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THE GASEOUS SPECIES OF THE BORON - BORIC OXIDE SYSTEM

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Abstract

The reaction between boron and beryllium oxide has been investigated at 1900°K by the Knudsen effusion method. From the results the heat of formation of BO gas is calculated to be 4.5 ± 3 kcal. mol.⁻¹, and it can be shown that boric oxide vaporizes without decomposition to lower oxides. Calculations based on experiments in the literature lead to a heat of sublimation of boron of 131 ± 4 kcal. mol.⁻¹ and to 8.0 ± 0.2 e.v. for the dissociation energy of BO gas. The vapor pressure of $ZrO_2 \times 10^{-7}$ atm. at 2073°K.

From a study of the vaporization characteristics of the aluminum-aluminum oxide system, Brewer and Searcy (1) have deduced the gaseous species which are important under various conditions for that system. Detailed vaporization data are not available for the related boron-boric oxide system. Although the vapor pressure of boric oxide has recently been measured by Speiser, Naiditch, and Johnston (2), the vapor pressure of boron itself has apparently never been determined, and no quantitative study of lower oxides of ~~boron~~ has been made except by spectroscopic means. These spectroscopic results have been differently interpreted by different authorities (3). Zintl, Morawietz, and Gastinger (4) have proved that a gaseous suboxide of

boron is produced when very carefully purified boron is heated with zirconium dioxide at 1800°C. They found that markedly greater volatilization occurred when mixtures of boron and zirconium dioxide were heated than when either substance was heated singly.

The sublimates collected by Zintl, Morawietz, and Gastiner from mixed heatings showed oxygen to boron atomic ratios averaging about 1.16 and negligible amounts of zirconium. They concluded that their boron had been oxidized to a mixture of BO and boric oxide vapors by the zirconium dioxide. This interpretation cannot be entirely correct because, although somewhat discordant values for the heat of formation of boric oxide have been reported by different investigators (5,6), none of the reasonable values for the heat of formation of boric oxide is high enough so that an appreciable weight of boric oxide could have volatilized from the boron-zirconium oxide mixtures.

The excess of oxygen detected in the sublimate may have arisen through partial oxidation of the finely divided, and possibly unstable, film of sublimate by air when the vacuum was broken. Probably Zintl, Morawietz, and Gastinger were correct in identifying the suboxide formed as BO. We shall see that the suboxide formed under conditions such as theirs has about the stability to be expected for BO from spectroscopic dissociation energies, and it seems unlikely that the oxygen to boron ratio found would have reached a value as high as 1.16 to one if B₂O had been the vaporizing species. But it should be emphasized that from the evidence available we can not definitely exclude the possibility that B₂O was the volatile oxide.

In the present research the reaction equilibrium between beryllium oxide and boron at 1900°K has been measured quantitatively by

the Knudsen effusion method. From the data so obtained, from the vapor pressures for B_2O_3 reported by Speiser, Naiditch, and Johnston, and from approximate vapor pressure calculations for boron based on the results of Zintl, Morawetz, and Gastinger we can determine almost unambiguously the important gaseous species of the boron-boric oxide system and can fix the equilibria among these species with fair accuracy.

Experimental

The boron used in this research was stated by the manufacturer to contain less than 0.5% impurity, principally carbon and iron. Spectroscopic analysis confirmed the purity claimed. By separate analysis the carbon content was found to be 0.13%. Before effusion runs were made, the sample of boron was heated in its degassed beryllium oxide container to remove any impurities more volatile than the desired reaction products. A spectrographic analysis made of the sublimate obtained from an effusion run showed less than 0.1% of any metal other than boron and beryllium.

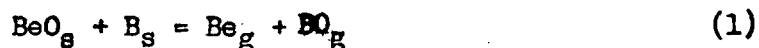
For an effusion run the boron was heated inside a beryllium oxide Knudsen cell whose lid was pierced by a 0.314 cm diameter knife-edged hole. The area of beryllium oxide in contact with finely powdered boron was approximately 100 times the area of the hole. The vapor pressure of boron metal was negligible under the conditions employed. The weight of material effusing during the known time of a run was determined both from the weight loss of the

crucible and from the weight gain of a platinum collector plate. The results indicate an average sticking (or accommodation) coefficient on the collector of 0.86 ± 0.05 . Spectroscopic analysis suggest that the sticking coefficient may have been higher for beryllium than for BO.

The apparatus and experimental techniques have been described previously (1).

Discussion

The equilibrium for the reaction between boron and beryllium oxide was assumed to be



in making the calculations of Table I. An exploratory run agreed well with the data reported, but was not listed because conditions were not then carefully controlled.

The entropy at 298°K for BO gas was taken from Kelley (7) and the heat capacity for BO gas was taken from the National Bureau of Standards Tables (8); data for boron were from Johnston, Hersh, and Kerr (6) and from Brewer (9); data for beryllium oxide and for beryllium gas were from the entropy compilations of Kelley (7) and from the National Bureau of Standards Tables. Using 147 kcal as the heat of formation for BeO (10) we find the standard heat of formation of BO gas to be 4.5 ± 3.0 at 298°K where the uncertainty is chiefly due to the uncertainty in the value for the heat of formation of BeO.

Speiser, Naiditch, and Johnston have argued that the agreement in weight loss by their Knudsen cells containing boric oxide with the weight gain of collectors above the cells indicates that boric oxide does not volatilize by decomposition to a lower oxide. This argument is inconclusive since a beam of BO and O₂ molecules impinging simultaneously on a cold surface might be expected to react together readily to re-form boric oxide just as ammonia and hydrogen chloride combine at a cold surface. The entropy of vaporization that these authors obtained, however, clearly rules out either B₂O and BO as principal species in vaporization of boric oxide.

The experimental entropy is about 31 cal. mol.⁻¹ deg.⁻¹ while the entropy calculated for vaporization by the reaction $B_2O_3(l) = 2BO(g) + 1/2O_2(g)$ is about 87 cal. mol.⁻¹ deg.⁻¹. The entropy of B₂O(g) at 1900°K would have to be about 35, more than 30 cal. mol.⁻¹ deg.⁻¹ less than we would estimate, in order to give the observed entropy of vaporization.

When the value for the heat of formation of BO gas that we have found is used with the lower value (5) for the heat of formation of boric oxide, the partial pressure of BO gas calculated to be present over boric oxide is less than one-hundredth the pressures observed by Speiser, Naiditch, and Johnston. If the species volatilizing from our boron-beryllium oxide mixture is assumed to be B₂O, we calculate that neither B₂O nor BO would contribute appreciably to the vapor pressure of boric oxide. We can conclude that boric oxide vaporizes without decomposition to lower oxides and, from entropy considerations again, probably vaporizes as the monomer B₂O₃ rather than as the dimer B₄O₆.

Calculations

The investigations by which Zintl, Morawietz, and Gastinger (4) demonstrated the volatilization of BO from mixtures of boron and zirconium dioxide powders provide all the data necessary for a calculation of the equilibrium pressures during their experiments except the area of the samples used. Combining the heat of formation of BO gas determined above with the heat of formation of zirconium dioxide, 258.3 ± 3.0 kcal (10), we calculate that the pressure of BO gas above the boron-zirconium dioxide mixtures should be 2×10^{-5} atm. at 2073°K. The open area of the top of the tantalum boats used by Zintl, Morawietz, and Gastinger would have to be 1.3 cm^2 to give the observed weight losses with this equilibrium pressure and a sticking coefficient near unity. From the kind of container and from the weights of samples used we would estimate the area of the openings in the boats to be between two and six cm^2 in area. Agreement in the calculated area, 1.3 cm^2 , and predicted area, $4 \pm 2 \text{ cm}^2$, is within the 4 kcal uncertainty arising from use of the heats of formation of beryllium oxide and zirconium dioxide.

The close agreement found between predicted and calculated area of the tantalum boat justifies our assumption that the boats may be considered effusion vessels. We can, therefore, use the weight losses that Zintl, Morawietz, and Gastinger reported for boron and zirconium dioxide heated individually to determine approximate vapor pressures for these substances. They found that the weight losses at 2073°K in one hour were 0.0291 g. when boron was heated

and 0.0295 g. when zirconium dioxide was heated. We calculate a vapor pressure of 8.5×10^{-7} atm. for boron and 2.5×10^{-7} atm. for zirconium dioxide using 3 cm^2 as the effusing area. The calculated vapor pressure of boron, using Brewer's heat content and entropy tables (9) corrected to agree with the entropy of crystalline boron found by Johnston, Hersh and Kerr, leads to a heat of sublimation at 298°K of $131 \pm 4 \text{ kcal mol.}^{-1}$. The vapor pressures of zirconium (11) and of boron are higher than the vapor pressures of the corresponding oxides, so neither oxide decomposes to the elements during vaporization.

The dissociation energy of BO gas can now be calculated from the heat of formation of BO and from the heat of sublimation of boron. The data yield 8.0 ± 0.2 electron volts for the dissociation energy compared to 7 ± 1 and 9.1 advocated by Gaydon and by Herzberg respectively from different interpretations of the spectroscopic data (3).

We conclude that the major gaseous species of the boron-boric oxide system are boron, BO, and a trivalent oxide, probably B_2O_3 . Boron, B_2O , and BO are not important in the vaporization of boric oxide. Only if a low heat of formation of boric oxide is accepted can the pressure of BO gas above a mixture of boron and boric oxide be as high as that of boric oxide itself. However, boron is capable of reducing oxides of greater stability than boric oxide at high temperatures provided that the oxides are relatively non-volatile.

I am indebted to Mr. John Conway and Mr. Milton Moore for the spectroscopic analyses and to Mrs. C. H. Dauben and Mr. Allan Zalkin for the X-ray diffraction analyses.

Table I

Data for reaction: $B_s + BeO_s = Be(g) + BO(g)$

Temp	P_{BO} (atm)	P_{Be} (atm)	Equilibrium Constant	ΔH_{298}
1889	1.06×10^{-5}	6.0×10^{-6}	6.4×10^{-11}	228.0
1910	1.4×10^{-5}	8.0×10^{-6}	1.1×10^{-10}	228.2

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