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Thermochemical data of boron subphosphide

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Abstract

Thermochemical data of boron subphosphide are derived from reported decomposition data of cubic boron monophosphide BP. Both reported boron subphosphides, i.e. B_6P and $B_{13}P_2$, are taken into account, without claiming either of these to have the reported stoichiometry. The standard heat of formation $\Delta_f H^0$, the standard entropy S^0, and the heat capacity as a function of temperature $C^0_{P,T}$ of B_6P and $B_{13}P_2$ are $\Delta_f H^0 = 69.2 \mp 11.4$ kJ/mol, $S^0 = 213 \mp 15$ J/mol K, and $C^0_{P,T} = (42.0 \mp 0.9) + (0.166 \mp 0.004) \times T$ J/mol K, and $\Delta_f H^0 = 175 \mp 4$ kJ/mol, $S^0 = 462 \mp 10$ J/mol K, and $C^0_{P,T} = (87.6 \mp 1.8) + (0.359 \mp 0.008) \times T$ J/mol K, respectively. © 1997 Elsevier Science B.V.

Keywords: Boron monophosphide; Boron phosphide; Boron subphosphide; BP; Thermochemical data

1. Introduction

Since the reports of Welker [1,2] regarding the semiconducting properties of the group III–V compounds, the research on the synthesis of these compounds has attracted interest. Among them, boron monophosphide (BP) is a semiconductor with an indirect band gap of 2 eV [3,4], it is quite hard [5,6], and resistant to chemical corrosion [7]. Apart from this cubic boron phosphide BP, another crystalline boron phosphide was reported by Perri et al. [8], Matkovich [9], and Spinar and Wang [10]. This boron phosphide was reported to be orthorhombic. However, its exact stoichiometry was not established [8]. Vickery [11] determined stoichiometries varying from BP to B_5P_2, synthesized by thermal dissociation of certain products. Williams [12] was the first to report the thermal decomposition of BP into a lower phosphide. On the basis of weight loss and chemical analyses, the decomposition product was believed to have the approximate formula of B_6P. However, Matkovich [9] calculated this lower boron phosphide to be $B_{13}P_2$, based on the rhombohedral unit-cell size and density. He also determined the boron-to-phosphorus ratio by weight loss during decomposition of BP at 1160°C to be ca. 6.3. Chemical analyses on the same samples resulted in ratios of 6.4 to 6.5. The formation of $B_{13}P_2$ upon dissociation of BP was confirmed by Spinar and Wang [10]. In this paper, we present the thermochemical data of the boron subphosphide, using free energy and entropy functions reported by Alikhanyan et al. [13]. They assumed the decomposition of BP to result in the formation of B_6P and certain volatile phosphorus species. In addition to these calculated thermochemical data of B_6P, the thermochemical data of $B_{13}P_2$ are derived using the same thermodynamic functions as reported by Alikhanyan

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Table 1
Thermodynamic functions of the vaporization of BP [13]

Reaction	ΔH_T^0/ kJ/mol	ΔS_T^0/ J/mol K	Temperature range K
(1)	466.5	176.1	1150–1400
(2)	447.7	236.8	1150–1400
(3)	681.2	328.0	1330–1420

[13] but with new decomposition reactions. However, we emphasize that it is not our aim to claim any structure or stoichiometry mentioned above to be the preferential one.

2. Results and discussions

For the calculation of the thermochemical data of B_6P, we used the thermodynamic functions of the vaporization of BP obtained by Alikhanyan et al. [13]. Alikhanyan assumed that the following reactions (Eqs. (1)–(3)) occurred. The data obtained are presented in Table 1.

$$6/5\,BP_{(s)} \rightleftarrows P_{(g)} + 1/5\,B_6P_{(s)} \quad (1)$$

$$12/5\,BP_{(s)} \rightleftarrows P_{2(g)} + 2/5\,B_6P_{(s)} \quad (2)$$

$$24/5\,BP_{(s)} \rightleftarrows P_{4(g)} + 4/5\,B_6P_{(s)} \quad (3)$$

The thermochemical data of the volatile phosphorus species P, P_2, and P_4 are taken from JANAF [14] and are listed in Table 2. The thermochemical data for cubic boron monophosphide BP are taken from Barin and Knacke [15]. In fact the data of BP were adapted from Gross et al. [16], which seems to be more accurate than the data given by Stone et al. [17], Medvedeva and Grinberg [18], and Gingerich [19]. The values given for $C_{P,T}^0$ are in good agreement with the calculations of Ohsawa et al. [20] and Kumashiro [21]. Stone et al. [17] and Williams and Ruehrwein [22] calculated the thermochemical data of the boron subphosphide B_6P from the decomposition of BP. In their paper, the data for B_6P formation are calculated from the thermodynamic functions [13] of the decomposition of BP into B_6P as determined experimentally by mass spectrometry [13].

The change in Gibbs free energy, which are the thermodynamic data of the reactions presented in Eqs. (1)–(3), actually observed by Alikhanyan et al. [13], is given by:

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \quad (4)$$

$$\Delta H_T^0 = \sum(\Delta_f H_{T,P}^0 - \Delta_f H_{T,r}^0) \quad (5)$$

$$\Delta S_T^0 = \sum(S_{T,p}^0 - S_{T,r}^0) \quad (6)$$

$$\Delta_f H_T^0 = \Delta_f H^0 + \int_{298}^{T} C_{P,T}^0\,dT \quad \Delta_f H^0 = \Delta_f H_{298}^0 \quad (7)$$

$$S_t^0 = S^0 + \int_{298}^{T} (C_{P,T}^0)dT \quad S^0 = S_{298}^0 \quad (8)$$

$$C_{P,T}^0 = A + B \times T + C \times T^{-2} + D \times T^2 + E \times T^{-3} + F \times T^{-0.5} \quad (9)$$

With A–F the fit parameters, $C_{P,T}^0$ the standard heat capacity at constant pressure and temperature T (J/mol K), ΔG_T^0 the standard Gibbs free energy of temperature T (J/mol), $\Delta_f H^0$ the standard enthalpy of formation at $T = 298$ K (J/mol), $\Delta_f H_T^0$ the change in standard enthalpy of formation at temperature T (J/mol), ΔH_T^0 the standard enthalpy of formation at temperature T (J/mol), $\Delta_f H_{T,p}^0$ the standard enthalpy of formation of products at temperature T (J/mol), $\Delta_f H_{T,r}^0$ the standard enthalpy of formation of reactants at temperature T (J/mol), ΔS_T^0 the change in entropy at temperature T (J/mol K), R the gas constant

Table 2
Thermochemical data of $P_{(g)}$, $P_{2(g)}$, $P_{4(g)}$ [14], and $BP_{(s)}$ [15]. The numbers A–F refer to the parameters of Eq. (9), with $E = 0$

Species	$\Delta_f H^0$/ (kJ/mol)	S^0/ (J/mol K)	A	$B \times 10^{-2}$	$C \times 10^5$	$D \times 10^{-6}$	$F \times 10^2$
$P_{(g)}$	316.4	163.2	20.79	—		—	—
$P_{2(g)}$	143.7	218.1	56.72	−0.90	1.93	2.18	−420
$P_{4(g)}$	58.9	280.0	105.4	−1.03	−6.34	2.38	−487
$BP_{(s)}$	−115.48	26.78	21.97	2.803	—	—	—

Table 3
Thermochemical data of BP, with A and B fit parameters of Eq. (9)

Reaction	$\Delta_f H0/$ (kJ/mol)	$S^0/$ (J/mol K)	A	B
(1)	57.55	226.1	28.19	0.1677
(2)	69.18	212.5	41.98	0.1658
(3)	80.15	231.9	32.24	0.1610

Table 4
Thermochemical data of $B_{13}P_2$, with A and B fit parameters of Eq. (9)

Reaction	$\Delta_f H^0/$ (kJ/mol)	$S^0/$ (J/mol K)	A	B
(1)	138.8	473.5	82.0	0.346
(2)	175.4	462.4	87.57	0.3594
(3)	215.5	494.0	66.79	0.3596

(8.314 J/mol K), S^0 the standard entropy at $T = 298$ K (J/mol K), S^0_T the standard entropy at temperature T (J/mol K), $S^0_{T,p}$ the standard entropy of products at temperature T (J/mol K), $S^0_{T,r}$ the standard entropy of reactants at temperature T (J/mol K), and T the absolute temperature (K).

First, we derived $\Delta_f H^0_T$ (B_6P) and S^0 (B_6P) using Eq. (5) for the reactions (1) to (3) at temperatures T between 1000 and 1500 K. The obtained $\Delta_f H^0_T$ values are subsequently fitted to Eq. (7) in order to determine $\Delta_f H^0$. Consequently, $C^0_{P,T}$ as a function of temperature was derived from Eq. (7) using the first two terms of Eq. (9) only. S^0 is derived from Eq. (8), using the $C^0_{P,T}$ function as obtained above. The results of the three reactions (Eqs. (1)–(3)) are given in Table 3.

The values listed in Table 3 reveal different values for different reactions. The average thermochemical values calculated for B_6P are $\Delta_f H^0 = 70 \mp 10$ kJ/mol, $S^0 = 220 \mp 10$ J/mol K, and $C^0_{P,T} = 34.4 \mp 7.0 + (0.165 \mp 0.004) \times T$ J/mol K.

According to Perri et al. [8], Matkovich [9], and Spinar and Wang [10], boron subphosphide consists of $B_{13}P_2$ rather than B_6P. Therefore, in addition to the obtained thermochemical data of B_6P, the thermochemical data of $B_{13}P_2$ were derived using the same method as described above, but with the reactions given by Eqs. (10)–(12). A same procedure was performed by Myers [23] who reviewed the data of Williams and Ruehrwein [22]. The same thermodynamic functions as reported by Alikhanyan [13] as shown already in Table 1 were used. The results are presented in Table 4.

$$13/11\,BP_{(s)} \rightleftarrows P_{(g)} + 1/11\,B_{13}P_{2(s)} \quad (10)$$

$$26/11\,BP_{(s)} \rightleftarrows P_{2(s)} + 2/11\,B_{13}P_{2(s)} \quad (11)$$

$$52/11\,BP_{(s)} \rightleftarrows P_{4(g)} + 4/11\,B_{13}P_{2(s)} \quad (12)$$

The values listed in Table 4 reveal different values for different reactions as was obtained for B_6P. The average thermochemical values calculated for $B_{13}P_2$ are $\Delta_f H^0 = 175 \mp 40$ kJ/mol, $S^0 = 480 \mp 20$ J/mol K, and $C^0_{P,T} = 78.8 \mp 12.0 + (0.355 \mp 0.010) \times T$ J/mol K.

The thermochemical data of both B_6P and $B_{13}P_2$ derived above, reveal a large error by comparing the different decomposition reactions (Eqs. (1)–(3) and Eqs. (10)–(12), respectively). Because the decomposition reaction which results in the formation of volatile P_2 was measured to be far the most abundant [13], we assumed the data obtained for Eqs. (2) and (11) to be the most reliable. In addition, the error in the observed thermodynamic function of this decomposition reaction was reported not to be more than 2% [13].

3. Conclusions

Without claiming the specific structure or stoichiometry of boron subphosphide, i.e. either B_6P or $B_{13}P_2$, the thermochemical data of B_6P and $B_{13}P_2$ were derived to be $\Delta_f H^0 = 69.2 \mp 1.4$ kJ/mol, $S^0 = 213 \mp 5$ J/mol K, and $C^0_{P,T} = 42.0 \mp 0.9 + (0.166 \mp 0.004) \times T$ J/mol K, and $\Delta_f H^0 = 175 \mp 4$ kJ/mol, $S^0 = 462 \mp 10$ J/mol K, and $C^0_{P,T} = 87.6 \mp 1.8 + (0.359 \mp 0.008) \times T$ J/mol K, respectively.

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