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Abstract

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Determination of the Heat of Vaporization of Boron Oxide by the Mass-Spectrometric Method

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Boron oxide is one of the important products (intermediate or final) of chemical transformations of various boron-containing compounds, and therefore determination of its heat of vaporization (ΔH_T) is necessary for carrying out many thermodynamic calculations. The long-debated question of the composition of the vapor over boron oxide, after a series of mass-spectrometric studies (1,2), has received a definitive solution: the principal component of boron oxide vapor is the molecule B_2O_3. The first measurements of the vapor pressure of boron oxide, carried out by Koulom and Taylor (3) by the transpiration method, as was shown (4), proved to be erroneous because of the interaction of boron oxide with water vapor contained in the carrier-gas stream. In studies (5–9), the effusion method was used to measure the vapor pressure of boron oxide. In study (1), the effusion method was combined with mass-spectrometric analysis of the evaporation products,* in (10) the vapor pressure of boron oxide was measured by the effusion-torsion method, and, finally, in (11) the measurement was carried out with the aid of a time-of-flight mass spectrometer. Table 1 gives values of $\Delta H_T(B_2O_3)$ calculated from experimental data of various authors.** As can be seen, the discrepancy in the values of $\Delta H_T(B_2O_3)$ obtained, on the one hand, in studies (5,7,8), and, on the other, in studies (10,11), exceeds the experimental error. In our opinion, this may be connected with a number of specific difficulties that arise in working with boron oxide (measurement of the vapor pressure of B_2O_3 vapor in the absence of traces of water both in the preparation and in the apparatus; sufficient sensitivity and reliability of the analytical method,

Table 1

Temp., °K	$\Delta H_T(B_2O_3)$, kcal/mol	Source
1331–1642	76.9	(5)
1335–1515	77	(7)
1414–1621	87	(10)
1268–1593	78.7	(8)
1264–1641	82.9 ± 1.5	(11)

etc.) and are not accounted for in the same way by different authors. In this connection it should be noted that, in the presence of traces of water in the boron oxide preparation, measurements in the region of lower temperatures will give overestimated values of the vapor pressure (and consequently underestimated values of ΔH_T). Thus, for example, $\Delta H_T(B_2O_3)$, calculated from the data of (5) and the data of (7), has the following values (in kcal/mol): 76.9 (in the interval 1331–1642°K) and 80.0 (in the interval 1449–1642° K); 77.0 (in the interval 1335–1515° K) and 82.0 (in the interval 1402–1505° K), respectively. In works (5,7) the samples were heated for 1–2 h at 900° C, which is insufficient. There were therefore grounds to suppose that the values of $\Delta H_T(B_2O_3)$ obtained in works (5,7) were somewhat underestimated. The data (10), obtained in the interval 1414–1621° K, give a higher value $\Delta H_T(B_2O_3) = 87$ kcal/mole; (12) recommends using for calculations the value $\Delta H_T(B_2O_3) = 84 \pm 5$ kcal/mole.

In view of the foregoing, it seemed advisable to us to undertake an investigation to refine the value of $\Delta H_T(B_2O_3)$ by a method combining evaporation from an effusion cell with mass-spectrometric determination of the composition and absolute pressure of the vapor.

We used a boric oxide preparation of "chemically pure for analysis" grade, well dehydrated in a nickel crucible on a vacuum pumping station at a temperature of 1200°C for 1–3 h. To determine the heat of evaporation of boric oxide we used an MS-3 mass spectrometer. The ion source of the mass spectrometer was equipped with a high-temperature evaporator enclosed in a copper jacket cooled by flowing water. Boric oxide was evaporated from a molybdenum effusion cell (ratio of the area of the effusion orifice to the evaporation area 1 : 500). A thermoregulator was used, which made it possible during the measurements to stabilize the temperature of the effusion cell to an accuracy of ±0.5°C. The apparatus, experimental procedure, and temperature-measurement procedure have been described previously (13, 14). After being placed in the effusion cell of the ion source, the boric oxide was subjected to additional dehydration at a temperature of 1100°C and above directly in the mass spectrometer. The vapors of boric oxide leaving the effusion cell passed through a slit system and were ionized by electrons with an energy of 70 eV. To allow for the background, a shutter was used that blocked the access of vapor to the ionization region of the source. In the mass spectrum of boric oxide vapor the ions B^+, BO^+, $B_2O_2^+$, and $B_2O_3^+$ were detected, with relative intensities 2; 7; 7; 100.

Ion currents were measured electrometrically with an amplifier having an input resistance of $5 \cdot 10^{11}$ ohm. To determine the heat of evaporation of boric oxide, the dependence of the ion current $B_2O_3^+$ on the temperature of the effusion cell

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* The authors report that their data differ by no more than a factor of 2 from the data of (5), but they do not give their own experimental data.

** Values of $\Delta H_T(B_2O_3)$ from the data of (6,9) are not given, since they were obtained in a narrow temperature interval.

was studied. The temperature of the effusion cell was varied stepwise every 25–30° by means of the thermoregulator. The establishment of temperature equilibrium was monitored from the readings of self-recording instruments used to measure temperature and ion current. The experimental data obtained were treated by the method of least squares; from a plot of the dependence of $\lg(I \cdot T)$ on $\frac{1}{T}$, the heat of evaporation of boric oxide was calculated.

Table 2

Experiment No.	Temperature interval	Number of measurements	$\Delta H_T(B_2O_3)$, kcal/mole	$\sigma(\Delta H_T)$, kcal/mole
1	1288–1625	110	84.2	0.6
2	1321–1573	66	85.9	1.0
3	1315–1529	155	84.1	1.1

Weighted mean 84.5 ± 0.5

Table 2 gives the values of $\Delta H_T(B_2O_3)$ obtained by us in three experiments (the mean square error is indicated as the deviation). To check the operation of the apparatus and determine the sensitivity of the instrument, silver was evaporated from the same effusion cell, which then made it possible, following the procedure described in works (15, 16) and also used by us (17), to calculate the absolute values of the vapor pressure of B_2O_3. Our experimental data on the vapor pressure of boric oxide are described by the equation:

$$\lg p_{\text{atm}} = (7.44 \pm 0.16) - \frac{84\,500}{4.576T}.$$

The experimental value obtained for the heat of vaporization, ΔH_T $(B_2O_3) = 84.5 \pm 0.5$ kcal/mole (in the range 1315-1529° K), appears to us sufficiently reliable to recommend it for thermodynamic calculations.

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