7

Report No. CCC-1024-TR-231

STRUCTURES AND THERMODYNAMIC PROPERTIES
OF HIGH TEMPERATURE GASEOUS SPECIES
IN THE $B_2O_3-H_2O$ SYSTEM

UNIVERSITY OF WISCONSIN

March 14, 1957

Do Not
STAT

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STRUCTURES AND THERMODYNAMIC PROPERTIES
OF HIGH TEMPERATURE GASEOUS SPECIES
IN THE $B_2O_3-H_2O$ SYSTEM

by

J. L. Margrave

J. R. Soulen

G. E. Leroi

S. P. Randall

This document is
PUBLICLY RELEASABLE
Hugh Kinser H. Kinser
Authorizing Official
Date 10/28/06

UNIVERSITY OF WISCONSIN

Madison, Wisconsin

March 14, 1957

878 - 1

ABSTRACT

Vaporization of liquid boric oxide at high temperatures has been studied in inert and moist atmospheres to determine (1) the vapor pressure, heat of vaporization, and the boiling point of B_2O_3 ; (2) the molecular weight and structures of the major vapor species in oxidizing, reducing, and inert atmospheres, as well as in vacuum; (3) the formulas and stabilities of any gaseous hydroxide (hydrated oxide) species in the presence of water vapor; and (4) thermodynamic equilibrium constants describing this system.

In flow measurements, spectroscopic and photometric studies, the major species over B_2O_3 (l) in an inert or oxygen-rich atmosphere was found to be B_2O_3 (g).¹¹ Direct determinations and extrapolations of lower temperature work indicate a normal boiling point of $2400^\circ \pm 100^\circ K$ for boric oxide, and a heat of sublimation at $0^\circ K$ of 89 ± 1 kcal./mole. The structure of the gaseous pentatomic molecule is predicted to be a bipyramid of symmetry D_{3h} on the basis of visible and infrared spectral data.

When water is added to the flow gas, vaporization of B_2O_3 is greatly enhanced and is easily measurable at $500^\circ C$. From studies of weight loss as a function of water, partial pressure, and temperature, it appears that the reaction proceeds to produce gaseous H_3BO_3 and possibly some gaseous HBO_2 .

Thermodynamic properties and heats of formation may now be evaluated for BO (s and g), B_2O_2 (g), B_2O_3 (s, l, and g), H_3BO_3 (s and g), and HBO_2 (s and g), and equilibria calculated for B-H-O systems.

CONTENTS

ABSTRACT	Page i
INTRODUCTION	1
RESULTS AND DISCUSSION	1
REFERENCES	6

INTRODUCTION

A detailed understanding of the various equilibria involved in the vaporization of a liquid at high temperatures requires considerable experimental work, since little can be predicted about such processes on the basis of present theories.

In this work on vaporization of boric oxide, the known facts about the structures of the solid and the liquid compounds have been considered. The crystalline solid, on the basis of powder patterns only, has been described by a hexagonal unit cell with two sets of interconnected BO_4 tetrahedra.¹ In glassy B_2O_3 , there are apparently triangular BO_3 units and some BO_4 tetrahedra.² This structure tends to break up in the liquid as the temperature rises, yet the liquid is extremely viscous.³ X-ray diffraction, infrared and Raman spectra of boric oxide have not yet been interpreted fully to describe all the known properties of the solid, glass, and liquid.⁴ The viscosity³ and surface tension⁵ of the liquid and the dielectric constant⁶ of solid and liquid have also been measured, and must be related to the structure. In an earlier paper in this series,¹¹ flow and effusion vapor pressure measurements and spectroscopic observations in the visible and ultraviolet regions were used to elucidate the vaporization processes for B_2O_3 .

RESULTS AND DISCUSSION

Vaporization of Boric Oxide in the Absence of Water

Interpretation of all vapor pressure work depends on a knowledge of the molecular species which are vaporizing. Mass spectrographic observations by Bradt⁷ and by Inghram, Chupka and Porter⁸ show only B_2O_3^+ and lighter species in the vapor over the region 1300°-1500°K, unless there is a polymer formed which undergoes ionization in the mass spectrograph with no parent peak. One may thus assume monomeric $\text{B}_2\text{O}_3(\text{g})$ as the main vapor species in treating Knudsen effusion and flow vapor pressure data, at least up to 1800°-1900°K.

The results of all published studies of the vapor pressure of boric oxide are indicated in Figure 1 (page 2), including the Knudsen cell measurements of Speiser, Naiditch and Johnston;⁹ the mass spectrographic Knudsen cell data of Inghram, Chupka and Porter;⁸ flow studies of Cole and Taylor¹⁰ and of Soulen and Margrave;¹¹ direct boiling point measurements of Soulen,¹² Leroi and Margrave;¹³ and older data of Mott¹⁴ and of von Wartenberg.¹⁵ Searcy and Myers¹⁷ and Scheer¹⁸ have also confirmed the Knudsen data in ordinary and torque cell measurements. From the slope of a $\log P$ vs. $1/T$ plot the heat of vaporization may be determined as 77.3 ± 1 kcal./mole at an average temperature of 1500°K. It appears that the flow measurements may indicate a slight upward trend in the vapor pressure at the highest temperatures studied, or else that some systematic error is included in the flow results. Early flow data were incorrectly obtained, and the calculated vapor pressures are too high.

If a model for the $\text{B}_2\text{O}_3(\text{g})$ molecule is assumed, the thermodynamic functions can be calculated.^{19, 20} With a highly symmetrical, bipyramidal model as suggested by Woolley, Wacker and Fair,¹⁹ it can be shown that $\Delta H_0^0 = 89 \pm 1$ kcal./mole = the heat of sublimation at 0°K.²¹

Figure 1

Vapor Pressure of Boric Oxide

870-5

Extrapolation of an equation derived for the Knudsen data leads to a normal boiling point of about 2500°K for boric oxide. The validity of this extrapolation involves first, the assumption that $B_2O_3(g)$ does not dissociate appreciably to $B_2O_2(g)$, $BO(g)$, or $O(g)$ and $O(g)$ at high temperatures, and second, the assumption that polymeric species— $(B_2O_3)_x(g)$ —do not become of importance at least up to the boiling point. The first assumption can be shown to be valid on the basis of the data on $BO(g)$ and $B_2O_2(g)$ obtained by Searcy,^{16a} Searcy and Myers^{16b} and by Inghram, Chupka and Porter⁸ as interpreted by Soulen and Margrave¹¹ to yield the heats of formation and dissociation energies listed in Table I.

TABLE I

Thermodynamic Properties of Important Species in the B—O System

Compound	Free Energy Functions $-\left(\frac{F-H_0^0}{T}\right)$ cal. deg ⁻¹ mole ⁻¹					$(H_{298}-H_0)$ cal. mole ⁻¹	ΔH_0 kcal. mole ⁻¹
	298°K	500°K	1000°K	1500°K	2000°K		
B(g)	0.43	1.17	2.99	4.6	6.1	290	0
B(g)	31.587	34.190	37.664	39.689	41.123	1510	135.8 ± 4
BO(s)	(3.5)	(4.5)	(8)	(12)	(16)	(800)	(-100)
BO(g)	41.652	45.255	50.210	53.258	55.504	2073	≥ +5
B ₂ O ₂ (g)	(48)	(53)	(61)	(66)	(71)	(1800)	-110.9 ± 7
B ₂ O ₃ (s)	5.42	10.36	23.34	33.96	41.85	2222	-303.8
B ₂ O ₃ (g)	(50)	(55)	(66.0)	(73.1)	(78.8)	(2000)	-214.4 ± 5
O ₂ (g)	42.061	45.675	50.697	53.808	56.104	2075	0

The possibility of polymeric species cannot be so easily eliminated since the flow measurements seem to indicate an experimental vapor pressure higher than predicted from the extrapolated data at higher temperatures. Since the trend indicated in the vapor pressure profoundly affects the boiling point, Soulen, Leroi and Margrave^{12, 13} have attempted direct boiling point determinations in molybdenum and tantalum foil boats heated in a graphite resistance furnace. In one run, Soulen reported no boiling observed at 2400°K; Leroi, however, observed bubbling in $B_2O_3(l)$ at temperatures as low as 1938°K. X-ray examination of the boats after the study showed the formation of molybdenum boride (MoB) and tantalum boride (TaB). It is apparent that reactions such as

probably occur, and make the apparent boiling point too low. Studies of B_2O_3 in the presence of carbon indicate the $\text{CO}(g)$ partial pressure from the reactions

reaches one atmosphere at about 1850° - 1900°K , to be compared with Mott's observation of 1773°K in the carbon arc.¹⁴

Apparent boiling of B_2O_3 must therefore be carefully interpreted to distinguish the effects of chemical reaction from true boiling. If Leroi's low boiling point observation is considered the lowest possible and if the vapor at one atmosphere is primarily dimeric, then one may place limits on the thermodynamic properties of the dimer in its reactions as follows:

Entropy requirements do not allow a compact, symmetrical molecule but favor an open, high entropy structure for the dimer which has very nearly twice the entropy of a monomer molecule.

Optical Spectra of Boric Oxide Vapors

The equilibrium gases over B_2O_3 are green and have been examined spectroscopically. Absorption and emission spectra show many closely spaced lines and a complex structure with few regularities, identical with the "fluctuation bands" listed by Pearse and Gaydon,²² except that no BO lines are present. A repeating frequency of 1059 Kaysers appears. Infrared emission studies by Dows and Porter²³ gave frequencies of 2013, 2059, and 2114 Kaysers. Isotopic substitution with B^{10} shifted all the band systems in the visible spectrum except the strong system at 5460 Å and gave an infrared isotope shift consistent with the bipyramidal model (D_{3h}) and not with a linear or bent model.

A photoelectric cell was used along with a prism spectrograph to monitor the relative intensities of the absorption and emission bands at various temperatures. From the ratios for a given band system the heat of vaporization of the species associated with the green "fluctuation" bands was shown to be identical with that of $B_2O_3(g)$ as determined from the Knudsen and mass spectrographic work. It thus appears that the green bands must be identified with an electronic transition in the $B_2O_3(g)$ molecule and not with an excited state of $BO(g)$ as suggested by Singh.²⁴

Effect of Water on Boric Oxide Vaporization

Quantitative analyses of boron compounds have often been found unreliable because of the losses by volatilization with water as indicated by DeFord, Lucchesi and Thoburn.²⁵ The species $H_3BO_3(g)$ and $HBO_2(g)$ were postulated by Quatram, Dressel and von Stackelberg²⁶ to explain boron transfer from boric acid in the vapor phase at temperatures up to $180^\circ C$.

Damron and Margrave²⁷ made preliminary studies of the weight losses from a platinum boat containing B_2O_3 at various water pressures and temperatures at a constant flow rate. The plot of $\log P_{\text{boron compound}}$ vs. $\log P_{H_2O}$ was interpreted to favor $HBO_2(g)$ as the species, although the slope was very uncertain, and seemed to be nearer $3/2$ at low pressures as predicted for $H_3BO_3(g)$. Further careful flow measurements by Randall have given equilibrium weight losses at $900^\circ K$ and $1273^\circ K$ determined by extrapolating several flow observations to zero flow rate after suitable corrections. From the two equilibrium measurements, if the reaction is

$$\log K = \log \frac{(P_{H_3BO_3})^2}{(P_{H_2O})^3} = -3.903 \text{ at } 900^\circ K$$

$$= -2.538 \text{ at } 1273^\circ K.$$

The heat of reaction is then 19,200 calories in this temperature region. From the early studies of von Stackelberg et al., one calculates a heat for this reaction of $23,000 \pm 5000$ calories, in fair agreement. Thermodynamic data for H_3BO_3 (s and g) and HBO_2 (s and g) are given in Table II.

TABLE II

Thermodynamic Properties of Important Species in the B-O-H System

Compound	$\frac{F-H_0}{T}$				$H_{298}-H_0$ cal.mole ⁻¹	ΔH_0 kcal.mole ⁻¹
	298°K	500°K	1000°K	1500°K		
$H_3BO_3(s)$	21.21	23.62	(31)	(37)	3201	-260.2
$H_3BO_3(g)$	67.5	71.2	80.5	(88)	(2400)	-237
$HBO_2(s)$	9.5	13.6	(20)	(23)	(2000)	-188
$HBO_2(g)$	(50)	(52)	(57)	(63)	(2200)	>-125
$H_2O(g)$	37.165	41.293	47.010	50.598	2368	-57.104

It appears that early prediction of HBO_2 as a molecule of importance at low temperatures was incorrect. It is not more than equal, and probably is less important than $\text{H}_3\text{BO}_3(\text{g})$, even at 1273°K . This makes it more unstable by at least 35 kcal./mole than suggested by von Stackelberg, Quatram, and Dressel. Perhaps at still higher temperatures, where the reaction

takes place, HBO_2 will be of importance. HBO_2 has been observed in high temperature vaporization products from metallic boron in the mass spectrograph, probably because of surface coatings of H_3BO_3 .²⁸

REFERENCES

1. S. V. Berger, *Acta Cryst.*, 5, 389 (1952)
2. (a) K. Fajans and S. W. Barber, *J. Am. Chem. Soc.*, 74, 2761 (1952)
(b) S. Anderson, R. Bohon, and D. Kimpton, *J. Am. Ceram. Soc.*, 38, 370 (1955)
3. B. Rabinowich, *J. Phys. Chem. (USSR)* 16, 23 (1942)
4. K. Grjotheim and J. Krogh-Mow, *Det. Kon. Norske Videnskabers Selshabers Forhandling*, Bind 27, 1954, Nr. 18
5. L. Shartsis and A. W. Smock, *J. Am. Ceram. Soc.*, 30, 130 (1947)
6. R. Kruh, K. Stern, and F. Hornyak, Report No. CCC-1024-TR-152, (1955)
7. P. Bradt, National Bureau of Standards, Report 3016, Jan. 1, 1954
8. M. G. Inghram, R. F. Porter, and W. A. Chupka, *J. Chem. Phys.*, 25, 498 (1956)
9. R. Speiser, S. Naiditch, and H. L. Johnston, *J. Am. Chem. Soc.*, 72, 2578-80 (1950)
10. S. S. Cole, and N. W. Taylor, *J. Am. Ceram. Soc.*, 18, 82-5 (1935)
11. J. R. Soulen and J. L. Margrave, *J. Am. Chem. Soc.*, 78, 2911 (1956); cf. CCC-1024-TR-86, Jan. 14, 1955
12. J. R. Soulen, Ph.D. Dissertation, University of Wisconsin (1955).
13. G. E. Leroi, B. S. Thesis, University of Wisconsin (1956)
14. W. R. Mott, *Trans. Amer. Electrochem. Soc.*, 34, 255-95 (1918)
15. H. von Wartenberg and O. Bosse, *Zeit. Chem. Apparatenkunde*, 28, 384 (1922)

16. (a) A. W. Searcy, AEC Report UGRL-1404, 1951
(b) A. W. Searcy and C. E. Myers, Technical Report on Contract No. N7onr-394/12 Project No. NR-032-331, June 1953
17. A. Searcy and C. E. Myers, Dissertation Abstracts, May, 1956
18. M. D. Scheer, Private Communication (1956)
19. P. F. Wacker, H. W. Woolley, and M. F. Fair, Technical Report to Bureau of Aeronautics, Navy Department, from Heat and Power Division, National Bureau of Standards, Jan. 25, 1945.
20. H. K. Kallmann and F. J. Kreiger, Rand Corp. Report P-120, 1949
21. J. R. Soulen, P. Sthapitanonda, and J. L. Margrave, J. Phys. Chem., 59, 132-6 (1955)
22. R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," John Wiley and Sons, Inc., New York, 1950
23. D. A. Dows and R. F. Porter, To be published, 1957
24. N. R. Singh, (a) Proc. Indian Acad. Sci. 29A, 424 (1949); (b) J. Sci. Res. Benares Hindu Univ. 2, 147 (1951-1952)
25. D. D. DeFord, C. A. Lucchesi, and J. M. Thoburn, "Analytical Chemistry of Boron," Northwestern University (1953), pp. 3-5
26. M. von Stackelberg, F. Quatram, and J. Dressel, Z. Elektrochem. 43, 14 (1937)
27. J. Damron and J. L. Margrave, Unpublished Work, University of Wisconsin (1955)
28. W. Chupka, Private Communication (1956)