tions and experimental results from different laboratories. The Committee plans to maintain this set of recommended values of the fundamental constants for physical chemistry up-to-date by revision at appropriate intervals and will appreciate being advised of any new information and data which may affect the values.

CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
12 EAST STANWORTH DRIVE, PRINCETON, NEW JERSEY

JANUARY 31, 1952

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Reaction of Beryllium Oxide with Water Vapor

BY LEONARD I. GROSSWEINER AND RALPH L. SEIFERT[1]

RECEIVED OCTOBER 4, 1951

At high temperatures the volatility of beryllium oxide is greatly increased by the presence of water vapor. Measurements of the effect of temperature and partial pressure of water on the rate of volatilization of beryllium oxide indicate that the increased volatility results from the reaction $BeO(s) + H_2O(g) \rightarrow Be(OH)_2(g)$ for which $\log_{10} K_p = 1.63 - 9060/T$.

The volatility of a number of oxides is greatly increased by the presence of water vapor. This has been shown to be true by quantitative measurements with silicon dioxide,[2,3] boron trioxide,[4,5] beryllium oxide,[6,7] and the oxides WO_3, W_4O_{11}, WO_2 and MoO_3.[8,9] The volatile species may result from a reaction between the oxide and water

$$MO(s) + nH_2O(g) \longrightarrow MO{\cdot}nH_2O(g) \qquad (1)$$

or between the oxide and a decomposition product of water

$$MO(s) + nX(g) \longrightarrow MO{\cdot}nX(g) \qquad (2)$$

where X may be H_2, O_2, OH, H or O. The partial pressures of H_2, O_2 and OH in water vapor are proportional to the 2/3 power of the partial pressure of water. The partial pressures of H and O in water vapor are proportional to the 1/3 power of the partial pressure of water. Whether reaction (1) or (2) occurs can be determined experimentally together with the correct value of n by plotting the logarithm of the equilibrium pressure of the volatile complex as a function of the logarithm of the partial pressure of water at constant temperature. If only one reaction is involved an integral value will be found for the slope if it is reaction (1) that occurs and n will equal the slope. If reaction (2) occurs and involves H_2, O_2 or OH the slope will equal $2n/3$. If the reaction involves H or O the slope will equal $n/3$. Obviously ambiguous results will be obtained if n is a multiple of 3.

The necessary data may be obtained by observing the loss in weight of a sample of oxide when known volumes of gas containing known pressures of water vapor are passed over the sample. The following experimental conditions must exist: the temperature must be maintained constant; the gas phase must come into equilibrium with the solid; and the solid must lose weight by only one mechanism. Of the earlier work only in the case of boric acid were the experimental requirements met sufficiently well to permit an unambiguous determination of n. However, the results of this earlier work[3,4,9] are not inconsistent with the conclusion that the volatile species in the cases of SiO_2, B_2O_3 and WO_3 are, respectively, $SiO_2{\cdot}2H_2O$, H_3BO_3 or HBO_2 depending upon the temperature, and $WO_3{\cdot}H_2O$. (The work with B_2O_3[4] was carried out at temperatures where H_3BO_3 and HBO_2 were stable in the solid phase so that the treatment of these data differs somewhat from the procedure indicated above.)

In the earlier work with beryllium oxide[6,7] the gas phase did not come into equilibrium with the solid beryllium oxide. However, it was observed that the volatility of beryllium oxide in water vapor increased with increasing temperature and with increasing pressure of water vapor. Crystalline needles of beryllium oxide were deposited from the vapor phase in the cool part of the apparatus.

This investigation was undertaken to study the influence of water vapor on the volatility of beryllium oxide under conditions that permit a much closer approach to the equilibrium state than was possible in the apparatus used by Berkman and Simon.[6]

Experimental

Apparatus.—The apparatus was designed so that a stream of gas, containing either helium and water vapor or water vapor alone, could be preheated, passed over beryllia chips that were heated to constant temperature, and could then be cooled to condense the water and beryllium oxide. The beryllia chips were contained in a platinum gauze basket that fitted closely inside a platinum–10% rhodium tube. The platinum–rhodium tube, 2.5 ft. long with an internal diameter of $^7/_{16}$ in., was placed vertically inside a 1.0 foot long platinum-wire wound alundum tube furnace. The power input to the furnace was controlled by a Wheelco Proportioning Potentiotrol with a platinum platinum–10% rhodium thermocouple placed at the outer surface of the

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[1] Consultant to Argonne National Laboratory; permanent address: Department of Chemistry, Indiana University, Bloomington, Indiana.

[2] C. J. van Nieuwenburg and H. B. Blumendal, *Rec. trav. chim.*, **49**, 857 (1930).

[3] C. J. van Nieuwenburg and P. M. van Zon, *ibid.*, **54**, 129 (1935).

[4] M. v. Stackelburg, F. Quatram and Jutta Dressel, *Z. Elektrochem.*, **43**, 14 (1937).

[5] H. Tazaki, *J. Sci. Hirosima Univ.*, **A10**, 109 (1940).

[6] M. G. Berkman and S. L. Simon, Argonne National Laboratory Report ANL-4177, July 15, 1948.

[7] C. A. Hutchison and J. G. Malm, THIS JOURNAL, **71**, 1338 (1949).

[8] C. J. van Nieuwenburg and H. B. Blumendal, *Rec. trav. chim.*, **50**, 994 (1931).

[9] T. Millner and J. Neugebauer, *Nature*, **163**, 601 (1949).

furnace windings. The furnace temperature was constant to ±5°.

A preheating furnace was placed about the platinum tube immediately above the platinum-wound furnace. It consisted of a 6-in. stainless steel tube that was heated to 800° by a small nichrome-wound heating element.

Each of the two ends of the platinum tube was connected to the adjacent glass portion of the apparatus *via* a brass flare fitting, a brass Sylphon bellows and a Housekeeper seal. Thus a leak-tight, flexible path was provided between the glass portions of the apparatus. An optical window was provided above the upper end of the reaction tube for viewing the sample with a Leeds and Northrup optical pyrometer. A small tube furnace prevented condensation of water on the window.

Two means were used to supply a gas stream. For measurements involving pure water vapor at atmospheric pressure, steam was generated in a one-liter flask that was heated by a Glas-Col heater. For lower partial pressures of water, a mixture of helium and water was used. Helium was metered by a calibrated rotometer and bubbled through water that was heated by a Glas-Col heater, controlled by a Capacitrol. The gas mixture was passed through an 8-in. preheating furnace maintained at about 200°. In each case the gas stream entered the top of the platinum reaction tube after passing through a 1.0 ft. length of quartz tubing that was heated to 600° by a nichrome muffle.

When no carrier gas was used the water vapor leaving the reaction tube was condensed in a standard water-jacketed condenser. When helium carrier was used the exit gas from the reaction tube was passed through a short, vertical, water-cooled condenser into a round-bottom flask cooled by a Dry Ice–acetone mixture. To check the efficiency of the condensation in the flask an Anhydrone drying tube was attached to the outlet during several runs. There was no observed increase in weight of the drying tube during the runs.

Material.—The beryllium oxide samples consisted of chips of hot-pressed beryllia, shown by spectroscopic and chemical analysis to be 99.6% pure BeO. The density of the chips was 2.3 g. per cc. The chips were acid washed and carefully sized by sieving. Two different sizes were used. The "small" chips were between sieve sizes U.S. 20 and U.S. 40 and the "large" chips were between U.S. 12 and U.S. 20. A rough statistical calculation of the surface of the samples[10] indicated that the small chips had a superficial surface area of 46 cm.^{2} per gram and the large chips had a superficial area about half as great.

Procedure.—The platinum gauze basket was filled to a depth of 2 in. In the runs reported as no. 1 to 12 the sample weight was approximately 3 g., in runs 17 to 20, 2.2 g.; and in runs 21 to 25, 1.4 g. Runs reported as 13 to 16 were made in an earlier apparatus, using a Mullite tube, 2 in. in diameter, and using samples of the order of 15 g. in a funnel shaped platinum gauze basket, 1$^7/_8$ in. in diameter and 1 in. high. The above data indicate that in the platinum tube furnace about 40% of the tube volume at the position of the sample was occupied by solid beryllia, leaving 60% of the volume for gas flow.

Prior to the introduction of the platinum basket the temperature gradient along the reaction tube was investigated by means of a platinum platinum–10% rhodium thermocouple, the junction of which was coated with Alundum cement. The thermocouple was moved up and down in the reaction tube while steam was passed through the tube. These traverses with the thermocouple indicated that the temperature did not vary by more than 10° throughout the length to be occupied by the beryllia sample. The steam flow rate had a small effect on the temperature, but did not disturb the position of the constant temperature region.

The weighed basket with sample was introduced into the reaction tube following which the furnace was heated to constant temperature. Water vapor was then passed through the tube for exactly 150 minutes (except runs 1, 8 and 32, which lasted 154, 156 and 154 minutes, respectively, and runs 13 to 16 which lasted 152 minutes each). The temperature of the hot beryllia during each run was measured to within ±15° by optical pyrometry.

After each run the sample basket was removed and weighed and the weight of condensed water was determined. The amount of beryllium oxide lost per liter of gas passing over the sample was calculated from the temperature of the beryllia, the weight data and the rotometer readings. The partial pressure of the volatile beryllium oxide complex in the vapor phase was then calculated, assuming that each molecule of the volatile species contained one atom of beryllium and that the vapor approximated an ideal gas at the temperatures and pressures involved.

Results

Effect of Steam Flow Rate on Rate of Volatilization.—To determine whether equilibrium conditions could be achieved, a series of measurements (no. 1 to 12) was made with water vapor at atmospheric pressure passing over the beryllia at different rates of flow. Small chips of beryllia were used for measurements at both 1460 and 1535°. Large chips of beryllia were used for measurements at 1535°. The results of these measurements are given in Table I.

TABLE I

VOLATILIZATION OF BeO AT CONSTANT TEMPERATURE BUT VARIABLE FLOW RATE OF WATER VAPOR AT ATMOSPHERIC PRESSURE

No.	Size chips	Temp., °C.	Wt. of water, g.	Wt. loss of BeO, g.	Av. flow rate, l./hr.	Partial pressure BeO complex mm.
1	Small	1460	369	0.1560	1119	0.235
2			227	.0999	726	.238
3			175	.0700	560	.216
4			152	.0756	486	.269
5	Small	1535	108	.0797	361	.399
6			160	.1310	534	.442
7			145	.1025	484	.382
8			80	.0578	257	.390
9	Large	1535	131	.0949	437	.391
10			141	.1198	471	.459
11			180	.1423	601	.427
12			185	.1173	618	.343

The extreme values of flow rate used in this series of measurements correspond to linear velocities of 75 and 320 cm. per sec. in the reaction tube and velocities of 125 and 530 cm. per sec. past the chips. Therefore the gas stream was in contact with the chips for 0.05 to 0.01 sec. At 1535° only 5×10^{-1} sec. would be required to obtain 99% saturation of the gas stream if a pure substance of molecular weight 43 were vaporizing under the same conditions of surface area and free volume. This calculation assumes unit accommodation coefficient and infinite rate of mixing in the gas phase. Whether the conditions of these measurements permitted saturation of the gas stream depends on the turbulence in the gas flowing through the sample. As shown by Table I, a fourfold variation in flow rate and a twofold variation in surface area of beryllia produced no perceptible trend in the partial pressure of the volatile complex at constant temperature. Therefore within the accuracy of the measurements equilibrium conditions must have been achieved.

Effect of Temperature on Rate of Volatilization.—A series of measurements (no. 13 to 25) was made at different furnace temperatures. In each case water vapor at atmospheric pressure was passed over small beryllia chips. The results of these

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(10) J. M. Dalla Valle, "Micromeritics, the Technology of Fine Particles," Pitman Publishing Corp., New York, N. Y., 1943, pp. 261-265.

TABLE II

VOLATILIZATION OF BeO IN WATER VAPOR AT ATMOSPHERIC PRESSURE

No.	Temp., °C.	Wt. of water, g.	Wt. loss of BeO, g.	Av. flow rate, l./hr.	Partial pressure BeO complex, mm.
13	1400	471	0.110	1436	0.126
14	1550	469	.339	1558	.390
15	1475	472	.215	1503	.246
16	1600	480	.349	1638	.393
17	1350	197	.0340	590	.0932
18	1350	197	.0311	590	.0853
19	1390	100	.0235	307	.127
20	1395	165	.0418	508	.137
21	1400	223	.0599	689	.145
22	1313	260	.0360	761	.0748
23	1215	383	.0262	1052	.0370
24	1261	233	.0177	660	.0410
25	1199	251	.0134	682	.0288

measurements are given in Table II and shown graphically in Fig. 1. The data of Table I are included in Fig. 1. No correction need be made for the partial pressure of BeO itself since this is equal to only 4.8×10^{-7} mm. at 1600°,[11] which was the highest temperature used in these measurements.

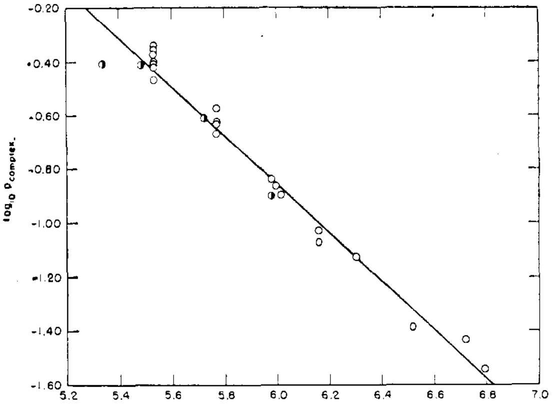

Fig. 1.—Volatility of BeO in water vapor at atmospheric pressure. p_{complex} is the partial pressure of the vapor molecule containing BeO. ◑ indicates points 13–16, which were obtained with an earlier apparatus.

The straight line in Fig. 1 corresponds to the equation

$$\log p_{\text{mm}} = 4.584 - 9060/T \qquad (3)$$

the constants of which were evaluated by the method of least squares. The runs numbered 13 to 16 were made in an earlier apparatus in which conditions for producing saturation were not as favorable as in the later apparatus. The agreement of these runs with the remaining ones is further evidence that saturation was closely approached in all cases.

Effect of Partial Pressure of Water on Rate of Volatilization.—Helium was used to dilute the water vapor in a series of measurements that was made using small beryllia chips at 1400° and varying the partial pressure of the water vapor from 76 mm. to atmospheric pressure. The results of these measurements are given in Table III and shown graphically in Figs. 2 and 3 together with the two measurements at 1400° given in Table II. In Fig. 2 the logarithm of the partial pressure of the volatile beryllium oxide complex is plotted as a function of the logarithm of the partial pressure of water. The slope of the line in Fig. 2 is 0.765. It has been shown earlier that if the observed loss in weight of beryllia and basket is due to only one process the observed slope of this plot should be an integral multiple of $^1/_3$. Even when allowance is made for the small change in equilibrium concentration of the

TABLE III

VOLATILIZATION OF BeO AT 1400° AS A FUNCTION OF THE PARTIAL PRESSURE OF WATER VAPOR

No.	Moles of He	Moles of H_2O	Moles BeO lost × 10⁴	Pressure of H_2O, mm.	Partial pressure BeO complex, mm.
26	8.26	0.93	2.88	76	0.0235
27	6.36	.72	2.00	76	.0212
28	5.90	.78	2.48	88	.0278
29	5.90	1.28	3.72	134	.0389
30	5.90	1.56	3.56	157	.0358
31	5.90	2.11	4.80	198	.0449
32	6.05	3.07	6.96	252	.0572
33	3.26	3.06	5.80	363	.0688
34	1.24	2.79	5.04	519	.0938
35	0.00	3.00	5.36	750	.134
36	.00	5.94	11.00	750	.139

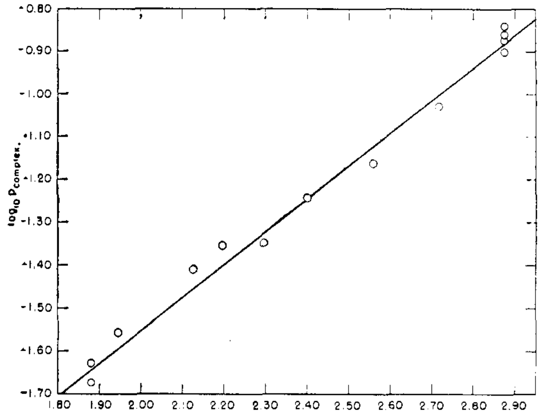

Fig. 2.—Variation of the logarithm of the partial pressure of the volatile BeO-H_2O complex with the logarithm of the partial pressure of water.

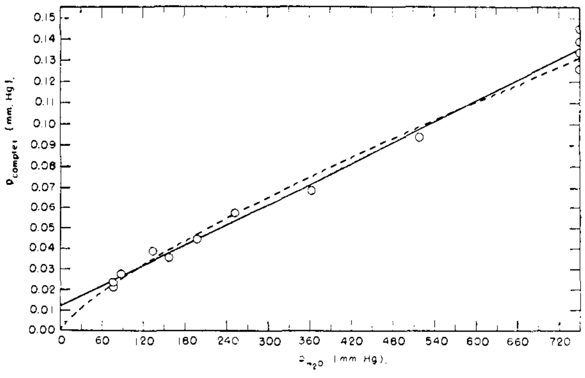

Fig. 3.—Variation of the partial pressure of the volatile BeO-H_2O complex with the partial pressure of water. The dotted curve corresponds to the straight line in Fig. 2.

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[11] N. D. Erway and R. L. Seifert, *J. Electrochem. Soc.*, **98**, 83 (1951).

decomposition products of water that would accompany the reaction of any one of them with beryllium oxide, no simple reaction can be found that is consistent with a slope of 0.765. Further evidence that the decomposition products of water are not involved was obtained from a series of measurements in which dry hydrogen and dry oxygen were passed over the beryllia chips. Within the limit of error of these measurements there was no loss in weight of the beryllia. Berkman and Simon[6] observed a decrease in volatility of beryllium oxide when hydrogen or nitrogen was added to the water vapor. The decrease in volatility was greater with nitrogen than with hydrogen and was attributed in both cases to the decreased diffusion rate of reaction products from the beryllia surface.

To investigate the possibility that more than one process is involved in the observed loss of weight of beryllia and basket the results may be plotted as shown in Fig. 3. If the partial pressure of the volatile beryllium oxide complex is thus plotted as a function of the partial pressure of water, the data may be represented by a straight line with slope of 0.000163 and intercept of 0.0126 mm. for zero partial pressure of water. The dotted curve in Fig. 3 corresponds to the straight line in Fig. 2. It is seen that the experimental data are equally well represented by either curve. The behavior is similar to that shown by the volatility of solid HBO_2 in atmospheres containing water vapor,[4] in which case the intercept corresponds to the partial pressure of HBO_2 above the solid HBO_2. The intercept of 0.0126 mm. corresponds to a total weight loss of sample and basket of 3.6 mg. during a 150-min. run at 500 l./hr. A measurement was made of the volatility of the beryllium oxide in a stream of dry helium. No loss in weight was observed, in agreement with the low values for the vapor pressure of beryllia previously reported.[11] Therefore the intercept in Fig. 3 cannot be interpreted as the vapor pressure of pure beryllium oxide.

The small loss in weight corresponding to this intercept must have been related to the deterioration of the platinum gauze basket that was observed after long usage. Holes, 1 to 2 mm. in diameter, appeared in the platinum gauze at points where it was in contact with the beryllia chips. The appearance of the holes resembled that of local melting of the gauze. In view of the results of the dry helium run loss of weight could accompany the deterioration only if the presence of water vapor is essential for the deterioration to occur. Unfortunately, the dry helium run was not of sufficient duration to indicate whether further deterioration occurred under dry conditions.

Whatever the cause of small additional loss in weight it seems clear that the weight loss resulting from volatilization of the BeO in the presence of water vapor is a linear function of the partial pressure of the water. Therefore the volatilization must result from the reaction

$$\mathrm{BeO(s)} + \mathrm{H_2O(g)} \longrightarrow \mathrm{BeO{\cdot}H_2O(g)} \qquad (4)$$

It may be assumed that the small error in p_{complex} indicated by the intercept in Fig. 3 is independent of the partial pressure of water and that it varies with temperature in approximately the same manner as p_{complex}. Since the magnitude of this error is small such an approximate correction is adequate. Then combining the slope of Fig. 3 with equation (3) one obtains the following equation for K_p of reaction (4)

$$\log K_p = 1.63 - 9060/T \qquad (5)$$

From equation (5) it follows that ΔH^0 for this reaction is 41.5 kcal./mole and at 1400° ΔF^0 is 29 kcal./mole. Combined with the vapor pressure data for beryllium oxide[11] this gives (at 1400°) $\Delta H^0 = -108._5$ kcal./mole, $\Delta F^0 = -57._5$ kcal./mole, and $\Delta S^0 = -30$ e.u. for the gaseous reaction

$$\mathrm{BeO(g)} + \mathrm{H_2O(g)} \longrightarrow \mathrm{BeO{\cdot}H_2O(g)} \qquad (6)$$

However, the value of $-\Delta H^0$ is too large for a simple molecular association, as indicated in equation (6). The values of ΔH^0, ΔF^0 and ΔS^0 are more consistent with the formation of $Be(OH)_2$ by the reaction

$$\mathrm{BeO(g)} + \mathrm{H_2O(g)} \longrightarrow \mathrm{Be(OH)_2(g)} \qquad (7)$$

Though $Be(OH)_2$ is unstable in the solid phase at atmospheric pressure above 300°,[12] it is not necessarily unstable in the gas phase. An approximate value may be calculated for the average Be–OH bond energy in $Be(OH)_2(g)$, assuming ΔC_p for reaction (7) to be -7 cal./mole deg. and using the dissociation energies of BeO and H_2O given by Gaydon[13] and Herzberg,[14] respectively. The resulting average Be–OH bond energy is 109 kcal./mole, which is a reasonable result since the assumptions made herein and in the interpretation of the beryllium oxide vapor pressure data would make this calculated value large. It may therefore be concluded that all the experimental evidence indicates the formation of gaseous $Be(OH)_2$ in the reaction occurring between beryllium oxide and water at high temperatures.

Acknowledgment.—The authors wish to express their appreciation to Dr. S. L. Simon (now at the NACA Laboratories, Cleveland, Ohio) for many helpful suggestions and stimulating discussions during the course of this work.

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