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**ESTIMATION OF HEAT CAPACITIES AND OTHER
THERMODYNAMIC PROPERTIES OF REFRACTORY BORIDES**

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Contents

Abstract	1
Introduction	1
Heat Capacity Relations	2
Dilatation Term	2
Harmonic Lattice Vibrations	9
Anharmonic Lattice Vibrations	12
Conduction Electrons	12
d and f Electrons	14
Lattice Defects	16
Enthalpy of Fusion	18
C_p of the Liquid	18
Calculational Procedures	19
Input Parameters	21
Results	21
Acknowledgment	35
References	36

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Abstract

High-temperature heat capacities and other related thermodynamic functions of the refractory borides were calculated and the results tabulated.

Theoretical expressions describe the contributions of various factors to the heat capacities (C_p) of crystalline solids. To apply these expressions to borides, however, a number of parameters need to be determined, so correlation methods are developed here for estimating many of these parameters. The correlations are based upon known properties of borides, carbides, nitrides, metals, and other compounds. Heat capacity factors that are taken into account are the dilatation term, harmonic and anharmonic lattice vibrations, the separate contributions of conduction electrons and d or f electrons, and contributions of lattice defects.

An important parameter in the dilatation factor is the thermal expansivity. It is found that thermal expansivity correlates with atomization energy (ΔE_a) and degree of ionic or covalent bonding in the compound. Thermal expansivity also varies with temperature as $T^{0.4}$. If the

Knoop microhardness (h) is used as an approximate measure of the degree of covalent bonding, the thermal expansivity of borides can then be expressed as

$$\alpha = 10 h^{-1/2} \Delta E_a^{-1} T^{0.4},$$

where α is the volume thermal expansivity in $^{\circ}\text{K}^{-1}$, h is in kg/mm^2 for 50-100 g loads, ΔE_a is in $\text{kcal}/\text{g-atom}$, and T is in $^{\circ}\text{K}$.

Other parameters that have been derived by correlation methods are the Grüneisen constant, empirical Debye temperatures for metal and nonmetal constituents, the anharmonic constant A , the heat capacity coefficient of conduction electrons, energy levels of f electrons in lanthanides and actinides, and energies and entropies of formation of defects.

Results of the heat capacity and entropy calculations are compared with the accurate data available for borides. Calculated room temperature entropies are uncertain by about $\pm 10\%$, but the calculated values of heat capacities at room temperature and above lie within the experimental uncertainties.

Introduction

A fair amount of information has accumulated in the literature on the basic properties of borides. Crystalline phases

have been identified and structures determined for a number of binary boron systems.¹ Phase diagrams are known for

many of the systems,^{2,3} and a variety of thermophysical properties have been measured.⁴ In spite of these advances, thermodynamic information on the borides is yet very fragmentary. A basic requirement for thermodynamic calculations is information on heat capacities. Although heat capacity data on borides are

very limited, significant advances have been made during the past few years in developing methods for estimating the heat capacities of refractory materials. These methods were reviewed and used, together with innovations developed here, to estimate heat capacities and other thermodynamic properties for the borides.

Heat Capacity Relations

The heat capacity at constant pressure, C_p , is the quantity that is ordinarily needed for calculations of thermodynamic equilibria. C_p is related to C_v , the heat capacity at constant volume, by the well-known thermodynamic relation

$$C_p = C_v + \frac{\alpha^2 \bar{V} T}{\beta} \quad (1)$$

where α is the volume thermal expansivity, $\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T} \right)_P$, $\bar{V}$ is the molar volume, and β is the isothermal compressibility, $-\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P} \right)_T$. The quantity, $\alpha^2 \bar{V} T / \beta$, is known as the dilatation term. C_v is made up of contributions from several factors that can be summarized as follows:

$$C_v = C_l + C_a + C_e + C_s + C_d \quad (2)$$

where C_l is the contribution of harmonic lattice vibrations and constitutes the main factor, C_a is a term that accounts for anharmonic lattice vibrations, C_e is the heat capacity of the conduction electrons, C_s is the heat capacity of electronic contributions of d or f electrons, and C_d is the heat capacity of lattice defects such as vacancies. These various heat capacity factors either are not known or cannot adequately be derived from experimental data or theoretical treatments for most of the materials of interest. To evaluate them, empirical or correlation methods must be used, at least in part.

Dilatation Term

Following the approach used by Hoffman and co-workers,⁵ the dilatation term may be rewritten in terms of the Grüneisen constant as

$$\frac{\alpha^2 \bar{V} T}{\beta} = \alpha \gamma_G T C_l \quad (3)$$

where γ_G , the Grüneisen constant, is equal to $\alpha \bar{V} / \beta C_l$. Evaluation of the dilatation term therefore will depend upon the evaluation of α and γ_G . The dilata-

tion term contributes less than 1% to the heat capacity of borides at room temperature, but increases to a contribution of about 15% at the boride melting point.

The estimation of thermal expansivity will be considered first. There are at present no satisfactory methods for making quantitative calculations; but useful correlations can be made, based on such factors as heat capacity, melting point, or bond energies. These correlations

are most successful if they are restricted to isotropic or nearly isotropic structures and to specific classes of substances.

Before thermal expansivities can be compared, an expression is needed to describe the temperature variation of thermal expansivity. For the special case of metals, it is convenient to use a corresponding states form based upon melting point. Assuming a power-dependence of volume with temperature gives

$$\frac{V - V_0}{V_m - V_0} = \left(\frac{T}{T_m} \right)^n, \quad (4)$$

where 0 and m refer to temperatures of 0°K and the melting point, and n is a parameter to be determined from experimental data. In terms of thermal expansivity, the expression becomes

$$\frac{\alpha}{\alpha_m} = \frac{V_m}{V} \left(\frac{T}{T_m} \right)^{n-1}, \quad (5)$$

where α_m represents the thermal expansivity at the melting point, and is given by

$$\alpha_m = \frac{n(V_m - V_0)}{T_m V_m}. \quad (6)$$

Examination of the available data (e.g., see Ref. 6) on metals with the common bcc, hcp, and fcc structures shows that with $n \approx 1.4$, and $(V_m - V_0)/V_m \approx 0.08$, an adequate description is obtained of the behavior of these metals from room tem-

perature to the melting point.^{*} Hence, for these metals, $\alpha_m \approx 0.11 T_m^{-1}$; and since V_m/V is about 1, or somewhat larger than 1, then

$$\alpha = 0.12 T_m^{-1.4} T^{0.4}. \quad (7)$$

Similarly, for refractory compounds,⁶ n is found to be ~ 1.4 , but α_m does not correlate well with T_m . A better correlation for refractory compounds is obtained between α and ΔE_a , the atomization energy per gram atom. This is illustrated in Fig. 1 by plotting $\alpha T^{-0.4}$ vs ΔE_a^{-1} for a number of borides, carbides, and nitrides. The sources of data are summarized in Table 1, where thermal expansivities are believed to be accurate to within $\pm 5\%$ for the borides and carbides, and within ± 10 -20% for the nitrides. For the metal-rich compositions such as MB, MB_2 , M_2C , MC, and MN, the data may be described by

$$\alpha = C \Delta E_a^{-1} T^{0.4}, \quad (8)$$

where C, the slope of the $\alpha T^{-0.4}$ vs ΔE_a^{-1} curve, is about 0.24 cal/g-atom-°K^{1.4}.

It is apparent from Fig. 1 that a considerable number of compounds lie both above and below the curve of slope 0.24.

* Thermal expansivity is generally given in the literature as the mean linear expansivity from room temperature to some higher temperature. Linear expansivity may be readily converted to volume expansivity by multiplying by 3. The mean expansivity over the temperature interval, $\alpha(T-298)$, may be converted to an instantaneous expansivity, α at temperature T, by use of Eq. (4); thus,

$$\begin{aligned} \alpha &= \frac{V_{298}}{V_T} \cdot \frac{n(1 - 298/T)}{1 - (298/T)^n} \cdot \alpha(T-298) \\ &\approx \frac{1.4(1 - 298/T)}{1 - (298/T)^{1.4}} \cdot \alpha(T-298). \end{aligned}$$

Fig. 1. Dependence of thermal expansivity on atomization energy for borides, carbides, and nitrides.

Table 1. A summary of atomization energy and thermal expansivity data for borides, carbides, and nitrides.^a

Substance	$-\Delta H_{f,298}^{\circ}$ kcal/mole	$\Delta H_{sub,298}^{\circ}(M)$, ^b kcal/mole	ΔE_a , kcal/g-atom	$\alpha_T T^{-0.4}$, ^c °K ^{-1.4} $\times 10^{-6}$
WB	$\sim 17^d$ (7)	203.4	177	1.24 (6)
TiB ₂	66.8 (8)	112.3	148	1.62 (6)
ZrB ₂	73.0 (8)	145.5	162	1.47 (6)
HfB ₂	80.0 (8)	148.0	165	1.47 (6)
NbB ₂	41.9 (8)	172.4	160	1.55 (6)
B ₄ C	14.0 (9)	—	144	1.17 (6)
ThB ₄	52 ^e (10)	137.3	144	1.45 (6)
CaB ₆	~ 72 (11)	42.6	130	1.49 (12)
SrB ₆	~ 72 (11)	39.3	130	1.54 (12)
BaB ₆	~ 72 (11)	43.9	131	1.56 (12)
YB ₆	~ 72 (11)	101.5	139	1.39 (12)
LaB ₆	~ 72 (11)	103.0	139	1.44 (12)
CeB ₆	~ 72 (11)	101	139	1.63 (12)
PrB ₆	~ 72 (11)	85.0	136	1.69 (12)
NdB ₆	~ 72 (11)	78.3	136	1.62 (12)
SmB ₆	~ 72 (11)	49.4	131	1.52 (12)
EuB ₆	~ 72 (11)	41.9	130	1.54 (12)
GdB ₆	~ 72 (11)	95.0	138	1.95 (12)
TbB ₆	~ 72 (11)	92.9	138	1.74 (12)
YbB ₆	~ 72 (11)	36.3	130	1.31 (12)
ThB ₆	54.5 ^e (10)	137.5	144	1.74 (12)
SiB ₆	$\sim 20^f$	107.7	132	1.12 (6)
B(β -rhd)	—	—	133	1.25 (18)
Mo ₂ C	5.5 (13)	157.3	164	1.26 (6)
Cr ₃ C ₂	5.5 (13)	95.0	127	2.18 (6)
SiC	16.5 (8)	107.7	148	1.09 (6)
TiC	44.1 (13)	112.3	164	1.57 (6)
ZrC	47.0 (13)	145.5	182	1.43 (6)
HfC	50.1 (13)	148.0	185	1.33 (6)
VC _{0.88}	24.5 (13)	122.9	159	1.29 (6)
NbC	33.6 (13)	172.4	169	1.46 (6)
TaC	34.1 (13)	186.9	196	1.32 (6)
WC	9.7 (13)	203.4	192	0.97 (6)
UC	23.3 (13)	126.3	160	2.33 (6)
PuC _{0.9}	12 (13)	84.1	132	2.18 (6)

Table 1 (continued).

Substance	$-\Delta H_{f,298}^\circ$ kcal/mole	$\Delta H_{\text{sub},298}^\circ(\text{M})^b$ kcal/mole	ΔE_a kcal/g-atom	$\alpha_T T^{-0.4}$ $^\circ\text{K}^{-1.4}$ $\times 10^{-6}$ ^c
La_2C_3	$\sim 50^g$	103.0	154	2.05 (4)
Ce_2C_3	$\sim 50^g$	101	153	2.15 (4)
U_2C_3	51 (13)	126.3	164	2.25 (6)
LaC_2	$\sim 25^g$	103.0	157	2.50 (4)
CeC_2	$\sim 25^g$	101	156	2.09 (4)
PrC_2	$\sim 25^g$	75.0	151	2.35 (4)
ThC_2	29.7 (13)	137.5	170	2.18 (6)
$\text{UC}_{1.9}$	20.0 (13)	126.3	163	2.15 (4)
Ta_2N	64.7 (9)	186.9	184	1.11 (4)
Cr_2N	27.3 (9)	95.0	110	1.95 (4)
TiN	80.4 (9)	112.3	153	1.79 (6)
ZrN	87.3 (9)	145.5	173	1.65 (6)
HfN	88.2 (9)	143.0	175	1.42 (4)
VN	51.9 (9)	122.9	144	1.68 (4)
UN	70.4 (9)	126.3	155	1.85 (15)

^aThe numbers in parentheses are Reference numbers.

^bThe enthalpies of sublimation are from Honig and Kramer.¹⁶ The values for boron and carbon are 133.0 (Ref. 8) and 171.3 kcal/g-atom (Ref. 15) respectively. The enthalpy of formation of atomic nitrogen is 113.0 kcal/g-atom.⁸

^cThe $\alpha_T T^{-0.4}$ values are derived from thermal expansivity data extending from room temperature to somewhere in the range of 800-1500°C.

^dBrewer and Haraldsen estimate $\Delta H_{f,298}^\circ$ of WB to be between -22 and -12 kcal/mole.¹⁷

^eThe $\Delta H_{f,298}^\circ$ of ThB_4 and ThB_6 are assumed to be equal to their free energies of formation at 850°C.¹⁰

^fThe $\Delta H_{f,298}^\circ$ of SiB_6 is assumed to be about the same as that of B_4C and SiC .

^gThe group IIIB and lanthanide carbides are assumed to have about the same $\Delta H_{f,298}^\circ$ as carbides of thorium and uranium.

Compounds with the highest and lowest expansivities are identified with formulas in Fig. 1 and show that the highest expansivities correspond to carbides of the group IIIB, lanthanide, and actinide elements, whereas the lowest expansivities are represented by compounds that have a high degree of covalent bonding. The group IIIB, lanthanide, and actinide carbides show a number of properties that

are characteristic of ionic bonding. For example, the ease of hydrolysis of these carbides to form acetylene and other hydrocarbons attests to their salt-like character. Similar values of thermal expansivity are anticipated for CaC_2 and other group IIA carbides. For these salt-like carbides, $C \approx 0.35/\text{g-atom-}^\circ\text{K}^{1.4}$, or

$$\alpha = 0.35 \Delta E_a^{-1} T^{0.4} \quad (9)$$

For the highly covalent compounds such as the tetraborides and hexaborides, $C \approx 0.20 \text{ cal/g-atom-}^\circ\text{K}^{1.4}$, and

$$\alpha = 0.20 \Delta E_a^{-1} T^{0.4}. \quad (10)$$

Although borides such as hexaborides or dodecaborides are expected to have a large ionic contribution to the bonding between metal and the boron network,¹² the structural framework that primarily determines the thermal expansivity is provided by covalent B-B bonds.

It would appear that if a quantitative measure of the degree of ionic or covalent bonding in the bonds that determine thermal expansivity can be found, then a more quantitative expression can be given for thermal expansivity. A property that shows promise for such a correlation is microhardness. Knoop microhardness values^{4,13} range from $\sim 600 \text{ kg/mm}^2$ near the top of Fig. 1 to $\sim 4000 \text{ kg/mm}^2$ near the bottom. Empirically, the thermal expansivity may be related to microhardness by,

$$\alpha = 10 h^{-1/2} \Delta E_a^{-1} T^{0.4}, \quad (11)$$

where h is the Knoop microhardness in kg/mm^2 for loads of 50-100 g. This relationship is illustrated in Fig. 2 for the compounds from Table 1 for which microhardness data are available.

In order to evaluate γ_G , a tabulation is made of the available room temperature data on borides, carbides, nitrides, and several typical oxides (see Table 2). Thermal expansivities have been extrapolated to room temperature, when necessary, by assuming that α is proportional to $T^{0.4}$. When several values of compressibility were given for a single compound in the references to Table 2, the

values were averaged. The heat capacity values are actually C_p values, but the error is negligible in assuming them to be equal to C_l at room temperature. Similarly, no distinction is made between isothermal and adiabatic compressibilities. The uncertainties in $\bar{V}$ and C_l are believed to be negligible, and the uncertainties in α and β are believed to be about $\pm 10\%$ each. Hence, γ_G is uncertain by about $\pm 15\%$.

Examination of the γ_G data shows that a definite trend exists in γ_G with class of substance. It seems reasonable to assign a γ_G value of 1.2 for the borides and carbides, and 1.4 for the nitrides and oxides. These values may be compared with an average γ_G value of 1.84 for the common metals—Na, K, Al, Mn, Fe, Co, Ni, Cu, Ag, and Pt—while the rare earths (with the exception of Eu) have values in the range of 0.3 to 1.2.²⁷

The temperature dependence of γ_G has been determined for TiB_2 , ZrB_2 , and HfB_2 by Wiley and co-workers,²⁰ who found γ_G values that are nearly constant from room temperature to 1300°K . Manning and Hunter²⁸ found values in the range of 1.0-1.2 for γ_G of Y_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , and Lu_2O_3 from room temperature to 1300°K . The values either remained constant or decreased by a few percent over the temperature interval. Similarly, Soga and Anderson²⁹ found γ_G to be approximately constant at 1.3 for Al_2O_3 from 300 - 1400°K , and 1.5 for MgO from 300 - 1100°K . From the thermal data on tungsten,^{8,21} γ_G values are calculated to increase uniformly from 1.6 at 300°K to 1.8 at 1500°K . Kleppa³⁰ found that, for most low-melting-point metals, γ_G shows no appreciable change in going

Fig. 2. Dependence of the product $\alpha \Delta E_a T^{-0.4}$ on microhardness (h).

Table 2. Room temperature values of thermal expansivity, molar volume, compressibility, heat capacity, and Grüneisen gamma for a number of refractory substances.^a

Substance	α , °K ⁻¹ × 10 ⁻⁵	$\bar{V}$, cm ³ /mole	β , cm ² /dyne × 10 ⁻¹²	C_p , ergs/mole-°K × 10 ⁸	γ_G
B(β -rhd)	1.3 (18)	4.60 (1)	0.56 (19)	1.11 (25)	1.0
C(diam)	0.4 (6)	3.42 (19)	0.19 (19)	0.61 (25)	1.2
TiB ₂	1.6 (6)	15.38 (4)	0.47 (20)	4.39 (8)	1.2
ZrB ₂	1.4 (6)	18.53 (4)	0.46 (20)	4.82 (8)	1.2
HfB ₂	1.4 (6)	17.87 (4)	0.49 (20)	5.02 (8)	1.0
B ₄ C	1.1 (6)	21.94 (4)	0.39 (21)	5.26 (25)	1.2
TiC	1.6 (6)	12.18 (4)	0.48 (4)	3.36 (25)	1.2
ZrC	1.4 (6)	15.50 (4)	0.47 (21)	3.79 (25)	1.2
UC	2.3 (6)	18.35 (4)	0.61 (22)	5.01 (13)	1.4
TiN	1.8 (6)	11.38 (4)	0.34 (4)	3.71 (25)	1.6
UN	2.1 (6)	17.60 (4)	0.54 (23)	4.78 (26)	1.4
BeO	1.8 (6)	8.32 (19)	0.46 (24)	2.54 (25)	1.3
MgO	2.9 (6)	11.25 (19)	0.62 (19)	3.78 (25)	1.4
Al ₂ O ₃	1.7 (6)	25.57 (19)	0.38 (19)	7.90 (25)	1.4
ThO ₂	2.0 (6)	26.38 (19)	0.56 (21)	6.10 (25)	1.5
UO ₂	2.3 (6)	24.62 (19)	0.62 (21)	6.41 (25)	1.4

^aThe numbers in parentheses are Reference numbers.

from the solid at room temperature to the liquid at moderately elevated temperatures. As exceptions, Kleppa noted that bismuth and gallium undergo a decrease in γ_G from about 2.2 to 1.1 upon melting, which is an effect that can be attributed to a structural change associated with the melting of these metals. From these observations it is concluded that γ_G is

nearly independent of temperature for crystalline substances, provided that drastic changes in structure do not occur. Caution should be exercised in extending this conclusion below room temperature, where γ_G could change considerably and, in exceptional cases, as with Si and InSb,³¹ may actually become negative.

Harmonic Lattice Vibrations

The heat capacity contribution of harmonic lattice vibrations, C_p , will be examined next. Hoffman et al.⁵ found that Debye functions were suitable for

describing the low-temperature heat capacities of binary compounds of metals with nonmetals, provided that two Debye temperatures were assigned to each

compound: one for the metal and the other for the nonmetal constituent. Pairs of Debye temperatures were thus selected for a series of compounds to give a best fit to the low-temperature heat capacity data (see Table 3). Hoffman et al. further showed that if all atoms in a crystal have equal mean-square displacements, then the metal and nonmetal Debye temperatures will be inversely proportional to the square roots of the corresponding masses; i.e., $\theta_R/\theta_X = (M_X/M_R)^{1/2}$. For eleven compounds consisting of carbides, nitrides, oxides, and fluorides (see Table 3), the ratio θ_R/θ_X was found to agree within a factor of two with $(M_X/M_R)^{1/2}$ (see Ref. 5).

Kaufman³² calculated θ_R and θ_X values for diborides of Ti, Zr, Hf, Nb, and Ta (see Table 3) by using Hoffman's relation, $\theta_R/\theta_X = (M_X/M_R)^{1/2}$, together with the condition that S_{298}° values calculated by Debye functions (with suitable dilatation and electronic terms added) must be in agreement with the experimental S_{298}° values. Kaufman presents a comparison between the heat capacities calculated on the basis of θ_R and θ_X values and experimental data. Agreement between calculation and experiment is generally poor at 50°K or lower; but, with the exception of HfB₂, agreement is within 7% at 100°K and improves to within 2% at 350°K. For HfB₂, the comparison shows large discrepancies throughout the temperature range and indicates failure of the equal mean-square displacement assumption in this case.

Schick⁸ calculated θ_R and θ_X for refractory borides by means of a modified form of the Lindemann relation, i.e., $\theta_i = KT_c^{1/2} M_i^{-1/2} V_i^{-1/3}$. Here, θ_i represents θ_R (or θ_X), K is the Lindemann

constant (which is taken to be 137), T_c is the melting point of the compound, and M_i and V_i represent the atomic weight and atomic volume of pure element R (or X). A comparison of Schick's results with those of Kaufman (see Table 3) shows that Schick's θ_R values are lower and his θ_X values higher than Kaufman's. Schick's calculated S_{298}° and $C_{p,298}$ values are in general agreement with experimental data for the diborides listed in Table 3; but, for the diborides of chromium and molybdenum, Schick's S_{298}° values are about 2 cal/mole-°K higher than the experimental data.⁸

Examination of the data in Table 3 suggests yet a simpler method for estimating θ_R and θ_X . θ_R seems to show little change with type of refractory compound, as, for example, a θ_R of about 251-320°K for HfB₂ may be compared with 275°K for HfO₂. Furthermore, a θ_R appears to correlate well with θ_R° , the Debye temperature for the pure elemental metal. The ratio θ_R/θ_R° is found to have a mean value of 1.38 and an uncertainty of about ± 0.3 (see Table 3). For borides, a value of 1.7 for θ_R/θ_R° provides a better fit to the data. The nonmetal contributions, θ_X , also appear to be reasonably constant for a given class of compound. For borides, a θ_X of approximately 1210°K is consistent with a θ_R/θ_R° value of 1.7. There is an obvious decrease in θ_X and an increase in ionic bonding, in going from borides to carbides, nitrides, oxides, and fluorides.

The method developed here will be used for the heat capacity calculations. It has an advantage over Hoffman's method in that it does not require low-temperature calorimetric data for input. The estimated

Table 3. Debye temperatures of the metal (θ_R) and nonmetal (θ_X) constituents of various compounds, and a comparison of θ_R with θ_R° , the Debye temperature of the elemental metal.

Compound	θ_R° , $^\circ\text{K}^a$	θ_X° , $^\circ\text{K}^a$	θ_R° , $^\circ\text{K}^b$	θ_R/θ_R°
TiB ₂	620, 498	1302, 1422	362	1.71, 1.38
ZrB ₂	440, 342	1277, 1479	254	1.73, 1.35
HfB ₂	320, 251	1299, 1503	206	1.55, 1.22
VB ₂	—, 489	—, 1328	408	—, 1.20
NbB ₂	425, 370	1245, 1481	286	1.49, 1.29
TaB ₂	320, 270	1309, 1514	229	1.40, 1.18
VC	475	1400	408	1.16
Cr ₃ C ₂	500	1000	492	1.02
VN	375	1100	408	0.92
ZrN	400	900	254	1.57
Al ₂ O ₃	750	1100	390	1.92
Ga ₂ O ₃	360	1075	253	1.42
HfO ₂	275	850	206	1.33
ThO ₂	250	775	148	1.69
MgF ₂	375	750	323	1.16
CaF ₂	375	550	232	1.62
ZnF ₂	250	620	230	1.09

Average 1.38

Debye Temperatures of Additional Elemental Metals^b

Metal	θ_R° , $^\circ\text{K}^b$	Metal	θ_R° , $^\circ\text{K}^b$	Metal	θ_R° , $^\circ\text{K}^b$
Be	1094	Pr	144	C(diam)	1861
Sr	140	Nd	147	Si	635
Ba	109	Sm	141	Mo	384
B	1280	Eu	(100)	W	317
Sc	321	Gd	162	U	176
Y	216	Tb	166	Pu	(165)
La	142	Yb	94		
Ce	135	Lu	166		

^aThe first entries of θ_R and θ_X for the diborides are from Kaufman,³² and the second entries are from Schick.⁸ The single entries of θ_R and θ_X for the remaining compounds are from Hoffman et al.⁵

^bThe θ_R° values for the lanthanide metals are from Gschneidner.²⁷ When data were given on both sound velocity and heat capacity results,²⁷ the values were averaged. θ_R° for Eu and Pu were estimated. For the remaining metals, θ_R° was calculated from the low-temperature heat capacity data given by Hultgren et al.³³ Suitable corrections were applied for electronic heat capacity contributions in making these calculations. θ_R° for boron, carbon, and silicon were derived from heat capacity data at 150–400°K. For Sr and Ba, the temperature range used was 7–20°K; for the other metals, 50–100°K was used.

θ_R and θ_X values may not give reliable heat capacity estimates at low temperatures, but

should give reasonable values for S_{298}° and for C_p at room temperature and above.

Anharmonic Lattice Vibrations

The contributions to the heat capacity from anharmonic lattice vibrations have the theoretical form

$$C_a = AC_l T, \quad (12)$$

where A is a parametric constant that depends in a complex manner on the harmonic and anharmonic coefficients of the potential energy curve.³⁴ The functional dependence of thermal expansivity on the harmonic and anharmonic coefficients is generally similar to that of A ,³⁴ and a correlation should exist between α and A .

Experimental determinations of A are limited to those of Overton,³⁵ who made measurements on sodium and copper. He found that A for sodium from 0-200°K is $6 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$, but, from 200-300°K, A increases very rapidly. A likely explanation of this rapid increase is that it originates from vacancy contributions to the heat capacity. The lower temperature value is therefore taken to be the correct one. In the case of copper, Overton concluded that the anharmonic contributions to the heat capacity are approximately zero at room temperature. His data show considerable scatter, with anharmonic

contributions ranging from 0-1% of the total heat capacity from 70-300°K. It is conceivable that the anharmonic contribution may be as much as 0.5% at 300°K, which would give an A value of $1.7 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$.

From the expectation that A values should correlate with thermal expansivity, they should also correlate with ΔE_a^{-1} . Using the sodium A value and taking 25,755 cal/g-atom for ΔE_a (Ref. 16) gives

$$A = 1.5 \Delta E_a^{-1} \quad (13)$$

as a possible correlation expression. Similarly, using the estimated A value for copper and 80,500 cal/g-atom for ΔE_a (Ref. 16) gives $A = 1.4 \Delta E_a^{-1}$, which is better agreement than could be expected. Considering the general lack of data on the anharmonic factor, Eq. (13) will be assumed to apply to the borides or, indeed, to substances in general. Fortunately, the anharmonic contribution to the heat capacity is sufficiently small that little error is introduced into the C_p calculations from the large uncertainties in this term.

Conduction Electrons

The contribution of conduction electrons to the heat capacity is represented by

$$C_e = \gamma_e T, \quad (\text{Refs. 5, 34}) \quad (14)$$

where γ_e is the heat capacity coefficient of the conduction electrons. It may be shown theoretically that γ_e depends on the concentration of conduction electrons

and on the density of energy states of the conduction electrons at the Fermi energy level.³⁴ The theory is not adequate to permit quantitative calculations of γ_e , so experimental means are needed for its determination. It is determined most easily from low-temperature C_p data. Below $\sim 20^\circ\text{K}$, C_e is a major contributor to the heat capacity of metallic materials, and C_p is given by

$$C_p = \gamma_e T + BT^3, \quad (15)$$

where BT^3 is the Debye contribution. A plot of C_p/T vs T^2 may be used to determine γ_e as the 0°K intercept.³⁴

The available values of γ_e for borides are summarized in Table 4, where a number of γ_e values for metals ($\gamma_{e,M}$) have been included for comparison. The boride γ_e values generally tend to correlate with $\gamma_{e,M}$ but several inconsistently high values also occur. Perhaps this should not be surprising, since the functional dependence of the density of energy states with Fermi energy (or with electron-to-atom ratio) is irregular across a row of the periodic table (e.g., see Ref. 43), and may show several sharp peaks.

The temperature dependence of γ_e is usually assumed to be small; but, if the Fermi energy is at or near a peak in the density of energy states, then γ_e will have a large temperature dependence. Theoretical calculations by Ostenburg and co-workers⁴³ on the temperature-dependence of γ_e for niobium and molybdenum, and for alloys of Nb-Mo, Nb-Tc, and Mo-Tc, show that high values of γ_e , as is found for Nb, will decrease markedly with temperature; and low values, as in Mo, will show a slight increase. At high temperatures, the γ_e values of these

metals approach roughly a common value. It thus appears that unusually high values of γ_e derived from low-temperature data should not be used at high temperatures. An estimate of the high-temperature $\gamma_{e,M}$ may be made from comparisons with neighboring elements.

Examination of the data in Table 4 shows that, for the diborides, $\gamma_e \approx 0.3 \gamma_{e,M}$. With lower boron contents, γ_e should approach the metal value. For MB_6 and MB_{12} , Matthias³⁷ has suggested that γ_e should be representative of the value for pure boron with a cubic structure. The data of Table 4, however, would suggest that the metal atoms have an influence in determining γ_e . A factor that may be significant for these higher borides is the valence of the metal atom. For example, ytterbium, which is believed to be partly in the +2 state in a number of its compounds,²⁷ has a relatively low γ_e in the hexaboride as compared to the pure metal value ($\gamma_{e,M}$). Conversely, for the higher-valence metals, γ_e is relatively high, as in ThB_6 and ZrB_{12} . On the basis of these various qualitative observations, predictions for γ_e of the various borides are summarized as follows:

Boride	γ_e , cal/mole- $^\circ\text{K}^2$
MB_n , where $n \leq 2$	$\left(\frac{1}{n+1}\right) \gamma_{e,M}$
$\text{M}(+2)\text{B}_{4,6,12}$	$0.4 \gamma_{e,M}$
$\text{M}(+3)\text{B}_{4,6,12}$	$0.8 \gamma_{e,M}$
$\text{M}(+4, +5, +6)\text{B}_{4,6,12}$	$1.2 \gamma_{e,M}$

The uncertainties in these estimates for γ_e at high temperatures are believed to be $\pm 50\%$.

Table 4. Comparisons of the electronic gamma for borides with those for elemental metals.^a

Boride	γ_e (boride), cal/mole-°K ²	$\gamma_{e,M}$ (metal), ³³ cal/g-atom-°K ²	Boride	γ_e (boride), cal/mole-°K ²	$\gamma_{e,M}$ (metal), ³³ cal/g-atom-°K ²
	$\times 10^{-4}$	$\times 10^{-4}$		$\times 10^{-4}$	$\times 10^{-4}$
Mn ₂ B	16.4 (36)	30	MnB ₂	6.7 (36)	30
MnB	13.1 (36)	30	UB ₂	22.5 (38)	24.6
TiB ₂	2.3 ^b (32)	8.25	YB ₆	6.8 (37)	20
ZrB ₂	1.7 ^b (39)	7.0	LaB ₆	24.9, 15.3 ^c (40)	27.5
HfB ₂	1.8 ^b (41)	5.8	YbB ₆	2.4 (40)	6.93
NbB ₂	5.8 ^b (42)	18.75 ^d	ThB ₆	11.5 (40)	11.2
TaB _{2.1}	4.7 ^b (32)	13.5 ^d	ZrB ₁₂	13.5 (37)	7.0

Electronic Gamma for Additional Elemental Metals³³

Metal	$\gamma_{e,M}$ ³³ cal/g-atom-°K ²	Metal	$\gamma_{e,M}$ ³³ cal/g-atom-°K ²	Metal	$\gamma_{e,M}$ ³³ cal/g-atom-°K ²
	$\times 10^{-4}$		$\times 10^{-4}$		$\times 10^{-4}$
Be	0.41	Ce(β)	25	C	0.03
Mg	3.04	Pr	25	Si	0.0
Ca	7.17	Nd	27 ^e	V	23 ^d
Sr	8.70	Sm	29	Cr	3.8
Ba	6.5	Eu	14	Mo	5.0
B	0.0	Gd	27	W	2.7
Al	3.23	Tb	25	Pu	25 ^e
Sc	24.6	Lu	26.9		

^aThe numbers in parentheses are Reference numbers.

^bThe γ_e values were calculated from the low-temperature C_p data.

^cThe first value corresponds to a sample prepared by the reduction of La₂O₃ with a mixture of boron and carbon, while the second corresponds to a sample prepared by reduction with boron alone.

^d $\gamma_{e,M}$ for V, Nb, and Ta at high temperatures are estimated to be 10×10^{-4} , 9×10^{-4} , and 8×10^{-4} cal/g-atom-°K, respectively.

^e $\gamma_{e,M}$ values for Nd and Pu were estimated.

d and f Electrons

The electronic heat capacity of d or f electrons, C_g , arises either from spin-order magnetic transitions^{19,44} or from Schottky anomalies corresponding to the

thermal excitation of electronic energy states.⁴⁵ These effects are generally found in elements or compounds of the 3d transition series, the lanthanides, and

actinides. The crystal field interaction with d electrons is very strong in the 3d series, so it becomes difficult to distinguish d electron contributions from other heat capacity effects. Magnetic transitions may be readily identified for this series when experimental data are available, but otherwise are difficult to predict. For the lanthanides and actinides and their compounds, the 4f and 5f electrons are well screened so that the crystal field interaction is weak. Consequently, these substances have energy states at levels comparable to those in the free atom or ion. Since lanthanides and actinides typically have a large number of low-lying levels, the Schottky contribution to the heat capacity will be large. Magnetic spin-order transitions are also common in the lanthanide and actinide series.

Magnetic ordering transitions characteristically show a lambda-shaped heat capacity curve that is a consequence of cooperative order-disorder transformations. The ordered state is ferromagnetic, antiferromagnetic, or ferrimagnetic, and the disordered state, paramagnetic. For lanthanides and actinides and their compounds, magnetic transitions generally occur well below room temperature and involve a relatively small number of energy levels.^{44,46-48} Because of the smallness of the effect, it is adequate for our purposes to treat the heat capacity of these substances in the same manner as for Schottky anomalies. For elements and compounds of the 3d transition series, however, magnetic transitions may occur above or below room temperature and may make a significant contribution to the heat capacity. Because of the uncertainties involved in predicting the existence

and magnitude of magnetic transitions in the 3d series, predictions will not be made.

For Schottky anomalies, the heat capacity is calculated from the expression^{45,47}

$$C_s = \frac{1}{RT^2} \left\{ \frac{\sum_i E_i^2 g_i \exp(-E_i/RT)}{\sum_i g_i \exp(-E_i/RT)} - \left[\frac{\sum_i E_i g_i \exp(-E_i/RT)}{\sum_i g_i \exp(-E_i/RT)} \right]^2 \right\}, \quad (16)$$

provided that the energy levels are known. Dennison and Gschneidner⁴⁵ calculated the Schottky heat capacity contributions of a number of trivalent lanthanide ions and of divalent samarium. Contributions to C_s above room temperature were found to be of the order of 2 cal/g-atom-°K. Below room temperature, C_s was negligible except for Sm^{+2} and Eu^{+3} .

A serious drawback of Dennison and Gschneidner's calculations is that they did not take into account the effects of crystal field on the energy levels. This is particularly important for the ground state, where degenerate energy levels within a few hundred cm^{-1} of the lowest energy state contribute significantly to C_s at room temperature and below. An empirical treatment of low-temperature heat capacity data by Westrum and co-workers on NdB_6 (Ref. 47) indicates that the ten-fold degenerate $^4I_{9/2}$ ground state is split into two levels at 0 cm^{-1} , four levels at 80 cm^{-1} , and four levels at 224 cm^{-1} . Similar studies on GdB_6

(Ref. 48) indicate, for the $^8S_{7/2}$ ground state, two levels at 0 cm^{-1} , four at 51 cm^{-1} , and two at 80 cm^{-1} . The heat capacity curves for NdB_6 and GdB_6 show thermal anomalies extending over most of the $0\text{--}298^\circ\text{K}$ range. Unpublished work on CeB_6 (Ref. 46) shows similar behavior. A Schottky anomaly for UB_2 (Ref. 38) may be interpreted to correspond to one level at 0 cm^{-1} and two levels at 122 cm^{-1} . Other levels are too far removed to contribute to the heat capacity up to 350°K . Data on lambda and Schottky anomalies have been presented by Westrum and co-workers^{44,46} for several other lanthanide and actinide compounds.

From the limited information available, it may be surmised that the crystal field

splitting is generally greater for the actinides than for the lanthanides. The following scheme is therefore chosen for estimating the crystal field splitting of the ground state for the borides. For the lanthanide borides, two levels are assigned to 0 cm^{-1} , four levels to 60 cm^{-1} , and the balance of the multiplicity is placed at 180 cm^{-1} . For the actinide borides, one level is assigned to 0 cm^{-1} , two levels to 120 cm^{-1} , and the balance to 360 cm^{-1} . For the lanthanide ions, the multiplicity of the levels is given by $(2J + 1)$. For the actinide ions, a partial breakdown of spin-orbit coupling occurs.⁴⁴ Hence, for calculational purposes, an average of $2J + 1$ and $2S + 1$ will be used as a best guess of the multiplicity for actinide ions.

Lattice Defects

The heat capacity of lattice defects, C_d , depends upon the concentration of defects and upon their energies of formation. For a defect concentration in thermodynamic equilibrium with the lattice,

$$N_d = \exp(\Delta S_d/R) \exp(-\Delta E_d/RT), \quad (17)$$

where N_d is the ratio of defects to lattice sites, and ΔS_d and ΔE_d are the entropy and energy of defect formation, respectively. Assuming ΔS_d and ΔE_d to be independent of temperature and volume, the heat capacity of defects is obtained by differentiating $N_d \cdot \Delta E_d$ with respect to T , resulting in

$$C_d = (\Delta E_d^2/RT^2) \exp(\Delta S_d/R) \times \exp(-\Delta E_d/RT). \quad (18)$$

Equation (18) is similar in form to the Schottky heat capacity for a single excited

state given by Eq. (16), and consequently it is not possible to distinguish between the heat capacity of a Schottky anomaly and of a lattice defect on the basis of heat capacity data alone.

In the case of elemental metals, experimental studies of diffusion, thermal expansion, and quenching as well as heat capacity have established the primary importance of Schottky vacancies in the lattice.^{34,49,50} Vacancy concentrations are found to be of the order of 1% of the lattice sites near the melting point. Heat capacity measurements provide the most reliable values of the energies and entropies of vacancy formation, while methods based on thermal expansion or quenching tend to give vacancy concentrations that are too low.⁵⁰ Diffusion data are useful for setting an upper bound to the energy

of vacancy formation, since the activation energy for diffusion is the sum of the formation and migration energies. Typically, ΔE_d for vacancy formation is 0.5-0.6 of the activation energy for diffusion.^{34,48}

Examination of heat capacity data on vacancies in metals⁵⁰ shows that correlations may be made of both ΔE_d and ΔS_d with the atomization energy (Ref. 16), ΔE_a (see Fig. 3). These correlations are summarized by the equations

Fig. 3. Correlation of the energy and entropy of vacancy formation for metals with the energy of atomization.

$$\Delta E_d = 0.32 \Delta E_a \quad (19)$$

and

$$\Delta S_d = 5.0 + 3.5 \times 10^{-5} \Delta E_a. \quad (20)$$

Substitution of Eqs. (19) and (20) in (17) or (18) allows the calculation of the concentration and heat capacity of vacancies for metals.

For compounds, a variety of defects may result from Schottky or Frenkel disorder, impurity effects, or lattice vacancies in nonstoichiometric compounds.^{34,51} Taking a strictly empirical approach and ignoring the types of defects, there is

evidence that the activation energy for diffusion will still correlate with atomization energy. Based on data given by Swalin for halides and chalcogenides,⁵² the relation $\Delta E_{\text{diffusion}} = 0.6 \Delta E_a$ holds well for cation diffusion and is crudely correct for anion diffusion.* If one assumes that $\Delta E_d = 0.55 \Delta E_{\text{diffusion}}$ then $\Delta E_d = 0.33 \Delta E_a$, which is in substantial agreement with Eq. (19). On the basis of this agreement, it is assumed that Eqs. (19) and (20) are generally applicable to metals and compounds, including borides. Uncertainties in the predicted ΔE_d and ΔS_d are probably about $\pm 20\%$.

Enthalpy of Fusion

The enthalpy of fusion, ΔH_m° , may be obtained by estimating the entropy of fusion, and applying the relation, $\Delta H_m^\circ = T \Delta S_m^\circ$. For borides with boron contents less than in MB_4 , ΔS_m° is estimated to be 2.3 cal/g-atom-°K, a value that is comparable to that for close-packed metals.³³ For borides with boron contents equal to or higher than in MB_4 , ΔS_m° is taken to be an additive combination with 2.3 cal/g-atom-°K for the metallic constituent, and

4.0 cal/g-atom-°K for the boron. A high entropy of fusion for the boron part is justified on the basis of the rigid covalent-type bonding exhibited by borides with high boron contents. Other elements with covalent characteristics in the solid, such as Si, Ge, red P, Sb, Bi and Te, have entropies of fusion in the range of 4-8 cal/g-atom-°K. The estimates above for the enthalpies of fusion of borides are believed to be uncertain by about $\pm 25\%$.

C_p of the Liquid

There is no experimental information at the present time on the heat capacities of liquid refractory materials. Qualitatively, the heat capacity is believed to behave as follows. At temperatures within a few hundred degrees above the melting point, a complex behavior is expected to occur as remnants of the crystalline struc-

ture gradually break down. Within this interval, the heat capacity may decline, it may remain relatively constant, and/or it may show one or more humps. Be-

*On the basis of more limited information, a similar relationship is found between the free energy of diffusion and ΔE_a .⁵²

cause of the unknown structural changes upon melting, it is not possible to predict whether C_p for the liquid will be greater or less than for the solid at the melting point. As the temperature increases beyond the first few hundred degrees, C_p will rise because of the dilatation term,

as well as various contributions from vibrational, electronic, and other excitation processes. For purposes of thermodynamic calculations, C_p for the liquid boride will be assumed to be constant from the melting point to 4000°K, and to have a value equal to that of the solid at the melting point.

Calculational Procedures

In addition to C_p , calculations were made of S_{298}° , $H_{298}^\circ - H_0^\circ$, $H_T^\circ - H_{298}^\circ$, and $(F_T^\circ - H_{298}^\circ)/T$, where T goes from 298 to 4000°K. C_p values were calculated at intervals of 2°K up to 300°K, and at intervals of 5°K up to 4000°K. Other thermodynamic functions were derived from the C_p values by using appropriate summations to approximate the required integrals. (Calculations were made on a Control Data Corporation CDC-6600 computer.)*

For convenience in making computer calculations, the Debye heat capacity contributions were expressed in the form

$$C_\ell = \frac{dE_\ell}{dT} = \frac{d}{dT} \left[9RT \left(\frac{T}{\theta} \right)^3 D\left(\frac{\theta}{T}\right) \right], \quad (21)$$

where

$$D\left(\frac{\theta}{T}\right) = \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1}.$$

Equation (21) may be approximated by

$$\frac{dE_\ell}{dT} \approx \frac{\Delta E_\ell}{\Delta T} = \frac{9R}{2\theta^3 \Delta T}$$

$$\times \left[(T + \Delta T)^4 D\left(\frac{\theta}{T + \Delta T}\right) - (T - \Delta T)^4 D\left(\frac{\theta}{T - \Delta T}\right) \right], \quad (22)$$

where ΔT represents a sufficiently small temperature increment that errors in C_ℓ become negligibly small. The temperature increments of 2°K below room temperature and 5°K above room temperature adequately meet this requirement, as they introduce less than 0.01% error into C_ℓ or the other thermodynamic functions at temperatures of 298°K and higher. The Debye function, $D(\theta/T)$, may be evaluated by writing it in the form

$$D\left(\frac{\theta}{T}\right) = \int_0^\infty \frac{x^3 dx}{e^x - 1} - \int_{\theta/T}^\infty \frac{x^3 dx}{e^x - 1}. \quad (23)$$

The first integral is equal to $\pi^4/15$, and the second integral is solved by the series method given by Stegun.⁵³

The complete heat capacity equation for binary compounds may now be written as follows:

$$C_p = \left(1 + \Delta E_a^{-1} \gamma_G T^{1.4} + 1.5 \Delta E_a^{-1} T \right) (N_R C_{\ell,R})$$

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

$$+ N_X C_{\ell,X}) + \gamma_e T + N_R C_{s,R} + \frac{\Delta E_d^2}{RT^2} \exp\left(\frac{\Delta S_d}{R} - \frac{\Delta E_d}{RT}\right), \quad (24)$$

where C , the thermal expansion parameter, may be determined from Eqs. (8)-(11); γ_G is the Grüneisen constant; ΔE_a is the atomization energy per gram atom for the compound; N_R and N_X are the atom fractions of metal R or nonmetal X in the compound; $C_{\ell,R}$ and $C_{\ell,X}$ are the Debye heat capacities as calculated from Eqs. (22) and (23); and, based on θ_R and θ_X estimated by methods described in the text, γ_e is the heat capacity coefficient for conduction electrons and is also estimated by methods given in the text; $C_{s,R}$ is the Schottky heat capacity given by Eq. (16); and ΔE_d and ΔS_d are the energy and entropy of vacancy formation from Eqs. (19) and (20).

The method of summation used to approximate the integrals for the other thermodynamic functions is illustrated for the case of $H_{298,15}^\circ - H_0^\circ$ (which, for brevity, is written as $H_{298}^\circ - H_0^\circ$):

$$\begin{aligned} H_{298}^\circ - H_0^\circ &= \int_0^{298,15} C_p dT \\ &= \sum_{i=2,2}^{i=296} 1/2 (C_{p,i} + C_{p,i+2}) \Delta T \\ &\quad + 0.15 C_{p,298} \\ &= 1/2 (0 + C_{p,298}) \Delta T \\ &\quad + \Delta T \sum_{i=2,2}^{296} C_{p,i} + 0.15 C_{p,298}, \end{aligned}$$

and, since $\Delta T = 2^\circ K$,

$$\begin{aligned} H_{298}^\circ - H_0^\circ &= 1.15 C_{p,298} \\ &\quad + 2 \sum_{i=2,2}^{296} C_{p,i}. \quad (25) \end{aligned}$$

The summations used for the remaining functions are

$$\begin{aligned} S_{298}^\circ &= \frac{1.15 C_{p,298}}{297} \\ &\quad + 2 \sum_{i=2,2}^{296} \frac{C_{p,i}}{i} + N_R R \ln g_0, \quad (26) \end{aligned}$$

$$\begin{aligned} H_T^\circ - H_{298}^\circ &= 4.35 C_{p,300} \\ &\quad + 2.5 C_{p,T} + 5 \sum_{i=305,5}^{T-5} C_{p,i}, \quad (27) \end{aligned}$$

and

$$\begin{aligned} \frac{F_T^\circ - H_{298}^\circ}{T} &= \frac{H_T^\circ - H_{298}^\circ}{T} - S_{298}^\circ \\ &\quad - \frac{4.35 C_{p,300}}{300} - \frac{2.5 C_{p,T}}{T} \\ &\quad + 5 \sum_{i=305,5}^{T-5} \frac{C_{p,i}}{i}, \quad (28) \end{aligned}$$

where ΔT has been taken to be $5^\circ K$ above $300^\circ K$, and g_0 is the multiplicity of the lowest energy state. Suitable interpolations are made for nonincremental temperatures.

Input Parameters

The input parameters required for the calculations are C , ΔE_a , γ_G , θ_P , θ_X , γ_e , g_i , E_i , T_m , $\Delta S_{m,R}^\circ$, and $\Delta S_{m,X}^\circ$. For the borides, $\gamma_G = 1.2$, $\theta_X = 1210^\circ\text{K}$, and $\Delta S_{m,R}^\circ = 2.3 \text{ cal/g-atom-}^\circ\text{K}$; θ_R is taken to be $1.7 \theta_R^\circ$, using θ_R° values given in Table 3; and $\Delta S_{m,X}^\circ$ is taken to be $2.3 \text{ cal/g-atom-}^\circ\text{K}$ for boron contents up to MB_4 , and $4.0 \text{ cal/g-atom-}^\circ\text{K}$ for MB_4 and above. B_4C and the silicon borides are exceptions to this procedure, where ΔS_m° for the entire compound is taken to $4.0 \text{ cal/g-atom-}^\circ\text{K}$. Where several values of T_m are available, the values are generally

averaged. For peritectic melting compounds, the peritectic temperature is given for T_m . The values used for C , ΔE_a , γ_e , and T_m are listed in Table 5, and values for g_i and E_i for assumed lanthanide and actinide ionic states are given in Table 6. All other metal ions are assumed to be nondegenerate for the borides listed in Table 5. In compiling the input data, estimates were made whenever data were not available. The methods of estimation either have been described in the text or footnotes, or are based on trends in the periodic table.

Results

Values of S_{298}° and C_p at 298, 1000, and 2000°K , as calculated by the methods developed here, are compared in Table 7 with experimental data on borides. Only borides that have reasonably accurate data have been listed.

The experimental C_p data on borides are still quite uncertain at temperatures in the neighborhood of 2000°K . For example, C_p values reported for ZrB_2 at 2000°K by different investigators range from 5.8 to $9.0 \text{ cal/g-atom-}^\circ\text{K}$. Agreement at $\sim 1000^\circ\text{K}$ is much better, usually being within $\pm 10\%$ for different investigators. Values at room temperature are based on low-temperature calorimetric methods, and C_p values are believed to be accurate to $\pm 2\%$. Considering the experimental uncertainties, the calculated values provide as good a fit as can be expected for C_p . Unfortunately, the assumptions made here about conduction electron and vacancy contributions at high

temperatures cannot be tested because of the uncertainties in the experimental data.

Comparisons of calculated and experimental S_{298}° values present a more critical test of the assumptions made in the selection of Debye temperatures. Agreement between calculated and experimental values is found to be generally within $\pm 10\%$, which is surprisingly good, considering the empirical nature of the methods used to make the estimates.

Thermodynamic functions have been calculated for most of the known borides and are summarized in Tables 8, 9, and 10. The borides of dysprosium through thulium should be similar in properties to borides of terbium, and hence have not been listed. Borides of iron- and platinum-group metals, and of a number of actinides, also are excluded. It should be possible to make estimates for these borides by observing trends in the periodic table.

Table 5. Input parameters for heat capacity calculations.^a

Boride	C_p^b cal/g-atom-°K ^{1.4}	$-\Delta H_f^{\circ}, 298^c$ kcal/mole	ΔE_a kcal/g-atom	γ_e cal/mole-°K ² $\times 10^{-4}$	T_m °K
Be ₄ B	(0.24)	(8)	90	(0.33)	1430 (2)
Be ₂ B	(0.24)	(8)	99	(0.27)	1790 (2)
BeB ₂	(0.24)	(15)	120	(0.14)	(2250)
BeB ₆	(0.20)	(40)	131	(0.16)	2340 (2)
BeB ₁₂	(0.20)	(60)	133	(0.16)	(2000)
MgB ₂	(0.24)	22.0 (17)	108	(1.0)	(1300)
MgB ₄	(0.20)	25.1 (17)	118	(1.2)	(1400)
MgB ₆	(0.20)	(30)	123	(1.2)	1420 (2)
CaB ₆	0.194 ^d	~72 ^d	130	(2.9)	2510 (2)
SrB ₆	0.200 ^d	~72 ^d	130	(3.5)	2510 (2)
BaB ₆	0.204 ^d	~72 ^d	131	(2.6)	2540 (2)
AlB ₂	(0.24)	(15)	120	(1.1)	1250 (2)
AlB ₁₂	0.164 ^e	(80)	135	(2.6)	2450 (2)
ScB ₂	0.237 ^e	(30)	129	(8.2)	2520 (2)
ScB ₄	0.147 ^e	(50)	134	(19.7)	(3000)
ScB ₁₂	(0.20)	(120)	139	(19.7)	(2500)
YB ₂	(0.24)	(30)	132	(6.7)	2370 (2)
YB ₄	(0.20)	(50)	137	(16.0)	3970 (2)
YB ₆	0.193 ^d	~72 ^d	139	(16.0)	2870 (2)
YB ₁₂	(0.20)	(120)	140	(16.0)	2470 (2)
YB ₇₀	(0.20)	(130)	134	(16.0)	2270 (2)
LaB ₄	(0.20)	(50)	137	(22.0)	2070 (2)
LaB ₆	0.200 ^d	~72 ^d	139	(22.0)	2800 (2)
CeB ₄	(0.20)	(50)	137	(30.0)	(2400)
CeB ₆	0.226 ^d	~72 ^d	139	(30.0)	2510 (2)
PrB ₄	(0.20)	(50)	133	(20.0)	(2600)
PrB ₆	0.230 ^d	~72 ^d	136	(20.0)	(2700)
NdB ₄	(0.20)	(50)	132	(21.6)	(2800)
NdB ₆	0.220 ^d	~72 ^d	136	(21.6)	2810 (2)
SmB ₄	(0.20)	(50)	126	(11.6)	(2800)
SmB ₆	0.200 ^d	~72 ^d	131	(11.6)	2740 (2)
EuB ₆	0.201 ^d	~72 ^d	130	(5.6)	(2520)
Gd ₂ B ₂	(0.24)	(30)	130	(9.0)	2740 (2)
Gd ₄ B ₄	(0.20)	(50)	135	(21.6)	(2800)
Gd ₆ B ₆	0.268 ^d	~72 ^d	138	(21.6)	(2800)
Gd ₁₀₀ B ₁₀₀	(0.20)	(130)	134	(21.6)	(2270)
Tb ₂ B ₂	0.239 ^d	(30)	130	(8.3)	(2200)

Table 5 (continued).

Boride	C, ^b cal/g-atom-°K ^{1.4}	-ΔH _{f,298} , ^c kcal/mole	ΔE _a , kcal/g-atom	γ _e , cal/mole-°K ² × 10 ⁻⁴	T _m , °K
TbB ₄	(0.20)	(50)	135	(20.0)	(2800)
TbB ₆	(0.20)	~72 ^d	144	(20.0)	(2800)
TbB ₁₂	(0.20)	(120)	139	(20.0)	(2500)
YbB ₄	(0.20)	(50)	124	(2.8)	(2800)
YbB ₆	0.170 ^d	~72 ^d	130	(2.8)	(2800)
YbB ₁₂	(0.20)	(120)	135	(2.8)	(2500)
YbB ₁₀₀	(0.20)	(130)	133	(2.8)	(2270)
LuB ₂	(0.24)	(30)	133	(9.0)	(2500)
LuB ₄	(0.20)	(50)	137	(21.5)	(3000)
LuB ₆	(0.20)	(72)	139	(21.5)	(3000)
LuB ₁₂	(0.20)	(120)	140	(21.5)	(2500)
B ₄ C	0.168 ^d	14.0 (9)	144	(0.03)	2730 (2)
SiB ₄	(0.20)	(15)	131	(0.0)	2120 (2)
SiB ₆	0.148 ^d	~20 ^d	132	(0.0)	2220 (2)
TiB	0.191 ^e	38.3 (17)	142	(4.1)	2460 (3)
TiB ₂	0.240 ^d	66.8 (8)	148	2.3 (32)	3498 (3)
ZrB ₂	0.237 ^d	73.0 (8)	162	1.7 (39)	3520 (3)
ZrB ₁₂	(0.20)	(120)	143	(8.4)	2520 (3)
HfB	(0.24)	(45)	163	(2.9)	2370 (3)
HfB ₂	0.242 ^d	80.0 (8)	165	1.8 (41)	3653 (3)
ThB ₄	0.209 ^d	52 ^d	144	(13.4)	(2800)
ThB ₆	0.250 ^d	54.5 ^d	144	(13.4)	2470 (2)
V ₃ B ₂	0.209 ^d	~73 (54)	142	(6.0)	2170 (3)
VB	(0.24)	33.1 (54)	144	(5.0)	2840 (3)
V ₅ B ₆	(0.24)	182.5 (54)	145	(4.5)	(2850)
V ₃ B ₄	0.206 ^e	116.3 (54)	145	(4.3)	2880 (3)
V ₂ B ₃	(0.24)	82.5 (54)	145	(4.0)	(2950)
VB ₂	0.189 ^e	48.7 (54)	146	(3.3)	3020 (3)
Nb ₃ B ₂	0.209 ^e	(70)	171	(5.4)	2350 (3)
NbB	0.213 ^e	(30)	168	(4.5)	3190 (3)
Nb ₃ B ₄	0.209 ^e	(104)	165	(3.9)	3210 (3)
NbB ₂	0.248 ^d	41.9 (8)	160	5.8 (42)	3310 (3)
Ta ₂ B	(0.24)	(38)	182	(5.3)	2690 (3)
Ta ₃ B ₂	0.190 ^e	(73)	180	(4.8)	2450 (3)
TaB	0.179 ^e	(33)	176	(4.0)	3360 (3)
Ta ₃ B ₄	0.173 ^e	(120)	173	(3.4)	3300 (3)
TaB ₂	0.200 ^e	50.0 (8)	168	4.7 (32)	3310 (3)

Table 5 (continued).

Boride	C, ^b cal/g-atom-°K ^{1.4}	-ΔH _{f,298} ^c kcal/mole	ΔE _a ^c kcal/g-atom	γ _e ^c cal/mole-°K ² × 10 ⁻⁴	T _m ^c °K
Cr ₄ B	0.284 ^e	(30)	109	(3.0)	1960 (2)
Cr ₂ B	0.272 ^e	(27)	117	(2.5)	2070 (2)
Cr ₅ B ₃	(0.24)	(75)	119	(2.4)	2160 (2)
CrB	0.283 ^e	(20)	124	(1.9)	2310 (2)
Cr ₃ B ₄	0.263 ^e	(75)	127	(1.6)	2200 (2)
CrB ₂	0.218 ^e	(33)	131	(1.3)	2450 (2)
CrB ₆	(0.20)	(60)	136	(4.6)	(2400)
Mo ₂ B	0.200 ^e	25.5 (6)	158	(3.3)	2550 (3)
MoB	0.203 ^e	16.3 (6)	153	(2.5)	2870 (3)
MoB ₂	0.289 ^e	23 (6)	149	(1.7)	2650 (3)
Mo ₂ B ₅	0.206 ^e	50 (6)	147	(1.7)	2410 (3)
MoB ₄	(0.20)	(30)	144	(6.0)	2070 (3)
W ₂ B	0.203 ^e	23 (6)	188	(1.8)	2940 (3)
WB	0.219 ^d	~17 ^d	177	(1.4)	2940 (3)
W ₂ B ₅	0.194 ^e	~35 (6)	158	(1.4)	2640 (3)
WB ₄	(0.20)	(25)	152	(3.2)	2290 (3)
UB ₂	(0.24)	39.3 (38)	144	22.5 (38)	2660 (2)
UB ₄	(0.20)	63 ^f	144	(29.5)	2770 (2)
UB ₁₂	(0.20)	136 ^f	143	(29.5)	2510 (2)
PuB	(0.24)	(30)	124	(12.5)	2320 (2)
PuB ₂	(0.24)	(40)	130	(8.3)	2100 (2)
PuB ₄	(0.20)	(55)	134	(30)	2320 (2)
PuB ₆	(0.20)	(60)	135	(30)	2370 (2)

^aEstimated values are given in parentheses in the number columns. Numbers in parentheses to the sides of the columns indicate References.

^bC is a parameter that is related to the thermal expansivity by, $\alpha = C \Delta E_a^{-1} T^{6.4}$. Values of C are derived from existing data given in Table 1, or from hardness values using Eq. (11). Estimates of C are based on Eqs. (8) and (10).

^cEstimated ΔH_{f,293} values are based on trends in the periodic table.

^dSee Table 1.

^eBased on hardness values given by Samsonov.⁴

^fDifferences in free energies of formation of UB₂-UB₄ and UB₄-UB₁₂ were obtained from Alcock and Grievson.⁵⁵ It was assumed that these differences were equivalent to differences in ΔH_{f,298}, and were combined with the ΔH_{f,298} of UB₂ (Ref. 38) to obtain the values for UB₄ and UB₁₂ given in the table.

Table 6. Energy level assignments for lanthanide and actinide ions.^a

Ion	g_i	E_i, cm^{-1}	Ion	g_i	E_i, cm^{-1}
Ce ⁺³ (45)	(2)	(0)	Eu ⁺² (56)	(2)	(0)
	(4)	(60)		(4)	(60)
	(8)	2248		(2)	(180)
Pr ⁺³ (45)	(2)	(0)	Gd ⁺³ (56)	(2)	(0)
	(4)	(60)		(4)	(60)
	(3)	(180)		(2)	(180)
	11	2120	Tb ⁺³ (45)	(2)	(0)
	13	4237		(4)	(60)
	5	4860		(7)	(180)
	7	6250		11	2075
	9	6694		9	3370
	9	6731		7	4332
Nd ⁺³ (45)	(2)	(0)		5	5010
	(4)	(60)		3	5490
	(4)	(180)		1	5714
	12	1931	U ⁺⁴ ^b (56)	(1)	(0)
	14	3905		(2)	(120)
	16	5984		(3)	(360)
	4	11376			
	6	12409	Pu ⁺⁴ ^b (56)	(1)	(0)
	10	12514		(2)	(120)
	8	13406		(4)	(360)
	4	13414			
	10	14653			
Sm ⁺³ (45)	(2)	(0)			
	(4)	(60)			
	8	1072			
	10	2277			
	12	3586			
	14	4957			
	2	5731			
	4	6340			
	16	6640			
	6	7104			
	8	7937			
	10	9106			
	12	10530			

^a Estimated values are given in parentheses in the number columns. Numbers in parentheses to the sides of the columns indicate References.

^b For U⁺⁴, the ground state is ³H₄, 2S + 1 = 3, 2J + 1 = 9, and the multiplicity is assumed to be 1/2(2S + 1 + 2J + 1) = 6. For Pu⁺⁴, the ground state is ⁵I₄, 2S + 1 = 5, 2J + 1 = 9, and the multiplicity is taken to be 7.

Table 7. A comparison of calculated and experimental entropies and heat capacities of borides.^a

Boride	S_{298}° cal/g-atom-°K		C_p , cal/g-atom-°K, at various temperatures					
			298°K		1000°K		2000°K	
	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.
MgB ₂	2.63	2.87 (17)	3.71	3.81 (17)				
MgB ₄	2.19	2.48 (17)	3.41	3.36 (17)				
LaB ₆	2.73	2.84 (47)	3.47	3.31 (47)	6.13	6.02 (12)		
NdB ₆	3.34	3.53 (47)	3.50	3.38 (47)	6.41	6.46 (57)		
B ₄ C	1.24	1.30 (17)	2.45	2.54 (17)	5.37	5.46 (17)	6.39	6.70 (17)
TiB ₂	2.45	2.27 (33)	3.64	3.53 (33)	5.96	6.00 (33)	6.79	7.08 (33)
ZrB ₂	3.05	2.86 (17)	3.80	3.84 (17)	5.93	5.75 (17)	6.62	6.56 (17)
HfB ₂	3.44	3.41 (33)	3.87	3.96 (33)	5.94	6.41 (33)		
NbB ₂	2.88	3.05 (8)	3.80	3.83 (8)	6.08	6.54 (8)		
TaB ₂	3.27	3.28 (32)	3.86	3.82 (32)	6.01	6.12 (8)		
UB ₂	4.97	4.42 (38)	4.38	4.44 (38)	6.70	7.10 (58)		

^aReference numbers are given in parentheses.

Table 8. The enthalpy of melting and the heat capacities of solid and liquid borides.

Boride	T _m , °K	ΔH° of fusion, cal/ g-atom	C _p , cal/g-atom-°K, at various temperatures in °K							
			298	500	1000	1500	2000	2500	3000	Liquid
Be ₄ B	1430	3289	1.793	3.618	5.525	6.419	6.419	6.419	6.419	6.419
Be ₂ B	1790	4117	1.969	3.779	5.552	6.413	7.253	7.253	7.253	7.253
BeB ₂	2250	5175	2.480	4.188	5.657	6.229	7.153	8.112	8.112	8.112
BeB ₆	2340	8792	2.760	4.417	5.700	6.152	6.782	7.819	7.819	7.819
BeB ₁₂	2000	7738	2.358	4.500	5.730	6.159	6.749	6.749	6.749	6.749
MgB ₂	1300	2990	3.706	5.018	6.007	6.300	6.300	6.300	6.300	6.300
MgB ₄	1400	5124	3.410	4.643	5.889	6.237	6.237	6.237	6.237	6.237
MgB ₆	1420	5335	3.265	4.773	5.852	6.209	6.209	6.209	6.209	6.209
CaB ₆	2510	9430	3.349	4.803	5.865	6.270	6.906	8.757	8.813	8.813
SrB ₆	2510	9430	3.396	4.825	5.883	6.284	6.938	8.798	8.854	8.854
BaB ₆	2540	9543	3.403	4.823	5.872	6.276	6.900	8.711	8.835	8.835
AlB ₂	1250	2875	3.585	4.958	5.964	6.194	6.194	6.194	6.194	6.194
AlB ₁₂	2450	9480	3.113	4.673	5.780	6.159	6.887	8.052	8.052	8.052
ScB ₂	2520	5796	3.773	5.120	6.193	6.715	7.508	9.552	9.872	9.872
ScB ₄	3000	10980	3.514	5.005	6.186	6.720	7.429	9.240	12.977	12.977
ScB ₁₂	2500	9673	3.182	4.757	5.936	6.394	6.981	8.500	8.500	8.500
YB ₂	2370	5451	3.913	5.156	6.156	6.637	7.351	8.576	8.576	8.576
YB ₄	3070	11236	3.589	5.017	6.160	6.879	7.345	8.041	12.626	12.626
YB ₆	2870	10783	3.412	4.694	6.038	6.514	7.108	8.678	11.009	11.009
YB ₁₂	2470	9557	3.209	4.757	5.910	6.350	6.689	8.243	8.243	8.243
YB ₇₀	2270	9026	3.016	4.628	5.785	6.210	6.785	7.487	7.487	7.487
LaB ₂	2070	7576	3.673	5.095	6.284	6.861	7.586	7.746	7.746	7.746
LaB ₅	2800	10520	3.472	4.952	6.132	6.654	7.295	8.913	10.744	10.744
CeB ₄	2400	8784	3.733	5.216	6.645	7.313	8.075	9.378	9.378	9.378
CeB ₆	2510	9430	3.518	5.044	6.410	7.014	7.699	8.356	9.416	9.416
PrB ₄	2600	9516	3.703	5.213	6.780	7.284	7.908	9.710	10.294	10.294
PrB ₆	2700	10144	3.496	5.044	6.516	6.899	7.588	9.262	10.446	10.446
NdB ₄	2800	10248	3.716	5.177	6.648	7.446	8.238	10.084	12.121	12.121
NdB ₆	2800	10558	3.505	5.015	6.406	7.097	7.787	9.461	11.426	11.426
SmB ₄	2800	10248	3.716	5.367	6.887	7.146	7.744	9.764	11.954	11.954
SmB ₆	2740	10295	3.503	5.146	6.562	6.854	7.389	9.176	10.726	10.726
EuB ₆	2520	9468	3.440	4.854	5.917	6.342	7.002	8.676	8.990	8.990
GdB ₂	2200	5060	4.049	5.239	6.248	6.767	7.552	8.152	8.152	8.152
GdB ₄	2800	10248	3.690	5.100	6.282	6.857	7.607	9.438	11.431	11.431
GdB ₆	2800	10520	3.490	4.972	6.183	6.747	7.448	9.136	11.431	11.431
GdB ₁₀₀	2270	9042	3.008	4.623	5.792	6.208	6.782	7.484	7.484	7.484
TbB ₂	2200	5060	4.081	5.379	6.729	7.238	7.910	8.465	8.465	8.465
TbB ₄	2800	10248	3.704	5.175	6.553	7.114	7.787	9.546	11.502	11.502
TbB ₆	2810	10520	3.494	5.005	6.314	6.813	7.340	8.727	10.375	10.375
TbB ₁₂	2500	9673	3.253	4.818	6.062	6.518	7.061	8.580	8.580	8.580
YbB ₄	2690	10248	3.583	4.919	5.925	6.345	7.110	8.261	11.511	11.511
YbB ₆	2800	10520	3.405	4.817	5.849	6.224	6.851	8.679	10.706	10.706
YbB ₁₂	2500	9573	3.206	4.719	5.819	6.217	6.771	8.402	8.402	8.402
YbB ₁₀₀	2270	9042	3.003	4.615	5.775	6.184	6.765	7.481	7.481	7.481
LuB ₂	2500	5750	3.993	5.215	6.236	6.750	7.484	9.362	9.362	9.362

Table 8 (continued).

Boride	T _m , °K	ΔH° of fusion, cal/g-atom	C _p , cal/g-atom-°K, at various temperatures in °K							
			298	500	1000	1500	2000	2500	3000	Liquid
LaB ₄	3000	10980	3.656	5.085	6.273	6.845	7.566	9.315	12.957	12.957
LaB ₆	3000	11271	3.460	4.944	6.124	6.643	7.281	8.895	12.369	12.369
LaB ₁₂	2500	9673	3.235	4.783	5.954	6.414	6.974	8.483	8.483	8.483
B ₄ C	2730	10909	2.452	3.957	5.366	5.896	6.389	7.695	8.844	8.844
SiB ₄	2120	8472	3.054	4.651	5.789	6.194	6.805	7.087	7.087	7.087
SiB ₆	2220	8874	3.026	4.623	5.740	6.111	6.666	7.213	7.213	7.213
TiB	2460	5658	3.997	5.207	6.110	6.514	7.040	8.306	8.306	8.306
TiB ₂	3488	8045	3.640	4.981	5.856	6.344	6.791	8.012	10.941	15.028
ZrB ₂	3520	8086	3.805	5.035	5.934	6.281	6.619	7.471	9.745	14.417
ZrB ₁₂	2520	9750	3.179	4.722	5.846	6.252	6.728	8.081	8.168	8.168
HfB	2370	5451	4.336	5.323	6.095	6.448	6.813	7.363	7.363	7.363
HfB ₂	3653	8402	3.870	5.061	5.943	6.288	6.615	7.412	9.568	15.675
ThB ₄	2800	10248	3.617	5.006	6.108	6.591	7.155	8.578	10.244	10.244
ThB ₆	2470	9280	3.436	4.899	6.039	6.521	7.079	8.369	8.369	8.369
V ₃ B ₂	2170	4891	4.087	5.325	6.291	6.778	7.391	7.757	7.757	7.757
VB	2840	6532	3.889	5.185	6.173	6.635	7.199	8.631	10.585	10.585
V ₅ B ₆	2850	6555	3.799	5.120	6.113	6.557	7.091	8.469	10.444	10.444
V ₃ B ₄	2880	6824	3.745	5.078	6.060	6.478	6.979	8.321	10.486	10.486
V ₂ B ₃	2950	6785	3.694	5.048	6.053	6.483	6.998	8.354	11.066	11.066
VB ₂	3020	6946	3.562	4.949	5.945	6.328	6.776	8.039	11.043	11.208
Nb ₃ B ₂	2350	5405	4.449	5.454	6.282	6.672	7.072	7.543	7.543	7.543
NbB	3190	7337	4.189	5.289	6.134	6.517	6.888	7.689	9.786	11.109
Nb ₃ B ₄	3210	7383	4.007	5.176	6.051	6.420	6.777	7.603	9.787	11.317
NbB ₂	3310	7613	3.799	5.087	6.075	6.502	6.926	7.898	10.334	12.918
Ta ₂ B	2690	6187	4.776	5.615	6.340	6.749	7.143	7.816	8.287	8.287
Ta ₃ B ₂	2450	5635	4.583	5.487	6.221	6.588	6.931	7.472	7.472	7.472
TaB	3360	7728	4.301	5.315	6.092	6.432	6.743	7.384	9.155	11.652
Ta ₃ B ₄	3500	7590	4.102	5.186	6.009	6.336	6.630	7.286	9.131	11.192
TaB ₂	3310	7613	3.865	5.088	6.006	6.376	6.715	7.478	9.533	11.841
Cr ₄ B	1960	4508	4.029	5.319	6.319	6.939	8.149	8.149	8.149	8.149
Cr ₂ B	2070	4761	3.841	5.177	6.179	6.709	7.762	8.017	8.017	8.017
Cr ₅ B ₃	2160	4968	3.781	5.128	6.119	6.610	7.571	8.161	8.161	8.161
CrB	2310	5313	3.616	5.022	6.082	6.547	7.394	8.560	8.560	8.560
Cr ₃ B ₄	2220	5106	3.519	4.951	5.995	6.450	7.204	7.891	7.891	7.891
CrB ₂	2450	5635	3.391	4.857	5.903	6.313	6.948	8.509	8.509	8.509
CrB ₆	2400	9017	3.165	4.729	5.861	6.279	6.841	7.998	7.998	7.998
Mo ₂ B	2550	5865	4.241	5.345	6.153	6.526	6.929	7.918	8.285	8.085
MoB	2870	6601	3.913	5.139	6.016	6.376	6.774	7.847	9.631	9.631
MoB ₂	2650	6085	3.598	4.964	5.965	6.373	6.835	8.053	8.712	8.712
Mo ₂ B ₅	2410	5543	3.503	4.896	5.888	6.251	6.673	7.566	7.566	7.566
MoB ₄	2070	7576	3.369	4.846	5.832	6.347	6.834	6.948	6.948	6.948
W ₂ B	2940	6762	4.439	5.363	6.051	6.396	6.587	7.081	8.196	8.196
WB	2940	6782	4.068	5.179	5.964	6.271	6.540	7.129	8.535	8.535
W ₂ B ₅	2840	6072	3.597	4.926	5.866	6.200	6.529	7.434	7.917	7.917
WB ₄	2290	8381	3.421	4.846	5.873	6.244	6.633	7.112	7.112	7.112

Table 8 (continued).

Boride	T _m , °K	ΔH° of fusion, cal/ g-atom	C _p , cal/g-atom-°K, at various temperatures in °K							
			298	500	1000	1500	2000	2500	3000	Liquid
UB ₂	2660	6118	4.375	5.540	6.695	7.394	8.204	9.884	10.766	10.786
UB ₄	2770	10138	3.853	5.226	6.440	7.069	7.784	9.360	10.909	10.909
UB ₁₂	2510	9712	3.310	4.837	6.018	6.500	7.055	8.489	8.533	8.533
PuB	2320	5336	5.001	5.792	6.694	7.338	8.388	9.740	9.740	9.740
PuB ₂	2100	4830	4.283	5.325	6.249	6.743	7.511	7.779	7.779	7.779
PuB ₄	2320	8491	3.885	5.244	6.466	7.120	7.965	9.024	9.024	9.024
PuB ₆	2370	8904	3.624	5.059	6.265	6.845	7.596	8.790	8.790	8.790

Table 9. The room temperature entropy and free energy functions of solid and liquid borides.

Boride	S_{298}° cal/g-atom-°K	$-(F_T^{\circ} - H_{298}^{\circ})/T$, cal/g-atom-°K, at various temperatures in °K								
		500	1000	1500	2000	2500	3000	3500	4000	T_m
Be ₃ B	0.775	1.049	2.454	3.964	5.751	7.148	8.295	9.268	10.112	3.669
Be ₂ B	0.898	1.194	2.659	4.086	5.588	7.122	8.388	9.465	10.403	4.834
BeB ₂	1.208	1.560	3.178	4.679	5.959	7.320	8.692	9.865	10.891	6.537
BeB ₆	1.386	1.769	3.473	5.013	6.305	7.567	9.261	10.586	11.721	7.080
BeB ₁₂	1.448	1.842	3.577	5.134	6.435	8.327	9.814	11.038	12.077	6.435
MgB ₂	2.631	3.108	5.056	7.047	8.925	10.370	11.544	12.534	13.389	6.106
MgB ₄	2.187	2.635	4.510	6.390	8.593	10.230	11.531	12.699	13.529	5.843
MgB ₆	1.996	2.433	4.278	6.098	8.324	9.974	11.283	12.766	13.289	5.658
CaB ₆	2.254	2.696	4.554	6.179	7.524	8.682	10.351	11.766	12.984	8.704
SrB ₆	2.664	3.110	4.979	6.610	7.950	9.123	10.797	12.215	13.438	9.145
BaB ₆	2.870	3.316	5.184	6.814	8.161	9.320	10.954	12.378	13.606	9.408
AlB ₂	2.321	2.787	4.709	6.760	8.601	10.019	11.172	12.144	12.984	5.583
AlB ₁₂	1.707	2.127	3.930	5.521	6.838	8.047	9.698	11.069	12.247	7.862
ScB ₂	2.708	3.194	5.184	6.910	8.342	9.584	11.090	12.410	13.573	9.631
ScB ₄	2.288	2.760	4.701	6.408	7.830	9.062	10.195	11.822	13.275	10.195
ScB ₁₂	1.820	2.248	4.086	5.715	7.071	8.230	9.898	11.355	12.571	8.239
YB ₂	3.401	3.898	5.905	7.631	9.057	10.407	11.876	13.130	14.224	9.980
YB ₄	2.702	3.170	5.118	6.822	8.241	9.465	10.587	12.131	13.592	10.741
YB ₆	2.364	2.814	4.710	6.377	7.762	8.954	10.206	11.756	13.116	9.765
YB ₁₂	1.975	2.405	4.243	5.868	7.218	8.425	10.106	11.504	12.700	8.313
YB ₇₀	1.604	2.015	3.800	5.386	6.705	8.209	9.820	11.150	12.281	7.336
LaB ₄	3.215	3.692	5.673	7.409	8.859	10.739	12.339	13.667	14.801	9.044
LaB ₆	2.731	3.188	5.108	6.798	8.207	9.422	10.785	12.336	13.692	10.097
CeB ₄	4.024	4.509	6.545	8.358	9.883	11.355	13.135	14.631	15.921	10.954
CeB ₆	3.309	3.772	5.735	7.484	8.951	10.223	11.990	13.488	14.781	10.247
PrB ₄	4.037	4.519	6.562	8.397	9.932	11.255	12.948	14.508	15.862	11.504
PrB ₆	3.319	3.779	5.748	7.513	8.989	10.261	11.795	13.356	14.714	10.733
NdB ₄	4.063	4.545	6.567	8.375	9.908	11.246	12.724	14.381	15.841	11.993
NdB ₆	3.337	3.798	5.749	7.494	8.966	10.244	11.655	13.267	14.680	10.978
SmB ₄	3.889	4.377	6.474	8.345	9.888	11.209	12.664	14.301	15.743	11.942
SmB ₆	3.212	3.677	5.680	7.466	8.941	10.203	11.679	13.248	14.616	10.764
EuB ₆	3.531	3.981	5.862	7.503	8.962	10.034	11.704	13.134	14.368	10.078
GdB ₂	5.315	5.824	7.867	9.622	11.073	12.603	14.050	15.279	16.346	11.592
GdB ₄	3.870	4.348	6.331	8.068	9.517	10.774	12.174	13.760	15.154	11.474
GdB ₆	3.201	3.659	5.589	7.290	8.712	9.944	11.325	12.897	14.273	10.629
GdB ₁₀₀	1.637	2.047	3.830	5.415	6.734	8.237	9.849	11.179	12.311	7.365
TbB ₂	5.568	6.084	8.193	10.045	11.584	13.186	14.691	15.969	17.080	12.134
TbB ₄	4.017	4.498	6.516	8.308	9.806	11.101	12.531	14.140	15.553	11.820
TbB ₆	3.303	3.762	5.708	7.436	8.876	10.113	11.484	13.032	14.379	10.794
TbB ₁₂	2.480	2.915	4.781	6.440	7.821	9.008	10.724	12.155	13.392	9.008
YbB ₄	3.582	4.045	5.953	7.607	9.072	10.154	11.499	13.046	14.413	10.818
YbB ₆	2.991	3.438	5.303	6.928	8.270	9.423	10.737	12.252	13.579	10.066
YbB ₁₂	2.313	2.741	4.564	6.169	7.498	8.641	10.319	11.720	12.920	8.641
YbB ₁₀₀	1.622	2.032	3.811	5.292	6.707	8.208	9.817	11.146	12.276	7.336
LuB ₂	3.919	4.423	6.455	8.204	9.651	10.899	12.418	13.727	14.876	10.899

Table 9 (continued).

Boride	S_{298}° , cal/g-atom-K	$-(F_T^{\circ} - H_{298}^{\circ})/T$, cal/g-atom-K, at various temperatures in °K								T_m
		500	1000	1500	2000	2500	3000	3500	4000	
LuB ₄	3.032	3.507	5.483	7.216	8.663	9.915	11.065	12.704	14.165	11.065
LuB ₆	2.600	3.055	4.972	6.660	8.067	9.280	10.391	12.002	13.432	10.391
LuB ₁₂	2.101	2.534	4.384	6.020	7.381	8.552	10.253	11.672	12.987	8.552
B ₄ C	1.241	1.581	3.118	4.542	5.752	6.802	8.122	9.539	10.760	7.251
SiB ₄	1.592	2.008	3.801	5.390	6.709	8.453	10.013	11.297	12.387	6.996
SiB ₆	1.570	1.982	3.764	5.341	6.647	8.218	9.801	11.104	12.211	7.159
TiB	2.941	3.447	5.472	7.198	8.614	9.858	11.313	12.551	13.628	9.729
TiB ₂	2.450	2.921	4.853	6.520	7.891	9.058	10.108	11.122	12.442	11.117
ZrB ₂	3.051	3.536	5.492	7.164	8.532	9.688	10.712	11.679	12.922	11.717
ZrB ₁₂	1.888	2.315	4.139	5.748	7.082	8.225	9.870	11.263	12.454	8.268
HfB	4.413	4.947	7.025	8.768	10.186	11.502	12.910	14.092	15.110	11.037
HfB ₂	3.437	3.928	5.895	7.573	8.945	10.103	11.126	12.088	13.254	12.381
ThB ₄	3.113	3.582	5.526	7.221	8.627	9.834	11.173	12.685	14.005	10.458
ThB ₆	2.659	3.111	5.010	6.677	8.063	9.299	10.987	12.392	13.596	9.186
V ₃ B ₂	2.914	3.432	5.505	7.278	8.738	10.293	11.720	12.926	13.969	9.182
VB	2.668	3.166	5.181	6.913	8.342	9.564	10.754	12.147	13.351	10.324
V ₅ B ₆	2.557	3.045	5.034	6.747	8.159	9.366	10.573	11.912	13.103	10.137
V ₃ B ₄	2.494	2.977	4.948	6.646	8.043	9.237	10.408	11.738	12.925	10.081
V ₂ B ₃	2.427	2.905	4.863	6.555	7.951	9.143	10.260	11.609	12.819	10.116
VB ₂	2.267	2.731	4.649	6.309	7.675	8.838	9.887	11.204	12.405	9.927
Nb ₃ B ₂	3.963	4.512	6.642	8.432	9.891	11.263	12.700	13.906	14.946	10.773
NbB	3.543	4.066	6.127	7.871	9.294	10.497	11.559	12.755	13.961	11.841
Nb ₃ B ₄	3.246	3.751	5.766	7.478	8.878	10.061	11.107	12.280	13.483	11.524
NbB ₂	2.883	3.369	5.346	7.049	8.450	9.642	10.704	11.837	13.094	11.331
Ta ₂ B	5.032	5.610	7.819	9.637	11.122	12.374	13.710	14.988	16.095	12.806
Ta ₃ B ₂	4.670	5.229	7.375	9.164	10.616	11.884	13.324	14.631	15.570	11.723
TaB	4.133	4.664	6.738	8.479	9.894	11.085	12.128	13.187	14.393	12.827
Ta ₃ B ₄	3.752	4.264	6.288	7.997	9.389	10.559	11.586	12.672	13.857	12.163
TaB ₂	3.269	3.760	5.738	7.430	8.816	9.987	11.021	12.115	13.324	11.625
Cr ₄ B	2.660	3.173	5.242	7.018	8.544	10.285	11.720	12.940	14.000	8.387
Cr ₂ B	2.459	2.953	4.963	6.695	8.132	9.777	11.197	12.403	13.451	8.316
Cr ₅ B ₃	2.397	2.885	4.875	6.590	8.009	9.556	10.984	12.200	13.258	8.419
CrB	2.216	2.687	4.634	6.323	7.724	9.116	10.567	11.809	12.894	8.493
Cr ₃ B ₄	2.112	2.573	4.491	6.158	7.540	8.992	10.395	11.585	12.619	8.083
CrB ₂	1.976	2.424	4.303	5.942	7.297	8.510	9.942	11.169	12.241	8.352
CrB ₆	1.729	2.155	3.981	5.595	6.932	8.234	9.868	11.226	12.388	7.863
Mo ₂ B	3.205	3.735	5.817	7.571	9.001	10.210	11.624	12.860	13.932	10.322
MoB	2.772	3.270	5.266	6.967	8.357	9.535	10.686	11.979	13.121	10.321
MoB ₂	2.350	2.817	4.742	6.407	7.780	8.950	10.269	11.518	12.611	9.275
Mo ₂ B ₅	2.229	2.687	4.582	6.225	7.575	8.808	10.196	11.368	12.382	8.529
MoB ₄	2.042	2.487	4.363	6.005	7.364	9.153	10.665	11.912	12.971	7.536
W ₂ B	3.805	4.350	6.451	8.196	9.605	10.783	11.854	13.100	14.182	11.690
WB	3.229	3.739	5.754	7.453	8.834	9.993	11.053	12.300	13.388	10.891
W ₂ B ₅	2.496	2.962	4.871	6.515	7.862	9.002	10.287	11.487	12.529	9.295
WB ₄	2.214	2.664	4.539	6.172	7.517	8.969	10.530	11.814	12.905	8.200

Table 9 (continued).

Boride	S_{298}° cal/g- atom-°K	$-(F_T^{\circ} - H_{298}^{\circ})/T$, cal/g-atom-°K, at various temperatures in °K								T_m
		500	1000	1500	2000	2500	3000	3500	4000	
UB ₂	4.973	5.518	7.687	9.559	11.120	12.473	13.966	15.395	16.662	12.877
UB ₄	3.632	4.127	6.163	7.945	9.433	10.722	12.177	13.760	15.142	11.365
UB ₁₂	2.332	2.773	4.645	6.300	7.677	8.862	10.561	11.990	13.214	8.884
PuB	6.877	7.477	9.756	11.669	13.248	14.788	16.385	17.759	18.964	14.143
PuB ₂	5.050	5.579	7.661	9.430	10.887	12.507	13.926	15.125	16.164	11.151
PuB ₄	5.765	4.262	6.306	8.095	9.593	11.160	12.897	14.353	15.607	10.443
PuB ₆	3.123	3.595	5.561	7.289	8.733	10.182	11.903	13.343	14.580	9.673

Table 10. Enthalpy increments for solid and liquid borides.

Boride	$H_{298}^{\circ} - H_0^{\circ}$ cal/ g-atom	$H_T^{\circ} - H_{298}^{\circ}$ cal/g-atom, at various temperatures in °K								T_m (°K)
		500	1000	1500	2000	2500	3000	3500	4000	
Be_3B	166	560	2942	9273	12483	15693	18902	22112	25322	5535
Be_2B	191	598	3024	6010	13656	17283	20910	24536	28163	8016
BeB_2	254	693	3238	6217	9523	18665	22721	26777	30833	11462
BeB_6	290	747	3354	6325	9533	22076	25986	29895	33805	12034
BeB_{12}	302	766	3399	6360	9616	20729	24103	27477	30852	9616
MgB_2	495	901	3712	9840	12990	16140	19291	22441	25591	5590
MgB_4	424	855	3600	11807	14925	18044	21163	24281	27400	6059
MgB_6	393	836	3557	11957	15062	18166	21271	24375	27480	6125
CaB_6	424	845	3576	6615	9881	13725	27605	32012	36418	13857
SrB_6	461	851	3591	6640	9920	13783	27684	32111	36538	13915
BaB_6	474	851	3588	6631	9898	13729	27780	32248	36715	14127
AlB_2	452	884	3672	9647	12744	15841	18938	22034	25131	5224
AlB_{12}	348	810	3493	6485	9673	22865	26891	30917	34943	12983
ScB_2	506	918	3801	7032	10558	14750	25429	30265	35101	14990
ScB_4	440	882	3742	6975	10488	14588	20119	37587	44076	20119
ScB_{12}	364	825	3567	6658	9977	13823	27746	31996	36246	13823
YB_2	586	934	3813	7015	10486	20014	24302	28590	32878	13448
YB_4	487	889	3744	6960	10444	14476	19804	37732	44392	20778
YB_6	438	860	3657	6802	10188	14072	29848	35453	40857	17734
YB_{12}	382	827	3562	6635	9928	23278	27399	31520	35642	13473
YB_{70}	329	796	3473	6482	9707	22410	26153	29897	33640	11662
LaB_4	533	905	3809	7101	10682	22174	26047	29920	33793	11267
LaB_6	471	872	3706	6909	10377	14367	30019	35391	40762	17350
CeB_4	565	922	3950	7451	11277	24505	29194	33883	38572	14783
CeB_6	494	885	3814	7180	10839	15042	29228	33935	38643	15183
PrB_4	568	916	3996	7530	11302	15636	30320	35467	40614	16686
PrB_6	498	881	3848	7240	10864	15009	30305	35528	40751	17027
NdB_4	571	916	3927	7465	11367	15882	31927	37988	44048	18255
NdB_6	499	880	3795	7184	10888	15135	31137	36850	42563	18409
SmB_4	551	935	4100	7618	11303	15602	31539	37516	43493	18900
SmB_6	484	893	3913	7277	10808	14876	30391	35754	41117	17308
EuB_6	503	858	3613	6683	9991	13888	27895	32390	36885	14112
GdB_2	693	954	3875	7132	10683	19796	23871	27947	32023	12290
GdB_4	554	907	3811	7102	10685	14889	30582	36308	42023	18058
GdB_6	486	875	3726	6965	10493	14581	30378	35804	41430	17648
GdB_{100}	328	794	3471	6478	9702	22419	26161	29903	33645	11656
TbB_2	720	969	4060	7564	11323	20598	24631	29063	33296	12999
TbB_4	569	914	3914	7342	11045	15311	31055	36806	42557	18506
TbB_6	497	878	3777	7070	10593	14553	30046	35234	40422	17451
TbB_{12}	414	837	3628	6782	10158	14048	28011	32301	36591	14048
YbB_4	546	878	3647	6718	10047	14083	29787	35523	41279	17217
YbB_6	481	851	3580	6607	9850	13661	29265	34617	39970	16603
YbB_{12}	405	822	3524	6541	9765	13534	27408	31609	35810	13534
YbB_{100}	328	793	3463	6460	9673	23386	26127	29867	33608	11624
LuB_2	635	947	3860	7110	10643	14833	25264	29845	34626	14833

Table 10 (continued).

Boride	$H_{298}^{\circ} - H_0^{\circ}$, cal/g-atom	$H_T^{\circ} - H_{298}^{\circ}$, cal/g-atom, at various temperatures in °K									T_m (°K)
		500	1000	1500	2000	2500	3000	3500	4000		
LuB ₄	519	903	3801	7087	10669	14825	20369	37827	44305	20369	
LuB ₆	461	870	3700	6899	10360	14342	19631	37087	43272	19631	
LuB ₁₂	394	832	3584	6684	10012	13853	27773	32014	26356	13853	
B ₄ C	259	665	3067	5896	8955	12420	27655	32077	36499	14358	
SiB ₄	330	802	3483	6485	9708	21741	25285	28829	32372	10575	
SiB ₆	326	796	3459	6429	9598	22049	25656	29253	32870	11156	
TiB	551	949	3827	6988	10358	19875	24028	28181	32334	13885	
TiB ₂	470	891	3682	6764	10034	13682	18334	33116	41130	25039	
ZrB ₂	546	911	3706	6766	9984	13468	17694	23579	38933	23937	
ZrB ₁₂	372	821	3531	6564	9793	13437	27311	31395	35479	13640	
HfB	725	990	3885	7025	10334	14388	23069	26751	30432	12980	
HfB ₂	587	920	3722	6786	10006	13476	17645	23406	39583	25742	
ThB ₄	522	890	3728	6910	10331	14207	29360	34482	39604	17063	
ThB ₆	463	863	3660	6807	10191	23348	27533	31717	35902	13817	
V ₃ B ₂	552	970	3922	7194	10718	19593	23472	27351	31229	12043	
VB	511	937	3828	7035	10478	14378	25896	31189	36482	17671	
V ₅ B ₈	492	921	3783	6937	10353	14187	25641	30884	38086	17520	
V ₃ B ₄	482	912	3752	6892	10241	14010	25481	30724	35967	17598	
V ₂ B ₃	470	904	3735	6875	10230	14012	25712	31245	36778	18373	
VB ₂	443	881	3664	6739	10000	13649	18333	30937	36541	18611	
Nb ₃ B ₂	695	1016	3983	7222	10653	19776	23547	27319	31091	13240	
NbB	630	974	3874	7042	10388	13999	18294	31109	38684	20329	
Nb ₃ B ₄	584	945	3801	6924	10216	13776	18048	30978	36636	20313	
NbB ₂	528	917	3761	6912	10262	13927	18405	32118	38577	22050	
Ta ₄ B ₂	828	1062	4081	7357	10827	14543	24868	29011	33155	16112	
Ta ₃ B ₂	775	1030	3993	7199	10576	19846	23583	27810	31055	13838	
TaB	697	983	3880	7016	10306	13811	17878	31005	36831	21846	
Ta ₃ B ₄	641	956	3803	6896	10133	13583	17617	30529	36125	20701	
TaB ₂	571	922	3748	6850	10118	13632	17811	31023	36943	21160	
Cr ₄ B	518	965	3922	7230	15531	19605	23680	27754	31828	10697	
Cr ₂ B	483	932	3823	7044	10617	18417	23425	27433	31442	11209	
Cr ₅ B ₃	472	922	3787	6969	10472	19511	23592	27672	31752	11769	
CrB	440	895	3722	6877	10327	19764	24044	28324	32605	12825	
Cr ₃ B ₄	422	878	3674	6789	10170	19180	23125	27071	31016	11864	
CrB ₂	398	856	3608	6668	9956	19486	23740	27994	32249	13425	
CrB ₃	353	821	3537	6570	9837	22630	26630	30629	34628	12813	
Mo ₂ B	599	986	3904	7078	10433	14102	24045	28088	32130	14542	
MoB	526	934	3773	6877	10153	13761	24863	29678	34494	17010	
MoB ₂	456	886	3676	6767	10056	13726	24169	28525	32881	15025	
Mo ₂ B ₅	436	870	3625	6666	9884	19037	22820	26603	30385	12813	
MoB ₄	404	832	3611	6688	9668	21048	24522	27996	31470	10485	
W ₂ B	681	1008	3903	7005	10234	13626	24240	28337	32435	16988	
WB	589	952	3764	6848	10048	13438	24157	28425	32893	16883	
W ₂ B ₅	472	881	3637	6661	9835	13284	23318	27277	31236	14396	
WB ₄	427	856	3598	6635	9844	21740	25295	28851	32407	11885	

Table 10 (continued).

Boride	$H_{298}^{\circ} - H_0^{\circ}$, cal/g-atom	$H_T^{\circ} - H_{298}^{\circ}$, cal/g-atom, at various temperatures in °K								
		500	1000	1500	2000	2500	3000	3500	4000	T_m (a)
UB ₂	762	1016	4118	7645	11528	15993	27474	32857	38240	17696
UB ₄	590	935	3907	7291	10988	15217	30342	36096	41551	17995
UB ₁₂	422	844	3625	6762	10134	13962	27983	32249	38516	14090
PuB	1000	1098	4247	7754	11650	21669	26539	31409	36279	14580
PuB ₂	766	984	3920	7171	10705	19450	23339	27229	31118	11508
PuB ₄	605	940	3922	7324	11071	23934	28446	32958	37470	13818
PuB ₆	523	898	3787	7071	10658	23755	28150	32545	36940	13708

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