

Původní práce

VAPORIZATION OF SIMPLE SUBSTANCES USED IN GLASS MELTING

II. Vaporization of Boric Oxide

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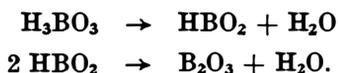
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Using the transpiration method, the density of B₂O₃ vapours was measured in the temperature range of 1000 to 1400 °C in dry nitrogen and in nitrogen-water vapour with a partial pressure of 0.01—0.05 MPa. The results were confronted with data from the literature and with calculations based on thermodynamic data.

INTRODUCTION

Boric oxide is one of the essential glass-forming oxides in industrial glasses. For melting it is usually introduced in the form of orthoboric acid H₃BO₃ or as hydrated sodium tetraborate, and only exceptionally in the form of predehydrated B₂O₃.

Dehydration of orthoboric acid takes place at elevated temperature, possibly combined with reduced pressure, via metaboric acid according to the equations



The dehydration product is a colourless, transparent and hygroscopic mass of amorphous B₂O₃; on heating it produces a viscous melt which only reluctantly gives up its last residual water. After melting in air at 1200 °C B₂O₃ would still contain about 0.1 % H₂O. The water content can further be reduced by melting in vacuo or by bubbling the melt with a dry inert gas.

The physical properties of B₂O₃ depend on the content of residual water. The transformation temperature is then in the range from 287—240 °C (0—0.28 % H₂O), the viscosity attaining 10² dPa s at about 1000 °C. Cooling down of the melt always yields a glass resisting crystallization; the crystalline form of B₂O₃ can only be obtained by special techniques. The melting temperature of crystalline B₂O₃ is 450 °C, its boiling point being given at 2200—2250 °C.

B₂O₃ is known to have a comparatively low vapour pressure but to become strongly volatile in the presence of water vapour, with which it combines producing vapours of HBO₂ and H₃BO₃ (the so-called reactive vaporization).

LITERARY DATA

Vaporization of anhydrous B₂O₃ into an inert atmosphere was dealt with by a number of authors, so that a number of data on B₂O₃ vapour pressure are available; however, the values differ quite considerably. Much less information has been pub-

lished on the reactive vaporization in a water vapour containing atmosphere, although it is just this behaviour of boric oxide which is of considerable practical significance.

Cole and Taylor [1] measured the B_2O_3 vapour pressure by the transpiration method on specimens prepared by dehydration of boric acid at temperatures above $1500^\circ C$ in an oxygen-hydrogen flame; nitrogen was used as the carrier gas in the measurements. The vapour pressure values were obtained by extrapolation to a zero rate of flow, which usually leads to incorrect, too high vapour pressure values. The vapours were assumed to consist of B_2O_3 molecules.

Soulen et al. [2] likewise applied the transpiration method. The B_2O_3 specimens were prepared by heating pure commercial B_2O_3 at $1000^\circ C$ for 1 hour. Nitrogen served as the carrier gas, the experiments being carried out in an apparatus with a porcelain tube either unprotected, or lined with a Pt sheet. The results obtained in the ceramic tube were close to the values reported by Cole and Taylor [1] whereas those from the Pt sheet were lower and close to the data from effusion measurements [5]. The following equation holding for the temperature range of $1331-1808$ K was derived for the B_2O_3 vapour pressure:

$$\log p \text{ (atm)} = -\frac{16\,960}{T} + 6.742. \quad (1)$$

The vaporization was assumed to occur in the form of B_2O_3 molecules, and this was confirmed spectrometrically. The spectrometrical measurements carried out by Bradt [3] likewise revealed the B_2O_3 monomer as a sole significant type of molecule present in the vapours emanating from Knudsen's cell containing B_2O_3 at 1300 K.

Malcev and Matvejev [4] confirmed in a study of emission and absorption spectra that B_2O_3 is mostly vaporized as a monomer. In the presence of water vapour, these authors found HBO_2 molecules, and in the presence of oxygen also BO_2 .

Speiser, Naiditsch and Johnston [5] employed the effusion method for B_2O_3 produced by dehydration of H_3BO_3 at $400^\circ C$ and in vacuo at $900^\circ C$. Their results for the $1331-1642$ K range are in a satisfactory agreement with equation (1) given above. The heat of vaporization calculated from their data amounts to $\Delta H_{1500} = 324.9$ kJ mole⁻¹.

Hildenbrand, Hall and Potter [6] measured by the effusion technique the vapour pressure on B_2O_3 specimens prepared by vacuum dehydration at $1100^\circ C$. For the temperature range of $1410-1590$ K, the results can be described by the equation

$$\log p \text{ (atm)} = -\frac{20\,381}{T} + 8.921. \quad (2)$$

The heat of vaporization obtained from this equation amounts to $\Delta H_{1500} = 390.6$ kJ mole⁻¹, whereas the earlier measurements [5], [8] led to the value of 325 kJ mole⁻¹. The authors ascribe the significant differences in the temperature dependence of B_2O_3 vapour pressure and thus in the heat of vaporization calculated, to the possible influence of water which has absorbed in the specimens during interrupted measurements, and to the subsequent vaporization of HBO_2 .

A higher heat of vaporization is also indicated to by the earlier results of Scheer [7] who worked with the torsion effusion technique in vacuo without interrupting the measurements. The B_2O_3 specimen was prepared by dehydration of H_3BO_3 at $500^\circ C$ in an open Pt crucible and then at $950^\circ C$ while degassing the entire apparatus. The dehydration was concluded when the pressure in the apparatus fell

down to 10^{-4} Pa. The molecular weight of the vapours established was 62 ± 9 (69.64 corresponds to B_2O_3) which implies that within the temperature interval measured, 1414–1621 K, the vapours contain mostly monomeric B_2O_3 molecules. The heat of vaporization ΔH_{1500} was 364 kJ mole^{-1} .

The effusion method was likewise used by Nesmeyanov and Firsova [8] in the 1299–1515 K range for B_2O_3 dehydrated at 900°C and 10^{-3} – 10^{-4} Pa. Determination of oxygen content in the vapours showed that the dissociation to BO and oxygen did not exceed 3% at 1500 K.

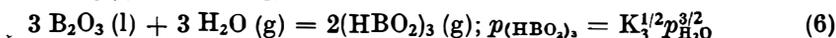
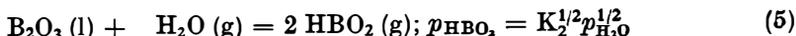
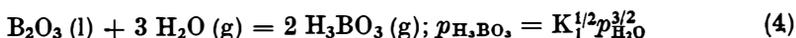
Greene and Margrave [9] used the technique of direct determination of boiling temperatures under variable pressures, and additionally the transpiration method. On the assumption that the vaporization of B_2O_3 may be affected by oxygen in addition to water vapour, they paid special attention to careful purification of the argon carrier gas (copper metal at 400°C and freeze-drying on silica gel). The initial H_3BO_3 was dehydrated at 1200°C for at least 6–8 hours; the degassing was checked by repeated boiling with the first measuring method. Both methods provided identical results, which can be expressed by the following equation for the 1946–2419 K temperature interval:

$$\log p \text{ (atm)} = -\frac{17\,630 \pm 550}{T} + (7.124 \pm 0.064). \quad (3)$$

The heat of vaporization for the given temperature range was $335.3 \text{ kJ mole}^{-1}$. The boiling point established by extrapolation was 2475 K. In view of the induction heating and of a lower accuracy in the determination and in temperature control, the results at the highest temperatures may have involved an error of up to 50°C . The results showed no dependence on the crucible materials: Mo, Al_2O_3 , ZrO_2 .

For the sake of comparison, Fig. 1 shows the vapour pressure of B_2O_3 according to the data of various authors. The data obtained within the present study are also plotted (see below).

Vaporization of liquid B_2O_3 in the presence of water vapour was dealt with by Randall and Margrave [11] who also summarized the results of previous studies. In their measurements they used the transpiration method and introduced the carrier gas over the melt surface in a Pt boat placed in a Vycor glass tube. The loss in weight was determined by weighing after about 1 hour and the pressure of boric vapours was calculated according to the equation $p_B = (\bar{n}_{B_2O_3}/\bar{n}_{total}) P$, where \bar{n} is the number of moles per unit time for B_2O_3 and for the total number of gas moles including vapours, and P is the overall pressure of the system. The measuring temperatures were between 1000–1273 K. The apparatus did not allow to accomplish regular saturation, so that the results had to be corrected. The interpretation of results was based on the work by Chupka and Berkowitz [12] who applied mass spectroscopy and found H_3BO_3 , HBO_2 and the trimer $(HBO_2)_3$ as the products of the reaction of B_2O_3 with water vapour at 1250°C . The following reactions with the appropriate equilibrium constants K_1 – K_3 thus come into consideration:



The total pressure of boric vapours is then given by the equation

$$p_B = p_{H_3BO_3} + p_{HBO_2} + p_{(HBO_2)_3}. \quad (7)$$

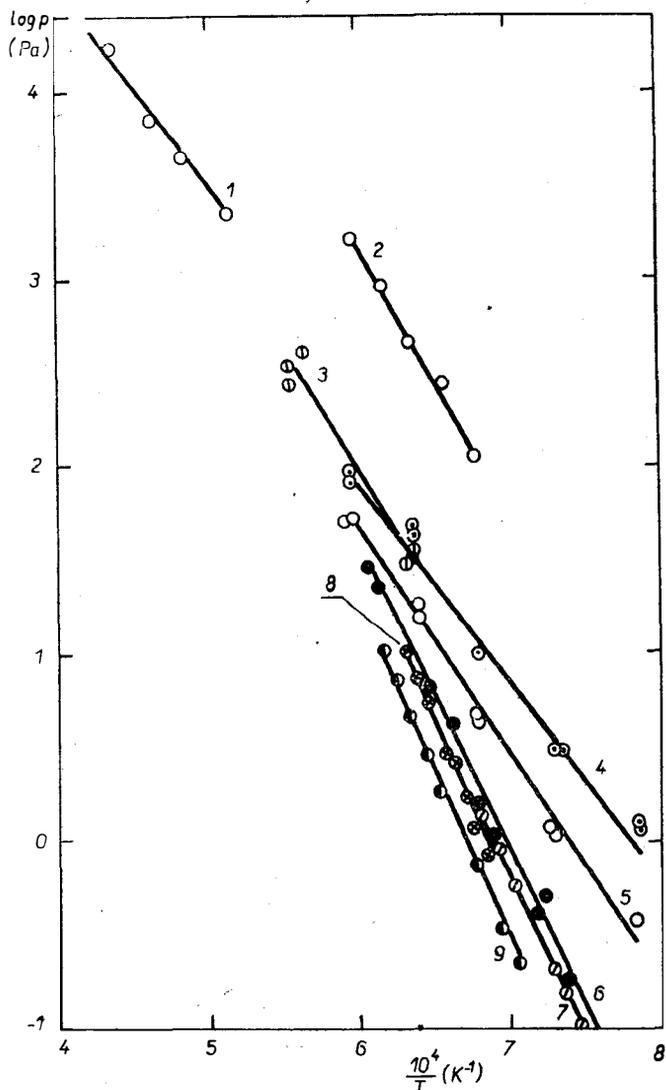


Fig. 1. A comparison of B_2O_3 vapour pressure measured by various authors;
 1 — Greene and Margrave [9], 2 — Cole and Taylor [1], 3 — Soulen et al. [2],
 4 — this work, samples dehydrated at $1400^\circ C$, 5 — this work, vacuum dehydration,
 6 — Speiser et al. [5], 7 — Nesmeyanov and Firsova [8], 8 — Hildenbrand et al. [6],
 9 — Scheer [7].

The equilibrium constants of the respective reactions indicate that the logarithmic dependence of vapour pressure p_B and water vapour pressure may have an incline with a tangent between the limit values of $1/2$ and $3/2$. The experimental results produced a slope of $3/2$ for 1073 K , while for 1273 K and low pressures its value approached $1/2$.

A recent study by Wenzel and Sanders [13] presents the results of transpiration vapour pressure measurements of B_2O_3 (p_B) under water vapour pressures in the range of 1.5–20 kPa at 1376 K, and measurements of the temperature dependence of p_B in the range of 1328–1579 K under a constant water vapour pressure of 2.5 kPa. The authors report that the results of two independent measurements differed by 23 %. On the whole, however, the results are in a satisfactory agreement with the calculation based on the JANAF thermodynamic data. H_3BO_3 and HBO_2 are considered as the sole reaction products. The results bring positive evidence for the model according to which HBO_2 alone is vaporized under low pressure, whereas the H_3BO_3 molecules arise at lower temperatures or at a high water vapour pressures only. The slope of the temperature dependence of p_B corresponds to the value $\Delta H = 168.3 \text{ kJ mole}^{-1}$, which is virtually the value of the heat of formation of HBO_2 ($167.1 \text{ kJ mole}^{-1}$).

It may be concluded that the literature presents many data on B_2O_3 which, however, show considerable differences in their absolute values and also in the temperature dependence slope (heat of vaporization). Incomplete information only is available on reactive vaporization; quantitative data have only been determined for the lower temperature region and under lower water vapour pressures compared to the present study.

EXPERIMENTAL

The apparatus was described in detail in part I [14] together with the measuring procedure. Light-bulb nitrogen served as carrier gas, saturation with water vapour was effected concurrently in the packing of a tempered tube. The borate vapours condensed in a collecting platinum tube and the rest was retained by an aerosol filter. The temperature was measured by a Pt-PtRh thermocouple calibrated by means of a standard thermocouple. The evaporation area of the melt in the boat was 7 cm^2 , the times of exposure were varied between 60 and 240 minutes.

The amount of the vaporized substance was determined from the weight loss of the boat as well as by analyzing the condensate transferred quantitatively into a measuring flask. The analysis was carried out by converting the boric acid to glycerinoboric acid and by titrating the latter with NaOH to phenolphthalein. The results of the analytical determination were lower by 5–13 % than the loss in weight. This result was considered satisfactory as some of the vapours obviously escaped through the filter. Most of the measurements were carried out by weighing the specimens. The results are given as the concentration (density) of B_2O_3 vapour or as apparent vapour pressure calculated for B_2O_3 molecules. This method was chosen to allow direct comparison of the results in dry and in moist nitrogen. Insofar as the vapours contain solely the molecules H_3BO_3 and HBO_2 with a single B atom each, the actual pressure of borate vapours is equal to the value p_B mentioned in the introduction, which in this instance amounts to double the apparent pressure $p_{B_2O_3}$, i.e. $p_B = 2p_{B_2O_3}$. Ideal behaviour of the gases and vapours involved was assumed in the calculation; the volumes were converted to normal conditions (101 325 Pa, 293 K).

The measurements in dry nitrogen were carried out at 1000–1400 °C, those in mixtures with water vapour (0.01–0.05 MPa) at four temperatures in the range of 1000–1300 °C. The dependence of vapour density on the rate of flow of the carrier gas was measured at each temperature and the final result was calculated for the region within which the vapour density was independent of flow rate. For the

given experimental arrangement this was the region of rate of flow over 150 ml min^{-1} . An example of one series of measurements is plotted in Fig. 2.

The B_2O_3 specimens were obtained by dehydration of H_3BO_3 A.R. in a platinum dish heated at first over a burner. The dish was then placed in a silite furnace and heated for 1 hour at 1400 °C. On cooling down the specimen was ground and fused into a boat in a transpiration furnace with the carrier gas flow turned off. It was found that at constant temperature, the vapour pressure in dry N_2 decreases in terms of time, obviously as a result of continuing dehydration (cf. Fig. 3). For this

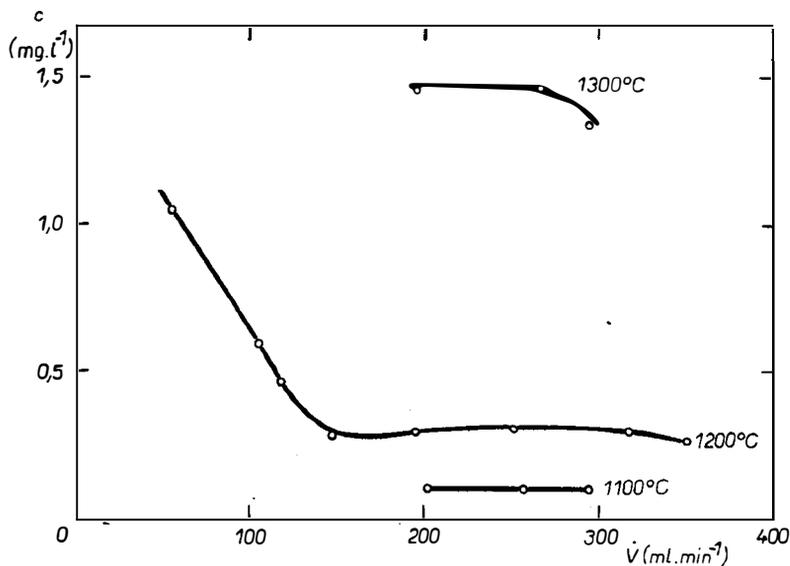


Fig. 2. Carrier gas saturation vs. its rate of flow for B_2O_3 dehydrated at 1400 °C.

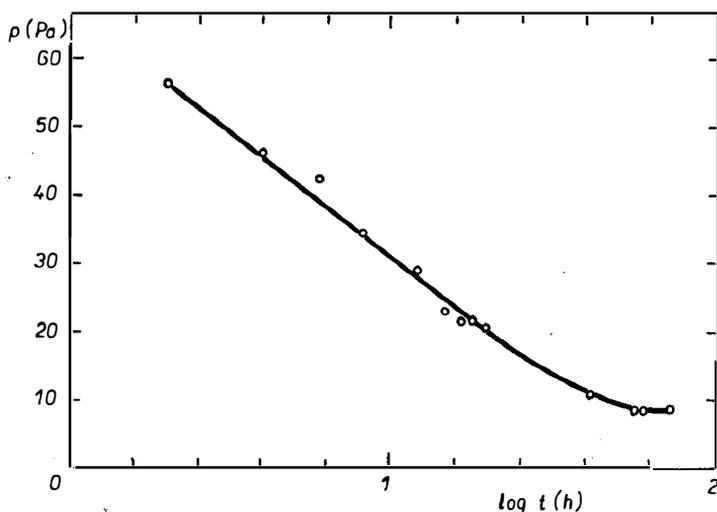


Fig. 3. Apparent vapour pressure of incompletely dehydrated B_2O_3 vs. the time of thermal exposure.

reason the specimen was always subjected to long-term exposure (50–60 h) in the dry nitrogen stream at the respective measuring temperature, and the actual measurements were only then performed with the specimen prepared in this manner. In addition to this, another specimen was prepared by dehydration at 1100 °C under reduced pressure (of units Pa, as a lower pressure would lead to boiling of the melt). The specimen was then kept in a desiccator with P₂O₅.

The results of the measurements are listed in Table I and plotted in the diagram in Fig. 4, together with the results of Wenzel and Sanders for the water vapour pressure of 0.0025 MPa.

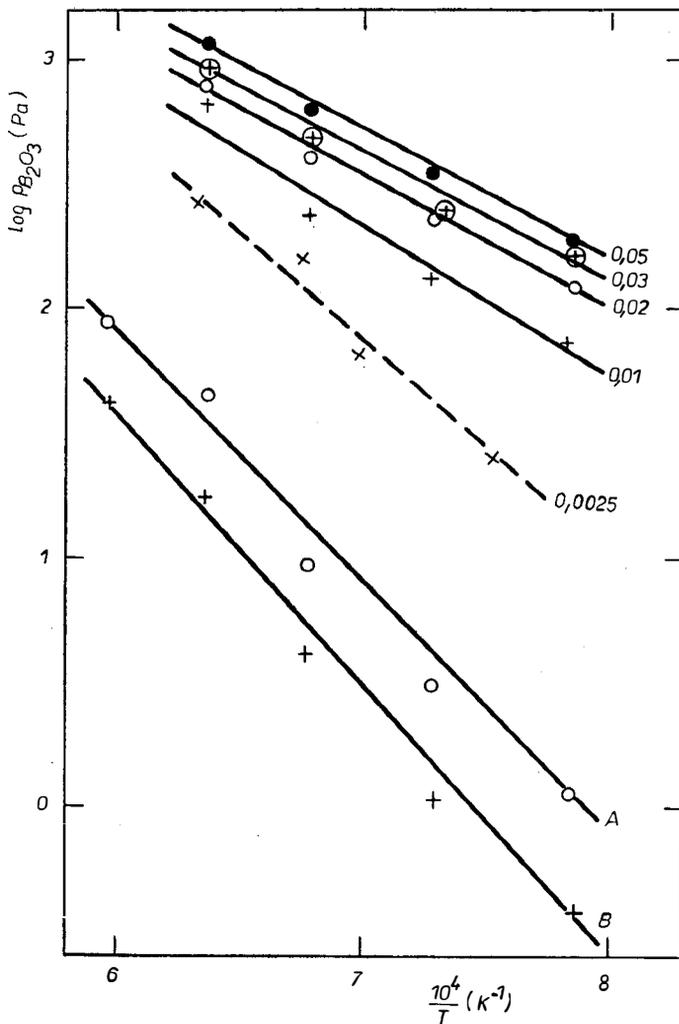


Fig. 4. The results of measuring the B₂O₃ vapour pressure in terms of temperature. The numbers at the curves indicate the water vapour pressure in MPa, the dashed line corresponds to the data by Wenzel and Sanders [13]. The bottom two curves are those for B₂O₃ dehydrated at 1400 °C (A) and in vacuo (B).

Table I

B₂O₃ vapour pressure vs. temperature

Specimen No.	Temperature [K]	Vapour density [mg/l]	Vapour pressure [Pa]
1	1275	0.037	1.21
	1373	0.098	3.20
	1473	0.300	9.78
	1571	1.451	47.26
	1678	2.780	90.60
2	1272	0.011	0.383
	1371	0.033	1.12
	1476	0.132	4.21
	1571	0.551	17.9
	1673	1.311	42.7

Specimen 1: B₂O₃ dehydrated in air at 1400 °C

Specimen 2: B₂O₃ dehydrated in vacuo at 1100 °C

The measurements in the carrier gas containing water vapour were likewise performed on specimens after their long-term dehydration in a dry nitrogen stream at the given temperature. The water vapour content in the carrier gas was checked by absorbing the water in CaCl₂ and by weighing. In the saturating with water thermostated at 47, 61 and 70 °C, the water vapour contents were found to be 10.13, 19.83 and 30.05 % respectively. The highest content was not checked, since at 50 % water vapour saturation the tube with CaCl₂ tended to clog rapidly.

Table II

Vapour density and pressure vs. temperature and water vapour pressure in the carrier gas

p_{H_2O} [Pa]	Temperature [K]	Vapour density [mg/l]	Apparent vapour pressure [Pa]
1.0×10^4	1277	2.18	71.06
	1376	4.12	133.9
	1473	7.61	247.5
	1572	20.92	674.1
2.0×10^4	1273	3.79	123.2
	1375	7.05	228.0
	1475	12.32	404.2
	1573	24.80	802.0
3.0×10^4	1272	5.11	165.0
	1374	7.48	242.6
	1473	14.56	474.0
	1570	29.04	938.0
5.0×10^4	1275	6.00	194.4
	1376	11.03	357.1
	1474	18.70	604.6
	1571	37.12	1194.2

The results of measurement in terms of water vapour pressure in the carrier gas are listed in Table II and plotted in Fig. 4. They are given as apparent pressures of B_2O_3 vapours regardless of the actual form in which B_2O_3 was present.

DISCUSSION

Fig. 3 shows that the B_2O_3 vapour pressure depends considerably on a minute amount of water bound relatively strongly in the melt. Although it was possible to attain a constant vapour density after a suitably long period of time, the density still remained higher than the data obtained by the effusion methods (cf. Fig. 1). It is interesting to note that the results of all the authors who worked by the transpiration method, are relatively high. This may be due to imperfect dehydration of the specimen or rather to interaction with the minute amount of water vapour originating from the furnace atmosphere.

The measuring results plotted in Fig. 4 demonstrate well a strong influence of water vapour, particularly at lower concentrations. The dashed straight line corresponding to the data by Wenzel and Sanders [13] is in a good agreement with our results. The slope of the linear dependence for a moisture of 0.01 MPa corresponds to an enthalpic value of as little as 118 kJ mole⁻¹.

According to most of the studies published so far, vaporization of B_2O_3 in the presence of water vapour mainly involves formation of metaboric acid molecules according to equation [5] mentioned in the introduction. According to this equation, the water vapour pressure and the HBO_2 vapour pressure should be related by the expression which has the following logarithmic form:

$$\log p_{HBO_2} = \frac{1}{2} \log p_{H_2O} + \frac{1}{2} \log K_2 \quad (8)$$

where K_2 is the equilibrium constant of reaction [5]. A graphic plot should therefore produce a straight line with a slope of 1/2. The results of the measurements have been treated in this way in Fig. 5. The slopes of the straight lines have the following values for the temperatures given in the diagram (from the bottom upwards): 0.75, 0.68, 0.57 and 0.45. The slope values obtained at the highest temperatures of 1200 and 1300 °C are very close to the theoretical value of 1/2. It may thus be assumed that metaboric acid HBO_2 prevails in the vapours at these temperatures.

A comparison with the results of Wenzel and Sanders shows a very good agreement; the values measured by these authors link up satisfactorily to the straight lines in Fig. 5 extrapolated towards the water vapour pressure of 0.0025 MPa. A linear dependence between the logarithm of boric vapour pressure and the logarithm of ambient water vapour pressure was thus established within a broad range of temperatures and pressure.

The higher value of the slope of the linear relations in Fig. 5, found for the lower temperatures, is obviously caused by the simultaneous formation of orthoboric acid molecules (H_3BO_3) according to reaction [4]. In this instance the definition relationship for the equilibrium constant is such that its conversion to the logarithmic form yields:

$$\log p_{H_3BO_3} = \frac{3}{2} \log p_{H_2O} + \frac{1}{2} \log K_1. \quad (9)$$

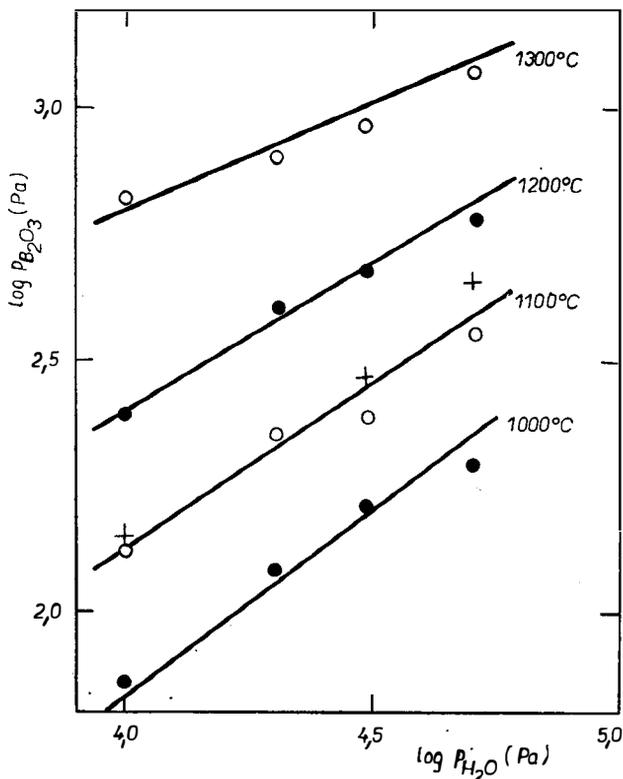


Fig. 5. Apparent B₂O₃ vapour pressure vs. water vapour pressure in the carrier gas at various temperatures.

With increasing H₃BO₃ content in the vapours the slope value of the linear relationships would therefore increase up to 3/2 (an angle of 56 deg.). Our results imply that measureable amounts of H₃BO₃ are also formed at low temperatures and that its relative content in the vapours does not essentially depend on the ambient water vapour pressure. The H₃BO₃ content decreases with increasing temperature, so that HBO₂ is the prevailing species above 1200 °C.

The theoretical vapour pressures of the B₂O₃ calculated by means of equilibrium constants for the reactions producing HBO₂ and H₃BO₃ mentioned above are given in Fig. 5 by crosses. Their values, calculated from the JANAF thermodynamic data for 1376 K, are [13]:

log K₁ = -3.8838 and log K₂ = -4.2926. The apparent pressure of B₂O₃ vapour was calculated from the equation:

$$p_{B_2O_3} = \frac{1}{2} (K_2^{1/2} p_{H_2O}^{1/2} + K_1^{1/2} p_{H_2O}^{3/2}). \quad (10)$$

At the given temperature and under the water vapour pressure of 0.05 MPa, the two products should be present in about the same proportion, while at 0.01 MPa the share of H₃BO₃ amounts to as little as 15 %. This is the cause of a higher theoretical value at the highest water vapour pressure, where the non-linearity of the

theoretical dependence has a significant effect. In view of the ready water vapour condensation at a higher saturation degree, the highest experimentally determined $p_{\text{H}_2\text{O}}$ value may involve an error which would lead to a lower result for $p_{\text{B}_2\text{O}_3}$. Another possible cause is a lower stability of the H_3BO_3 molecules than that assumed by the theory, or possibly gradual saturation of the B_2O_3 melt with water. Apart from the value at $p_{\text{H}_2\text{O}} = 0.05$ MPa, the agreement between experiment and theory is very satisfactory.

CONCLUSION

The results of this work supplement the available data on reactive vaporization of B_2O_3 for a wider temperature and pressure region. In this way they provide information on real behaviour of B_2O_3 melts under the conditions of contact with water vapour. The results are in a good agreement with the recent data reported by Wenzel and Sanders [13]. The agreement with thermodynamic calculations is likewise satisfactory.

References

- [1] Cole S. S., Taylor W.: J. Am. Ceram. Soc. 18, 82 (1935).
- [2] Soulen J. R., Shapitmonda P., Margrave J. L.: J. Phys. Chem. 59, 132 (1955).
- [3] Bradt P.: NBS Report 3016, Jan. 1954.
- [4] Malcev A. A., Matvejev V. K.: Dokl. AN SSSR 137, 123 (1961).
- [5] Speiser R., Naiditsch S., Johnston H. L.: J. Am. Chem. Soc. 73, 2911 (1950).
- [6] Hildenbrand D. L., Hall W. F., Potter N. D.: J. Chem. Phys. 39, 296 (1963).
- [7] Scheer M. D.: J. Phys. Chem. 61, 1184 (1957).
- [8] Nesmeyanov A. N., Firsova L. D.: Zh. fiz. chim. 5, 1032 (1960).
- [9] Greene F. T., Margrave J. L.: J. Phys. Chem. 70, 2112 (1966).
- [10] Kasha W. E. et al.: J. Chem. Phys. 34, 570 (1961).
- [11] Randall S. P., Margrave J. L.: J. Inorg. Nucl. Chem. 16, 29 (1960).
- [12] Chupka W. A., Berkowitz J.: J. Chem. Phys. 33, 530 (1960).
- [13] Wenzel J. T., Sanders D. M.: Phys. Chem. Glasses 23, 47 (1982).
- [14] Hlaváč J., Karásek M., Rybaříková L.: Silikáty 27, 355 (1983).

VYPAŘOVÁNÍ TAVENIN JEDNODUCHÝCH LÁTEK POUŽÍVANÝCH K TAVENÍ SKLA

II. Vypařování oxidu boritého

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Transpirační metoda popsaná v první části práce byla použita pro studium vypařování roztaveného oxidu boritého za atmosférického tlaku, v prostředí suchého dusíku a ve směsích dusíku s vodní parou o parciálním tlaku 0,01—0,05 MPa. Efektivní tlak páry B_2O_3 v suchém dusíku silně závisel na způsobu a stupni dehydratace vzorku (obr. 3). Vodní pára v nosném plynu výrazně ovlivňuje tlak boritých par (obr. 4 a 5). Výsledky dobře navazují na nedávné údaje Wenzela a Sanderse (1982), jež byly získány v prostředí o nižší vlhkosti. Závislost efektivního tlaku boritých par na tlaku vodní páry svědčí o tom, že při 1200—1300 °C převládá v parách HBO_2 , zatímco při nižší teplotě jsou ve značné míře přítomny i molekuly H_3BO_3 . Byl nalezen dobrý souhlas naměřených údajů s výsledky výpočtů z termodynamických dat.

- Obr. 1. Srovnání tlaků par B_2O_3 naměřených různými autory: 1 — Greene a Margrave [9], 2 — Cole a Taylor [1], 3 — Soulen et al. [2], 4 — tato práce, dehydratace při 1400 °C, 5 — tato práce, vakuová dehydratace, 6 — Speiser et al. [5], 7 — Nesmejanov a Firsova [8], 8 — Hildenbrand et al. [6], 9 — Scheer [7].
- Obr. 2. Závislost syčení nosného plynu na jeho průtoku pro B_2O_3 dehydratovaný při 1400 °C.
- Obr. 3. Závislost zdánlivého tlaku par neúplně dehydratovaného B_2O_3 na čase tepelné expozice.
- Obr. 4. Výsledky měření tlaku páry B_2O_3 v závislosti na teplotě. Číslice u křivek značí tlak vodní páry v MPa, čárkovaná křivka přísluší údajům Wenzela a Sanderec [13]. Dolní dvě křivky přísluší B_2O_3 dehydratovanému při 1400 °C (A) a vakuově (B).
- Obr. 5. Závislost zdánlivého tlaku par B_2O_3 na tlaku vodní páry v nosném plynu při různých teplotách.

ИССЛЕДОВАНИЕ ИСПАРЕНИЯ РАСПЛАВОВ ПРОСТЫХ ВЕЩЕСТВ, ПРИМЕНЯЕМЫХ ДЛЯ ВАРКИ СТЕКЛА

II. Испарение оксида трехвалентного бора

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Транспирационный метод, описываемый в первой части работы, использовали для исследования испарения расплавленного оксида трехвалентного бора при атмосферном давлении в среде сухого азота и во смесях азота с водяным паром парциальным давлением 0,01—0,05 МПа. Эффективное давление пара B_2O_3 резко зависит от способа и степени дегидратации пробы (рис. 3). Водяной пар в газе-носителе оказывает сильное влияние на давление паров бора (рис. 4 и 5). Результаты являются продолжением последних данных Венцела и Сандерса (1982), которые были авторами получены в среде с более низкой влажностью. Зависимость эффективного давления паров бора от давления водяного пара является свидетельством того, что при 1200—1300 °C преобладает в парах HBO_2 , в то время как при более низкой температуре в значительной степени присутствуют даже молекулы H_3BO_3 . Было найдено хорошее согласие измеренных данных с результатами расчетов, полученных из термодинамических данных.

Рис. 1. Сравнение давлений паров B_2O_3 , измеренных разными авторами: 1 — Грин и Марграв [9], 2 — Кол и Тейлор [1], 3 — Сулен и сотр. [2], 4 — измерения авторов, дегидр. при 1400 °C, 5 — измерения авторов, дегидр. под вакуумом, 6 — Спейсер и сотр. [5], 7 — Несмеянов и Фирсова [8], 8 — Гильденбранд и сотр. [6], 9 — Шер [7].

Рис. 2. Зависимость насыщения газа-носителя от его протока для B_2O_3 , дегидр. при 1400 °C.

Рис. 3. Зависимость кажущегося давления паров не вполне дегидратированного B_2O_3 от времени термической экспозиции.

Рис. 4. Результаты измерения давления паров B_2O_3 в зависимости от температуры. Числительные у кривых обозначают давление водяного пара в МПа, штриховая кривая — данные Венцела и Сандерса [13]. Нижние две кривые отвечают B_2O_3 , дегидратированному при 1400 °C (A) и под вакуумом (B).

Рис. 5. Зависимость кажущегося давления паров B_2O_3 от давления водяного пара в газе-носителе при разных температурах.

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