THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES

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THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES

Volume 3

Elements B, Al, Ga, In, Tl, Be, Mg, Ca, Sr, Ba and Their Compounds

Part One

Methods and Computation

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Errata: In Volume 1, Part 1, page 158, line 9, "$B_vJ(J+1)/1+DJ)(J+1)/B_v^{2}$" should appear as "$B_vJ(J+1)/1+DJ(J+1)/B_v^{2}$."

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CONTENTS

From the Foreword to Volume 3

The third volume of this work deals with the properties of ten elements (boron, aluminum, gallium, indium, thallium, beryllium, magnesium, calcium, strontium, and barium) and their compounds with oxygen, hydrogen, halogens, sulphur, and some others. The second part of this volume contains 343 tables of thermodynamic properties including 93 substances in the condensed state and 273 substances in the gaseous state. For about 80 substances the tables of thermodynamic properties are published for the first time in the literature.

In the course of preparation of this volume the authors had the opportunity to discuss the evaluation of different data with many Soviet and Western scientists. The evaluation of key thermochemical values for this volume coincided in time with the work of the CODATA-ICSU Task Group on Key Values for Thermodynamics, in which several authors of this book took part. Discussions with other members of the task group (Drs. W. Evans, D. D. Wagman, and J. Drowart) and also with Drs. I. L. Khodakovsky (Geokhi AN USSR), M. Chase (JANAF Group), and D. Hildenbrand (SRI) were extremely fruitful. The editors express sincere appreciation to them and to many other scientists for useful discussions and for providing results of their studies before publication.

Foreword to Volume 3 of the English Edition

Although ten years have passed since the publication of the third volume of the Russian edition of this book, the basic materials of this volume as well as of Volumes 1 and 2 are still applicable and most recommendations remain reliable even today. In cases when new data have appeared after the publication of the Russian edition that make it possible to substantially improve recommended thermodynamic properties, these data were used to update the recommendations. In general, the tables of thermodynamic properties of more than 90 substances were recalculated mainly due to improvement of the molecular constants of gases and the heat capacity and phase transition data for substances in the condensed state. The thermochemistry of many other substances (e.g., compounds of strontium and barium) was changed using new data, more accurate processing of old data, and new estimations. In addition, 47 tables of the thermodynamic properties of substances that were not included in the Russian edition are given in this volume, mainly for compounds of gallium, indium, and thallium with halogens.

After Prof. Vadim Medvedev died during the course of preparation of this volume, Dr. A. Gusarov served as the editor of paragraphs devoted to thermochemical data. Drs. N. Aristova, Yu. Khodeev, and Mrs. A. Efimova participated in the evaluation of data for several substances each.

CHAPTER

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BORON AND ITS COMPOUNDS

$B(cr, l)$, $B(am)$, B, B^+, B_2, BO, BO^-, BO_2, BO_2^-, B_2O, B_2O_2, $B_2O_3(cr, l)$, $B_2O_3(vit)$, B_2O_3, BH, BH_2, BH_3, B_2H_6, HBO, BOH, $HBO_2(cr, l)$, HBO_2, $HBOH$, $B(OH)_2$, H_2BOH, $HB(OH)_2$, $H_3BO_3(cr, l)$, H_3BO_3, $B_2(OH)_4$, $H_3B_3O_3$, $H_3B_3O_6$, BF, BF_2, BF_2^-, BF_3, BF_4^-, B_2F_4, FBO, F_2BO, $F_3B_3O_3$, BHF, BH_2F, BHF_2, $FBOH$, $FB(OH)_2$, F_2BOH, BCl, BCl_2, BCl_3, B_2Cl_4, $ClBO$, Cl_2BO, $Cl_3B_3O_3$, $BHCl$, BH_2Cl, $BHCl_2$, $ClBOH$, $ClB(OH)_2$, Cl_2BOH, $BFCl$, BF_2Cl, $BFCl_2$, $F_2ClB_3O_3$, $FCl_2B_3O_3$, $BHFCl$, BBr, BBr_2, BBr_3, BI, BI_2, BI_3, BS, BS_2, B_2S, B_2S_2, $B_2S_3(cr, l)$, B_2S_3, $BN(cr, l)$, BN, BH_3NH_3, $B_3N_3H_6$, BC, BC_2, B_2C, $B_4C(cr)$.

The thermodynamic properties of 77 substances including boron and its compounds with oxygen, hydrogen, halogens, sulphur, nitrogen, and carbon are discussed in this chapter. For six substances the properties are given for the condensed and gaseous states, for one substance only for the condensed state, and for all other substances only for the gaseous state. For elementary boron and boron oxide the properties are given in the crystalline, amorphous, and vitreous states. The thermodynamic properties of four gases (B, B^+, BO, and BO_2) were calculated up to 10,000 K, the others up to 6000 K.[1]

The thermodynamic properties of all substances are calculated for the natural mixture of isotopes of boron[2] and other elements. Differences between the molecular constants of isotopomers of boron

[1] Comment for the English edition: In the course of translation of this chapter thermodynamic properties of $BH_2(g)$, $HBOH(g)$, $B(OH)_2(g)$, $HB(OH)_2(g)$, $H_3BO_3(cr, l)$, $H_3BO_3(g)$, $B_2(OH)_4(g)$, $H_3B_3O_3(g)$, $H_3B_3O_6(g)$, $F_3B_3O_3(g)$, $FBOH(g)$, $FB(OH)_2(g)$, $F_2BOH(g)$, $Cl_3B_3O_3(g)$, $ClBOH(g)$, $ClB(OH)_2(g)$, $Cl_2BOH(g)$, $F_2ClB_3O_3(g)$, $FCl_2B_2O_3(g)$, $BN(g)$, and $BC(g)$ were recalculated using new data. Many thermochemical values were improved.

[2] Comment for the English edition: The atomic weight of B in this book was taken to be equal to 10.81; see Vol. 1, App. 1. According to the recommendation of IUPAC 1985 [2914a] it is 10.811. The errors in the thermodynamic functions due to this difference do not exceed 0.0012 $J \cdot K^{-1} \cdot mol^{-1}$.

compounds substantially affect the thermodynamic properties of the natural mixture of the isotopes, because the atomic masses of the isotopes ^{10}B and ^{11}B differ considerably, and the content of the ^{10}B isotope with a smaller abundance is considerable. Therefore in all cases when the molecular constants are known for different modifications, or differences between modifications can be estimated, they are taken into consideration. That allows refining calculations of the thermodynamic functions, and it is discussed in appropriate texts.

Unlike the JANAF Tables [1543, 1544], this reference book does not include data for many known positive ions such as BO^+, HBO^+, and BF_2^+. Ionization potentials of the corresponding neutral molecules are high, and the formation of these ions in the equilibrium conditions at temperatures up to 6000 K can be neglected.

B(cr, l). The thermodynamic properties of crystalline and liquid boron in the standard state at temperatures of 100–6000 K are given in Table 582.

The values of the constants used for calculating the thermodynamic functions are given in Table 20.1.

Similar to other reference books the β-rhombohedral (high temperature) modification[3] was selected as a standard state of boron in the interval from $T = 0$ to T_m.

At $T < 298.15$ K the thermodynamic functions are calculated using the heat capacity measurements of β-boron (99.9% B) at 16–280 K by Bogdanov et al. [40], and crystalline boron with an unidentified structure by Johnston et al. [1590] (17–308 K). The data of [40] are selected for $T < 50$ K; in the interval 50–280 K the data of [40] and [1590] are averaged. The uncertainties in the selected values of the heat capacity of boron at $T < 100$ K are estimated as 10% and at $T > 100$ K as 1%.[4]

The uncertainties in the adopted values of $S°(298.15\ K)$ and $H°(298.15\ K)–H°(0)$, estimated as 0.08 $J·K^{-1}·mol^{-1}$ and 0.008 $kJ·mol^{-1}$, respectively, coincide with the CODATA-ICSU [864] recommendations. In the interval 298.15–2348 K, the $C°_p$(B, cr) equation is derived by a combined mathematical treatment of results of measurements of the enthalpy of boron in studies of McDonald and Stull [1991] (333–1668 K, less than 0.2% impurities in the sample), Wise et al. [2862] (821–1103 K, two samples, phase composition was not determined carefully), and Stout et al. [2624] (1820–2218 K, the sample contained 99.96% B). The accuracy of the data of [1991] and [2624] amount to 0.4%, and of [2862] to 1.1%. The melting point of boron, 2348 ± 50 K, is selected from the measurements of Kimpel and Moss [1708], who considered the influence of impurities on the melting point. This value agrees within the uncertainty limits with the results of other determinations [1458] (2365 K), [2624] (2343 K), [1940] (2315 ± 20 K), and [911, 912] (2270–2350 K). Higher values, observed in [2486] (> 2420 K), [859] (2423 K), and [334] (2453–2543 K) have not been confirmed. The enthalpy of melting of boron 50.2 ± 1.7 $kJ·mol^{-1}$ is taken from the only experimental measurement [2624]. The estimated value of $C°_p$(B, l), 31.4 $J·K^{-1}·mol^{-1}$, is taken from the reference book [1503]. Results of estimations in [1543] and [2452] are 30.5 and 31.4 $kJ·mol^{-1}$, respectively. The uncertainties in the

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[3] The literature data on the polymorphism of boron are incomplete and contradictory (more than ten polymorphic modifications were described in [366]). The formation of several modifications can be explained by a thermal pre-history of samples, vacancies in a crystal lattice [2408], and presence of impurities [2857]. According to [2408], α-rhombohedral boron, stable at low temperatures, on heating up to ~ 1643 K transforms into an intermediate β'-modification, at ~ 1863 K into β''-modification, and at 1913 K into β-rhombohedral modification (the enthalpies of transformations are not known). The β-rhombohedral modification, formed during crystallization of liquid boron, can be easily quenched down to low temperatures; the thermodynamic properties of this modification are determined rather reliably.

[4] The differences between heat capacities of boron measured in [40] and [1590] are considerable and reach 30% at $T < 50$ K and 2–5% at $T > 50$ K. However, the values of $S°(298.15\ K)$ and $H°(298.15\ K)–H°(0)$ calculated from the data of [40] and [1590] by chance occurred to be close, because the heat capacity curves intersect several times.

Table 20.1 Adopted values of the thermodynamic quantities for boron and its compounds in the crystalline and liquid states

Substance	State	H° (298.15 K) − H°(0)	S° (298.15 K)	C_p° (298.15 K)	Coefficients in the equation for $C_p^\circ(T)$[a]			Temperature range	T_{tr} or T_m	$\Delta_{tr}H$ or $\Delta_m H$
		$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$		a	$b \cdot 10^3$	$c \cdot 10^{-5}$	K		$kJ \cdot mol^{-1}$
B	crI, hex.(β)	1.222	5.90	11.09	14.924	16.171	7.208[b]	298.15–2348	2348	50.2
	liq	—	—	—	31.4	—	—	2348–6000	—	—
B	amorph.	1.318	6.53	11.95	16.050	10.013	6.296	298.15–2000	—	—
B_2O_3	crI, hex.	9.301	53.97	62.76	64.141	64.643	18.359	298.15–723	723	24.56
	liq	—	—	—	127.047	—	−31.380	723–3200	—	—
B_2O_3	vitr.	10.3	80.5	62.97	22.309	154.440	4.786	298.15–723	—	—
HBO_2	crI, cub.(γ)	8.46	49.0	54.71	37.240	58.580	—	298.15–509	509	14.3
	liq	—	—	—	105	—	—	509–1500	—	—
H_3BO_3	cr, tricl.	13.52	89.95	86.06	4.804	272.533	—	298.15–444.1	444.1	22.3
	liq	—	—	—	180	—	—	444.1–800	—	—
B_2S_3	cr, monocl.	17.2	100	111.72	98.950	72.430	7.841	298.15–840	840	48.5
	liq	—	—	—	146	—	—	840–2000	—	—
BN	cr, hex.	2.628	14.81	19.71	18.732	38.886	8.456[b]	298.15–1200	—	—
	cr, hex.	—	—	—	51.635	—	68.731	1200–3240	3240	81
	liq	—	—	—	67	—	—	3240–3500	—	—
B_4C	cr, hex.	5.611	27.11	53.09	105.922	0.507	47.944[b]	298.15–2700	2700	—

[a] $C_p^\circ(T) = a + bT - cT^{-2} + dT^2 + eT^3$ (in $J \cdot K^{-1} \cdot mol^{-1}$)

B: [b] $d \cdot 10^6 = -6.496$, $e \cdot 10^9 = 1.053$

BN: [b] $d \cdot 10^6 = -12.464$

B_4C: [b] $d \cdot 10^6 = 10.694$

calculated values of $\Phi°(T)$ at 298.15, 1000, 3000, and 6000 K are estimated as 0.08, 0.2, 1.5, and 5 $J \cdot K^{-1} \cdot mol^{-1}$, respectively.

The thermodynamic functions of B(cr) given in Table 530 do not differ significantly from those calculated in reference books [105, 1503, 1543] (within the limits of 0.4 $J \cdot K^{-1} \cdot mol^{-1}$ in the values of $\Phi°(T)$ up to 2348 K). For B(l) the corresponding discrepancies increase and reach 3.5 and 7 $J \cdot K^{-1} \cdot mol^{-1}$ at 3000 and 5000 K, respectively. The differences occurred mainly because reference books [105, 1503, 1543] adopted estimated values for the enthalpy of melting of boron.

Crystalline boron (the β-rhombohedral modification) is selected as a standard state in this reference book:

$$\Delta_f H°(\beta\text{-B, cr}) \equiv 0$$

The vapor pressure of boron B(cr, l) = B(g) is calculated on the basis of the enthalpy of sublimation of boron:

$$\Delta_s H°(\text{B, cr, } 0) = 559.906 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$$

This value is based on data given in Table 20.2.

The analysis of these data was done in the course of preparation of the Russian edition of this book and showed that more reliable measurements were made by Akishin et al. [3], Paule and Margrave [2198], Robson and Gilles [2353], Hildenbrand and Hall [1415], Mar and Badford [1941], and Storms and Mueller [2622] (the listed uncertainties define only the reproducibility of measurements). The enthalpy of sublimation of boron can be calculated from the data [2622] only by the Second Law method, but the accuracy of thus obtained value is comparable with the Third Law calculation as the measurements were performed in a broad temperature range and temperatures were measured with very high precision. The adopted value

$$\Delta_s H°(\text{B, cr, } 298.15) = 565 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$$

is a weighted mean obtained from the six selected studies. Later the same value was recommended by CODATA-ICSU [864] as the key thermochemical value.[5]

B(am). The thermodynamic properties of amorphous boron[6] at temperatures of 100–2000 K are given in Table 583.

The values of the constants adopted for calculating the thermodynamic functions of B(am) are given in Table 20.1. Johnston et al. [1590] measured the heat capacity of B(am) in the interval 18–305 K; a sample was prepared by thermal decomposition of diborane 99.8% purity at 700°C. The results of [1590] are used in this book for the calculation at $T < 298.15$ K. The $C_p°(T)$ curve determined in [1590] has a minimum at $\sim$ 30 K; the extrapolation below 18 K yields the value of

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[5] Comment for the English edition: New analysis of vapor pressure data was done in the course of translation of this chapter. It permits conclusion that among six mentioned studies, the next three [1415, 1941, 2353] are the most accurate. The mean value calculated from these measurements is equal to 562 ± 5 $kJ \cdot mol^{-1}$ and coincides in the limit of uncertainties recommended by CODATA-ICSU and in the Russian edition. (Comment for the proofs: New precise measurements of boron vapor pressure were finished by P. Nordine et al. in 1991 (private communication; the paper was published in *High Temp. Sci.*, 1990, vol. 30, p. 163). The derived value of $\Delta_s H°$(B, cr) at 298.15 K is equal to 565.6 ± 3.6 $kJ \cdot mol^{-1}$ in accelent agreement with that adopted in the book.)

[6] The amorphous state of boron should be distinguished from the hypothetical vitreous state. Amorphous boron is characterized by disorder of icosahedron groups (B_{12}), which appear in all crystalline modifications of boron.

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