[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, CHICAGO, ILLINOIS]

The Volatilization of Beryllium Oxide in the Presence of Water

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Introduction

It has been noted by many observers[1b] in connection with the use of beryllium oxide as a refractory that: (a) under certain conditions it is quite volatile at temperatures as low as 1800° as evidenced by weight losses; (b) that firing of beryllium oxide produces relatively rapid vapor phase transfer at temperatures as low as 1500° as shown by changes in individual crystals; (c) that beryllium oxide condenses in the cooler portion of furnaces with maximum temperatures not in excess of 1800°. Similar phenomena were noted in this Laboratory[2] under conditions involving the presence of water in the vapor phase. The data of Erway and Seifert,[3] however, showed equilibrium vapor pressures of beryllium oxide too low to account for the observed rates of volatilization (3.2×10^{-8} mm. at 1500° and 1.5×10^{-4} mm. at 1800°). Their vapor pressure data are also inconsistent with the phenomena mentioned in (a), (b) and (c). We have performed experiments showing that the volatilization is due to the presence of water in the gas in contact with the beryllium oxide. A reaction with the water results in the formation of a volatile compound which condenses at lower temperatures with decomposition to beryllium oxide. Previous studies on the $BeO-H_2O$ system in a lower temperature range have been made by HaldunTerem[4] and Hackspill and Kieffer.[5]

Experimental Description

Pure beryllium oxide half cylinders weighing $\sim$2 g. and $\sim$19 mm. in diameter and $\sim$8 mm. in altitude, of density 2.38 g. cc.^{-1} were prepared by bisecting fired pellets made from a pressed dry paste by adding 0.5 cc. of 6 *M* nitric acid to 5 g. of 200-mesh Brush high fired beryllium oxide powder. This beryllium oxide powder was of high purity. Spectrographic analyses on the samples taken gave these results in p.p.m.

Fe	Mg	Mn	Si
50	50	<2	<500

More extensive spectrographic analyses on a similar sample of beryllium powder gave the results shown, in p.p.m.

Ag	Ba	Ca	Cd	Co	Cr	Cu
< 10	< 100	100	0.5	< 10	< 10	50
Fe	Li	Mg	Mn	Na	Ni	
400	< 20	100	5	300	< 100	
Pb	Si	Sn	Ti	V	Sb	
10	100	< 10	100	< 500	< 200	

The pellets were fired at 1650° for one hour. When such samples were placed in a platinum boat in a mullite tube and water at $\sim$1 atm. passed through the tube, the per cent. weight losses listed in Table I were observed in the temperature range 1483–1528°.

TABLE I

Time, hours	4.13	6.80	10.80	15.05
Weight loss, %	1.7	5.6	10.3	13.3

Condensation of beryllium oxide crystals in the form of a white cotton-like mass in the cooler portion of the tube and on the downstream side of the sample was observed. This material was shown to be nearly pure beryllium oxide by X-ray examination by W. H. Zachariasen.

Similar experiments were then performed with nitrogen–hydrogen mixtures passing over the sample at $\sim$1 atm. and in stagnant air with no measurable volatilization of the beryllium oxide.

In a series of similar experiments[6] with water at 1 atm. the effect of temperature (shown in Table II) was observed when the water was passed over the samples at a rate of 0.11 mole min.^{-1} in a tube of 3.6 cm. inside diameter.

TABLE II

Temperature, °C.	1000	1250	1400	1500	1550
BeO lost in 2.5 hr., %	0.01	0.19	0.66	1.58	2.24

Similar experiments performed with samples of magnesia and beryl resulted in no measurable volatilization.

Conclusions

1. The presence of water vapor in contact with beryllium oxide results in its relatively rapid volatilization at temperatures at which the vapor pressure of beryllium oxide is too low to account for the observed rates.
2. Reaction of water with beryllium oxide results in the formation of a volatile compound at temperatures of 1250° or greater. This volatile substance condenses with decomposition to beryllium oxide.

The reported observations (a, b and c) may be

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[1b] For a review of such observations reference may be made to F. H. Norton, "Pure Beryllium Oxide as a Refractory," United States Atomic Energy Commission, MDDC-126, 4/30/46.

(2) J. G. Malm and J. E. Willard, unpublished results, approximately January, 1946.

(3) N. D. Erway and R. L. Seifert, "Vapor Pressure of Beryllium Oxide," United States Atomic Energy Commission, MDDC-1030, September, 1946.

(4) HaldunTerem, *Rev. Faculté sci. univ. Istanbul*, **8A**, 99 (1943).

(5) Hackspill and Kieffer, *Ann. chim.*, **14**, 227 (1930).

(6) These measurements were carried out by M. G. Berkman.

accounted for by assuming the presence of moisture in the gases in contact with the beryllium oxide (flame gases, etc.).

3. The volatilization rate increases with increasing temperature.

4. The volatilization does not occur in the cases of beryl or magnesia.

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The Distillation of Mixtures Containing Diborane and the Identification of Two Azeotropes

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Depending upon the method of manufacture diborane may be contaminated with hydrogen halides, boron halides and ethane. Thus in Schlesinger's[2] and Stock's[3] methods of preparation hydrogen chloride and boron trichloride, and hydrogen bromide and boron tribromide are possible contaminants. In Schlesinger's later preparation[4] ethane might also contaminate the diborane. In other reactions described by Hurd[5] boron trifluoride as well as boron trichloride and hydrogen chloride may be impurities. A knowledge of the various possible mixtures of diborane with these materials becomes important both for the purification of diborane and the analytical distillation of the products of the reactions.

Experimental

Apparatus.—The apparatus used to perform the distillations was the Automatic Recording Low Temperature Fractional Distillation Apparatus, Hyd Robot Model, Serial No. H 576, manufactured by the Podbielniak Centrifugal Super Contactor Company. The entering stopcock of the "Super Cool" column was attached to a vacuum line that was equipped with bulbs of known volume. This part of the system was not thermostated, and all measurements of the gases entered into the column were made at room temperature. All values reported in the tables, however, have been reduced to 0° and 760 mm. Samples were mixed in the column by entering each gas separately. No van der Waals corrections were applied to any of the gases. The time under total reflux was ordinarily about thirty minutes to one hour long.

Chemical Analysis.—In Expt. 1 of Table I a chemical analysis was made for hydrogen chloride. This was accomplished by freezing a known volume of the gases into a sample bulb and then expanding through two bubblers of distilled water. A slow stream of dry nitrogen was used to prevent water from sucking back into the sampling bulb. The water was analyzed for hydrogen chloride by titration with a sodium hydroxide solution to a methyl orange end-point.

Materials.—The hydrogen chloride and diborane used in Expt. I, Table I, were distilled and only the middle cuts were saved. All boron trichloride was distilled prior to use. The diborane, ethane and boron trifluoride of Tables III and IV were distilled before use. All other hydrogen chloride and diborane as well as the hydrogen bromide came from tanks in which the impurities were known to be mainly gases not condensable in liquid nitrogen. Accordingly, the purification procedure for these samples was to freeze some gas into a bulb in liquid nitrogen, and then pump on the bulb.

Results

The System Hydrogen Chloride–Diborane.—A few preliminary runs (not reported here) with rather impure materials served to indicate that an azeotrope was formed having the approximate composition 26–30% hydrogen chloride and 70–74% diborane. This material boiled at about −94° at 760 mm., 1.5° lower than the value for diborane, −92.5°.

In order to get an accurate value for the composition of the azeotrope at 760 mm., samples of distilled hydrogen chloride and diborane were used in Expt. 1 of Table I. It will be noticed that in this experiment the difference between the total volume of gas used and that found is only 2 cc. in 4,934. This is fortuitous as will be found by an inspection of other data in this and subsequent tables. Sometimes less and sometimes more gas was found than was originally used. This is attributed to solution and possibly reaction in some cases with the stopcock grease of the Podbielniak apparatus. Apiezon L was the lubricant used. In making calculations on azeotrope composition, it is convenient to have the total volumes found agree with the total volumes used. If there is a discrepancy, it is assumed to be due to the causes mentioned, and the volumes found are pro-rated with an appropriate factor to bring them into agreement with the volumes used. It is then a simple matter to make the azeotrope composition calculations. The value for the azeotrope at 755 mm. was found to be 29.9% hydrogen chloride on a molar basis. When 1984 cc. of the azeotrope at S.T.P. was analyzed for hydrogen chloride in water solution,[6] 0.957 g. of hydrogen chloride was found. This corresponds to 29.6 mole per cent. in the azeotrope.

Experiments 2, 3 and 4 of Table I are determinations of the azeotrope composition at a lower pressure (205–208 mm.). The average of the three determinations of the composition is 26.2% hydrogen chloride and 73.8% diborane. The boiling point of the azeotrope at 207 mm. is about −114.5°, whereas for pure diborane at 207 mm. the boiling point is −113°.

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[1] This work was done on Army Ordnance Contract TU1-2000.

[2] Schlesinger and Burg, THIS JOURNAL, 53, 4321 (1931).

[3] Stock and Sütterlein, *Ber.*, 67B, 407 (1934).

[4] Finholt, Bond and Schlesinger, THIS JOURNAL, 69, 1199 (1947).

[5] Hurd, *ibid.*, 71, 20 (1949).

[6] Analysis courtesy of L. B. Bronk.