VAPORIZATION OF SIMPLE SUBSTANCES USED IN GLASS MELTING

III. Vaporization of Sodium Tetraborate Melt

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The transpiration method was used to measure the density of melted borax vapours at 900 to 1115 °C in nitrogen atmosphere and in nitrogen-water vapour mixtures. The results imply a relatively small effect of water vapour on the density of borate vapours and are indicative of quasi-congruent vaporization resulting from the reaction of the melt with water vapour.

INTRODUCTION

In spite of being a quite common substance, information on high-temperature behaviour of dehydrated borax in the literature presents neither numerous nor complete data. The earlier works by Klooster [1], Jaeger [2] and Briscoe et al. [3] only state qualitatively volatilization above the melting point specified at 1015 K.

Cole and Taylor [4] measured the vapour pressure of B_2O_3, $NaBO_2$ and $Na_2B_4O_7$ melts by the transpiration method at 1423 to 1673 K in nitrogen atmosphere. To evaluate the results, they used the method based on extrapolating to zero flow of the carrier gas, which usually leads to lower values. For $Na_2B_4O_7$, the vapour pressure value thus obtained amounted to 0.28 kPa (1423 K) and 3.33 kPa (1673 K). The vapours had the mean composition of 51.6 wt. % Na_2O and 48.4 wt. % B_2O_3; the vapour therefore contained more Na_2O than the melt. The composition is close to that of metaborate, $NaBO_2$, whose molecule is very stable in vapours at high temperatures.

Tamura et al. [5] studied vaporization of melts in the systems $R_2O-B_2O_3$ at 1000—1300 °C. In a series of $Na_2O-B_2O_3$ melts of stepped-up composition, they found distinct peaks of vaporization rate close to the composition corresponding to $NaBO_2$. Up to 40 wt. % Na_2O in the melt, the Na_2O content in the vapours was substantially higher. The vaporization rate showed a decrease in terms of time as a result of Na_2O depletion of the melt. The KBO_2 melt vaporized at a rate roughly ten times higher than that of $NaBO_2$, which again showed vaporization several times faster than $LiBO_2$.

Büchler et al. [6] investigated vaporization of B_2O_3 and borates by Knudsen's effusion method and a mass spectrometer. In the vapours above $NaBO_2$, they found $NaBO_2$ molecules and a small amount of the dimer, $Na_2(BO_2)_2$. Traces of the trimer were also determined. The vapour pressures of the monomer and dimer at 1070 K were 5.03×10^{-2} Pa and 2.03×10^{-3} Pa respectively,

Cable [7] discussed in detail vaporization from melts of the system $Na_2O-B_2O_3$ from the standpoint of kinetics. He showed that the composition of vapour and melt was identical for metaborate, so that vaporization of the melt of this composition did not involve diffusion in the melt and the vaporization rate was independent

of time. The author also analyzed the unpublished data by Lawton [8]; the table allows the rate of vaporization from a melt having the approximate composition of $Na_2B_4O_7$ to be determined: on free vaporization from a Pt crucible into a static atmosphere the weight loss at 1200 °C after 2 hours amounted to $60-98$ mg/cm², and after 20 hours to $365-506$ mg/cm². The vaporization rate therefore decreased in terms of time.

Terai and Egushi [8] followed thermogravimetrically the effect of water vapour on the vaporization rate of B_2O_3 and $Na_2B_4O_7$. They found the vaporization rate to increase in the presence of water vapour. At low temperatures with melts with the molar ratio $Na_2O : B_2O_3$ higher than 1, the results were independent of the ambient water vapour pressure, while showing conversely a strong dependence at the ratio lower than 1 (assumed formation of HBO_2). The activation energy of the vaporization process at a content of 9.3% H_2O in the ambient atmosphere amounted to 161 kJ/mole, which according to the authors agrees with the heat of the reaction $B_2O_3 + H_2O = 2\,HBO_2$.

Frischat and Herr [9] compared the behaviour of various boric minerals at high temperatures. For tinalconite, which has the same $Na_2O : B_2O_3$ ratio as borax, and thus produces a melt of the same composition, they found higher volatilization losses than for B_2O_3 and colemanite in dry atmosphere. In moist atmosphere $(0-50\%$ $H_2O)$ the losses were higher than in the case of colemanite, but lower than in that of B_2O_3.

In the two latter studies, thermal analysis apparatus was used in the measurements, i.e. at a continuously increasing temperature. The conditions for saturating the ambient gas are not specified and the experimental data obviously pertain to non-equilibrial states.

EXPERIMENTAL

The transpiration apparatus described in [10] was used in the measurements. The carrier gas (N_2) was saturated with water vapour in a thermostatted gas washing bottle. In all the measurements, the rate of carrier gas flow was 200 cm³/min, the time of measurement being 180 minutes in all cases. Following thermal exposure, the loss in the sample weight was determined by weighing. Under the given conditions, the carrier gas was completely saturated, so that the saturated vapour concentration and the corresponding borate vapour pressure could be calculated from the loss in the sample weight and the known volume of carrier gas passed through. As the vaporization is assumedly incongruent and the vapour composition not precisely known, the borate vapour pressure is specified as an apparent one, being related to the hypothetical molecules of $Na_2B_4O_7$.

The measurement results are plotted in Figs. 1 and 2. The plot indicates that the water vapour in the carrier gas has a distinct but not much significant effect on the apparent pressure of borate vapours. Fig. 1 implies the linear temperature dependence for the carrier gas containing water vapour, whereas in dry nitrogen this dependence is curved.
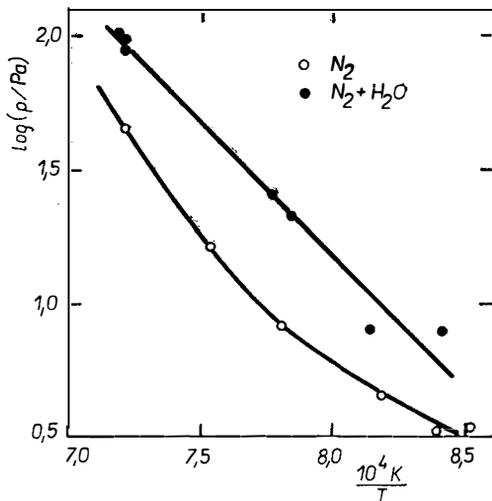
Fig. 1. *Temperature dependence of* $Na_2B_4O_7$ *vapour pressure in dry and moist carrier gas* (N_2 *and* N_2 *with 19.5 vol. %* H_2O).
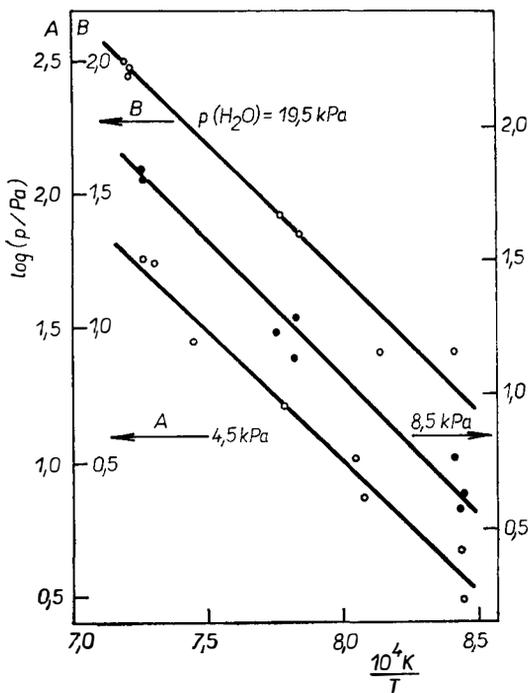

Fig. 2. *Temperature dependence of* $Na_2B_4O_7$ *vapour pressure for various partial water vapour pressures in the carrier gas.*

DISCUSSION

Direct comparison with the results given in the literature is impossible as the measurements were not carried out in the same temperature range. The data by Cole and Taylor [4] are somewhat higher than the extrapolated results of the present study. This is in agreement with the way the results were interpreted in the study quoted. According to Cole and Taylor, the vapour pressure of $Na_2B_4O_7$ in dry nitrogen (calculated for an $Na_2O + Na_2B_4O_7$ mixture with a mean molecular weight of 158.3 g mole^{-1}) at 1423'K is given by the value log $(p/Pa) = 2.44$, whereas the value extrapolated in Fig. 1 is approximately 2.1. The result by Büchler [6], obtained by the effusion method (0,05 Pa at 1077 K) for $NaBO_2$ is conversely lower than the extrapolated value from Fig. 1. No other comparable data on equilibrial vapour pressure were found.

A comparison with the study by Frischat and Herr [9] can be carried out on the assumption that the vaporization rate is proportional to the equilibrium vapour pressure. According to these authors, the $Na_2B_4O_7$ melt (of tinalconite) vaporizes about 3 times faster than that of B_2O_3 (dry atmosphere, 1000 °C); according to our results for borax and for B_2O_3 [11] the difference at the same temperature is about $10-50$ — fold according to the degree of B_2O_3 dehydration. The dynamic measurements by Frischat and Herr.could not lead to complete dehydration of B_2O_3, as this is very slow, and this circumstance must have had a significant effect on the vaporization of B_2O_3. As regards the effect of water vapour, according to the authors mentioned the vaporization rate of B_2O_3 at $p(H_2O) = 8.5$ kPa is higher roughly by 50 % than that from tinalconite melt (having the composition $Na_2B_4O_7$), while according to the measurements carried out by the present authors at the same temperature of 1000 °C, the difference in the concentration of vapours is three-fold. According to the former authors, the vaporization rate increases continuously and very steeply up to $p(H_2O) = 30$ kPa, where the ratio of the volatilization rates from the two melts amounts roughly to 2, being higher for B_2O_3. The results of our measurements show a significantly milder dependence of the $Na_2B_4O_7$ vapour pressure on $p(H_2O)$ compared to B_2O_3.

According to data from the literature, vaporization of the borax melt is incongruent, i.e. $NaBO_2$ vapours volatilize and the melt is enriched with boric oxide. This fact alone may be responsible for a non-linear dependence of log (p) on temperature. Under the conditions of measurement described above, with a standard exposure of 180 minutes, the free density convection occurs in the melt influencing the concentration relations at the melt-carrier gas boundary. The equilibrium concentration of vapours will be then time-dependent with respect to the instantaneous composition of the melt surface. This time dependence could be described either under the conditions of perfect mixing, or in a static melt free of density convection. However, such conditions are difficult to create. The results obtained for vaporization in dry nitrogen are therefore of only limited significance and relative validity.

A different situation occurs during vaporization into a moist medium, as indicated by Figs. 1 and 2. The temperature dependence of log (p) of borate vapours is linear, showing identical slopes at all the water vapour pressures employed. The regular course can be explained by quasi-congruent vaporization according to the reaction

$$Na_2B_4O_7 \text{ (l)} + H_2O \text{ (g)} = 2\,NaBO_2 \text{ (g)} + 2\,HBO_2 \text{ (g)} . \tag{1}$$
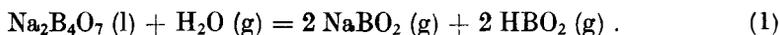
In this case, the ratio of Na_2O to B_2O_3 is identical with that in the melt[*] According to known experience, the melt proper does not contain any major amounts of H_2O, and the vapours do not contain molecules of $Na_2B_4O_7$ nor B_2O_3.

According to Figs. 1 and 2, the effect of water vapour in the carrier gas on the borate vapour pressure is relatively small. The equilibrium constant of reaction (1) is given by the equation

$$K = \frac{p^2(NaBO_2, g) \times p^2(HBO_2, g)}{p(H_2O, g)} \qquad (2)$$

The mass balance must be maintained during the reaction, where $p(NaBO_2) = p(HBO_2)$, and one obtains

$$K = \frac{p^4(B)}{p(H_2O, g)} \qquad (3)$$

where $p(B)$ is the total pressure of borate vapours, i.e. $NaBO_2 + HBO_2$.

The equilibrium constant expressed in this way indicates that

$$p(B) = \{K\, p(H_2O, g)\}^{1/4}, \qquad (4)$$

or

$$\log p(B) = 1/4 \log \{K\, p(H_2O, g)\}. \qquad (5)$$

For equation (1) these relationships indicate a very small effect of the ambient moisture content on the vaporization proper. The experimental data basically conform to the relationship between $\log p(B)$ and $\log p(H_2O)$ according to equation [5]: the points provide a straight line with a slope close to 1/4.

On assuming the above reaction to be valid, the data on the vaporized amount of $Na_2B_4O_7$ can be used to calculate the pressures of $NaBO_2$ and HBO_2 vapours; each of them will be double the apparent vapour pressure of $Na_2B_4O_7$.

To verify this assumption, the reaction according to equation (1) was subject to thermodynamical analysis. Using the JANAF tables (1971), standard changes of Gibbs energy were calculated for the reaction, and the following values were obtained for the equilibrium constant of reaction (1):

$$\log \{K_p(1200\ K)\} = -15.84 \quad \text{and} \quad \log \{K_p(1400\ K)\} = -10.11.$$

From these values, for the temperature range of 1200—1400 K, one obtains the heat of reaction $\Delta H_r^0 = 920$ kJ/mole.

Equation (5) indicates that the heat of reaction can also be calculated from temperature dependence $\log \{p(B)\}$ on $1/T$ (Fig. 2) according to the relationships derived from Clausius-Clapeyron equation for formal heat of vaporization by multiplying the result with four:

$$H_r^0 = 4 \left[\frac{2.303\, R T_1 T_2}{T_2 - T_1} \log \frac{p(B)_2}{p(B)_1} \right]. \qquad (6)$$

The linear relationships in Fig. 2 have roughly the same slope from which, using equation (6), one obtains for the heat of reaction value $\Delta H_r^0 = 750$ kJ/mole, i.e. a value lower by about 20 % than that obtained by calculation from tabelar data. In view of the relatively low accuracy of the transpiration method the results need not be regarded as not satisfying the given assumption. The significant point is the linear dependence of $\log \{p(B)\}$ on $1/T$ at various water vapour contents in the

carrier gas, and particularly the same slope of these linear relationships. Such a course can be expected in the case of the reaction according to equation (1).

CONCLUSION

The results characterize the behaviour of borax during the melting of glass from the point of view of vaporization. The initial vapour pressure of the borax melt is higher than that of completely dehydrated B_2O_3 in a dry medium. However, in the presence of water vapour the ratio is reversed, i.e. in the comparable temperature range of $900-1100\ °C$ the B_2O_3 will vaporize more extensively. This difference decreases with increasing temperature as a result of the different slope of the temperature dependence.

The experimental results and their analysis indicate that the following reaction takes place in the presence of water vapour:

$$Na_2B_4O_7\ (l) + H_2O\ (g) = 2\ NaBO_2\ (g) + 2\ HBO_2\ (g),$$
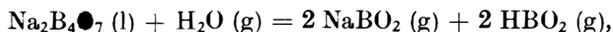
during which the melt composition does not change and the vaporization of borax into the medium containing water vapour then proceeds as quasi-congruent vaporization.

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VYPAŘOVÁNÍ JEDNODUCHÝCH LÁTEK POUŽÍVANÝCH PŘI TAVENÍ SKLA

III. VYPAŘOVÁNÍ TAVENINY TETRABORITANU SODNÉHO

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Transpirační metodou, popsanou v práci (10), byla měřena hustota par roztaveného boraxu $Na_2B_4O_7$ při teplotách 900—1115 °C v atmosféře dusíku a ve směsi dusíku s vodní parou o různém parciálním tlaku. Průtok nosného plynu 200 cm³/min zajišťoval regulární sycení parami, doba měření byla jednotně 180 min. Po tepelné expozici se vážením stanovil úbytek hmotnosti vzorku.

Výsledky jsou uvedeny v obr. 1 a 2 jako zdánlivé tlaky par hypotetických molekul $Na_2B_4O_7$, aby bylo možno srovnávat intenzitu vypařování v suchém a vlhkém prostředí, kdy skutečné složení par je odlišné. Podle grafů na obr. 1 a 2 má vodní pára sice zřetelný, ale nepříliš výrazný vliv na takto vyjádřený tlak par $Na_2B_4O_7$. Významným faktem je lineární závislost log $p(Na_2B_4O_7)$ na $1/T$ ve vlhkém nosném plynu, zatím co v suchém prostředí je tato závislost

zakřivená. Vysvětlení spočívá v tom, že inkongruentní charakter vypařování v suchém dusíku (vypařování $NaBO_2$) se mění ve vlhkém prostředí na quasi-kongruentní ve smyslu rovnice (I). Poměr látkových množství Na_2O a B_2O_3 je v tomto případě v parách stejný jako v tavenině. Termodynamický rozbor (rovnice 2—5 v textu) ukázal dobrou shodu predikce se skutečným chováním, pokud se týká závislosti tlaku boritých par na $p(H_2O)$ v nosném plynu (rov. 4 a 5). Reakční teplo vypočtené pro uvedenou reakci (1) z experimentálních dat činí $\triangle H^\circ_r = 750$ kJ/mol, což je hodnota o 20 % nižší než vypočtená z termodynamických dat (JANAF). Vzhledem k poměrně malé přesnosti transpirační metody není tento rozdíl pokládán za nevyhovující představě o quasi-kongruentním vypařování $Na_2B_4O_7$ v přítomnosti H_2O.

Obr. 1. Teplotní závislost tlaku par $Na_2B_4O_7$ v suchém prostředí (N_2 a N_2 a *19,5 % obj.* H_2O).
Oar. 2. Teplotní závislost tlaku par $Na_2B_5O_7$ pro různé dílčí tlaky par v prostředí.

ИСПАРЕНИЕ ПРОСТЫХ ВЕЩЕСТВ, ПРИМЕНЯЕМЫХ ПРИ ПЛАВЛЕНИИ СТЕКЛА
III. ИСПАРЕНИЕ РАСПЛАВА ТЕТРАБОРАТА НАТРИЯ

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С помощью транспирационного метода, описанного в работе [10], измеряли плотность паров плавленой буры $Na_2B_4O_7$ при температурах 900—1115 °C в атмосфере азота и во смеси азота в водяным паром разного парциального давления. Протоком газа-носителя 200 см³/мин. обеспечивалось насыщение парами, время измерения составляло всегда 180 мин. После термической экспозиции взвешиванием устанавливали убыль массы образца.

Результаты приводятся на рис. 1 и 2 в виде кажущихся давлений паров гипотетических молекул $Na_2B_4O_7$, чтобы можно было сопоставлять интенсивность испарения в сухой и влажной средах, когда действительный состав паров является различным. Хотя и согласно графикам на рис. 1 и 2 водяной пар заметен, однако он не оказывает весьма резкое влияние на таким образом выражаемое давление паров $Na_2B_4O_7$. Важным фактом является линейная зависимость $\log p(Na_2B_4O_7)$ от $1/T$ во влажном газе-носителе, в то время как в сухой среде приводимая зависимость имеет криволинейную форму. Объяснение заключается в том, что инконгруентный характер

испарения в сухом азоте (испарение $NaBO_2$) изменяется во влажной среде в квазиконкруентный согласно уравнению (1). Отношение количества вещества Na_2O и B_2O в парах в данном случае одинаково как в расплаве. Термодинамический анализ (уравнения 2—5 в тексте) показал хорошее согласие предполагаемого поведения с реальным поведением относительно зависимости давления паров бора на $p(H_2O)$ в газе-носителе (уравнения 4 и 5). Теплота реакции, рассчитанная для приводимой реакции (1) на основании экспериментальных данных составляет $\Delta H^\circ_r = 750$ кдж/мол, что представляет собой величину на 20 % более низкую по сравнению с рассчитанной величиной на осноавнии термодинамических данных (JANAF). Имея в виду относительно низкую точность транспирационного метода, нельзя приводимое различие считать непригодным в связи с представлением о квазиконгруентном испарении $Na_2B_4O_7$ в присутствии H_2O.

Рис. 1. Температурная зависимость давления паров $Na_2B_4O_7$ *в сухом и влажном газе-носителе* (N_2 *и* N_2 *с 19,5 % по объему* H_2O).
Рис. 2. Температурная зависимость давления паров $Na_2B_4O_7$ *для разных парциальных давлений пара в газе-носителе.*