

Vapour pressure and standard enthalpy of sublimation of H_3BO_3

R. Pankajavalli, S. Anthonysamy, K. Ananthasivan, P.R. Vasudeva Rao *

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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Abstract

A horizontal thermal analysis instrument was adapted as a transpiration apparatus for the measurement of vapour pressure of solid boric acid, H_3BO_3 . The experimental parameters necessary for establishing a dynamic isothermal congruent vapourisation equilibrium of H_3BO_3 were identified. Using these optimized transpiration experiments, the vapour pressures were measured in the temperature range 326–363 K. The temperature dependence of the measured values of vapour pressures could be expressed using the expression, $\log(p/\text{Pa}) = 26.83(\pm 0.09) - 9094(\pm 246)/T$ (K). The standard enthalpy of sublimation, ΔH_{sub}^0 , of H_3BO_3 was estimated to be $174.1 \pm 4.7 \text{ kJ mol}^{-1}$ at the mean temperature of the present measurements, viz., 345 K.

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1. Introduction

Compounds of boron containing ^{10}B are used as neutron absorbers in the nuclear industry. In fast reactors boron carbide is used as a control rod material [1]. Boron carbide containing boron enriched in ^{10}B isotope will be used in the control rods of the first Indian Prototype Fast Breeder Reactor (PFBR) [2].

The carbothermic reduction of boric acid or its anhydride is used in the large scale commercial production of boron carbide [3]. In this process, a significant quantity of boron is lost during the reduction and subsequent process steps. An alter-

nate process which does not involve significant loss of boron would be more suitable for the production of boron carbide from boric acid (enriched in ^{10}B). Recently a new scheme was proposed by Bhabha Atomic Research Centre, India [4]. This scheme involves the following steps: (i) conversion of boric acid into potassium fluoroborate, (ii) production of boron from potassium fluoroborate through fused salt electrolysis, (iii) purification of the cathode deposit by ‘acid-leaching’, (iv) production of boron carbide by direct reaction of the elements and (v) consolidation of the boron carbide powder. In order to generate the fundamental data required for building a facility for the production of elemental boron (steps (i)–(iii)) based on the above scheme, a ‘demonstration facility’ is currently being operated at the Indira Gandhi Centre for Atomic Research, India.

* Corresponding author. Tel.: +91 44 27480 229; fax: +91 44 27480 065.

E-mail address: vasu@igcar.ernet.in (P.R. Vasudeva Rao).

The enriched boric acid obtained after the enrichment process would be in the form of a 5% solution. This would be converted to solid boric acid in a drying equipment. In this step boric acid could encounter temperatures significantly above the ambient. Hence, care need to be exercised to prevent loss of the precious enriched boron through vapourisation of the volatile boric acid. Hence, it would be instructive to know the vapour pressure of boric acid over a temperature range of relevance to this application. However, reliable vapour pressure data for boric acid are not available in the literature. Hence, in this study, the vapour pressure of H_3BO_3 (s) was measured in the temperature range 326–363 K by a transpiration technique.

2. Experimental

2.1. Materials

Analytical Reagent grade H_3BO_3 (>99% pure, M/s Ranbaxy, Mumbai, India) was used in the vapour pressure experiments.

2.2. Thermogravimetry (TG)

TG experiments were carried out using a TG/DTA thermal analysis system (Model – Seiko 320, Japan). In a typical experiment about 35 mg of H_3BO_3 held in a platinum crucible was heated in a flowing stream of helium (flow rate, $5.7 \text{ dm}^3 \text{ h}^{-1}$) at a linear heating rate of 0.17 K s^{-1} . Using these experiments the mass-loss steps as well as the decomposition/melting temperature of H_3BO_3 were identified.

2.3. Vapour pressure measurements

The transpiration experiments were carried out using an experimental set-up based on the horizontal thermal analysis system mentioned above. The block diagram of this thermal analysis system, details of modification made to it in order to carry out the transpiration experiments and the corrections made for apparent weight losses during isothermal experiments are described in detail elsewhere [5–7].

In a typical experiment finely divided boric acid powder was spread over a shallow Pt crucible placed on the arm of the TG apparatus. High purity helium gas was passed at a pre-determined rate over this sample at a given temperature. A Pt–13% Rh/Pt

thermocouple (Type-R) was used for the measurement of temperatures with an accuracy of $\pm 0.5 \text{ K}$. The thermocouple was calibrated at the freezing point of pure metals such as tin, lead, antimony and silver. The mass loss of boric acid was recorded as a function of time using the TG analyzer. The apparent vapour pressure, p^{app} , was then calculated from the mass loss of the sample per unit volume of the carrier gas ' V_c ' at temperature T_c , using the relation

$$p^{\text{app}} = WRT_c/MV_c, \quad (1)$$

where M is the molecular weight of the vapour species, W is the mass loss of the sample and R is the universal gas constant. Further, Eq. (1) assumes that the vapour is ideal and that a monomeric moiety is the only gaseous species in equilibrium with the solid. These conditions are fulfilled in the congruent sublimation of boric acid below 365 K. It is seen from the literature [8–10] that the vapour phase, in equilibrium with solid H_3BO_3 , contains only the monomeric H_3BO_3 .

The horizontal design of the dual arm thermal analyzer minimises errors arising in weight measurement due to convection, buoyancy and thermal expansion of the beam. A Pt–13% Rh/Pt thermocouple which formed an arm of the microbalance beam was used for temperature measurement.

3. Results and discussion

3.1. Non-isothermal TG

The results obtained in the non-isothermal experiments carried out with boric acid are shown in Fig. 1, which reveal that the decomposition of

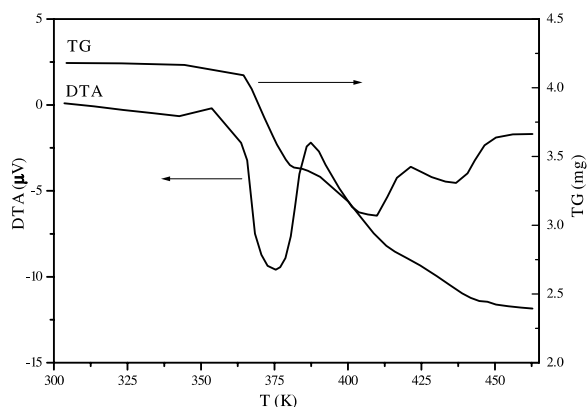


Fig. 1. TG and DTA trace of H_3BO_3 .

H_3BO_3 commences at 365 K. The three broad endotherms with the onset temperatures of 365, 387 and 420 K could be assigned to the progressive dehydration steps, resulting in the conversion of H_3BO_3 into HBO_2 , $\text{H}_2\text{B}_4\text{O}_7$ and B_2O_3 , respectively. The decomposition of H_3BO_3 into HBO_2 , $\text{H}_2\text{B}_4\text{O}_7$ and B_2O_3 at progressively higher temperatures has been reported in the literature [11]. The weight loss of boric acid measured in this study confirms the decomposition of H_3BO_3 into HBO_2 , $\text{H}_2\text{B}_4\text{O}_7$ and B_2O_3 at temperatures 365, 387 and 420 K, respectively. Thus, the decomposition of boric acid limits the maximum temperature for the present study of its congruent vapourisation to 365 K.

3.2. Vapour pressure measurements

A carrier gas flow regime pertaining to a dynamic congruent vapourisation of H_3BO_3 (s) under isothermal conditions was identified through the following procedure. Mass-loss experiments were carried out employing different carrier gas flow rates, viz., 5–34 $\text{dm}^3 \text{h}^{-1}$. The regime in which the values of the derived vapour pressures were independent of the flow rate of the carrier gas was identified using the classical transpiration curve constructed using the above data (Fig. 2). It is seen from this plot that the carrier gas is saturated with the vapour in the flow rate region between 11 and 18 $\text{dm}^3 \text{h}^{-1}$. Hence in the present study, vapour pressure measurements were carried out at a flow rate of 11–18 $\text{dm}^3 \text{h}^{-1}$ over the temperature range 326–363 K.

Prior to transpiration experiments, blank runs were conducted with flow rates of 11 and

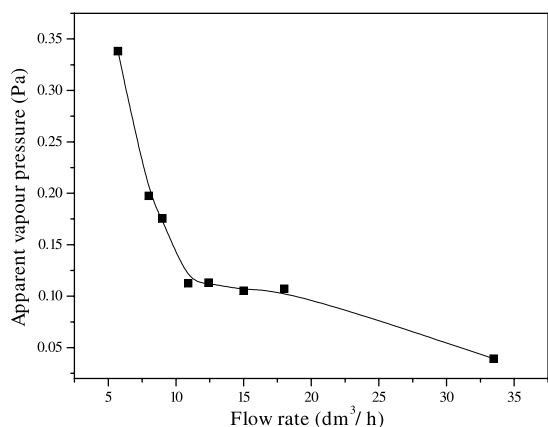


Fig. 2. Plot of apparent vapour pressure of H_3BO_3 against flow rate of the carrier gas at 326 K.

18 $\text{dm}^3 \text{h}^{-1}$ of He gas at temperatures within 300–500 K and keeping both sample and reference pans empty. The apparent mass gain was of the order of 2.0 μg for the above temperature range encompassing the full range of flow rate. However, at any given temperature in this range, the drift in mass with time was of the same magnitude namely 2.0 $\mu\text{g} \text{h}^{-1}$. This apparent mass loss was subtracted from all the recorded isothermal mass losses. The lowest mass loss measured in this study is 28 μg which is very significantly higher than the isothermal drift in the mass during the measurements.

The mass-loss data obtained in the present study along with the vapour pressure of H_3BO_3 obtained from the same are summarized in Table 1 and Fig. 3. The temperature dependence of the vapour pressure of H_3BO_3 could be represented by the following least-squares expression:

$$\log(p/\text{Pa}) = 26.83(\pm 0.09) - 9094(\pm 246) / T \text{ (K)}(326\text{--}363 \text{ K}). \quad (2)$$

From the above equation, the vapour pressure of solid boric acid in the temperature range 326–363 K was found to vary from 0.1 to 68 Pa. From the slope of the above equation, a value of 174.1(± 4.7) kJ mol^{-1} was derived to be the standard enthalpy of sublimation, ΔH_{sub}^0 (second law) of H_3BO_3 at the mean temperature of 345 K.

Stackelberg et al. [10] measured the vapour pressure of boric acid over the temperature range 382–413 K and reported a value of 102 (± 2.5) kJ mol^{-1} as the enthalpy of sublimation. It is known that H_3BO_3 undergoes a melting transition at 444 K

Table 1
Vapour pressure of H_3BO_3 by the TG transpiration method

Experiment number	T (K)	Mass loss (μg)	V_c (dm^3)	Pressure (Pa)
1	326	28	10.909	0.103
2	326	32	12.414	0.1034
3	326	36	15	0.963
4	326	44	18	0.981
5	331	64	12.414	0.2069
6	335	120	12.414	0.3879
7	340	284	12.414	0.918
8	341	454	10.909	1.670
9	341	342	12.414	1.1055
10	344	668	12.414	2.1592
11	347	1950	12.414	6.3032
12	351	2028	10.909	7.4597
13	355	4880	10.909	17.950
14	363	20940	12.414	67.686

Initial weight of the sample: 35 mg.

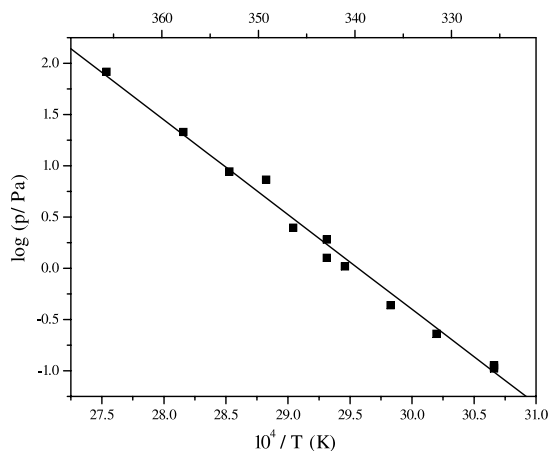
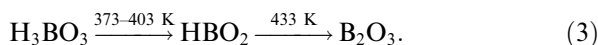


Fig. 3. Temperature dependence of equilibrium vapour pressure of H_3BO_3 .

when heated at a faster rate [8,12] while at lower heating rates it decomposes through the consecutive reactions represented by Eq. (3) [12]



The temperature range employed in the present investigation is below 373 K. Therefore, the above reactions may not interfere with the present investigations. From the TG–DTA data obtained in the present study, it is evident that in the temperature range of investigation employed by Stackelberg et al. [10] H_3BO_3 is thermodynamically not stable. Thus, the vapour pressures reported in Ref. [10] would have been influenced by the water vapour produced as during the decomposition of H_3BO_3 . In view of the above, the values reported in Ref. [10] could not be considered any further.

In order to assess the temperature dependent errors in the present measurements, a third-law analysis of the vapour pressure data was carried out. The third-law enthalpies pertaining to the values of the equilibrium pressures measured at different temperatures were computed using the appropriate Gibbs energy functions obtained from Ref. [8]. These values showed a systematic variation with temperature. It is surmised that the narrow temperature range of the present investigation (40 K) is not large enough to permit a meaningful ‘third-law’ analysis. The ‘second-law’ enthalpy

derived at the mean temperature of the present investigation, 345 K is $177.4 \pm 4.7 \text{ kJ mol}^{-1}$.

4. Conclusion

A horizontal thermal analyzer was used as a transpiration set-up for the measurement of the vapour pressure of solid H_3BO_3 . The attainment of equilibrium was ensured using the classical transpiration procedure of identifying a flow regime over which the derived vapour pressures were independent of the carrier gas flow at 326 K. From the vapour pressure measurements, a value of $174.1 \pm 4.7 \text{ kJ mol}^{-1}$ was obtained as the standard enthalpy of sublimation, ΔH_{sub}^0 at the mean temperature of 345 K. The results reported in this study are consistent with the thermodynamic stability of $\text{H}_3\text{BO}_3(\text{s})$ and supersede the data reported earlier in Ref. [8]. From the present investigation it is clear that prolonged heating at 343 K would not decompose H_3BO_3 and would help remove the adsorbed moisture.

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