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GASEOUS METABORATES. III.
THE BERYLLIUM OXIDE-BORON OXIDE SYSTEM

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Research on Thermodynamics of
The Al-B-O, Be-B-O and Al-Be-O Systems

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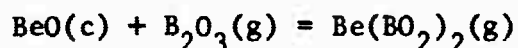
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GASEOUS METABORATES. III.
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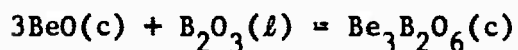
ABSTRACT

Gaseous beryllium metaborate, $\text{Be}(\text{BO}_2)_2$, has been identified mass spectrometrically in the vapor above the beryllium-boron-oxygen system. A study of this system by differential thermal analysis and Knudsen effusion using a vacuum balance and mass spectrometer, showed solid $\text{Be}_3\text{B}_2\text{O}_6$ to be the only condensed mixed oxide phase present with a melting point of $1495 \pm 5^\circ\text{C}$. The following thermodynamic values were obtained for the formation of gaseous beryllium metaborate from beryllium oxide and gaseous boron oxide:



$$\Delta H_{1500} = 22 \pm 5 \text{ kcal/mole} \quad \Delta S_{1500} = 6 \pm 1 \text{ eu/mole}$$

For the formation of solid $\text{Be}_3\text{B}_2\text{O}_6$ from the condensed oxides,



$$\Delta H_{1500} = -23 \pm 5 \text{ kcal/mole} \quad \Delta S_{1500} = -13 \pm 2 \text{ eu/mole}$$

The metal-anion bond strengths in the gaseous lithium and beryllium metaborates show the same relation to each other as the bond strengths in the corresponding chlorides, thus further confirming the pseudo-halide character of the gaseous metaborates.

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INTRODUCTION

In earlier papers^{1,2} we have described mass spectrometric and infrared spectroscopic studies of lithium and sodium metaborate, and pointed out the similarity of these compounds to the gaseous alkali metal halides. We were therefore led to investigate the existence of group II metaborates in the vapor phase. Gaseous beryllium metaborate, $\text{Be}(\text{BO}_2)_2$, was in fact identified mass spectrometrically in the vapor above a mixture of beryllium oxide and boron oxide.³ To derive reliable thermodynamic data for the gas phase compound, condensed phase data for the $\text{BeO-B}_2\text{O}_3$ system are required. While one condensed beryllium borate has been identified,^{4,5} no phase diagram for the entire system has been reported, nor are thermodynamic data available. A study of the phase relations in the $\text{BeO-B}_2\text{O}_3$ system by means of weight-loss effusion experiments and melting point measurements was therefore undertaken. The results of both these and the mass spectrometric studies are reported here.

EXPERIMENTAL

The experiments to be discussed below include (1) weight change measurements by means of an automatically recording microbalance, (2) melting point measurements by differential thermal analysis, (3) mass spectrometric measurements of heats of vaporization of individual vapor species.

Microbalance Measurements

Vapor pressure as a function of composition in the $\text{BeO-B}_2\text{O}_3$ system was obtained by determining the rate of effusion from a Knudsen cell whose weight change was continuously measured by means of an automatic recording microbalance.

The microbalance (Fig. 1) consists of a quartz truss beam supported at the fulcrum by steel pivots resting in sapphire cups. The pan-support knife edges at the end of each arm are replaced by quartz fibers sealed directly to the beam and to quartz hooks.

The balance is held at its null position automatically by an electromagnet acting on a magnet rod suspended from one arm of the balance. The null position is detected with a variable permeance transducer which surrounds a steel rod hanging below the magnet rod. When the balance is displaced from its null point, a signal is generated by the transducer-controller which drives a potentiometer through a servo mechanism. The potentiometer changes the current flowing in the electromagnet restoring the balance to its null position. The current, which is proportional to the weight change, is recorded continuously. Cochran's control design⁶ was used for governing the balance.

The vacuum system, designed to achieve pressures in the high vacuum range, is pumped with a Consolidated PMCU 721 diffusion pump, a foreline trap, and a 5 cubic ft/min mechanical pump. The system is surrounded by a large degassing oven, and hence can be baked out at a temperature of about 500°C. The vacuum system is made of stainless steel, Pyrex glass and Kovar. All joints are sealed with metal gaskets

of gold or copper. Both the electromagnet and the transducer mentioned above are mounted outside the system so that they may be removed during bakeout.

After bakeout, pressures as low as 2×10^{-9} torr have been achieved. With the vacuum furnace at 1300°C , the pressure generally rises to the 10^{-7} - 10^{-8} torr range.

The furnace consists of a water-cooled stainless shell containing a 10-inch long resistance-heated platinum-40% rhodium tube with three platinum radiation shields. The furnace ends are platinum rings clamped between water-cooled nickel flanges. The electrical leads are water-cooled tubing brought through the furnace wall with Varian high current feedthroughs. A platinum-10% rhodium-platinum control thermocouple is welded to the center of the furnace tube. The leads are insulated from the radiation shields by sapphire tubes. The furnace is calibrated with a thermocouple inside the vacuum system. This calibration is checked against the melting point of gold.

The furnace is fed by a stepdown transformer, governed by a Leeds and Northrup CAT controller through a magnetic amplifier and saturable reactor. Voltage from the control thermocouple is recorded together with the weight change.

The experiments were carried out both in platinum Knudsen cells of conventional design, and in $1/4$ " dia. x $3/8$ " high platinum cells with a conical base projecting into the cylinder. The sample was contained in the groove between the cylindrical wall and the conical base. The orifice was at the vertex of the cone. These cells, designed

after Freeman,⁷ were used to direct the effusing gas toward the bottom of the apparatus, thus reducing condensation on the support wire. Since temperature is noted and controlled automatically, continuous measurements may be made for weeks at a time.

Differential Thermal Analysis

The experimental procedure used is described below together with the measurements.

High Temperature Mass Spectrometry

The experiments were carried out with a Nuclide Corporation 12"-radius, 60°-sector, magnetic deflection mass spectrometer. Two types of crucibles were used. The first was a two-piece nickel crucible of the design described earlier.¹ The second, illustrated in Fig. 2, was a platinum-lined two-piece molybdenum crucible into which a small platinum cell was placed.

Materials

Crystalline B_2O_3 was furnished by the U.S. Borax and Chemical Corp. No significant impurities were indicated by spectrographic analysis. A water content of 4.5 wt % in material as received was found by titrating samples acidimetrically for their B_2O_3 content, then calculating for water by difference. Samples were therefore carefully dried under vacuum before using. High purity BeO was supplied by Nuclear Metals, Inc.

BeO- B_2O_3 samples were prepared from the pure oxides and loaded into Knudsen cells at Nuclear Metals. Weighed powders were thoroughly

mixed, fused at 950°C in vacuum for two hours, ground and mixed again. Samples from a single batch were analyzed photometrically for BeO and B_2O_3 to test for uniform mixing.

Mass spectrometric samples were prepared in our laboratories. To obtain the mixed oxide $Be_3B_2O_6$, a mixture of BeO and B_2O_3 powders was reacted in sealed platinum capsules at 1300°C for 100 hours.

RESULTS

Weight Change Measurements

The first weight change measurements were made in the temperature range between 1080° and 1250°C, with orifice areas between 2.3×10^{-3} and $1.8 \times 10^{-2} \text{ cm}^2$. These data indicated the existence of a two-phase region extending from $B_2O_3(l)$ to at least 50 mole % BeO, as manifested by a constant pressure equal to that of $B_2O_3(l)$. The existence of at least one compound was revealed, for the pressure decreased in the range from 50 to 75 mole % BeO. In none of these measurements, however, was equilibrium established after the pressure dropped. This is evidenced by the lack of constant pressure regions corresponding to other two-phase domains. To obtain consistent results, as shown by well-defined two-phase areas, it was necessary to use very small orifices. Two separate measurements were made, one at 1562°K with an orifice area of $5.5 \times 10^{-4} \text{ cm}^2$, a second at 1398°K with an orifice area of $1.4 \times 10^{-3} \text{ cm}^2$. The larger orifice was necessary at the lower temperature because of time limitations. Even with an orifice of this size, the measurement required three weeks.

The results of the two experiments are shown in Fig. 3, in which the logarithm of the B_2O_3 activity with $B_2O_3(l)$ as standard state is plotted against composition. The data of Fig. 3 indicate that the compound $Be_3B_2O_6$ identified earlier by low temperature X-ray studies,^{4,5} is in fact the only stable intermediate phase in this system. The drop-off in B_2O_3 activity as the 75% composition is approached is typical of a phase change in binary systems.^{8,9} A drop-off in activity as pure BeO is approached may be due to a decrease in effective evaporating surface through formation of BeO and to a low evaporation coefficient for the vaporization of B_2O_3 from $Be_3B_2O_6$.

Differential Thermal Analysis Measurements

To construct a phase diagram for the BeO- B_2O_3 system consistent with the vaporization data, it was necessary to establish the melting point of the compound $Be_3B_2O_6$. The liquidus in the neighborhood of this compound was found by differential thermal analysis. In this procedure, the difference in temperature between a sealed capsule containing a mixture of BeO and B_2O_3 in the ratio $3BeO : 1.15B_2O_3$ and a second capsule containing aluminum oxide was measured during cooling. The two capsules, placed side by side, were heated in a globar tube furnace. Platinum-platinum 10% rhodium thermocouples inserted in wells inside each capsule were used to measure temperature. One recorder was used to indicate the temperature of the capsule containing the experimental mixture, while a second recorder was used for the temperature difference between the two capsules. Three inflections

were observed: (1) the point at which freezing started, 1488°C; (2) the temperature where freezing ceased, i.e. the eutectic temperature, 1441°C; (3) the point where the cooling differential between the two capsules was re-established. No other inflections were observed in the differential curve, indicating the absence of other phases stable at lower temperatures. Our data yields a melting point for the stoichiometric compound $\text{Be}_3\text{B}_2\text{O}_6$ of $1495 \pm 5^\circ\text{C}$. Thus, all vapor pressure measurements were made over solid $\text{Be}_3\text{B}_2\text{O}_6$ and either $\text{BeO}(c)$ or $\text{B}_2\text{O}_3(l)$. On the basis of the data a phase diagram of the B_2O_3 - BeO system can be drawn as shown in Fig. .

Mass Spectrometric Studies

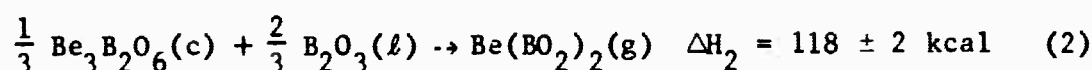
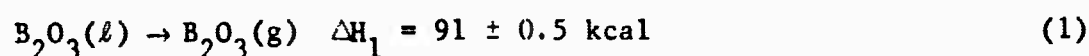
Four series of mass spectrometric measurements were made, three over the two phase region $\text{B}_2\text{O}_3(l) + \text{Be}_3\text{B}_2\text{O}_6(c)$ and one over the two phase region $\text{Be}_3\text{B}_2\text{O}_6(c) + \text{BeO}(c)$. In each case, the principal ionic species observed was B_2O_3^+ , corresponding to the neutral boron oxide $\text{B}_2\text{O}_3(g)$. The principal beryllium-containing ionic species was $\text{Be}(\text{BO}_2)_2^+$, corresponding to neutral beryllium metaborate $\text{Be}(\text{BO}_2)_2(3)$.

The three measurements on the sample containing excess B_2O_3 yielded results apparently unaffected by the quantity of sample material or the cell orifice areas. Two of these measurements were made with nickel cells, of the design described earlier,¹ one containing about 5 mg each of BeO and B_2O_3 and one containing 26 mg B_2O_3 and 10 mg $\text{Be}_3\text{B}_2\text{O}_6$. Both cells had orifices of $7.8 \times 10^{-3} \text{ cm}^2$. In the

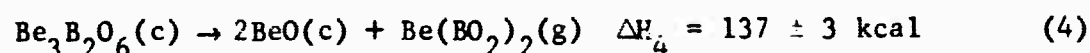
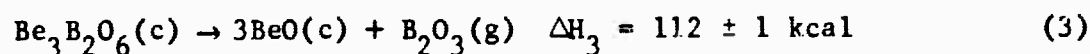
third experiment the crucible design of Fig. 2 was used with the platinum cell having an orifice area of $4.8 \times 10^{-4} \text{ cm}^2$. The results of the three experiments were combined to give the data shown in Fig. 5 which gives the temperature dependence of the B_2O_3^+ and $\text{Be}(\text{BO}_2)_2^+$ ion intensities. The second-law heat of vaporization for B_2O_3 found from these experiments is 91 kcal/mole, in good agreement with 93 ± 3 kcal/mole obtained in earlier experiments. To obtain data for the BeO-rich side of the diagram a molybdenum crucible was used with a platinum cell liner containing 68 mg of $\text{Be}_3\text{B}_2\text{O}_6$ and 12 mg of BeO and having an orifice area of $4.8 \times 10^{-4} \text{ cm}^2$. The data obtained for both B_2O_3 and beryllium metaborate gas are shown in Fig. 6

The second-law heats indicated on Figs. 5 and 6 correspond to the following reactions:

(a) $\text{B}_2\text{O}_3(\ell) - \text{Be}_3\text{B}_2\text{O}_6(\text{c})$ (Fig. 5)

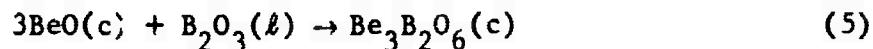


(b) $\text{Be}_3\text{B}_2\text{O}_6(\text{c}) - \text{BeO}(\text{c})$ (Fig. 6)



From these least square data the heats of formation of the condensed phase mixed oxide, $\text{Be}_3\text{B}_2\text{O}_6(\text{c})$, and the gaseous mixed oxide, $\text{Be}(\text{BO}_2)_2(\text{g})$,

can be obtained. The heat of reaction for:



can be obtained from the pairs of reactions (1) and (3) and (2) and (4), respectively:

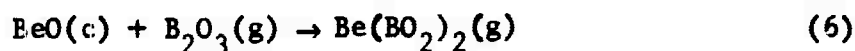
$$\Delta H'_5 = \Delta H_1 - \Delta H_3 = -21 \text{ kcal/mole}$$

$$\Delta H''_5 = \frac{3}{2}(\Delta H_2 - \Delta H_4) = -28.5 \text{ kcal/mole}$$

A third value for the heat of this reaction can be obtained from the B_2O_3 activity data obtained in the weight loss experiments, which give:

$$\Delta H'''_5 = -20 \text{ kcal/mole}$$

The best estimate for reaction (5) is $\Delta H_5 = -23 \pm 5 \text{ kcal/mole}$. For the heat of formation of the gaseous metaborate from the oxides



a value can be obtained directly from the gaseous equilibrium on the BeO-rich side.

$$\Delta H'_6 = \Delta H_4 - \Delta H_3 = 25 \text{ kcal/mole}$$

An additional value may be obtained by combining the heat of formation of $\text{Be}_3\text{B}_2\text{O}_6(c)$ from the oxides obtained above, ΔH_5 , with the $\text{Be}(\text{BO}_2)_2(g)$ data on the B_2O_3 -rich side:

$$\Delta H''_6 = \Delta H_2 - \Delta H_1 + \frac{1}{3}\Delta H_5 = 19 \text{ kcal/mole}$$

From these we obtain as best estimate for reaction (6)

$$\Delta H_6 = 22 \pm 5 \text{ kcal/mole.}$$

In order to obtain entropy values consistent with the measured pressures and second-law heats, entropy changes for reactions (1) through (4) were calculated from

$$\Delta S_{1500} = \frac{\Delta H_{1500}}{1500} + R \ln p \quad (7)$$

where p is the vapor pressure of the gaseous species and ΔH_{1500} is the heat of reaction computed from the values in Table I. The B_2O_3 pressure at 1500°K given by our vacuum balance data is 2.70×10^{-5} atm. Using this pressure, the ion intensities of $B_2O_3^+$ and $Be(BO_2)_2^+$ from the mass spectrometric data, and Otvos and Stevenson's¹¹ ionization cross sections, the pressures were computed at 1500°K for reactions (2) through (4). The data taken from platinum cells over the BeO - $Be_3B_2O_6$ system were normalized to the orifice area and sample-to-ion source distance of the nickel cells.

Using the above procedure, the following pressures (in atmospheres) and entropy changes were calculated for reactions (1) through (4): (1) $p_{B_2O_3} = 2.7 \times 10^{-5}$, $\Delta S_1 = 39.6$ eu; (2) $p_{Be(BO_2)_2} = 2.5 \times 10^{-7}$, $\Delta S_2 = 50.3$ eu; (3) $p_{B_2O_3} = 9.3 \times 10^{-6}$, $\Delta S_3 = 53.0$ eu; (4) $p_{Be(BO_2)_2} = 1.1 \times 10^{-7}$, $\Delta S_4 = 59.1$ eu.

The entropies for reactions (5) and (6) were calculated from the entropy changes for reactions (1) through (4) by the same methods used to calculate ΔH_5 and ΔH_6 . For reaction (5)

$$\Delta S'_5 = \Delta S_1 - \Delta S_3 = -13 \text{ eu/mole}$$

$$\Delta S''_5 = \frac{3}{2}(\Delta S_2 - \Delta S_4) = -13 \text{ eu/mole}$$

while the activity measurements give a third value

$$\Delta S'''_5 = -12 \text{ eu/mole}$$

These may be combined to give $\Delta S_5 = -13 \pm 2 \text{ eu}$ at 1500°K . For reaction (6)

$$\Delta S'_6 = \Delta S_4 - \Delta S_3 = 6.2 \text{ eu/mole}$$

$$\Delta S''_6 = \Delta S_2 - \Delta S_1 + \frac{1}{3} \Delta S_5 = 6.5 \text{ eu/mole}$$

We obtain as the best estimate for reaction (6), $\Delta S_6 = 6 \pm 1 \text{ eu/mole}$. ΔS_1 , ΔS_5 , and ΔS_6 are combined with the JANAF¹⁰ entropies at 1500°K for $\text{B}_2\text{O}_3(l)$ and $\text{BeO}(c)$ to give the remaining entropies in Table I.

It should be noted that our value of $S_{1500} = 101 \text{ eu}$ for $\text{B}_2\text{O}_3(g)$ compares well with Sommer, White, Linevsky and Mann's¹² value $S_{1500} = 100.2 \text{ eu}$. The model assumed by these authors is that of a V-shaped molecule.

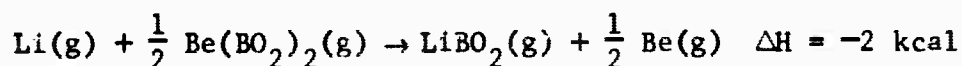
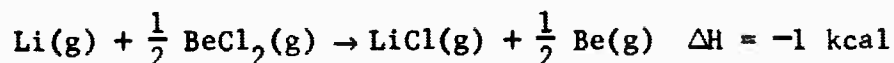
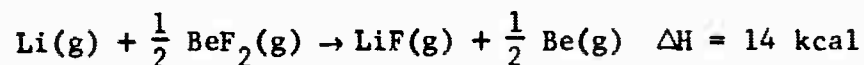
DISCUSSION

Phase Diagram

The $\text{BeO-B}_2\text{O}_3$ phase diagram of Fig. 4 has been drawn in analogy with the diagram for the $\text{MgO-B}_2\text{O}_3$ system.¹³ The alkaline

earth oxide-boron oxide systems all show regions of liquid miscibility. However, from magnesium onwards boron-oxide rich solid oxides with low melting points are also stable. $\text{BeO-B}_2\text{O}_3$ appears to be the highest melting system. The thermodynamic data for the various compounds in this system are summarized in Table I.

The properties of the gaseous alkali metaborates suggested that these compounds could be regarded as pseudo-halides and the existence of gaseous beryllium metaborate was originally postulated on this basis. It is therefore of interest to compare the heats of formation of beryllium and lithium metaborate with those of the corresponding fluorides and chlorides. Using heats of formation of the atoms and halides given by the JANAF Tables¹⁰ we obtain the following heats of reaction at 1500°:



The first of these reactions shows that the beryllium fluoride single bond is actually stronger than the lithium fluoride bond, whereas in the corresponding chlorides the two bond strengths are essentially equal. The relation of the lithium-metaborate and beryllium-metaborate single bond strength is very close to that of the chlorides and supports the description of the gaseous metaborates as pseudo-halides.

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The present work shows that the phases present were in fact $\text{Be}_3\text{B}_2\text{O}_6\text{(c)} + \text{B}_2\text{O}_3\text{(l)}$.
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Table I. Thermodynamic values for Be-B-O System.

	$\Delta H_{1500}^{\circ}(f)$ kcal/mole	S_{1500}° eu/mole
$\text{BeO}(c)^a$	-142.3	19.8
$\text{B}_2\text{O}_3(l)^a$	-294.7	61.3
$\text{B}_2\text{O}_3(g)^b$	-204	101
$\text{Be}_3\text{B}_2\text{O}_6(c)^b$	-745	108
$\text{Be}(\text{BO}_2)_2(g)^b$	-324	127

a. Reference 10.

b. This work.

FIGURE CAPTIONS

- Fig. 1: Automatic recording vacuum microbalance.
- Fig. 2: Molybdenum-platinum crucible.
- Fig. 3: Boric oxide activity as a function of composition.
- Fig. 4: B_2O_3 -BeO phase diagram.
- Fig. 5: Plots of I^+T vs $1/T$ for vaporization of $B_2O_3(g)$ and $Be(BO_2)_2(g)$ from the system $Be_3B_2O_6(c)$ - $B_2O_3(l)$.
- Fig. 6: Plots of I^+T vs $1/T$ for vaporization of $B_2O_3(g)$ and $Be(BO_2)_2(g)$ from the system $Be_3B_2O_6(c)$ - $BeO(c)$.

