

HEATS OF FORMATION OF Zn(II), Al (III) AND B(III) PHOSPHIDES

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The heats of combustion of zinc phosphide, aluminium phosphide and boron phosphide have been determined using oxygen bomb calorimetric techniques. Also the heats of combustion of mixtures of red phosphorus and the corresponding metals (Zn, Al and B), in the stoichiometric ratios as found in each phosphide were determined. From these data, the following heats of formation in kcal/mole, of the respective phosphides have been computed at ca. 298°K :

Zinc phosphide, Zn_3P_2 , $\Delta H_{298}^\circ = -90.3 \pm 5.2$; aluminium phosphide, AlP , $\Delta H_{298}^\circ = -29.0 \pm 1.7$; boron phosphide, BP , $\Delta H_{298}^\circ = 60.2 \pm 4.6$.

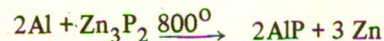
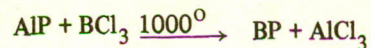
INTRODUCTION

Only a few phosphides have been studied previously with reference to their heats of formation due to difficulties in finding appropriate reactions and the hazards of handling phosphorus and phosphine. Some measurements have been made in this direction for such phosphides as could be prepared easily in the laboratory [1 - 3]. The reported values have been obtained generally by methods [4,5] other than calorimetric. The phosphides of boron and aluminium have been much less investigated in this regard because of the relatively minor importance of these compounds until recently. With the discovery of semiconducting properties of silicon and germanium, considerable interest has generated in the investigation of compound semiconductors such as Group III antimonides, arsenides and phosphides. Phosphides of gallium and indium have been prepared in the form of single crystals [6,7] for use as electroluminescents and high temperature rectifiers. Similar properties are expected for the phosphides of boron and aluminium. The present study was undertaken to determine the heats of formation of the said phosphides which may provide an insight into the structural characteristics of these compounds. Zinc phosphide was also included in this study to compare the value of its heat of formation with the reported values obtained by others.

MATERIALS AND METHODS

Reagents. Boron phosphide and aluminium phosphide were prepared in the laboratory by the methods of Ruehr-

wein [8] and Addamiano [9] respectively using the reactions:



$AlCl_3$ and Zn sublimed off at the temperatures of the experiments and the phosphides were left behind. The products were analysed at Materials Research Laboratories of Texas Instruments Inc., Dallas, U.S.A. The spectroanalysis results reported the impurities less than 0.1% in each case.

Purified zinc phosphide powder (Fisher Scientific Co., U.S.A.), was resublimed in an inert atmosphere and then used for all purposes.

Purified amorphous boron and aluminium powder were supplied by Fisher Scientific Co., and Denver Fire Clay Co., U.S.A., respectively.

Amorphous, technical grade red phosphorus powder, granular zinc and sodium carbonate, both analytical grade, were all supplied by J.T. Baker Chemical Co., U.S.A. All these reagents met ACS specifications.

Benzoic acid used in the standardisation of the calorimeter, was supplied by Parr Instrument Co., Illinois, U.S.A. It was of calorimetric grade with reported heat of combustion as 6318 cal/8.

Commercially available compressed oxygen furnished by Denver Oxygen Co., U.S.A., was used for firing the samples.

Equipment. The heat of combustion measurements were made on Emerson Fuel Calorimeter, adiabatic type. Adiabaticity was achieved by a thick felt lining all around

the double-walled calorimeter jacket developed by Daniels [10]. The internal capacity of the special acid resistant stainless-steel bomb was 500 ml and it was filled with oxygen at a pressure of 300 psi each time before ignition. The bomb was fitted with a loop electrode to hold the combustion cup. The calorimeter can made of thin sheet metal, had a capacity to hold 3250 ml water.

Throughout the experiments, glazed silica cups were used to hold the samples instead of metal cups which melted due to excessive heat liberated during the combustion.

Standard iron wire of 0.004 in dia was used as ignition wire with a heat of combustion as 1600 cal/g. Measured 8–12 cm length of the wire was coiled in the form of a spiral, ends of which were connected to the electrodes and the central loop touched the sample in the silica cup.

The combustion was achieved by short circuiting the fuse wire with the help of a resistance type ignition circuit. Approximately 35 ohms resistance and a current of 1.7 amperes were required.

The temperature rise in the calorimeter was measured with a Fisher calorimeter thermometer, 24 in long with a range of 18–28° (subdiv 0.001°). The temperatures observed with a thermometer reading lens were corrected with Master Standards certified by National Bureau of Standards, Washington, D.C. The temperature of the calorimeter jacket was recorded with an 18-in calorimeter thermometer having a range of 15–35° with subdiv. 0.05°.

Procedure

(a) *Standardisation.* It implies the operation of the calorimeter with a standard sample from which the energy equivalent of the system could be calculated. This factor includes the heat capacity of water bucket, water itself, bomb and its contents, dipped parts of the thermometer, stirrer and supports for the water bucket.

Standardisation of the calorimeter was done each time before a fresh sample was used. The method recommended by Parr [11] was employed. 5–7 parallel measurements were made for each standardisation. One g of powdered benzoic acid was compressed into a pellet for each measurement and it was weighed before use. The calorimeter bucket was filled with weighed 1950 g of water for every determination.

(b) *Ignition of Phosphide Samples.* This was carried out in the same manner as the standardisation except that the benzoic acid pellets were replaced by finely powdered phosphide samples. The oxygen pressure in the bomb was built up very slowly to avoid sweeping away of the samples.

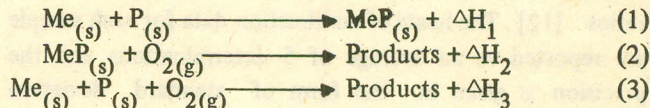
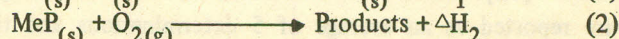
After the run was made, the solid firing products were collected for subsequent analyses. The gaseous products were allowed to escape.

(c) *Ignition of the Mixtures.* Exactly 1 g of a mixture of phosphorus and metal dust was weighed. The mixture contained the exact stoichiometric ratio of the elements to give a particular phosphide. The elements were intimately mixed and the weighed sample was ignited under identical conditions as used in (b). The combustion products were retained for analysis as before.

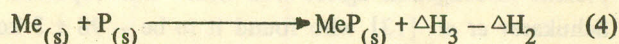
(d) *Analysis of the Combustion Products.* The solid products obtained from the combustions above were subjected to qualitative analysis on a General Electric XRD-5 X-ray diffraction unit with spectrogoniometer. The dried products were also studied as nujol mull on a Beckman IR-5 spectrophotometer using very low concentration to get better peaks.

Calculations

The heat of formation of metal phosphides was computed from the combustion data on the basis of the following scheme of reactions in which Me stands for metal and P for phosphorus:-



Considering the products to be the same in reactions (2) and (3), reaction (1) results by subtraction of (2) from (3):



$$\text{Thus } \Delta H_1 = \Delta H_3 - \Delta H_2$$

By definition, $\Delta H_3 = \Delta \bar{H}_{\text{comb. (Me+P)}}$

$$\Delta H_2 = \Delta \bar{H}_{\text{comb. (MeP)}}$$

$$\Delta H_1 = \Delta \bar{H}_{f(\text{MeP})}$$

Therefore equation (4) may be rewritten as

$$\Delta \bar{H}_{f(\text{MeP})} = \Delta \bar{H}_{\text{comb. (Me+P)}} - \Delta \bar{H}_{\text{comb. (MeP)}} \quad (5)$$

Equation (5) on per gram basis is expressed as

$$\Delta H_{f(\text{MeP})} = \Delta H_{\text{comb. (Me+P)}} - \Delta H_{\text{comb. (MeP)}}$$

RESULTS AND DISCUSSION

The analysis of the combustion products revealed beyond any doubt that the end-products of the ignition

Table 1. Heats of formation of phosphides of Zn (II), Al (III) and B (III) at 298°K

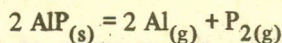
Compound or mixture	Energy equivalent of calorimeter (cal/°C)	Heat of combustion (kcal/g) ΔH_{comb}	Difference in the heats of combustion (kcal/g) $\Delta H_f = \Delta H_{(\text{Me}+\text{P})} - \Delta H_{(\text{MeP})}$	Heat of formation (kcal/mole) ΔH_f
Zinc phosphide, Zn_3P_2	2576 ± 20	- 2.35 ± 0.01	- 0.35 ± 0.032	- 90.3 ± 8.3
Zinc+phosphorus	2577 ± 22	- 2.70 ± 0.03		
Aluminium phosphide, AIP	2579 ± 35	- 5.67 ± 0.01	- 0.50 ± 0.022	- 29.0 ± 1.3
Aluminium+phosphorus	2605 ± 34	- 6.17 ± 0.02		
Boron phosphide, BP	2562 ± 17	- 7.42 ± 0.04	- 1.44 ± 0.081	- 60.2 ± 3.4
Boron + phosphorus	2576 ± 19	- 5.98 ± 0.07		

of phosphide samples and metal-phosphorus mixtures were identical. Further the extent of combustion and the amount of products obtained were also identical. As such, the heats of formation of the phosphides could be calculated as a difference between the heats of combustion of the phosphides and the metal-phosphorus mixtures in which the elements were present in stoichiometric ratios [12]. The heats of combustion data for each sample are reported as an average of 5 determinations and the precision is given in the form of standard deviation (Table 1). Heats of formation of individual phosphides as obtained in this study are discussed below:

Zinc Phosphide, Zn_3P_2 . The value obtained in the present investigation agrees well with that reported by Schukarev *et al.* [13] who found it to be -98 ± 3 kcal/mole from the heat of combustion of zinc phosphide. Karvelis [4] has also reported a value, $\Delta H_{298^\circ} = 55.03 \pm 1.5$ kcal, for the same phosphide which is considerably less than our value. Karvelis used a similar technique as is under report but his value was calculated only from one combustion using the reaction between zinc dust and red phosphorus in an adiabatic calorimeter. The reported yield of zinc phosphide was 53–67% at 360–420°K. The low value of heat of formation obtained by Karvelis is obviously due to incomplete reaction between zinc and phosphorus and may also be the result of some side reactions yielding products other than zinc phosphide. These products are not unexpected to be formed at the high temperatures which develop during calorimetric combustions. In the present study, complete combustion was obtained due to better technique and high efficiency of the calorimeter. Further our value has been calculated as a difference between two large values of heats of combustion which eliminates the errors due to possible side reactions which

are expected to be similar because of identical conditions of experiment. As such their effects would cancel out. Agreement with Schukarev *et al.* suggests that the basis of calculations for our value is also valid and sound.

Aluminium Phosphide, AIP. The heat of formation found in this study is not conclusive because very few studies have been made for this compound. A value of -28.2 ± 3.2 kcal/mole for its heat of formation has been reported earlier by De Maria *et al.* [14]. They obtained this value theoretically from the 2nd and 3rd law enthalpies for the reaction, $4 \text{Al}_{(\text{g})} + \text{Al}_2\text{O}_3(\text{s}) = 3 \text{Al}_2\text{O}_3(\text{g})$, combined with the enthalpy of decomposition of aluminium phosphide,



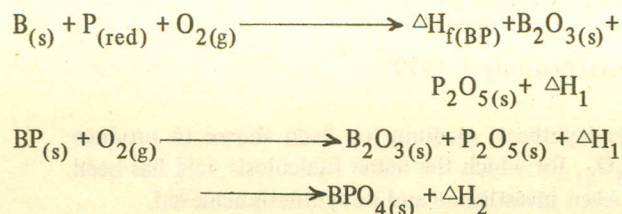
at the same temperature.

Experimental value found by us is quite consistent with the observed properties of aluminium phosphide reported by White and Bushey [15]. This compound is very stable and resistant to fusion and vaporisation in the absence of moisture. The value under report would predict such properties for this compound.

Boron Phosphide, BP. Heat of formation of boron phosphide, $\Delta H_{298^\circ} = +60 \pm 5$ kcal, obtained in this study appears very unusual considering the stability of this compound at ordinary temperatures. Phillip, Hayman and Stuart [16] found $\Delta \bar{H}_f(298^\circ) = -27.6 \pm 1.1$ kcal for it. They determined it calorimetrically by comparing the heat of combustion of B phosphide in F with that of stoichiometric mixtures of beta-rhombohedral boron and white phosphorus. Another value of -59.15 kcal/mole at 298°K has been found by Gardner [17].

Boron phosphide employed in the present study was identified by X-ray diffraction as metastable hexagonal

close-packed crystalline variety. This form undergoes a very slow transformation to the face-centered cubic form at room temperature. The relatively high value for the heat of formation of BP(H.C.P.) may be the result of a different mechanism of the reactions taking place during the ignition of the BP and (B + P) mixtures. This scheme of reactions is given below:



$$\Delta H_{comb(B+P)} = \Delta H_{f(BP)} + \Delta H_1$$

$$\Delta K_{comb(BP)} = \Delta H_1 - \Delta H_2$$

$$\Delta H_{comb(B+P)} - \Delta H_{comb.(BP)} = \Delta H_{f(BP)} + \Delta H_2$$

If ΔH_2 in the above equation is much larger than $\Delta H_{f(BP)}$, the observed value of heat of formation of BP would be +ve. ΔH_2 is the heat of formation of boron phosphate from boron oxide and phosphorus pentoxide. This value is not available in the literature. As such the postulated mechanism as above cannot be verified conclusively.

The combustion products obtained from the firing of BP and B+P mixture were amorphous in nature. Similar products were obtained by Dworkin, Sasmore and Van Artsdalen [18] in their attempt to determine the heat of combustion of boron nitride calorimetrically. The amorphous nature of the products refused to yield any reliable information regarding their nature and extent of production.

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