by the abrupt termination of the step adsorption in the first layer by the sharp cut-off, and it has no physical significance. The cut-off for isotherm 2 is smaller and $\bar{S}$ has lost its deep minimum at $\theta = 1$.

Discussion.—Because of the exponential distribution, the upper limit of $-\bar{E}/kT$ has the unrealistic value infinity for the examples treated here. We refrained from using an upper cut-off, which would have given $-\bar{E}/kT$ a finite limit, in order to keep the number of parameters down. None of the integral entropies has a minimum near the monolayer[5] because we have kept the entropy of binding to the surface equal to that in the bulk phase. This restriction is easily removed[8] (with still another parameter) and the observed minimum in S could be reproduced.

As yet, we are unable to make any generalizations connecting the limited number of parameters and the thermodynamic functions that result; for instance the negative value of $-\bar{E}/kT$ in Fig. 7 came as a complete surprise. If anything, this difficulty demonstrates the folly of making deductions about the model for adsorption from qualitative examination of, and *ad hoc* calculations on, experimental heats and entropies.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Tantalum, Niobium and Zirconium Oxides, and Tantalum Carbide

BY GEORGE L. HUMPHREY

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The heats of formation of tantalum pentoxide, niobium (columbium) pentoxide, zirconium dioxide and tantalum carbide were measured by combustion calorimetry. The results are, respectively, −488.8 ± 0.5, −455.2 ± 0.6, −261.5 ± 0.2, and −38.5 ± 0.6 kcal./mole at 298.16°K. Corresponding free energy values were calculated.

The present availability of zirconium almost completely free of hafnium and of substantially pure tantalum and niobium (columbium) made it desirable that new determinations be obtained of the heats of formation of the oxides of these metals. This was accomplished through combustion calorimetry and the results are reported in this paper, together with determinations of the heats of combustion and formation of substantially pure tantalum carbide.

Materials and Method.—The tantalum metal was obtained from Fansteel Metallurgical Corp. in the form of half-inch bar stock. Spectrographic analysis[1] showed 0.08% niobium, 0.01% silicon, 0.01% iron and 0.005% titanium, indicating a purity of 99.89%. The increase in mass on complete conversion to oxide agreed with the result calculated from this analysis to within 0.02%. Very thin lathe-turnings, cut from the interior of the bar with a Carboloy tool were used in the measurements.

The niobium metal also was a Fansteel Metallurgical Corp. product. It was received in 0.005-inch thick sheets that were cut into narrow strips for use in the measurements. Spectrographic analysis[1] showed 0.20% tantalum, 0.05% tungsten, less than 0.01% each of silicon, molybdenum, iron and boron, less than 0.005% each of aluminum, manganese, nickel and zirconium, less than 0.003% titanium and 0.001% copper. The indicated purity, therefore, is about 99.69%.

The zirconium metal was furnished by the Albany (Oregon) Station of the Bureau of Mines, along with the results of chemical and spectrographic analyses. The impurities are less than 0.1% hafnium, 0.09% iron, 0.053% chlorine, 0.03% carbon, 0.011% magnesium, 0.009% aluminum, 0.009% lead, 0.007% nitrogen, 0.006% titanium, 0.002% chromium, 0.002% manganese, 0.001% silicon, 0.001% copper and less than 0.001% each of boron, molybdenum, nickel and tin. The indicated purity thus is 99.67%. Part of the metal was in the form of vacuum purified sponge, which was used as received, and part in the form of a machined bar, from which very thin lathe-turnings (cut from the interior with a Carboloy tool) were taken for the measurements.

The tantalum carbide was obtained, in powder form, from Fansteel Metallurgical Corp. Spectrographic analysis[1] showed 0.27% niobium, 0.10% titanium, 0.05% silicon, 0.01% iron and 0.01% zirconium. Assuming these are lattice impurities, the composition would be 0.30% niobium carbide, 0.13% titanium carbide, 0.07% silicon carbide, 0.01% iron carbide, 0.01% zirconium carbide and 99.48% tantalum carbide. This composition theoretically would contain 6.27% carbon, which was checked reasonably well by actual analysis as 6.24%.

The heat of combustion determinations were conducted with previously described apparatus.[2] All weights were corrected to vacuum and all heat values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules). The calorimeter was calibrated before each set of measurements by means of benzoic acid (National Bureau of Standards sample 39 g.), the mean value being 32411.1 (±0.02%) cal./ohm.

All combustions were made with 30 atm. oxygen pressure. Ignition of the samples was by means of an electrically heated platinum spiral and a filter paper fuse, for which proper corrections were made. Each substance was tested and found to show no oxidation on standing in the bomb under 30 atm. oxygen pressure before ignition. The bomb gases, after combustion, were tested for oxides of nitrogen. The correction for this was negligible (less than 0.002%) except in the case of zirconium, for which it averaged 0.012% of the heat generated during combustion.

The tantalum combustions employed both plain silica-glass capsules and silica-glass capsules heavily lined with tantalum pentoxide and strongly ignited. In all instances the bomb walls remained entirely clean. No significant difference was noted between the final results with and without the capsule liner, although the combustions were much more nearly complete when no liner was used. Completion of combustion was evaluated for each individual run by means of the observed weight increase of the calorimeter combustion product on prolonged ignition in air. This method showed percentage completion of combustion ranging from 97.23 to 99.99+, and corresponding corrections were applied to the measured heats. (The efficacy of this test was confirmed by experiments with tantalum metal turnings.) X-Ray examination of the combustion product showed it to be the same variety of tantalum pentoxide used previously in low-temperature heat capacity[3] and high-temperature heat content[4] measurements.

The niobium combustions were conducted in silica-glass

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[1] This analysis was conducted by George M. Gordon, Division of Mineral Technology, University of California.

[2] G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).

[3] K. K. Kelley, *ibid.*, **62**, 818 (1940).

[4] R. L. Orr, *ibid.*, **75**, 2808 (1953).

capsules without linings. In conformity with the experience noted for tantalum, there was no evidence of any actual chemical attack of the capsules, although shattering by thermal shock occurred. About 99% of the combustion product remained in the capsule, while 1% appeared as a fine white deposit on the bomb walls. X-Ray diffraction of the product from the capsules showed it to be the same variety of niobium pentoxide as was employed in previous high-temperature heat content determinations.[4] The wall deposit was niobium pentoxide of a different crystalline form; however, the amount of this deposit was so small that no attempt was made to correct for its difference in energy content. As oxidation of niobium metal in air was found to be very slow, it was not practical to use strong ignition in air as a means of testing the combustion products for completion of combustion. Also the highly hygroscopic nature of the oxide added a further difficulty. Consequently, in this instance the combustion products were tested by strong ignition in pure oxygen, with simultaneous determination of the moisture pick-up during transfer and preparation of the samples for this test. The percentage completion of combustion ranged from 97.63 to 99.38, and correction of the measured heats was made accordingly.

The zirconium combustions were made in silica-glass capsules that were heavily lined with the monoclinic variety of zirconium dioxide and strongly ignited. In all instances the bomb walls remained entirely clean. The combustion products from the bomb were strongly ignited in air as a test for completion of combustion, and in all instances virtually 100% completion was observed. X-Ray examination of the combustion products showed the presence of only the monoclinic variety of zirconium dioxide.

The tantalum carbide combustions were conducted in plain silica-glass capsules, as was done for part of those for tantalum metal. Each combustion product was tested for completion of combustion by strong ignition in air, and the percentage completion ranged from 97.02 to 99.72. The bomb walls remained clean in all instances. The bomb gases after combustion were tested for carbon monoxide which was found to be absent. The X-ray diffraction pattern of the tantalum pentoxide product was identical with that from the tantalum metal combustions.

Heat of Combustion Results.—The measured heats of combustion at 30°, together with correction terms, appear in Table I. The assigned uncertainties were calculated according to the procedures of Rossini and Deming.[5]

No significant difference, depending upon the presence or absence of a tantalum pentoxide lining in the combustion capsule, appears in the final results for tantalum. However, the marked superiority in the completion of combustions in the unlined capsules is evident from the corrections in the next to last column of Table I. No significant effect of sample size was noted in any instance. The larger precision uncertainty of the results for niobium reflects the greater difficulty in this instance in determining the extent of completion of combustion. There appears to be no significant difference between results for the turnings of massive metal and the sponge metal in the case of zirconium. Impurity corrections, indicated in Table I, are based upon the previously mentioned chemical and spectrographic analyses and heat of formation data from the N. B. S. Tables.[6]

Heats of Formation.—The data in Table I are energy values for combustions under bomb conditions at 30°. To obtain the corresponding heat content values under standard conditions it is necessary to correct to a constant pressure process at 25°, with all gaseous substances reduced to 1 atm. fugacity. These corrections will be applied after first converting to a molal basis by means of 1951 International Atomic Weights.[7]

TABLE I

ENERGIES OF COMBUSTION AT 30°

Mass of substance, g.	Total heat evolved, cal.	Heat from EIT, fuse, and HNO_3, cal.	Cor. for incomplete comb., cal.	$-\Delta U_B/m$, cal./g.
		Tantalum		
3.00208[a]	4033.31	17.74	24.23	1345.7
3.00145[a]	3947.23	14.06	112.04	1347.8
1.00435[a]	1357.52	13.71	11.79	1349.7
2.99967[b]	4062.03	19.15	1.20	1348.2
1.99907[b]	2703.60	11.29	0.10	1346.8
2.00103[b]	2714.84	15.41	1.08	1349.6
			Mean	1348.0 ± 1.3
			Cor. for impurities (−0.126%)	1346.3 ± 1.3
		Niobium		
2.00110	4852.58	9.45	33.76	2437.1
2.00150	4844.05	8.55	54.14	2443.0
2.00337	4809.93	13.64	79.53	2433.8
2.00334	4840.39	16.57	64.61	2440.1
2.00501	4842.17	14.46	49.70	2432.6
2.00391	4796.86	14.23	116.09	2444.6
1.29956	3159.39	13.36	19.73	2436.0
1.30388	3179.76	18.34	19.82	2439.8
2.00210	4866.27	17.63	30.41	2437.0
			Mean	2438.2 ± 2.7
			Cor. for impurities (+0.0828%)	2440.2 ± 2.7
		Zirconium		
1.99975[c]	5724.14	17.08	Nil	2853.9
2.00005[c]	5724.72	12.35	Nil	2856.1
2.00093[c]	5727.74	15.87	Nil	2854.6
2.00023[c]	5730.56	15.16	Nil	2857.4
2.00091[d]	5729.55	13.99	Nil	2856.5
2.40084[d]	6869.09	12.27	Nil	2856.0
2.40055[d]	6771.23	15.85	Nil	2855.8
2.00053[d]	5724.60	12.46	Nil	2855.3
			Mean	2855.7 ± 0.8
			Cor. for impurities (+0.121%)	2859.2 ± 0.8
		Tantalum Carbide		
5.00881	7735.42	21.99	104.38	1560.8
4.48882	7012.71	13.56	15.17	1562.6
4.43808	6921.30	13.95	20.99	1561.1
2.22008	3456.87	32.16	43.56	1562.2
2.22066	3374.42	11.62	103.37	1560.9
4.42888	6918.64	11.75	19.66	1564.0
			Mean	1561.9 ± 1.0
			Cor. for impurities (−0.698%)	1551.0 ± 1.0

[a] Ta_2O_5 liner. [b] No liner. [c] Turnings. [d] Sponge.

The mean value for tantalum corresponds to −487.04 kcal./mole of tantalum pentoxide. Reduction to unit fugacity of oxygen was made using the value −1.556 cal./atm.[8] and a suitable modification of Washburn's equation[9]; conversion to a constant pressure process was made by the relationship $\Delta H = \Delta E + \Delta nRT$; and conversion to 25°

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(5) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(6) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Natl. Bur. Stands.*, Circ. 500 (1952).

(7) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

(8) F. D. Rossini and M. Brandsen, *Natl. Bur. Stands. J. Res.*, **9**, 733 (1932).

(9) E. W. Washburn, *ibid.*, **10**, 525 (1933). (Equation 43).

was made using heat capacity data listed by Kelley.[10] The net result is $\Delta H_{298.16} = -488.8 \pm 0.5$ kcal./mole, which is the heat of formation under standard conditions of tantalum pentoxide from the elements. The assigned uncertainty in this instance (and similarly for the other substances in this paper) takes account of uncertainties in the combustion heat of the metal, calibration of the calorimeter, combustion heat of benzoic acid, completion of combustion and correction for impurities in the metal.

The mean value for niobium corresponds to -453.44 kcal./mole of niobium pentoxide. The corrections to standard state conditions, made in the same manner as for tantalum, yield $\Delta H_{298.16} = -455.2 \pm 0.6$ kcal./mole as the heat of formation of niobium pentoxide from the elements.

The mean value for zirconium is equivalent to -260.82 kcal./mole of zirconium dioxide. Correction to standard conditions results in $\Delta H_{298.16} = -261.5 \pm 0.2$ kcal./mole as the heat of formation of zirconium dioxide.

The mean value for tantalum carbide corresponds to -299.17 kcal. for the reaction

$$TaC + {}^9/_4O_2 = {}^1/_2Ta_2O_5 + CO_2$$

under bomb conditions. Reduction to unit fugacity of oxygen and CO_2 were made jointly, using a suitable modification of Washburn's[9] equation; corrections to a constant-pressure process and to 25° were made as mentioned previously. The result is $\Delta H_{298.16} = -300.0 \pm 0.5$ for the above reaction under standard conditions. Combining with the heats of formation of carbon dioxide[6] and 0.5 mole of tantalum pentoxide leads to $\Delta H_{298.16} = -38.5 \pm 0.6$ kcal./mole as the heat of formation of tantalum carbide from the elements.

Previous heat of formation values of tantalum pentoxide, niobium pentoxide and zirconium dioxide were considered in compiling the N. B. S. Tables,[6] the adopted values being, respectively, -499.9, -463.2 and -258.2 kcal./mole. The present work is considered superior in that purer metals were available for study, the use of a kindler (such as paraffin oil) was avoided, and higher precision was obtained. No value for tantalum carbide is given in the N. B. S. Tables.

Using entropy values listed by Kelley[10] and the assumption that the tantalum and niobium oxides have the same entropy of formation, the following free energies of formation are derived: $\Delta F^\circ_{298.16} = -456.5 \pm 0.6$ kcal./mole for tantalum pentoxide, $\Delta F^\circ_{298.16} = -422.9 \pm 0.7$ kcal./mole for niobium pentoxide, $\Delta F^\circ_{298.16} = -247.7 \pm 0.2$ kcal./mole for zirconium dioxide, and $\Delta F_{298.16} = -38.1 \pm 0.6$ kcal./mole for tantalum carbide.

BERKELEY 4, CALIFORNIA

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[10] K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A Chromatographic Study of Carbonyl Compounds Present in a Hydrocarbon–Air Flame[1]

BY EARL W. MALMBERG

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A study has been made of the carbonyl compounds which are present in a hydrocarbon–air flame. The experimental methods included formation and chromatographic separation of the 2,4-dinitrophenylhydrazone derivatives. In addition to the carbonyl compounds which are to be expected in the light of presently accepted mechanisms, a number of synthesis products were obtained, compounds in which the length of the carbon chain was increased. These results are interpreted in terms of the free radicals which must have been present originally, including the formyl radical. Three products, glyoxal, methylglyoxal and formaldehyde were found to be common to eighteen hydrocarbon fuels. Quantitative analyses for these products showed no correlation with the type of fuel. This fact seems to indicate that the differences in the burning characteristics of hydrocarbons lie in the earlier stages of the combustion.

In the study of the mechanism of oxidation of hydrocarbons, the isolation of intermediates is difficult but yields important information as to the nature of the reactions. In the present investigation carbonyl compounds have been isolated from turbulent hydrocarbon–air flames which are quenched by an excess of fuel. A chromatographic study of derivatives of carbonyl compounds was initiated because of the great promise shown by this method for qualitative and quantitative analytical applications. This investigation is in two parts: the development of chromatographic procedures and the application of these methods to the study of flame combustion products.

Development of Chromatographic Methods

The work of Iddles and Jackson[2] has shown that water-soluble carbonyl compounds can be quantitatively precipitated as the 2,4-dinitrophenylhydrazones. At the time our study began Roberts and Green[3] had shown that chromatography on silicic acid adsorbent showed considerable promise. Further study showed that very good separations could be obtained with the derivatives of the lower carbonyl compounds. Gordon[4] and co-workers have since then reported essentially the same separations which were used in the present work. However, the procedures which we developed in-

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[1] This work was presented at the Meeting of the American Chemical Society in Atlantic City, N. J., September, 1952. The work was supported in part by the Air Force Research and Development Command under Contract No. AF 33(038)22959.

[2] H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

[3] J. D. Roberts and C. Green, *ibid.*, **18**, 335 (1946).

[4] B. E. Gordon, F. Wopat, H. D. Burnham and L. C. Jones, *Anal. Chem.*, **23**, 1754 (1951).