Carbides, ThC_x.

Mass Burned, Grams	Wt. Fuse, Mg.	Wt. ThO_2, Grams	Energy Equiv., Cal./Deg., Total	ΔT, ° C.	Energy from Firing, cal.	Energy from ThC_x, cal./gram	Dev. from Mean, Cal./Gram
			$x = 1.00$				
1.9654	23.52	33.0	2391.0	1.2014	1.4	−1445.9	2.1
1.7633	47.57	32.1	2390.8	1.0967	1.9	−1452.3	4.3
1.8927	51.13	32.2	2390.9	1.1665	2.5	−1438.5	9.5
1.7422	48.15	34.5	2391.0	1.0810	1.2	−1448.3	0.3
1.8715	27.51	35.5	2391.1	1.1498	1.5	−1449.9	1.9
1.6026	44.45	34.5	2390.9	0.9966	1.3	−1451.3	3.3
2.0988	50.26	35.5	2391.1	1.2967	2.1	−1446.4	1.6
1.7630	59.21	34.0	2390.9	1.1026	2.9	−1451.7	3.7
					Av.	−1448.0	3.3
					Std. dev. of the mean		1.6
			$x = 1.91$				
1.6261	61.88	34.2	2391.0	1.2060	7.9	−1720.8	11.9
1.9149	63.17	34.4	2391.0	1.4254	5.5	−1735.7	3.0
1.5279	63.48	33.5	2391.0	1.1364	6.3	−1722.2	10.5
1.8293	28.59	34.1	2391.0	1.3531	4.6	−1746.6	13.9
1.5143	64.20	33.7	2391.0	1.1328	4.8	−1732.4	0.3
1.5095	62.67	34.3	2391.0	1.1275	4.8	−1730.8	1.9
1.7079	61.44	34.2	2391.0	1.2821	4.4	−1747.4	14.7
1.5628	62.07	33.2	2391.0	1.1665	5.2	−1731.7	1.0
1.6232	33.33	33.5	2391.0	1.2015	6.2	−1740.3	7.6
1.6181	36.47	33.6	2391.0	1.1844	5.3	−1718.7	14.0
					Av.	−1732.7	7.9
					Std. dev. of the mean		3.2
			$x = 1.91$				
1.6451	30.21	33.7	2391.0	1.2080	5.7	−1729.3	5.9
1.5654	36.54	21.3	2390.3	1.1566	5.4	−1733.4	1.8
1.5410	18.62	22.9	2390.4	1.1330	3.1	−1740.4	5.2
1.6641	24.53	22.9	2390.4	1.2245	3.5	−1738.4	3.2
1.6889	23.56	22.6	2390.4	1.2491	2.9	−1748.7	13.5
1.7150	56.47	22.4	2390.4	1.2709	2.9	−1728.6	6.6
1.7261	57.92	22.5	2390.4	1.2842	3.4	−1734.5	0.7
1.6542	55.85	22.7	2390.4	1.2265	2.6	−1728.6	6.6
					Av.	−1735.2	4.4
					Std. dev. of the mean		2.5

ments, the heat of formation of thorium dioxide, and an estimated uncertainty for the correction for the impurities. The value given here for ThC agrees with that of Aronson (1). This work agrees with Westrum's second law calculation for $\mathrm{ThC}_{1.93}$ (*12*). The thorium carbides are somewhat more stable than the corresponding uranium carbides [$\Delta H^{\circ}_{f\,298^{\circ}}(\mathrm{UC}_{1.00}) = -23.2 \pm 0.7$ kcal. per mole; $\Delta H^{\circ}_{f\,298^{\circ}}(\mathrm{UC}_{1.93}) = -20.5$ kcal. per mole] (*3*).

ACKNOWLEDGMENT

The authors appreciate the efforts of Patrick L. Stone for preparing the samples, Group CMB-1 and Helen Cowan for chemical analyses, Finley Ellinger, x-ray analysis, Charles Javorsky, metallography, and Daniel Pavone, for the glass-window bomb experiments.

LITERATURE CITED

(1) Aronson, S., *Met. Soc., Am. Inst. Mining, Met. Petrol. Engrs., Inst. Metals Div., Spec. Rept. Ser.* No. 13, 247 (1964); *CA*64, 1416b (1966).

(2) Cameron, A.E., Wichers, E., *J. Am. Chem. Soc.* **84**, 4175 (1962).

(3) Holley, C.E., Jr., Storms, E.K., *Intern, At. Energy Agency, Symp. Thermodyn. Nucl. Mater.*, Vienna, Austria, 1967.

(4) Huber, E.J., Jr., Holley, C.E., Jr., Meierkord, E.H., *J. Am. Chem. Soc.* **74**, 3406 (1952).

(5) Huber, E.J., Jr., Matthews, C.O., Holley, C.E., Jr., *Ibid.*, **77**, 6493 (1955).

(6) JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., Sept. 30, 1964.

(7) Kornilov, A.N., Zaikin, I.D., *Zhur. Fiz. Khim.* **41** No. 2, 351 (1967).

(8) Kubaschewski, O., Evans, E.Ll., "Metallurgical Thermochemistry," p. 276, Pergamon Press, New York, 1958.

(9) Pavone, D., Holley, C.E., Jr., *Rev. Sci. Instr.* **36**, 102 (1965).

(10) Storms, E.K., "The Refractory Carbides," p. 155–170, Academic Press, New York, 1967.

(11) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B., Bailey, S.M., Schumm, R.H., *Natl. Bur. Std. Tech. Note* **270-1** (1965).

(12) Westrum, E.F., Takahashi, Y., Stout, N.D., *J. Phys. Chem.* **69**, 1520 (1965).

RECEIVED for review July 21, 1967. Accepted October 27, 1967. Work performed under the auspices of the U.S. Atomic Energy Commission. Presented in part at the Southwest Regional Meeting, ACS, Albuquerque, N. M., November 1966.

Diffusion Coefficient of Ethylene Gas in Water

AMINUL HUQ and TREVOR WOOD

Department of Chemical Engineering, University of Sydney, Sydney, Australia

Data on ethylene diffusivity obtained by absorbing the gas in a laminar jet of pure water at temperatures of 20°, 25°, and 30° C. are presented and compared with those quoted in the literature. The experimentally determined diffusion coefficients are consistent with results already reported. Various correlations describing the variation of diffusivity with temperature are reviewed and a convenient means of correlating ethylene gas diffusivity with temperature is presented.

AS part of an investigation into the reactions of ethylene gas with aqueous solutions of bromine, measurements were made of the diffusivity of the gas in water. The values of the diffusion coefficient, determined from a laminar jet absorber, were compared with data quoted in the literature and a certain amount of discrepancy was found between the various sources (*2, 5, 6, 23*). The purpose of this paper is to present the available data, to examine them critically, and to put forward a convenient correlation for estimating diffusion coefficients over a range of temperature from 20° to 30° C.

The background of diffusion or molecular transport has been discussed in detail by Longwell and Sage (*15*) and need not be reviewed here. It is desirable for practical purposes to define the proportionality constant between the flux density of the diffusing species and the gradient of the appropriate potential. Coefficients based on concentration gradient are now almost universally employed for both gas and liquid system. Diffusion in a binary system, like ethylene-water, is described by the mutual diffusion coefficient, often called the Chapman-Cowling coefficient (*4*), of the binary system.

THEORY

Absorption of gas by a liquid jet was used to measure the diffusivities of ethylene in pure water at various temperatures and at atmospheric pressure. Absorption into the jet may be analyzed using the "penetration theory" provided that the gas molecules penetrate only a short distance into the jet in comparison with its radius, and the velocity across the jet is uniform. The first condition is satisfied in the normal range of contact times and the flow pattern of the jet is very nearly, but not exactly, uniform. This is due to: frictional drag exerted by the inside surface of the nozzle, causing the velocity to be reduced in the boundary layer near the surface; drag of the surrounding gas on the surface; acceleration of the fluid motion due to gravity; and occurrence of ripples together with a stagnant surface at the receiver, where the jet terminates.

The drag of the surrounding gas on the jet surface and the receiver end effects are small and may be neglected; the nozzle drag and gravity effects have been studied in detail by Scriven (*20*) and Beek (*3*).

The diffusion equation and the boundary conditions describing the absorption process are:

$$U \frac{\partial c}{\partial x} + V \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \tag{1}$$

$$c(o, y) = c(x, \infty) = c_i,\ c(x, o) = c_e \tag{2}$$

For a jet in which the velocity throughout is constant, and equal to U_{av}, the instantaneous absorption rate is given by:

$$n^* = (c_e - c_i) \left[\frac{D\,U_{\mathrm{av}}}{x} \right]^{1/2} \tag{3}$$