pressure of bromine trifluoride and bromine pentafluoride at 75 and 100° using this apparatus agree very well with the literature values obtained with a nickel and Monel ebulliometer. This comparison at 75° is as follows:

	Our values, mm.	Lit. values, mm.
BrF_3	111	110.91[5]
BrF_5	2247	2249.2[5]

A similar comparison at 100° is

BrF_3	309	308.87[5]

The experimental values for the vapor pressure of bromine shown in Table I agree with values calculated from eq. 1, with an average deviation of ±0.2%. The temperatures were measured to ±0.01° and may be assumed to be accurate to ±0.02°. The pressure measurements are accurate to ±0.5 mm.

(5) R. D. Long, Argonne National Laboratory Document ANL-5405.

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Heats of Formation of Niobium Carbide and Zirconium Carbide from Combustion Calorimetry

BY ALLA D. MAH AND B. J. BOYLE

Refractory metal carbides, although of constantly increasing technical importance, are difficult to prepare in a form adequately pure for thermodynamic measurements. As a consequence, the available thermodynamic data are scattered and incomplete. This note presents the results of combustion calorimetric investigations of two substances, niobium carbide (columbium carbide) (NbC) and zirconium carbide (ZrC). Although the purity of the substances available for study leaves much to be desired, it is believed that useful heat of formation data have been obtained. The literature contains no previous directly measured values for these substances.

Materials and Methods.—The niobium and zirconium carbides were prepared by Professor Leo Brewer and co-workers of the Chemistry Department of the University of California.

Niobium carbide was prepared from niobium metal (containing no impurities other than trace amounts of silver, calcium, copper, iron, silicon and tantalum) and Acheson graphite. These substances were mixed and heated *in vacuo* in a graphite container to 2300–2400°. The product appeared uniform upon microscopic examination and X-ray diffraction showed the presence of only the niobium carbide phase. Analysis gave 10.82% carbon and 89.10% niobium (corresponding to $NbC_{0.939}$), as compared with the theoretical 11.45 and 88.55%. The unaccounted for 0.08% was considered to be oxygen and nitrogen.

Zirconium carbide was prepared similarly from Acheson graphite and part of the same sample of hafnium-free zirconium sponge used by Humphrey[1] in his heat of formation determinations of zirconium dioxide. In this case also a uniform appearing product, showing only the zirconium carbide phase upon X-ray examination, was obtained. Analysis gave 11.07% carbon and 88.15% zirconium, as compared with the theoretical 11.63 and 88.37%. The unaccounted for 0.78% could be attributed only to nitrogen and oxygen picked up during the course of preparation.

(1) G. L. Humphrey, THIS JOURNAL, **76**, 978 (1954).

The energy of combustion determinations were made 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). National Bureau of Standards benzoic acid sample No. 39g was used for calibration. Two bombs were employed and the calibration values were 32,480.6 (±0.02%) cal./ohm for the niobium carbide combustions and 32,426.2 (±0.02%) cal./ohm for the zirconium carbide combustions.

All combustions were made under 30 atm. oxygen pressure, with no water added to the bomb. Ignition of the samples was by means of an electrically heated platinum spiral and a filter paper fuse. The bomb gases, after combustion, were tested for carbon monoxide, which was found to be negligible (less than 0.00003%). The bomb gases also were analyzed for oxides of nitrogen for which a small energy correction, ranging from 0.001 to 0.002%, was required.

The niobium carbide was held in the bomb on a niobium pentoxide plate, supported in turn by an alundum disc. About 91% of the niobium pentoxide from the combustion appeared as a fused layer upon the niobium pentoxide plate and the remainder appeared as a fine wall deposit on the bomb. X-Ray diffractions of the original niobium pentoxide plate and the adhering layer of niobium pentoxide from the combustion showed them to be the high temperature variety reported by Brauer.[3] The wall deposit was a mixture of this variety and another, similar to Humphrey's[1] findings in his niobium metal combustions. The combustion products were examined visually for evidence of incomplete combustion, and three runs in which blackish specks were observed were discarded.

The zirconium carbide was held in silica glass capsules heavily lined with monoclinic zirconium dioxide. Over 99.9% of the zirconium dioxide formed by combustion remained in the capsule and less than 0.1% appeared as a wall deposit on the bomb. X-Ray diffraction of both fractions showed only monoclinic zirconium dioxide. Comparison of the mass of the combustion product with the original mass of the carbide (taking into account its analysis) indicated that the combustions were complete.

Energy of Combustion Results.—The results of the measurements are given in Table I. In both instances the precision uncertainty is about 0.03%.

Two assumptions were made regarding the composition of the niobium carbide sample to permit calculation of the correction to be made for impurities; both are consistent with the chemical analysis. First, the sample was considered as composed of 99.39% of the carbide phase, $NbC_{0.945}$, and 0.61% niobium nitride (NbN). This assumption leads to a correction of 6.8 cal./g. Second, it was assumed that the sample is 99.46% carbide of composition $NbC_{0.944}$ and 0.54% oxide (as NbO). This leads to a correction of 8.0 cal./g. The mean value 7.4 cal./g. has been applied in Table I. In obtaining these values the heats of solid solution of the nitride and oxide in the carbide phase are assumed to be zero.

Two similar assumptions were made for correcting the zirconium carbide results. First, the sample was assumed to be 94.01% zirconium carbide (ZrC), 5.86% zirconium nitride (ZrN) and 0.13% free carbon. This leads to 72.7 cal./g. correction. Second, it was assumed that the sample contains 94.72% zirconium carbide (ZrC), 5.23% zirconium oxide (as ZrO) and 0.05% free carbon, which leads to 92.0 cal./g. correction. Again, the heats of solid solution of the nitride and oxide in the carbide phase are taken as zero. In the absence of a decisive criterion for choice between these corrections, it was considered best to apply the mean value, 82.4 cal./g., in Table I.

(2) G. L. Humphrey, *ibid.*, **73**, 1587 (1951).
(3) G. Brauer, Z. *anorg. Chem.*, **248**, 1 (1941).

TABLE I

COMBUSTION DATA

Mass of sample, g.	Total energy cor. to 30°, cal.	Cor. for fuse. EIt, and HNO₃, cal.	Net energy, cal.	$-\Delta U_B$, cal./g.
		NbC		
1.99869	5437.12	8.17	5428.95	2716.3
1.99918	5438.46	8.24	5430.22	2716.2
1.99896	5440.45	8.33	5432.12	2717.5
2.00062	5439.36	8.41	5430.95	2714.6
1.50086	4080.99	7.39	4073.60	2714.2
1.51236	4113.67	8.33	4105.34	2714.5
1.51224	4116.26	8.14	4108.12	2716.6
1.50986	4109.41	8.27	4101.14	2716.2

	Mean	2715.8 ± 0.8
	Cor. for imp.	7.4
		2723.2

Mass of sample, g.	Total energy cor. to 30°, cal.	Cor. for fuse. EIt, and HNO₃, cal.	Net energy, cal.	$-\Delta U_B$, cal./g.
		ZrC		
1.11036	3264.50	12.08	3252.42	2929.2
1.11014	3264.49	12.46	3252.03	2929.4
1.11022	3264.77	14.26	3250.51	2927.8
1.11021	3264.06	12.71	3251.35	2928.6

	Mean	2928.8 ± 0.8
	Cor. for imp.	82.4
		3011.2

Heats of Formation.—The corrected mean result for niobium carbide corresponds to $\Delta E_{303.16}$ = −283.89 kcal./mole of $NbC_{0.9445}$, the energy evolution under bomb conditions. Correction to unit fugacity of oxygen (−37 cal.), to a constant pressure process (−753 cal.), and to 25° (−2 cal.) leads to $\Delta H_{298.16}$ = −284.69 kcal./mole as the standard heat of combustion of $NbC_{0.9445}$. Employing Humphrey's[1] value of the heat of formation of niobium pentoxide and the N. B. S. value[4] for carbon dioxide, there is obtained $\Delta H_{298.16}$ = −31.75 ± 0.8 kcal./mole as the heat of formation of niobium carbide ($NbC_{0.9445}$) from the elements. Assuming zero heat of solution of niobium metal in carbide of stoichiometric composition, there is obtained $\Delta H_{298.16}$ = −33.6 ± 0.8 kcal./mole as the heat of formation of $NbC_{1.000}$ from the elements.

Similarly, the corrected mean value for zirconium carbide corresponds to $\Delta E_{303.16}$ = −310.85 kcal./mole as the energy evolution under bomb conditions. Correction to unit fugacity of oxygen (−15 cal.), to a constant pressure process (−602 cal.), and to 25° (2 cal.) gives $\Delta H_{298.16}$ = −311.5 kcal./mole as the standard heat of combustion of zirconium carbide. Applying Humphrey's[1] heat of formation of zirconium dioxide and the N. B. S. value[4] for carbon dioxide, there is obtained $\Delta H_{298.16}$ = −44.1 ± 1.5 kcal./mole as the heat of formation from the elements.

It is believed that the uncertainties assigned to the heat of formation values are large enough to account for errors in the corrections to exact stoichiometric composition. All other errors are minor in comparison to those associated with the impurity contents of the samples.

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

It is of interest to compare the present heat of formation values with those of tantalum carbide,[5] $\Delta H_{298.16}$ = −38.5 kcal./mole, and titanium carbide,[5] $\Delta H_{298.16}$ = −43.85 kcal./mole. As the entropies of formation should not differ greatly, it is evident that zirconium and titanium carbides have about the same thermodynamic stability, while niobium carbide is somewhat less stable than tantalum carbide.

(5) G. L. Humphrey, THIS JOURNAL, **73**, 2261 (1951).

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Some Phosphates of Aliphatic Diamines[1]

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Although both aliphatic diamines and the phosphoric acids are common chemicals, the salts which form during the reaction between solutions of these substances have not been described.[3] The primary objective of this investigation was the preparation of some of these salts. Diamines are diprotic bases which always react with two equivalents of acid in salt formation; therefore the various series of salts which could be isolated were due to changes in the phosphate ion with varying pH.

Experimental

Reagents.—Ethylenediamine was obtained from the Eastman Kodak Company, 1,2-diaminopropane from the Union Carbide and Carbon Company, and 1,3-diaminopropane and 1,3-diaminobutane from the Sharples Company. All were distilled shortly before use and were water white. Merck "Reagent Grade" orthophosphoric acid was used without further treatment. Lumpy pyrophosphoric acid was obtained from City Chemical Company, New York City. The material was stored under refrigeration, and only the required amount dissolved immediately before use. Such solutions of pyrophosphoric acid were kept cool (under 30°), and were not allowed to remain below pH 4 any longer than necessary. These precautions prevented any significant hydrolysis to orthophosphate during the reactions.

General Procedure.—All systems investigated were taken through the following systematic steps.

1. Approximately 6 N aqueous solutions were prepared. Solutions of this strength made it possible to obtain an appreciable amount of solid product from a relatively small volume of reaction mixture.

2. The changes in pH resulting from the slow addition of diamine solution to the acid were followed with a pH meter. The resulting curves of both ortho- and pyrophosphoric acids with all of the diamines studied have the same general form.[4] An inflection point near pH 4 (the dihydro-