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THE VAPOR PRESSURE OF BERYLLIUM FLUORIDE

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by

K. A. Sense, M. J. Snyder, and J. W. Clegg

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ABSTRACT

Vapor pressures of BeF_2 were measured over the temperature range of 746-968° using the transpiration method. The extrapolated boiling point is shown to be 1159°. The melting point is about 803°.

INTRODUCTION

Since no experimental data on the vapor pressure of beryllium fluoride are available in nonclassified literature, it is considered of interest to report our findings. Because the pressure range was approximately 0.5 - 50 mm mercury, the so-called "difficult" range, the streaming (or transpiration) method of measuring vapor density was employed.^{1,2,3}

Outline of the Method

An inert gas is passed over the salt to be investigated, becomes saturated with it (or nearly so), passes through a condenser where the salt is deposited, and finally passes into a gas-measuring device. Assuming that the ideal gas laws hold, and that Dalton's law of partial pressure is applicable, the following relation holds:

$$p = \frac{m_1 - m_2}{M + m_1 - m_2} P \quad (1)$$

- * Work performed under AEC Contract W-7405-eng-92
(1) H. Von Wartenberg, Z. f. Elektrochem., 19, 485 (1913)
(2) E. Thiele, Ann. d. Physik, 14, 937 (1932)
(3) K. Jellinek, G. A. Rosner, Z. phys. Chem. (A), 143, 51, (1929)

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RESTRICTED DATA

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~~CONFIDENTIAL~~

-2-

where p = vapor pressure of salt,

P = total pressure of salt and carrier gas,

m_1 = total moles salt collected in condenser,

m_2 = moles salt collected in condenser due to diffusion, and

M = moles carrier gas collected.

Salt is deposited in the condenser as the result of two effects, transpiration and diffusion. From equation (1), it is evident that neglect of the diffusion factor would lead to erroneous results, for then, $p \rightarrow P$ as $M \rightarrow 0$. Hence, the amount deposited in the condenser due to diffusion must be subtracted from the total amount. A mathematical analysis of this problem has been made.⁴

Description of Apparatus

The carrier gas used in these runs was highly purified nitrogen which was passed for further purification over heated copper oxide for hydrogen removal, Ascarite[®] for carbon dioxide, magnesium perchlorate for water, and heated metallic copper for oxygen removal. This highly purified nitrogen was then passed into a McDanel[®] tube, 30-inches long, having an I.D. of 1-1/8 inches. Because of the corrosive properties of BaF_2 , the McDanel tube contained a nickel liner, 16-inches long, with an I.D. of $\frac{15}{16}$ inches, within which was placed a nickel boat, 14-inches long. The nickel liner was open at one end to admit the boat and closed at the other end except for a hole large enough for the nickel shield which contained the thermocouple. To insure a central position in the McDanel tube for the boat and liner, alumina plugs, 1-1/2-inches long, and spacers, 4-1/2-inches long, cut from

(4) J. V. Lepore and J. R. Van Wager, A Discussion of the Transpiration Method for Determining Vapor Pressure - MDDC-1188, U. S. Atomic Energy Commission.

* An absorbent of asbestos impregnated with sodium hydroxide manufactured by the A.H. Thomas Company.

**An unglazed, vitreous refractory porcelain tube manufactured by the McDanel Refractory Porcelain Company.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

-3-

a 1-inch O.D. McDanel tube, were used. The plugs had concentric holes of 1/4-inch diameter to admit the nickel thermocouple shield and the condenser from either end of the McDanel tube. To reduce the possibility of contamination from the air when condensers were changed at the start of a run, a short stainless steel tube, 1/2-inch I.D., was inserted concentrically in the rubber stopper which was used to stopper the outlet end of the McDanel tube. The condensers were nickel, about 13-inches long, with an 1/8-inch I.D., and 1/4-inch O.D. The condenser and the nickel thermocouple shield were inserted the same distance from opposite ends of the McDanel tube, being separated by 3/8 inch in the hot zone, each being 3/16 inch from the exact center. Figure 1 shows the details.

After passing through the condenser, which collected the salt, the nitrogen passed through a drying tube (to prevent water vapor from diffusion into the McDanel tube) into a Mariotte flask, where the nitrogen was collected over water. The amount of nitrogen collected was determined from the weight of water displaced. Account was taken of the specific gravity of water displaced, the barometric pressure, the temperature and pressure of the displaced nitrogen, and the vapor pressure of water. Because the outlet spout of the Mariotte flask was at a fixed height, variations of pressure in the McDanel tube resulted only from atmospheric pressure changes.

The furnace was 16-inches long, with a diameter of 12 inches. A 2-inch I.D. liner was wound with 14-gauge Chromel A wire. The hottest region of the furnace turned out to be exactly in the center. At 866°, the temperature was found to be 1/4° lower 3/8 inch from the exact center. Only calibrated chromel-alumel thermocouples were used. The temperature gradients across the nickel shield or a quartz shield were established over the temperature range by inserting into the hot zone a couple without a shield and one with a shield. The voltages generated by the thermocouples were measured by a potentiometer. Temperature was controlled by the

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~~CONFIDENTIAL~~

-4-

use of a Brown Electronic controller-recorder in conjunction with a resistance coil which cut the power to 90 per cent of its full value with the recorder relay in the off position. Temperature stabilization was further aided by the use of a Thermometer*** a commercially available device designed to compensate for power as well as room temperature fluctuations. The result was that the temperature fluctuated by $\pm 1.4^\circ$ or less about a mean temperature.

The quantity of BeF_2 deposited in the condenser was determined in two ways, by direct weighings on an analytical balance, and by chemical analysis. Upon removal of the condenser from the apparatus, the outside was very carefully cleaned with the aid of damp tissue paper and steel wool, and then weighed. It was weighed again after the BeF_2 was removed from the interior of the condenser by repeated washings with water and subsequent drying. The difference in weight of the condenser represented the weight of the BeF_2 . The salt washed out of the condenser was subsequently analyzed. In this manner, one result could be checked against another.

The rate of diffusion of the salt into the condenser at various temperatures was determined by simply clamping off the exit end of the condenser while in the McDanel tube for a given length of time. For each run then, the amount of BeF_2 deposited by diffusion alone could be determined and subtracted from the total deposited.

Material

The BeF_2 used was supplied by the Brush Beryllium Company and reportedly had the following composition: a minimum of 99.0 per cent BeF_2 , with about 0.02 per cent iron, 0.02 per cent aluminum, and 0.01 per cent magnesium. The remainder was made up primarily of BeO and moisture.

*** A voltage regulator manufactured by the Thermo Electric Mfg. Co., Dubuque, Iowa.

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~~CONFIDENTIAL~~

-5-

Experimental Procedure

After a charge of about 20g BeF_2 was placed in the boat and the apparatus was assembled, the system was purged by passing a rapid stream of nitrogen through the system. Then the temperature was raised to about 200° for approximately 4 hours while nitrogen was passed through fairly rapidly. This served to drive moisture out of the BeF_2 , which is hygroscopic. Then, using a moderate nitrogen flow rate, the temperature was raised for several hours to that at which the run was to be made. This served to purify the charge further by driving off any low boiling components which might be present. During this procedure, a "dummy" condenser with the exit end sealed off from the atmosphere by dibutyl-phthalate, was inserted into the McDanel tube. When the run was started, the dummy condenser was removed and the regular condenser inserted. This operation was performed speedily to reduce air contamination to a minimum. Immediately upon insertion of the condenser, the clamped-off rubber tubing leading to the Mariotte flask was attached. This procedure permitted the air in the condenser to be flushed out. The amount of BeF_2 deposited in the condenser during this operation was negligible. Generally, about 10 minutes were allowed to let the condenser get up to temperature. Then, the clamp on the rubber tubing to the Mariotte flask was released, and the run was started. Readings were taken at regular intervals throughout the runs to insure proper control. At the end of the runs, the rubber tubing leading to the Mariotte flask was removed from the condenser, the latter was quickly removed from the McDanel tube and a dummy condenser was replaced just as quickly. Upon cooling, the outside of the condenser was very carefully cleaned with damp tissue paper and steel wool, and the amount of BeF_2 collected was determined as described previously.

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RESULTS

The stability of BeF_2 was established by Brewer⁵, who calculated, from Herzberg's⁶ data, that with a total pressure of 2×10^{-6} atm., BeF_2 is not 50 per cent dissociated until about 3000°K. Since BeF_2 does not dissociate appreciably at the temperatures studied, the vapor pressure of BeF_2 can be calculated directly from the data obtained in the runs. Data on the results of runs conducted in this work are given in Table 1.

With the limits of experimental error, it is apparent from these data that extrapolation to zero flow rate is unnecessary, since saturation of the carrier gas was achieved at the fastest flow rate. Hence, the data were plotted without regard to the flow rate. The following relations were derived:

From 740° - 830°:

$$\log p \text{ (mm Hg)} = 11.822 - \frac{12385}{T, ^\circ\text{K}} \quad (2)$$

$$\Delta H_{\text{sublimation}} = 56.64 \frac{\text{Kcal}}{\text{mole}} \quad (3)$$

Above 803°:

$$\log p \text{ (mm Hg)} = 10.651 - \frac{11125}{T, ^\circ\text{K}} \quad (4)$$

$$\Delta H_{\text{vaporization}} = 50.88 \frac{\text{Kcal}}{\text{mole}} \quad (5)$$

$$\text{Extrapolated boiling point} = 1159^\circ \quad (6)$$

Equation (2) was obtained by application of the least squares method. From (2) and (4), the melting point is found to be 803°.

In a recent paper⁷, the melting point of BeF_2 was determined to be 543°. However, visible evidence from our work indicates that BeF_2 is still in the solid

(5) L.L. Quill, "The Chemistry & Metallurgy of Miscellaneous Materials, Thermodynamics" McGraw-Hill Book Company, 215, (1950)

(6) G. Herzberg, "Molecular Spectre and Molecular Structure", Prentice-Hall, Inc. (1939)

(7) D. Roy, R. Roy, and E. F. Osborn, J. Am. Ceram. Soc., 31, 85-90, (1950)

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-7-

state at a temperature of 754° . Moreover, Novoselova, et al⁸ determined the melting point of BaF_2 to be close to 800° .

The reliability of this vapor pressure apparatus was checked by making runs with KCl. The only change in the apparatus when KCl determinations were made was the use of quartz instead of nickel.

Of the available literature data, Flock and Rodebush's⁹ seem to be the best near the temperature region under consideration. Figure 2 is a plot of their data as well as that of Hackspill and Grandadam¹⁰, together with data resulting from the present work. The agreement is satisfactory.

(8) A. V. Novoselova, M. E. Levina, Y. P. Simanov, and A. G. Zhasmin, J. Gen. Chem., (U.S.S.R.), 14, 385-402 (1944)

(9) E. F. Flock and W. H. Rodebush, J. Am. Chem. Soc., 48, 2522 (1926)

(10) L. Hackspill and R. Grandadam, Ann. chim., 5, 218 (1926)

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-8-

TABLE 1

Temperature, °C	Vapor Pressure, mm Hg		Flow Rate of Ni- trogen, cm ³ /min.
	Obs.	Calc.	
745.9	0.484	0.467	4.89
745.9	0.493	0.467	2.84
746.4	0.519	0.473	7.64
746.5	0.453	0.474	8.75
762.9	0.656	0.740	2.84
762.9	0.704	0.740	8.46
763.1	0.698	0.743	4.62
776.4	1.04	1.05	4.41
777.2	1.12	1.08	2.84
778.9	1.28	1.12	7.12
781.1	1.15	1.19	7.24
781.4	1.12	1.20	2.82
781.6	1.25	1.20	4.55
820.5	2.96	2.01	8.30
820.5	3.11	3.01	2.83
820.6	2.87	3.02	4.62
833.5	4.38	3.97	2.58
833.7	4.46	3.98	7.55
834.0	3.80	4.01	4.04
879.2	10.46	9.93	4.39
879.2	10.60	9.93	2.26
879.7	10.12	10.01	2.85
880.6	11.37	10.21	8.17
916.8	20.0	20.0	2.26
917.0	20.1	20.1	4.60
917.0	17.4	20.1	7.13
940.5	30.7	30.6	7.12
941.1	34.3	30.8	7.27
941.4	30.9	31.0	2.80
941.7	32.4	31.2	4.07
967.4	50.1	48.3	2.73
968.1	48.2	48.9	7.13
968.1	48.4	48.9	4.09

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FIGURE 2. VAPOR PRESSURE OF KCl: x, FLOCK AND RODEBUSH; □, HACKSPILL AND GRANDADAM; O, SENSE, SNYDER, AND CLEGG

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