of *ca.* 5 ± 1. Stackelberg and Freyhold[3] have reported that ferric iron reduces with an $E_{1/2}$ of -1.36 volt in 0.04 to 0.8 *M* potassium fluoride. Shoemaker[4] has recently reported the irreversible reduction of FeF^{++} at a rotating platinum microelectrode. Recent study in this Laboratory clarifies some of these discordant reports.

At 25° and within a *p*H range of about 5 to 6.5, a small reduction wave is observed with the dropping mercury electrode at -1.36 volt *vs.* S.C.E. in 0.3 to 1.0 *M* potassium fluoride. However this wave is found with or without ferric ion present, and is apparently due to hydrogen discharge or other phenomena. At a *p*H of 5.8 a reversible (based on slope if $n = 1$) ferric to ferrous reduction wave does occur with an $E_{1/2}$ of -0.49 volt *vs.* S.C.E. in 1.0 *M* fluoride. The wave is observed within a very limited range of *p*H, however. Only about one-third of the diffusion current remains on lowering the *p*H to 5.4 or on raising it to 6.2.

The $E_{1/2}$ of this wave is not appreciably *p*H dependent.

At a *p*H of 5.8 the relation of $E_{1/2}$ to log $[F^-]$, for $[F^-] = 0.3$ to 1.0 *M*, fits the conclusion that one (or, one *additional*) fluoride ion is being complexed. A plot of these data is shown in Fig. 1.

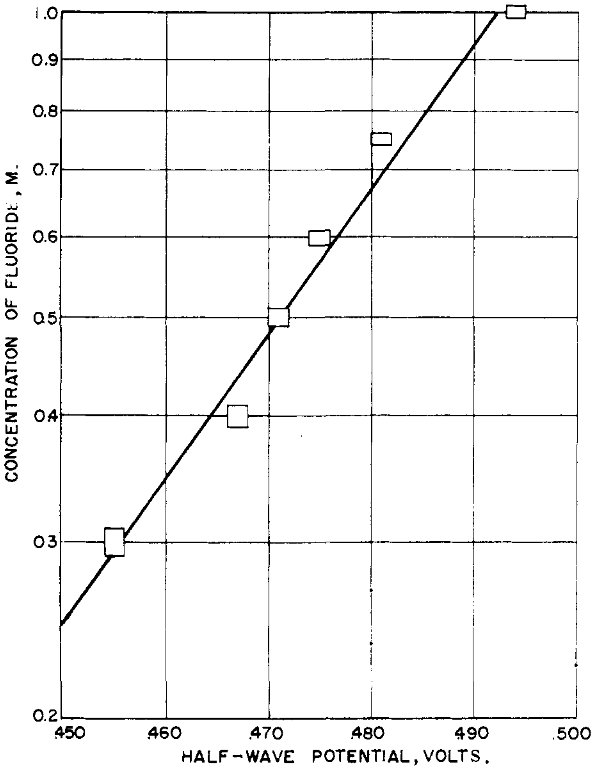

Fig. 1.—Variation of half-wave potential of ferric ion with fluoride concentration.

At 25° in 1 *M* KF and at a *p*H of 5.8, the diffusion coefficient of the ferric fluoride complex is estimated as being 5.8×10^{-6} cm.^{2} sec.$^{-1}$. The capillary characteristics were $t = 2.35$ sec. and $m = 3.48$ mg. sec.$^{-1}$ at -0.47 volt.[5]

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[3] M. von Stackelberg and H. von Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[4] C. E. Shoemaker, paper presented at American Chemical Society Meeting, Kansas City, March, 1954.

[5] This work was performed under Contract No. AF 18(600)-379 with the Air Research and Development Command, Wright Air Development Center.

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The Heats of Combustion and Formation of Boron Carbide

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There appear to be no published data for the heat and free energy of formation of boron carbide, B_4C, a compound of considerable technical interest as a possible refractory and neutron absorber. We decided to measure the heat of combustion of boron carbide since we are interested in the thermochemistry of boron compounds and had developed methods for their combustion and analysis. Although a more direct measurement of heat of formation would be desirable, it is possible to derive a reasonably reliable value from the heat of combustion.

Experimental

Boron Carbide.—A sample of high purity boron carbide together with its analysis was supplied to us through the courtesy of Dr. G. R. Finlay of Norton Company, Research and Development Department. The analysis showed B = 77.81%, C = 21.63%, corresponding to 3.99 boron atoms per carbon atom, or within experimental error to the stoichiometric composition B_4C. There was apparently no free boron or carbon in the sample. However, because of the small heat of formation of B_4C, traces of the free elements would cause negligible errors. The sample contained 0.16% iron. Calculation showed that if the iron impurity were present as either free iron or cementite, Fe_3C, and burned to Fe_2O_3 an error no greater than 0.03% would be introduced, while if the iron were already partially or completely converted to oxide the error would be smaller. Therefore, we have made no allowance for the presence of iron impurity in the absence of exact knowledge about its fate.

The following atomic weights were used: B, 10.82; C, 12.110; O, 16.000.

Apparatus.—Heat of combustion measurements were made in a Parr oxygen bomb calorimeter, modified as described by Dworkin, Sasmor and Van Artsdalen.[2] The bomb itself, a double valve type, constructed of illium, has a volume of about 360 cc. A smaller weight of water than in our previous work was used in the calorimeter during the present study; the standard amount was 1990.0 g. and corrections were applied for slight deviations from this amount from run to run. Three different types of crucibles were used to contain the charge of boron carbide: namely, stainless steel, platinum and quartz, of which quartz was most satisfactory and least attacked, though it seemed to hinder combustion somewhat. Available stainless steel and platinum crucibles were light weight and ruptured in most combustions. The calorimeter was calibrated by combustion of N.B.S. benzoic acid, standard sample 39g, according to Bureau of Standards recommendations at 30 atm. of oxygen when there was one ml. of water in the bomb and the pelleted benzoic acid was contained in a stainless steel crucible. A series of five calibrations made during the course of work with boron carbide gave 2437.7 ± 1.7 cal./deg. for the thermal equivalent of the calorimeter containing 1990.0 g. of water. The temperature rise in calibration was comparable with that in B_4C experiments. Appro-

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[2] A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 837 (1954).

TABLE I

HEAT OF COMBUSTION OF B_4C

1 Crucible material	2 Approx. % B_4C burned	3 B_4C burned (from B_2O_3 titre), mmoles	4 CO_2 found, mmoles	5 C (by diff.), mmoles	6 Q measured (with fuse and Washburn corrections), cal.	7 Q^*, cal.	Q_c, cal.	9 $-\Delta H_c$, kcal./mole
Pt	41	5.110	4.916	0.194	3467.0	18.2	3485.2	682.0
S.S.	33	4.294	3.340	0.954	2856.9	89.7	2946.6	686.2
Quartz	26	3.287	2.301	0.986	2143.6	92.7	2236.3	680.3
Quartz	25	3.195	1.996	1.199	2063.2	112.8	2176.0	681.1
Quartz	21	3.745	1.776	1.969	2382.0	185.2	2567.2	685.5
Pt	30	3.951	3.296	0.655	2627.1	61.6	2688.7	680.5
Quartz	27	3.467	2.401	1.066	2250.8	100.3	2351.1	678.1
								682.0 ± 2.2

priate corrections were applied to the thermal equivalent to account for different heat capacity of the three types of crucibles which were used. No water was used in the bomb during combustion of boron carbide and an appropriate correction for this was also made. Aside from these changes, the operation of the calorimeter and the methods of applying corrections for fuse wire, temperature, etc., were identical with our previous work.[2] No detectable oxides of nitrogen were produced in either calibration or B_4C measurements.

Procedure.—Approximately 0.7 g. of powdered boron carbide was weighed into an appropriate combustion crucible which was placed in the holder in the bomb and a length of special iron fuse wire was looped through the boron carbide. The bomb was flushed twice with 10 atm. of oxygen before final filling with 30 atm. of oxygen. With the bomb in place, the calorimeter was filled with 1990 g. of water and, when appropriate temperature conditions were reached, the charge was fired and the temperature rise was measured. After combustion the bomb was vented slowly through two tared weighing bottles of fresh *ascarite* in series and flushed twice with 10 atm. of oxygen. The increase in weight of the first bottle of ascarite was taken equal to the carbon dioxide produced in the combustion. The second ascarite bottle was to check for complete absorption and in no case did it show a significant change in weight. The correct stoichiometric yield of carbon dioxide was obtained in the calibration runs using benzoic acid. The bomb was opened after venting and the boric oxide, present as an amorphous deposit, was rinsed from the bomb and leached from unburned B_4C with warm water, the washings combined and titrated for boric acid in the presence of excess mannitol as described previously.[2] Blank runs showed the absence of boric oxide or acid in the original boron carbide. The result of the titration was assumed to represent the amount of boron carbide which burned in the bomb. The residue of unburned material was filtered, dried and weighed to obtain a material balance check.

All weights have been reduced to vacuum.

Results and Discussion

The experimental results for the heat of combustion of boron carbide are given in Table I. The first two columns of this table list the crucible material and the approximate proportion of the sample which burned; the actual amount of boron carbide burned, as determined by titration of the boric oxide which was produced, is shown in column three. The amount of carbon dioxide produced in the combustion is given in the next column and it will be noted that in all cases less carbon dioxide was produced than boric oxide on a stoichiometric basis. Since no carbon monoxide is formed in the bomb, it is evident that some of the carbon fails to burn and remains as free carbon. This amount is taken as the difference between B_4C burned and CO_2 found, and is listed in column 5. We believe this is warranted by the fact that a material balance[3] was obtained within an average of −1.6 mg. or −0.36% for all experiments. The number of calories, Q, produced by the combustion is given in column 6. In obtaining Q, corrections have been made not only for combustion of the fuse wire but also for conversion to 1 atm. pressure by the Washburn[4] method. The latter correction is about 1 cal. Had a stoichiometric amount of carbon (corresponding to the boron) actually burned, more heat would have been produced. We have computed this additional heat, called Q^*, (column 7) by multiplying the number of moles of free carbon produced times the heat of combustion of carbon to yield gaseous carbon dioxide, 94051.8 cal./mole.[5] The sum of the actual heat, Q, plus this additional amount, Q^*, is considered to represent the heat of combustion, Q_c, for the stoichiometric reaction

$$B_4C + 4O_2 = 2B_2O_3(\text{amorph.}) + CO_2(\text{gas}) \quad (1)$$

and is given in column 8. The molar heat of combustion, $-\Delta H_c$, is shown in the final column of the table. In view of incomplete combustion and non-stoichiometry, necessitating analyses for both boric oxide and carbon dioxide, the agreement ±2.2 kcal./mole (±0.32%) seems satisfactory.

The values for the molar heat of combustion given in Table I must be corrected for difference in the number of moles of gas in the bomb before and after combustion. According to equation 1 there is a decrease of 3 moles of gas per mole of B_4C burned. Thus, we write

$$\Delta H_c^\circ = -682.0 - 3(0.59) = -683.3 \pm 2.2 \text{ kcal./mole}$$

This value for the heat of combustion may be combined with the heats of formation of boric oxide[6] and carbon dioxide[5] to enable computation of

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(3) A material balance was assumed when the weight of the insoluble material remaining after combustion was equal to the original weight of B_4C before combustion plus the weight of free carbon produced (calculated as described in the text) plus the weight of iron oxide produced from the fuse wire minus the weight of B_4C burned (calculated from the titration for B_2O_3). The slight negative average material balance can be explained as resulting from small unavoidable losses, especially of traces of iron oxide which tend to stick to the electrodes in the bomb.

(4) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(5) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, D. C., 1952.

(6) E. J. Prosen, W. H. Johnson and F. Y. Pergiel, National Bur. Standards Rpt. No. 1552, March 26, 1952.

the heat of formation of boron carbide. Thus

$$\Delta Hf^0_{298} = -603.5 - 94.05 + 683.8 = -13.8 \pm 2.7 \text{ kcal./mole}$$

The entropies of boron, carbon and boron carbide have been tabulated by the Bureau of Standards[5] and from them one calculates that the standard entropy of formation of boron carbide is $\Delta Sf^0_{298} = -0.53$ eu. Combination of this value with that for heat of formation leads to the standard free energy of formation

$$\Delta Ff^0_{298} = -13.6 \pm 2.7 \text{ kcal./mole}$$

The results presented in this paper may be combined with other thermochemical data to give the heat of reaction for atomization of boron carbide.[7] One obtains

$$B_4C(c) = 4B(g) + C(g);\ \Delta H^0_{298} = 748.3 \text{ kcal.} \quad (2)$$

The lattice energy (average) per atom will be one-fifth of this value, or 149.7 kcal. It is interesting to observe that this value lies between those of boron and graphite as shown in Table II.

TABLE II

LATTICE ENERGIES PER GRAM ATOM AT 25°, IN KCAL.

B	140.9	Ref. 7
B_4C	149.7	This work
BN	157.3	Calcd. from ref. 2 using $D(N_2) = 225.93$[8]
C	170.9	Ref. 8

[7] The other values taken were: heat of sublimation of carbon to monatomic vapor, 170.9 kcal./mole (ref. 8); heat of vaporization of boron to monatomic vapor, 140.9 kcal./mole (Searcy and Myers, presented A.C.S. Meeting, Los Angeles, 1953).

[8] L. Brewer, private communication.

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A Survey of the Effects of Changes in *p*H, Solvent and Salt Concentration upon the Rate of the Periodate–Glycol Reaction[1]

BY JAY E. TAYLOR,[2] BENADETTO SOLDANO AND GEORGE A. HALL

RECEIVED DECEMBER 3, 1954

A quantitative study of the effect of the periodate–glycol complex upon the rate of the periodate–glycol reaction was made in an earlier paper.[3] The data for the present paper were taken before those of the previously published paper and, for the most part, before the importance of the periodate–glycol complex had been recognized.[4] It has not been possible therefore to interpret the present data with the degree of thoroughness of the earlier paper. However, certain very interesting conclusions can be made.

The Effect of Variation of *p*H.—The inhibiting effect of base upon the reaction of ethylene glycol, and *cis*- and *trans*-cyclohexandiol with periodic acid was first observed by Price and co-workers.[5,6]

A more complete survey of the effect of *p*H upon the reaction of 0.0025 M periodic acid and ethylene glycol has shown that at 25° there is a broad maximum in the *p*H–rate curve between *p*H 2.5 and 6.0 and as either acid or base is added the rate decrease (see Fig. 1). Periodic acid is known to be dibasic and may form the monovalent ion ($IO_4^- + H_4IO_6^-$) or the divalent ion ($H_3IO_6^=$). If the observed *p*H–rate curve is compared with a calculated curve in which the average maximum value for the rate constant is multiplied by the ratio of the monovalent ion to total periodate at the given *p*H, good agreement between the curves is obtained in acid solution, but only fair agreement may be observed in basic solution. The reason for the latter discrepancy appears to be extensive periodate–glycol complex formation in basic solution.[7,8] Thus, it may be concluded that at 25.1° the monovalent ion is the sole reactive form of periodic acid and that the undissociated acid or the divalent ion must first be transformed to this ion before reaction can occur. This differs in part from the conclusions of Buist and Bunton[8] based on recent work at 0°. Their work will be analyzed in detail in a later paper.

For pinacol[9] and certain carbohydrates[10] the effects of *p*H change do not correlate with the observations for glycol.

Effect of Changes in Solvent.—The addition of ethanol to a reaction mixture of ethylene glycol and periodic acid in 0.0025 M concentrations causes a marked lowering of the rate of reaction. The data which show these trends are graphed in Fig. 2.

The decrease in rate is accompanied by a variation in activation energy. The activation energy (0.3–25.1°) decreases from 12 kcal. in pure water to 8 kcal. in 28% alcohol concentration. As the alcohol concentration is further increased the activation energy then increases to 10 kcal. in 45% alcohol. It is quite possible that this minimum in activation energy may be the result of decreased hydration of the periodate ion and decreased periodate–glycol complex formation. Both of these factors make a positive contribution to the observed activation energy.[3]

The Effects of Certain Salts.—In concentration above 0.1 M neutral salts of the alkali metals effect an observable increase of the rate of the periodate-glycol reaction. For any individual salt this increase is proportional to the concentration of the salt. For example, the rate of reaction of 0.0025 M periodic acid with 0.0025 M glycol is increased by a factor of 1.20 upon adding 1 M $NaNO_3$ at *p*H 3.5 at 24.9°.

The effect of the presence of small quantities (0.003 M or less) of cobalt(II) nitrate or copper(II) sulfate upon the reaction of 0.0025 M periodic acid and glycol at 25.1° may be well explained upon assuming the precipitation or complexing of part of the periodic acid. The acid is thereby made unavailable for reaction with the glycol. The observed rate is essentially first order with respect to the periodic acid, and upon extrapolating the apparent concentration of periodic acid back to zero

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[1] From the Ph.D. Thesis of B. Soldano, University of Wisconsin, 1949.

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[3] J. E. Taylor, THIS JOURNAL, **75**, 3912 (1953).

[4] F. R. Duke, *ibid.*, **69**, 3054 (1947).

[5] C. C. Price and H. Kroll, *ibid.*, **60**, 2726 (1938).

[6] C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942).

[7] J. E. Taylor, unpublished work.

[8] G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1406 (1954).

[9] F. R. Duke and V. C. Bulgrin, THIS JOURNAL, **76**, 3803 (1954).

[10] G. Neumuller and E. Vasseur, *Arkiv Kemi*, **5**, 235 (1953).