# Study of Vaporization of Sodium Metaborate by Transpiration Thermogravimetry and Knudsen Effusion Mass Spectrometry

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ABSTRACT: The vaporization of solid sodium metaborate $NaBO_2(s)$ was studied by transpiration thermogravimetry (TTG) and Knudsen effusion mass spectrometry (KEMS). The transpiration measurements, performed for the first time on $NaBO_2(s)$, involved use of argon as the carrier gas for vapor transport and derivation of vapor pressure of $NaBO_2(g)$ (by assuming it as the sole vapor species) through many flow-dependence runs and temperature-dependence runs in the temperature range 1075−1218 K. The KEMS measurements performed in the temperature range 1060−1185 K confirmed

$NaBO_2(g)$ as the principal vapor species over $NaBO_2(s)$, in accord with the previously reported KEMS studies. The values of $p(NaBO_2)$ obtained by both TTG and KEMS are consistent within the uncertainties associated with each method and so are the second- and third-law values of enthalpy of sublimation, the latter aspect consistently missing in all previous vaporization studies. The results of both TTG and KEMS were combined to recommend the following thermodynamic parameters pertinent to the sublimation reaction, $NaBO_2(s) = NaBO_2(g)$: $Log\{p(NaBO_2)/Pa\} = -(17056 \pm 441)/(T/K) + (14.73 \pm 0.35)$ for the temperature range 1060−1218 K; $\Delta_r H^o_m(298.15\ K) = (346.3 \pm 9.4)\ kJ \cdot mol^{-1}$; and $\Delta_r S^o_m(298.15\ K) = (210.2 \pm 6.8)\ J \cdot mol^{-1} \cdot K^{-1}$.
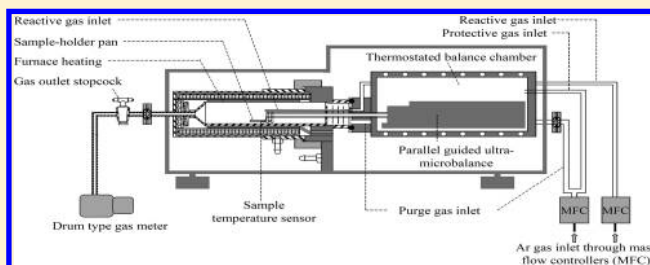
1. INTRODUCTION

In continuation of a detailed vaporization study of boric acid by transpiration thermogravimetry (TTG) and Knudsen effusion mass spectrometry (KEMS),[1] we have sought to undertake a similar study of another boron-containing system, sodium metaborate, an important component of sodium borosilicate glasses, the industrial development of which is of practical interest for nuclear waste disposal.[2,3] Sodium metaborate also finds important application in the energy field: for production of sodium borohydride, the catalytic hydrolysis of which will generate hydrogen and sodium metaborate as a byproduct that can be recycled.[4,5] Additional motivating factors for starting the present study are: (1) no transpiration measurements exist on $NaBO_2$-(s); (2) among the three previously reported KEMS studies on $NaBO_2(s,l)$,[6−8] the first two give vapor pressures only at one temperature (1070 K[6] and 1270 K[7]) and the third[8] gives the $p−T$ relations; but not only is this reference not easily accessible, the vapor pressure is given (by the same authors) only at one temperature in their subsequent easily accessible publication;[9] and (3) the value of partial pressure of $NaBO_2(g)$ obtained in the KEMS studies are not very consistent.

The congruently vaporizing nature of equimolar composition $(Na_2O)_{0.5}(B_2O_3)_{0.5}$ was identified by Cole and Taylor[10] way back in 1935 through their transpiration study of liquid samples of $(Na_2O)_x(B_2O_3)_{1-x}$ ($x = 0, 1/2, 1/3$). While the samples with $x = 0$ and $1/2$ volatilized without change in the composition, that with $x = 1/3$ volatilized by preferential loss of the Na_2O component. Uncertain of the molecular formula for the vapor species,

the authors reported two sets of vapor pressures for the equimolar composition sample (that pertinent to the present study) at five temperatures at 50 K intervals between 1423 and 1623 K: one for the vapor species $NaBO_2(g)$ and the other for the vapor species $Na_2O.B_2O_3(g)$. Kröger and Sörström[11] performed Knudsen effusion measurements on sodium metaborate in 1965, in the temperature range from 1110 to 1316 K. Their measurements essentially consisted of condensing the vapor effusing from the Knudsen cell on an aluminum foil and deducing the vapor pressures (from the rate of mass gain of the foil) with the assumption that vaporization is congruent. As Cole and Taylor[10] did, these authors also presented two sets of results, one each for the molecular formulas $NaBO_2$ and $Na_2O.B_2O_3$. Furthermore, taking the melting temperature of the substance as 1223 K, they reported the results corresponding to two temperature ranges, 1103−1223 K and 1223−1333 K, respectively.

The first mass spectrometric study of sodium metaborate was by Akishin et al.[12] in 1961. They performed the preliminary experiments by evaporating lithium and sodium metaborates from "a platinum band". The mass spectra of both substances were similar, and subsequent experiments were performed with lithium metaborate only using "an ion-source with an effusion chamber". From their conclusion of these experiments on lithium metaborate, it is evident that they attribute the formation of

MBO_2^+ to monomeric species and $M_2BO_2^+$ (M = Li or Na) to a more complex molecule (possibly M_3BO_3). These authors did not report vapor pressures or any other thermodynamic data. In 1963, Büchler and Berkowitz-Mattuck[6] performed the first detailed KEMS study of vaporization of sodium metaborate, the sample prepared by dehydration of $Na_2B_2O_4 \cdot 8H_2O$. They identified in the mass spectrum the ions Na^+, $NaBO_2^+$, $Na_2BO_2^+$, $Na_3(BO_2)_2^+$ in the ratio 2.7:1.0:0.37:0.001. From duplicate sublimation runs (990 to 1140 K), these authors gave the enthalpy values at $T = 1070$ for the sublimation reaction $NaBO_2(s) = NaBO_2(g)$ and for the dimerization reaction $2NaBO_2(g) = Na_2(BO_2)_2(g)$. Employing silver for pressure calibration, they also gave the partial pressure values again at $T = 1070$ K for $NaBO_2(g)$ (5×10^{-2} Pa) and $Na_2(BO_2)_2(g)$ (2×10^{-3} Pa). These results showed unambiguously for the first time that the vapor phase over sodium metaborate is composed of monomeric and polymeric species (with the latter, dimer and trimer together, being only $\leq 4\%$ of the monomer). The authors identified alkali metaborates as pseudohalides based on the resemblance in the composition and dimerization energies of metaborate vapors with those of alkali halide vapors. It is not clear as to why Büchler and Berkowitz-Mattuck[6] chose not to report $p-T$ relations for $NaBO_2(g)$ and $Na_2(BO_2)_2(g)$.

In 1971, Gorokhov et al.[7] studied the vaporization of sodium metaborate by KEMS as well as by the mass-loss Knudsen effusion method. They listed the ion intensities of Na^+, $NaBO_2^+$, and $Na_2BO_2^+$ (in the ratio 3.30:1.00:0.25), the values of total vapor pressure, and the dimer-to-monomer ratio at 1270 K. They also deduced the second-law enthalpies of sublimation for the monomer and the dimer from the temperature dependence of ion intensities (1080—1230 K). It is not clear as to why these authors did not report vapor pressures at temperatures other than 1270 K.

In 1985, Yasue and Asano[8] published a brief report (of Kyoto University - in Japanese) of mass spectrometric study of vaporization of $NaBO_2(s)$. They gave $p-T$ relations for $NaBO_2(g)$ (914 to 1129 K), $Na_2(BO_2)_2(g)$ (1005 to 1127 K), and $Na_3(BO_2)_3(g)$ (1149—1201 K). These results, while confirming the finding of Büchler and Berkowitz-Mattuck[6] that polymeric species constitute no greater than 4% of the vapor phase, yield at $T = 1070$ K a value of partial pressure for the monomeric species that is relatively 3.5 times higher (0.18 Pa). The enthalpy values for sublimation reactions, $iNaBO_2(s) = (NaBO_2)_i(g)$ ($i = 1$ to 3) as well as for polymerization reactions, $iNaBO_2(g) = (NaBO_2)_i(g)$ ($i = 2, 3$) were tabulated by Asano and Yasue[9] at selected temperatures of 1071 K ($i = 1$), 1066 K ($i = 2$), and 1175 K ($i = 3$). The enthalpy of sublimation to $NaBO_2(g)$ and that of dimerization of $NaBO_2(g)$ reported by these authors[9] are in reasonable accord (within error limits) with the values reported by Büchler and Berkowitz-Mattuck,[6] although it is not clear as to why the sublimation enthalpy for $NaBO_2(g)$ reported in ref 9 (Asano and Yasue) is about 9 kJ·mol^{-1} lower than that deducible from the $p-T$ relation given in ref 8 (Yasue and Asano).

Analysis of results of all three mass spectrometric studies revealed one common disconcerting feature - the third-law enthalpy of sublimation of $NaBO_2(s)$ to $NaBO_2(g)$ being distinctly higher than the second-law value: the difference is 28 kJ mol^{-1} (Büchler and Berkowitz-Mattuck[6]), 34 kJ mol^{-1} (Gorokhov et al.[7]), and 32 kJ mol^{-1} (Yasue and Asano).[8,9] On the other hand, the vapor pressures obtained in the studies of Cole and Taylor[10] and Kröger and Sörström[11] yield higher second-law enthalpies than the third-law values by 132 kJ mol^{-1} and 54 kJ mol^{-1}, respectively. Thus, the remark by Gorokhov et al.[7] is

still valid - that the second-law enthalpy of sublimation differed significantly from the third-law values in all vaporization studies performed so far on sodium metaborate.

The vaporization of solid sodium metaborate, practically to single vapor species (monomers), renders TTG[1,13,14] a convenient means of obtaining reliable vapor pressures and sublimation enthalpy values. With no TTG measurements reported so far on $NaBO_2(s)$, we conducted a systematic study for the first time to obtain vapor pressures over a temperature range of 150 K. A reasonably good consistency was obtained between second- and third-law values. We also conducted a KEMS reinvestigation not only to confirm whether the vapor phase is predominantly of monomers but also to resolve the discrepancy that existed within and among the results of previous KEMS studies. In conformity with the identification of alkali metaborates as pseudohalides by Büchler and Berkowitz-Mattuck,[6] the electron-impact ionization behavior of vapor species also appeared to be similar to that of alkali halides — dissociative ionization dominating over simple ionization, favoring the formation of positive ions with the loss of BO_2 from $NaBO_2(g)$ and $(NaBO_2)_2(g)$. The intensity of Na^+ was 3 to 4 times greater than that of $NaBO_2^+$, and the ion $Na_2(BO_2)_2^+$ was not detected at all. Very disconcerting results were obtained in the first two series of KEMS measurements though: the temperature dependence of ion intensities was often inconsistent between the runs, and they also corresponded to relatively lower enthalpy of sublimation than the TTG results. However, KEMS measurements in the last two series, performed with the samples that were fully predehydrated in the TTG apparatus, yielded results that were consistent among themselves as well as with those from the TTG experiments in terms of the vapor pressure and the sublimation enthalpy for $NaBO_2(g)$. There was good agreement between second- and third-law values for the sublimation reaction as well. All these aspects of the present study and comparison with previously reported results are presented and discussed in detail in the paper.

2. EXPERIMENTAL SECTION

$NaBO_2(s)$ was prepared by dehydration from $NaBO_2 \cdot 4H_2O$ (Sigma-Aldrich, USA, purity: 99 mass percent) in two steps. The first step involved heating ~ 12 g of the sample (taken in a quartz beaker) at 423 K for 24 h in a vacuum oven. From the mass loss, it was inferred that 0.85 mass fraction of water of hydration was removed from the original sample. The residue was stored in a plastic container, sealed with cellophane paper, and designated as 'bulk sample'. The second step of removal of remaining fraction of water of hydration from the bulk sample was performed in situ at higher temperatures — by heating the known aliquots of the bulk sample in a platinum crucible for TTG study (as well for the last two series of KEMS measurements) and in a platinum Knudsen cell for KEMS studies (in the first two series).

The transpiration measurements were performed by using the commercial thermogravimetric apparatus (Mettler Toledo TG/SDTA 851),[1,13,14] and the KEMS measurements were performed by using a magnetic sector mass spectrometer (VG MM 30 BK).[1,15] The details of both instruments are given in the references cited, and only the salient features pertinent to the present study are given here.

For TTG studies, the aliquot from the bulk sample was transferred to a cylindrical Pt-crucible (dia: 6 mm and depth: 4 mm), nearly up to its brim, and placed on the pan of the microbalance, positioned in the center of the horizontal furnace.
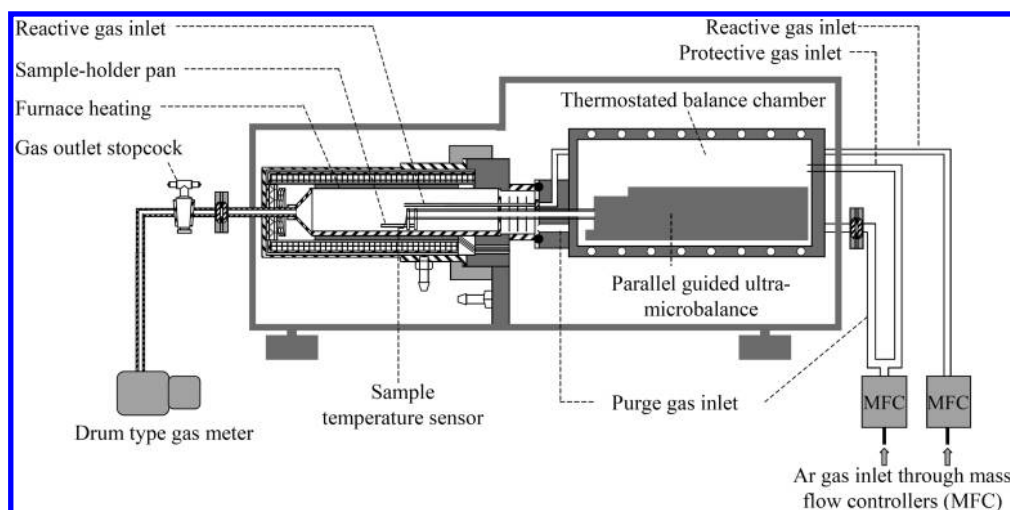
Figure 1. Schematic of the thermogravimetric apparatus used for transpiration measurements.

Experiments were performed on two aliquots (initial mass = 19.2 mg and 26.7 mg, respectively). The complete dehydration of the bulk sample was sought to be achieved by subjecting it to dynamic heating at the rate of 1−2 K per minute to various temperatures 393, 473, 573, 673, 773, 973, 1073, and 1173 K (and to isothermal heating at least for 1 h at each of these temperatures) before beginning the normal transpiration measurements. Figure 1 shows the schematic of the TTG apparatus used in the present study.[1,13] The apparatus has an horizontal furnace having three inlets and one common outlet for the passage of carrier gas, argon in the present study. While the admission of the carrier gas was effected through mass flow controllers, the overall flow through the furnace (after its exit through a stopcock) was measured using a drum-type wet test meter (Ritter, Germany; Type 05/6). As in other TTG studies, the flow through two inlets (purge gas and protective gas inlets) was kept constant and at as minimum level as measurable, and it was the flow through the third inlet (reactive gas inlet: a capillary tube, positioned immediately in front of but slightly above the sample crucible) that effectively transported the vapor species from the sample out of the furnace. The pattern of mass loss for a freshly loaded sample-aliquot led us to infer that conversion to anhydrous $NaBO_2$ was practically complete at $T \leq 673$ K, in accord with the findings of Figen and Pişkin.[16] However, we began to treat the mass-loss data as those due to vaporization of anhydrous $NaBO_2$ only after keeping the sample at $T = 1173$ K for about 10 h under flowing argon. Eleven flow dependence runs (five at 1173 K, three at 1200 K, one at 1155 K, and two at 1218 K) and nine temperature dependence runs were conducted. The flow dependence measurements were performed by constricting the exit stopcock opening to obtain previously determined flow values at a known mass-flow controller setting that facilitated good transpiration conditions - in terms of both dm/dt versus dV/dt and P versus dV/dt plots.[13] The temperature dependence runs were performed for different durations at different conditions of exit stopcock opening (fully open or constricted) and at different mass flow-controller settings. There were two long temperature dependence runs (each for 73 h) involving 29 isothermal segments, the latter selected such that an overall temperature range $\Delta T = 125$ K ($T/K = 1075−1200$) is covered once in the increasing, once in the decreasing, and once in the zigzag temperature directions, and that there is a minimum of one measurement at every 5 K interval.

We also conducted three DTA runs at the end of transpiration experiments to obtain information on melting of the sample used thus far. The first run was conducted at a fast heating rate of 5 K per minute between 1173 and 1263 K, while the subsequent two runs were performed at a slow heating rate of 1 K per minute between 1223 and 1253 K. All these runs led to confirmation of endothermic peaks at ∼(1236 ± 2) K, in reasonably good accord with the melting temperature of $NaBO_2$ adopted by JANAF[17] as (1240 ± 2) K. Visual examination of the sample showed it to be a white globule, confirming that the sample had indeed melted. One temperature dependence transpiration measurement was performed on this globule to compare the results with those obtained on the powder sample with a similar temperature program.

Four series of mass spectrometric measurements were performed. For the first two series, the aliquots from the bulk sample were taken in a platinum Knudsen cell that had a knife-edged orifice of ∼0.5 mm diameter. For the remaining series, the aliquots were first heated in a Pt crucible in the TTG apparatus to 773 K under flowing argon, and this crucible was then placed inside the Pt Knudsen cell. In the first two series, it took a very long time (a few days of slow heating at different increasing temperatures) before we reached the temperature at which we could observe ions such as Na^+, $NaBO_2^+$, $Na_2BO_2^+$ in the mass spectrum. The reason for such a situation presumably is the requirement that loss of water molecules has to occur through the orifice (unlike from a open crucible in TTG experiments). Furthermore, during most of this heating, H_2O^+ showed a shutter effect, and the vacuum in the Knudsen cell chamber remained just at the threshold level of furnace-trip, making it necessary to raise the temperatures very slowly. In the third and fourth series, we employed the samples that had been preheated in the TTG apparatus. We were able to begin ion intensity measurements much quicker than in the first two series. Pressure calibration was performed with $TeO_2(s)$, a congruently vaporizing system with $TeO_2(g)$ as one of the major vapor species.[15] The main reasons for choosing $TeO_2(s)$ for pressure calibration instead of silver, the common standard, are (1) in our previous KEMS study of $TeO_2(s)$,[15] we found the silver calibration yielding lower $p(TeO_2)$ than that deducible from the more absolute quantitative vaporization experiments (and we chose to select the result from the latter method reasoning that it would be less susceptible to errors in ionization cross
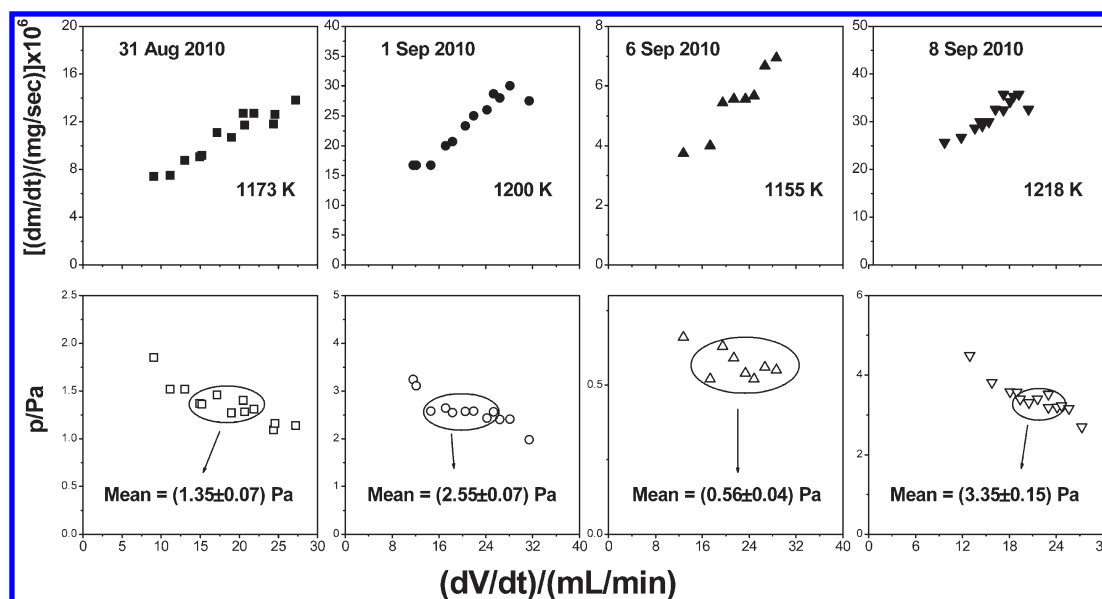
Figure 2. Variation of the rate of mass loss of $NaBO_2(s)$ and the corresponding apparent pressure of $NaBO_2(g)$ as a function of the volumetric flow rate of the argon carrier gas in the transpiration experiments at T = 1173, 1200, 1155, and 1218 K.

Table 1. Results from the Flow Dependence Experiments (TTG) on $NaBO_2(s)$ Sublimation

| | | | | | k in | | plateau region | | | |
T/K	run no.[a]	date	flow region covered (mL/min)	no. of points	$(dm/dt) = k \cdot (dV/dt)$	R(squared)	(mL/min)	no. of points	mean p/Pa	mean p/Pa at T/K
1173	1	17 Aug 2010	16.0−39.5	10	1.36×10^{-6}	0.96	23.5−39.5	8	1.63 ± 0.06	1.34 ± 0.30
	2	18 Aug 2010	11.8−56.6	17	4.82×10^{-7}	0.60	24.3−54.8	15	1.10 ± 0.14	
	3	19 Aug 2010	8.5−47.4	10	5.21×10^{-7}	0.04	34.1−47.4	12	1.09 ± 0.07	
	4	30 Aug 2010	8.6−22.2	7	7.19×10^{-7}	0.47	19.1−22.2	3	1.51 ± 0.02	
	5	31 Aug 2010	9.1−27.2	13	5.65×10^{-7}	0.61	14.9−21.9	7	1.35 ± 0.07	
1200	6	1 Sep 2010	11.6−31.4	8	1.08×10^{-6}	0.70	14.6−24.2	7	2.55 ± 0.07	2.37 ± 0.20
	7	2 Sep 2010	10.9−31.8	12	9.54×10^{-7}	0.26	18.9−24.5	4	2.23 ± 0.06	
	8	3 Sep 2010	11.7−31.0	11	1.02×10^{-6}	0.57	19.2−26.1	5	2.33 ± 0.08	
1155	9[b]	6 Sep 2010	12.8−28.9	8	2.48×10^{-7}	0.87	17.4−28.9	7	0.56 ± 0.04	0.56 ± 0.04
1218	10	7 Sep 2010	12.9−27.0	8	1.50×10^{-6}	0.18	19.5−27.0	5	3.27 ± 0.16	3.31 ± 0.23
	11	8 Sep 2010	12.9−27.3	13	1.46×10^{-6}	0.01	19.4−24.7	7	3.35 ± 0.15	

[a] Runs 1−3 performed with sample 1 and runs 4−11 performed with sample 2. [b] Last temperature of the long temperature dependence run 5.

sections, σ), and (2) since $NaBO_2(s)$ and $TeO_2(s)$ both are oxide systems that vaporize congruently to yield molecular species $NaBO_2(g)$ and $TeO_2(g)$ in the vapor phase, any inadequacy in the empirical relation to be employed to deduce σ for the molecular species will impart relatively much less error in the resulting $p(NaBO_2)$.

The starting sample, $NaBO_2 \cdot 4H_2O$, the "bulk sample", which is the product of the preheating in vacuum oven (starting sample for TTG and KEMS measurements), and the residue of the first aliquot after TTG experiments were subject to X-ray diffraction (XRD) examinations using a Siemens D500 Diffractometer (Cu Kα radiation 1.54 Å). While the XRD pattern of the bulk sample clearly gave the main lines known for $NaBO_2 \cdot 4H_2O$, the XRD pattern of the residue was broader, and only three main lines known for anhydrous $NaBO_2$ could be identified. Perhaps moisture absorption by the residue made the spectrum broader.

3. RESULTS AND DISCUSSION

3.1. TTG Measurements. Figure 2 shows the results of some selected flow dependence experiments. The top half of figure 2 displays the variation of rate of mass loss (dm/dt) with volumetric flow rate (dV/dt), and the bottom half displays the variation of apparent vapor pressure (P_{app}) with dV/dt. The apparent vapor pressure P_{app} at the sample temperature T_s was calculated using the following relation:

$$(P_{app}/Pa) \text{ at } (T_s/K) = 4.989 \times 10^5 \{(dm/dt)/(mg/sec)\}$$

$$/\{(dV/dt)/(ml/min)\}(T_c/K)/\{M/(g/mol)\} \quad (1)$$

where T_c = 298 K, the temperature at which the carrier gas flow was measured in this work, and M = 65.8 g·mol^{-1}, the molar mass of $NaBO_2(g)$, assumed to be the principal vapor species in

Table 2. Details of TTG Temperature Dependence Runs on Vaporization of NaBO$_2$(s)

						log [(dm/dt),mg/sec] = $-A/T + B$		
run no.	date	temp. range/K	flow mL/min	no. of points	T_m/K	A	B	$f = (p/\text{Pa})^c/(\text{d}m/\text{d}t)$
1[a]	4 and 5 Aug 2010	1093−1193	58	7	1143	15857 ± 505	8.45 ± 0.44	122661
2[a]	5 and 6 Aug 2010	1093−1193	52	7	1143	16993 ± 702	9.43 ± 0.61	122643
3[b]	30 and 31 Aug 2010	1093−1193	24	8	1143	16502 ± 270	9.17 ± 0.24	85706
4[b]	1 and 2 Sep 2010	1093−1200	25	10	1146.5	18103 ± 332	10.50 ± 0.29	99934
5[b]	3−6 Sep 2010	1075−1200	25	29	1137.5	17730 ± 206	10.14 ± 0.18	110187
6[b]	9 Sep 2010	1155−1218	19	4	1186.5	16773 ± 469	9.31 ± 0.40	105864
7[b]	9−12 Sep 2010	1075−1200	19	29	1137.5	17575 ± 342	9.96 ± 0.30	121862
8[b]	13 Sep 2010	1155−1218	19	4	1186.5	14428 ± 1170	7.36 ± 0.99	99621
9[b]	13 Sep 2010	1155−1218	22	4	1186.5	16087 ± 2079	8.75 ± 1.75	101526

[a] Exit stopcock completely opened. [b] Exit stopcock constricted. [c] p/Pa computed from eq 2: log [$p(\text{NaBO}_2)$/Pa] $= -(16606 \pm 2493)/(T/\text{K}) + (14.19 \pm 2.10)$.
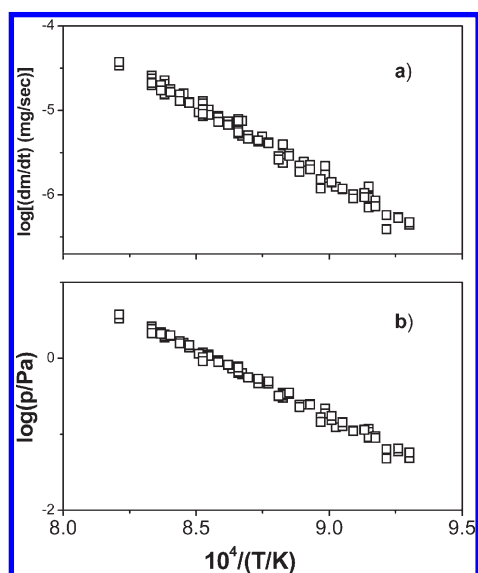

Figure 3. Temperature dependence of the rate of mass loss of NaBO$_2$-(s) and $p(\text{NaBO}_2)$. (a) Rate of mass loss vs $1/T$. (b) $p(\text{NaBO}_2)$ vs $1/T$ corresponding to all the data in a.

Figure 4. Ionization efficiency curves for the ions detected in the mass spectrum of the vapor over NaBO$_2$(s).

the equilibrium vapor over NaBO$_2$(s). Table 1 gives a summary of results from the flow dependence experiments. The mean of $p(\text{NaBO}_2)$ values in the so-called "plateau region"[13] is given in column 10 of Table 1 along with the standard deviation.

Column 11 of Table 1 gives the mean value of $p(\text{NaBO}_2)$ at each temperature, computed from the plateau region values obtained in each flow dependence experiment. The quoted uncertainties are the most probable values. These values given at 1218, 1200, 1173, and 1155 K were input to obtain a p−T relation:

$$\log[p(\text{NaBO}_2)/\text{Pa}] = -(16606 \pm 2493)/(T/\text{K})$$
$$+ (14.19 \pm 2.10) \qquad (2)$$

The main purpose of deducing the above equation was to use it for pressure calibration (as described below) in temperature dependence runs.

Table 2 gives the details pertinent to temperature dependence runs. Essentially, $p(\text{NaBO}_2)$ was computed from the rate of mass loss at a given temperature. The procedure employed was similar
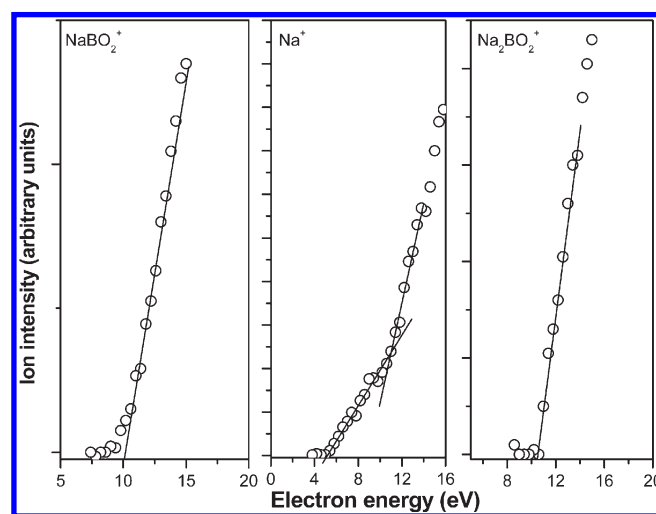
to that described earlier.[1,14] Mass (m) versus time (t) data at each temperature (accumulated through a computer) were fitted to a ($m = at + b$) straight line relation, the slope a representing the rate of mass-loss, dm/dt. The values of dm/dt at each temperature were then least-squares-fitted against $1/T$, and the coefficients of the resulting relations for each run are given in columns 7 and 8. The value of dm/dt at the mean temperature T_m (column 6) was computed for each run and so was the $p(\text{NaBO}_2)$ at T_m from eq 2. A normalization factor f (column 9) was then deduced as [$p(\text{NaBO}_2)/(\text{d}m/\text{d}t)$] at T_m. Subsequently, the $p(\text{NaBO}_2)$ corresponding to every dm/dt value was computed as [$f \cdot (\text{d}m/\text{d}t)$]. Figures 3a and 3b show, respectively, the plot of (dm/dt) versus $1/T$ and $p(\text{NaBO}_2)$ versus $1/T$. Figure 3b also contains the four mean $p(\text{NaBO}_2)$ values (column 11 of Table 1). The least-squares-fitted straight line corresponding to all the $p(\text{NaBO}_2)$ values (106 points) shown in Figure 3b yield the following p−T relation:

$$\log[p(\text{NaBO}_2)/\text{Pa}] = -(17234 \pm 148)/(T/\text{K})$$
$$+ (14.74 \pm 0.13) \qquad (3)$$

The above relation gives enthalpy of sublimation of 329.9 ± 2.8 kJ mol^{-1} (at T_m 1146.5 K) and 347.2 ± 2.8 kJ mol^{-1}

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(at T = 298 K) using auxiliary thermal functions from JANAF.[17] A third-law evaluation of these P_{app} values was performed by employing Gibbs free energy functions from JANAF,[17] and the mean value of $\Delta_{sub}H^{o}_{m}$(298.15 K) 350.7 ± 1.0 kJ mol^{-1} was obtained, where the uncertainty is the standard deviation.

The value of $p(NaBO_2)$ deducible from relation 3 at T = 1070 K is in excellent accord with that obtained by Kröger and Sörström[11] and Büchler and Berkowitz-Mattuck.[6] Interestingly, however, the second-law sublimation enthalpy at 298.15 K, deducible from this relation was lower than that of ref 11 (by ~50 kJ mol^{-1}) and higher than that of ref 6 (by ~26 kJ mol^{-1}).

3.2. Mass Spectrometric Measurements on Sodium Borate.
The ionic species detected in the mass spectrum of the vapor over $NaBO_2(s)$ are Na^+, $NaBO_2{}^+$, and $Na_2BO_2{}^+$. In the latter two cases, the natural isotope abundances of 10 and 11 for boron were confirmed, but the ion intensity measurements were generally performed on the ions representing the relatively more abundant isotope (^{11}B). Figure 4 shows the ionization efficiency curves for all the three ionic species. The appearance energies (AEs) deduced from these curves by using linear extrapolation method are 4.9 eV (Na^+), 10.1 eV ($NaBO_2{}^+$), and 10.6 eV ($Na_2BO_2{}^+$). There is a clear positive break in the ionization efficiency curve for Na^+ at ~11 eV; the uncertainty in the measured AE values is ±0.5 eV. The electron energy scale was previously calibrated with known AEs of Ag^+, In^+, Hg^+, Ar^+, and He^+. During the present study, the validity of the calibration was checked against the known AE for H_2O^+.

Although the low value of AE for Na^+ relative to that for $NaBO_2{}^+$ might be taken to indicate that, at electron energy less than 10 eV, the source of Na^+ could be atomic sodium, the increase in $I(Na^+)$ with electron energy was very steep (in contrast to near constant values of ionization of cross sections, σ, for atomic sodium). This led us to infer that it is the dissociative ionization of $NaBO_2(g)$ that is the main contributor to $I(Na^+)$ at electron energies above 11 eV. For instance, while the values of $\sigma(Na)^{18}$ are according to $[\sigma(14\ eV)/\sigma(11\ eV)]$ = 1.03 and $[\sigma(32.6\ eV)/\sigma(11\ eV)]$ = 0.82, the values of $I(Na^+)$ are according to $[I^+(14\ eV)/I^+(11\ eV)]$ = 5 and $[I^+(32.6\ eV)/I^+(11\ eV)]$ = 17. Thus at an electron energy of 32.6 eV at which we performed much of our measurements, the contribution to $I(Na^+)$ from atomic sodium, even if it exists in the vapor, is negligibly small (~ 5%). Büchler and Berkowitz-Mattuck[6] did not report or discuss the AEs of the ionic species, although in the case of lithium metaborate, they mentioned that the AEs of Li^+ and $Li_2BO_2{}^+$ were ~1 eV higher than the AE of $LiBO_2{}^+$, thus implying that the alkali metal ion might only be a fragment; Asano and Yasue[9] attributed the low value of AE for Na^+ to "positive−negative ion formation from $NaBO_2(g)$", the ionization reaction being $NaBO_2(g) + e^- \rightarrow Na^+ + BO_2{}^- + e^-$. Since in our instrument we cannot study negative ions, we are unable to confirm whether the ion-pair formation was responsible for obtaining the low value of AE for Na^+.

As for $Na_2BO_2{}^+$, we assume that it is formed by dissociative ionization of $(NaBO_2)_2(g)$, just as the authors of the previous KEMS studies did.[6−9] Akishin et al.[12] have confirmed by studying the ion velocity distribution (in the case of lithium borate vapors) that $M_2BO_2{}^+$ is formed only by dissociative ionization, but it is not clear as to why they mentioned M_3BO_3 as the possible precursor instead of $(MBO_2)_2$.

We were not able to detect $Na_3(BO_2)_2{}^+$. Perhaps the sensitivity of our instrument did not permit us to detect this ion that the previous investigators[6,8] could.

Table 3. Third-Law Evaluation of Results of KEMS Experiments (Series 3 and Series 4)

T/K	$I(NaBO_2{}^+)^a$	$p(NaBO_2)/Pa^b$	$\Delta_{sub}H^{o}_{m}$ (298.15 K)/ (kJ mol^{-1})
Series 3; Run 1; 3 March 2011; 8 Points			
1075	1.13×10^{-5}	1.24×10^{-1}	342.5
1090	1.58×10^{-5}	1.75×10^{-1}	343.9
1105	2.20×10^{-5}	2.49×10^{-1}	345.3
1120	3.41×10^{-5}	3.89×10^{-1}	345.5
1135	5.36×10^{-5}	6.20×10^{-1}	345.5
1145	7.11×10^{-5}	8.31×10^{-1}	345.7
1160	1.26×10^{-4}	1.49	344.3
1175	2.24×10^{-4}	2.69	342.8
Series 3; Run 2; 4 March 2011; 10 Points			
1175	1.93×10^{-4}	2.32	344.2
1160	1.43×10^{-4}	1.70	343.1
1145	9.85×10^{-5}	1.15	342.6
1135	7.75×10^{-5}	8.98×10^{-1}	342.1
1120	4.61×10^{-5}	5.27×10^{-1}	342.7
1105	2.58×10^{-5}	2.91×10^{-1}	343.8
1090	1.55×10^{-5}	1.72×10^{-1}	344.1
1075	8.00×10^{-6}	8.78×10^{-2}	345.6
1185	2.03×10^{-4}	2.46	346.4
1085	1.27×10^{-5}	1.40×10^{-1}	344.4
Series 4; Run 1; 29 March 2011; 11 Points			
1175	1.67×10^{-4}	2.01	345.6
1185	2.37×10^{-4}	2.86	344.9
1175	2.02×10^{-4}	2.43	343.8
1160	1.65×10^{-4}	1.95	341.7
1145	1.05×10^{-4}	1.23	341.9
1135	7.65×10^{-5}	8.86×10^{-1}	342.2
1120	4.98×10^{-5}	5.69×10^{-1}	342.0
1105	2.96×10^{-5}	3.34×10^{-1}	342.5
1090	1.66×10^{-5}	1.85×10^{-1}	343.5
1075	9.56×10^{-6}	1.05×10^{-1}	344.0
1060	5.83×10^{-6}	6.31×10^{-2}	343.9
Series 4; Run 2; 30 March 2011; 11 Points			
1175	1.76×10^{-4}	2.11	345.2
1185	2.12×10^{-4}	2.56	346.0
1175	1.83×10^{-4}	2.19	344.8
1160	1.34×10^{-4}	1.59	343.7
1145	8.76×10^{-5}	1.02	343.7
1135	4.56×10^{-5}	5.28×10^{-1}	347.1
1120	3.15×10^{-5}	3.60×10^{-1}	346.3
1105	1.74×10^{-5}	1.96×10^{-1}	347.4
1175	1.69×10^{-4}	2.02	345.6
1145	8.69×10^{-5}	1.02	343.7
1075	9.47×10^{-6}	1.04×10^{-1}	344.1
	mean of all 40 points	344.2 ± 1.5	

^{a} Ion intensity corresponding to m/z = 66 ($^{23}Na^{11}B^{16}O_2$). ^{b} $p(NaBO_2)/Pa = I(NaBO_2{}^+) \cdot T \cdot k_1$, where k_1 = 10.2 (see eq 4 and Table 4).

The electron energy chosen for temperature dependence experiments was 32.6 eV. Na^+ showed very similar temperature dependence as $NaBO_2{}^+$, while $Na_2BO_2{}^+$ showed a relatively steeper behavior. However, as mentioned already in the Introduction, the

Table 4. Details Pertinent to Computation of $p(NaBO_2)$ in KEMS Measurements[a]

equation	numerical values pertinent to the constants in the equation
$p(NaBO_2)/Pa = I(NaBO_2{}^+) \cdot T \cdot k_1$	$k_1 = 10.2 \pm 2.2$
where $k_1 = k_2 \cdot k_3 \cdot k_5$	$k_2 = \text{mean } \{[p(TeO_2)/Pa]/[I({}^{130}TeO_2{}^+) \cdot T]\} = 9.96 \pm 1.27$
	$k_3 = 3.27 \pm 0.57$
	$k_5 = 0.314$
$k_3 = \{1 + k_4 \cdot [\gamma(Na^{11}BO_2{}^+)/\gamma(Na^+)] \cdot \eta(Na^{11}BO_2)\}$	$k_4 = \text{mean } [I(Na^+)/I(Na^{11}BO_2{}^+)] = 4.8 \pm 1.2$
where $\gamma(i)^+ = [1/M(i^+)]^{0.5}$	$\gamma(Na^{11}BO_2{}^+)/\gamma(Na^+) = (23/66)^{0.5}$
	$\eta(Na^{11}BO_2) = 0.8$
$k_5 = [\sigma(TeO_2)/\sigma(NaBO_2)] \cdot [\gamma({}^{130}TeO_2{}^+)/\gamma(Na^{11}BO_2{}^+)] \cdot [\eta({}^{130}TeO_2{}^+)/\eta(Na^{11}BO_2{}^+)]$	$\sigma(Te) = 6.938$
where $\gamma(i)^+ = [1/M(i^+)]^{0.5}$; $\sigma(TeO_2) = 0.75 [\sigma(Te) + 2\sigma(O)]$;	$\sigma(Na) = 3.180$
$\sigma(NaBO_2) = 0.75 [\sigma(Na) + \sigma(B) + 2\sigma(O)]$	$\sigma(B) = 2.556$
	$\sigma(O) = 0.976$
	$[\gamma({}^{130}TeO_2{}^+)/\gamma(Na^{11}BO_2{}^+)] = (66/162)^{0.5}$
	$\eta({}^{130}TeO_2{}^+) = 0.34$
	$\eta(Na^{11}BO_2{}^+) = 0.80$

[a] σ at 32.6 eV for elements obtained from Mann's tables.[18] η for elements were taken from IUPAC technical report,[20] and those for the polyatomic species were computed. γ assumed to be inversely proportional to square root of mass of the ionic species.

results from series 1 and 2 KEMS experiments were really intriguing. The apparent enthalpies of sublimation of the ions $\Delta_{sub}H_{apparent}$ (I^+), deduced from the $\log(I^+ \cdot T)$ versus $1/T$ plots showed large variations from run to run (totally 13 runs; 11 in series 1, and 2 in series 2), far beyond the statistical uncertainties in the values for each run. For Na^+, the values were from 249 to 299 kJ mol^{-1} (mean = 266 ± 14); for $NaBO_2{}^+$, the values were from 240 to 289 kJ mol^{-1} (mean = 267 ± 16); and for $Na_2BO_2{}^+$, the values were from 254 to 351 kJ mol^{-1} (mean = 303 ± 35). The reason for the unusually high scatter in apparent enthalpies was hard to understand since we never observed such results on any system studied hitherto by us. Furthermore, measurements on elemental silver, performed on many days after series 1 and 2 measurements on sodium metaborate, yielded values of enthalpy of sublimation of $Ag(g)$ consistent among the runs, the mean value from 6 runs on different days being 279.5 ± 5.2 kJ mol^{-1} at T_{mean} = 1120 K. This value on conversion to T = 298.15 K is 285.2 ± 5.2 kJ mol^{-1}, in accord with the literature[19] value of 284.55 kJ mol^{-1}. We sought to reject the results of series 1 and 2 as suspect following some observations we made on inspection of the Knudsen cells after these experiments: (1) there was visually no sample left inside the Knudsen cell after completion of vaporization experiments in both series, and a glassy deposit was found at the bottom of the Knudsen cell lid clogging the orifice; and (2) the deposit was so strongly adherent in the case of series 1 that the deposit could not be even scraped off. While the actual reason for this is not evident to us, we suspected that the orifice clogging occurred from in situ dehydration. By performing the dehydration in the TTG apparatus (that is outside the Knudsen cell), this problem was solved in series 3 and 4 KEMS experiments. However there was very little sample left in the Knudsen cell as well, which we took as crude proof for the occurrence of congruent sublimation. We restricted our measurements to only $I(NaBO_2{}^+)$ to avoid peak switching (or to restrict the change in the magnetic field to just that which is necessary for staying at the $NaBO_2{}^+$ peak top). We also limited the measurements to only two runs in each series. The values of $I(NaBO_2{}^+)$ measured at different temperatures in four runs are tabulated in Table 3. On one day at the end of series 3, we additionally measured Na^+ and $Na_2BO_2{}^+$ at very few temperatures

to obtain the ratios $Na^+/NaBO_2{}^+$ (to correct for fragmentation) and $Na_2BO_2{}^+/NaBO_2{}^+$ (to deduce the abundance of dimer relative to that of monomer). The values were 4.8 ± 1.2 ($Na^+/NaBO_2{}^+$) and 0.26 ± 0.06 ($Na_2BO_2{}^+/NaBO_2{}^+$). Although Na^+ was the more dominant ion, we preferred to use the parent ion $NaBO_2{}^+$ as a better representative of $NaBO_2(g)$ because it was much easier to remain at the peak top of $NaBO_2{}^+$ than Na^+ during the shutter operations (the Na^+ peak being very sharp due to its relatively lower mass number).

Although our approach of giving sole attention on the major vapor species might amount to under utilization of the potential of KEMS, we reasoned that with the dimer constituting not more than 4% of the vapor phase, it was more important for us to examine (a) how well the KEMS values of $p(NaBO_2)$ agree with those of TTG experiments and (b) the consistency between the second- and third-law evaluations of KEMS results that was lacking in previous KEMS studies.

The values of $p(NaBO_2)$ were deduced from the following equation:

$$p(NaBO_2)/Pa = I(NaBO_2{}^+) \cdot T \cdot k_1 \qquad (4)$$

where $k_1 = k_2 \cdot k_3 \cdot k_5$.

In the above equation, k_2 is the pressure calibration constant obtained in the pressure calibration run performed using solid TeO_2:

$$k_2 = [p(TeO_2)/Pa]/[I({}^{130}TeO_2{}^+) \cdot T] \qquad (5)$$

where $p(TeO_2)$ is the partial pressure of $TeO_2(g)$ over solid TeO_2.[15] k_3 is the constant to account for the dissociative ionization of $NaBO_2(g)$ and k_5 is the constant to account for the differences in (a) the ionization cross sections (σ) of TeO_2-(g) and $NaBO_2(g)$, (b) the detection efficiencies of the secondary electron multiplier (γ) for the ions $^{130}TeO_2{}^+$ and $Na^{11}BO_2{}^+$, and (c) the relative isotopic abundances of these ionic species (η). Table 4 gives the details of the equations and the numerical values of the various constants employed in those equations. Table 5 gives the least-squares-fit p−T relations corresponding to the individual runs as well as the second-law enthalpy of sublimation deduced from the coefficient of the slopes (A).

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Table 5. Second-Law Evaluation of Results of KEMS Experiments (Series 3 and Series 4)

| | | | | log $[p(NaBO_2)/Pa]^a = -A/(T/K) + B$ | | | | |
| | | | | | | | $\Delta_{sub}H^o_m\ (T_m)^b/$ | $\Delta_{sub}H^o_m\ (298.15\ K)/$ |
run	date	temperature range/K	no. of points	A	B	T_m/K	(kJ mol^{-1})	(kJ mol^{-1})
				Series 3				
1	3 March 2011	1075−1175	8	16746 ± 859	14.59 ± 0.76	1125	320.6 ± 16.4	337.3 ± 16.4
2	4 March 2011	1075−1185	10	17247 ± 737	15.06 ± 0.66	1130	330.2 ± 14.1	347.0 ± 14.1
				Series 4				
1	29 March 2011	1060−1185	11	16876 ± 584	14.76 ± 0.52	1122.5	323.1 ± 11.2	339.7 ± 11.2
2	30 March 2011	1075−1185	11	17389 ± 777	15.13 ± 0.68	1130	333.0 ± 14.9	349.7 ± 14.9
	all points combined	1060−1185	40	16878 ± 375	14.72 ± 0.33	1122.5	323.2 ± 7.2	339.8 ± 7.2

$^a\ p(NaBO_2)/Pa = I(NaBO_2^+)\cdot T\cdot k_1$, where $k_1 = 10.2$ (see eq 4). ^{b} Deduced from the value of coefficient A (column 5).

Table 6. Comparison of Thermodynamic Quantities Pertinent to Sublimation of Solid NaBO₂

| | $p(NaBO_2)/Pa$ over NaBO$_2$(s,l) | | | | $\Delta_{sub}H^o_m\ (298.15\ K)/(kJ\ mol^{-1})^b$ | | |
| | | | | | | | $\Delta_{sub}S^o_m\ (298.15\ K)/$ |
reference	1070 K	1100 K	1150 K	1270 K^a	II law	III law	(J mol^{-1} K^{-1})^b II Law
this work, TTG (eq 3)	4.3×10^{-2}	1.2×10^{-1}	5.7×10^{-1}		347.2 ± 2.8	350.7 ± 2.8	210.6
this work, KEMS (eq 6)	8.9×10^{-2}	2.4×10^{-1}	1.1		339.8 ± 7.2	344.2 ± 1.5	209.6
this work, recommended (eq 7)	6.2×10^{-2}	1.7×10^{-1}	8.0×10^{-1}		343.6 ± 8.4	348.9 ± 7.2	210.2
Büchler and Berkowitz-Mattuck[6c]	5.1×10^{-2}	1.3×10^{-1}	5.5×10^{-1}		320.6 ± 12.6	349.0	185.7
Kröger and Sörström[11d]	3.9×10^{-2}	1.2×10^{-1}	7.5×10^{-1}		396.8	347.7 ± 1.6	256.0
Yasue and Asano[8e]	1.8×10^{-1}	4.4×10^{-1}	1.8		305.1 ± 1.5	336.5	186.4
Cole and Taylor[10f]				1.3×10^1	463.2	331.2 ± 6.9	300.3
Kröger and Sörström[11g]				3.0×10^1	421.6	342.5 ± 2.0	275.8
Gorokhov et al.[7h]				3.3×10^1	303.3	341.7	

^{a} Value for NaBO$_2$(l). ^{b} Thermal functions taken from JANAF[17] for calculation. ^{c} $p(NaBO_2)$ computed from the $p-T$ relation (log p/Pa = $-15868/T$ + 13.54), deduced by us using $p(NaBO_2)$ and $\Delta_{sub}H^o_m$ (1070 K) given in ref 6. II law value from $\Delta_{sub}H^o_m$ (1070 K), and III law value from the $p(NaBO_2)$ at $T = 1070$ K given in ref 6. ^{d} $p(NaBO_2)$ computed from the $p-T$ relation (log p/Pa = $-19800/T$ + 17.09) given in ref 11. II law value from $\Delta_{sub}H^o_m$ (1163 K) and mean III law value from the $p(NaBO_2)$ values tabulated at eight temperatures in ref 11. ^{e} $p(NaBO_2)$ computed from the $p-T$ relation (log p/Pa = $-15400/T$ + 13.64) given in ref 8; II law value from this relation and III law from the $p(NaBO_2)$ at $T_{mean} = 1021.5$ K. ^{f} $p(NaBO_2)$ computed from the $p-T$ relation (log p/Pa = $-20417/T$ + 17.18), deduced by us using the $p(NaBO_2)$ values tabulated at 5 temperatures in ref 10. II law value from this relation ($T_{mean} = 1523$ K) and mean III law value from the p(NaBO$_2$) values given in ref 10. ^{g} $p(NaBO_2)$ computed from the $p-T$ relation (log p/Pa = $-19100/T$ + 16.51) given in ref 11. II law value from $\Delta_{vap}H^o_m$ (1278 K) and mean III law value from the $p(NaBO_2)$ values tabulated at 13 temperatures in ref 11. ^{h} $p(NaBO_2)$ given in ref 7 at $T = 1270$ K. II law value from $\Delta_{sub}H^o_m$ (1155 K) given in ref 7, and III law value deduced from the $p(NaBO_2)$ at $T = 1270$ K.

The $p-T$ relation obtained by pooling together all points from four runs (see column 3 of Table 3) is

$$\log[p(NaBO_2)/Pa] = -(16878 \pm 375)/(T/K) + (14.72 \pm 0.33) \qquad (6)$$

The above relation yields an enthalpy of sublimation of 323.2 ± 7.2 kJ mol^{-1} (at $T_m = 1122.5$ K) and 339.8 ± 7.2 kJ mol^{-1} (at $T = 298.15$ K). The mean value of third-law enthalpy (see column 4 of Table 3) is 344.2 ± 1.5 kJ mol^{-1}, where the uncertainty is the standard deviation. It was gratifying to observe a good agreement between second- and third-law enthalpies, which was eluding in the case of previous KEMS studies.[6−9]

3.3. Recommended $p(NaBO_2)-T$ Relation and Enthalpy of Sublimation to NaBO$_2$(g). The $p(NaBO_2)-T$ relations obtained in TTG and KEMS experiments (eqs 3 and 6, respectively) are reasonably consistent with one another. Values of $p(NaBO_2)$

deduced from these relations at some selected temperatures are given in Table 6. Although the KEMS values are a factor of ∼2 higher than the TTG values, in view of the uncertainties associated with various constants employed in the computation of p(NaBO$_2$) in the case of KEMS measurements and also of those associated with TTG measurements, we believe that we can give equal weight to both equations and thus recommended the following $p-T$ relation (valid for the temperature range from 1060 to 1218 K) by taking the mean of the respective coefficients:

$$\log[p(NaBO_2)/Pa] = -(17056 \pm 437)/(T/K) + (14.73 \pm 0.36) \qquad (7)$$

The uncertainties quoted were deduced by error propagation of those in the coefficients of the component equations. Figure 5 shows all the values of $p(NaBO_2)$ represented by eq 7. We estimate an uncertainty of 50% in the $p(NaBO_2)$ deducible from
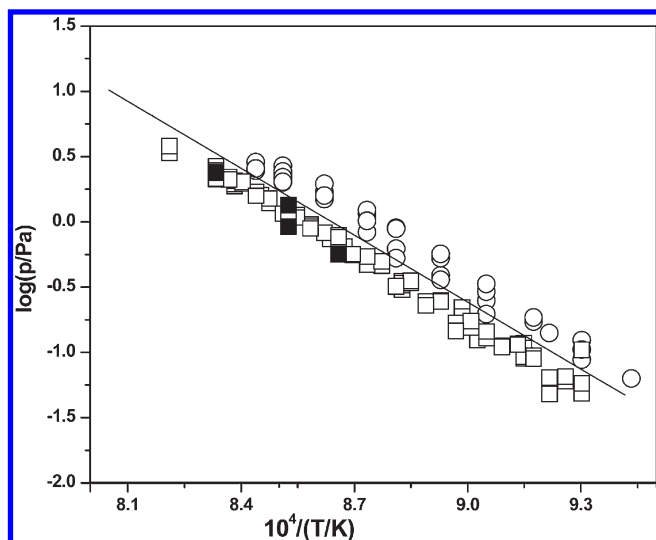
Figure 5. Temperature dependence of $p(NaBO_2)$. Results of transpiration runs (temperature dependence □ and flow dependence ■) and KEMS runs ○.

the above relation. The second-law enthalpy for the sublimation of $NaBO_2(s)$ to $NaBO_2(g)$ deduced from the coefficient (slope) of above equation is 326.5 ± 8.4 kJ mol^{-1} (at $T_{mean} = 1139$ K) and 343.6 ± 8.4 kJ mol^{-1} (at $T = 298.15$ K). The mean value of third-law enthalpy corresponding to all the $p(NaBO_2)$ values (146 points) shown in Figure 5 is (348.9 ± 3.1) kJ mol^{-1}, where the uncertainty is the standard deviation. We seek to recommend $\Delta_{sub}H^{\circ}_m$ (298.15 K) = (346.3 ± 9.4) kJ mol^{-1}, the mean of second- and third-law values. The uncertainty in the recommended value is deduced by error propagation. The entropy of sublimation at $T_{mean} = 1139$ K, also obtained from the coefficient (intercept) of eq 7 is (186.2 ± 6.8) J K^{-1} mol^{-1}. Combining with auxiliary thermal functions, the entropy of sublimation at $T = 298.15$ K is (210.2 ± 6.8) J K^{-1} mol^{-1}.

3.4. Comparison with Previous Studies. Table 6 compares the results from the present study with those from previous studies[6–8,10,11] The values of $p(NaBO_2)$ given in Table 6 are those computed from the $p–T$ relations (given by authors or deduced by us). In the case of Gorokhov et al.,[7] no $p–T$ relation was deducible since the authors reported $p(NaBO_2)$ at $T = 1270$ K (for liquid $NaBO_2$) while giving an enthalpy of sublimation valid for the temperature range 1080–1230 K (for solid $NaBO_2$). Table 6 shows that the values of $p(NaBO_2)$ obtained in the present study for $NaBO_2(s)$ lie close to those obtained by Büchler and Berkowitz-Mattuck[6] and Kröger and Sörström,[11] but the agreement with the latter may have to be considered only as apparent since the coefficients of the $p–T$ relation obtained by these authors are so very different. As for $p(NaBO_2)$ over $NaBO_2(l)$, the results of Kröger and Sörström[11] and Gorokhov et al.[7] are in good agreement, while the value from Cole and Taylor[10] is lower, but the reason might even be the need for extrapolation of their results (valid for the temperature range 1423–1623 K) to 1270 K.

The values of $\Delta_{sub}H^{\circ}_m$ (298.15 K) and $\Delta_{sub}S^{\circ}_m$ (298.15 K) listed in columns 6 and 8, respectively, of Table 6 were deduced from the $p–T$ relations (that is, by second-law method), while the values of $\Delta_{sub}H^{\circ}_m$ (298.15 K) listed in column 7 were deduced by third-law method. The necessary auxiliary thermal functions required for these computation were taken from JANAF.[17]

Use was made of thermal functions tabulated for $NaBO_2(s,l)$ so that evaluation of $p(NaBO_2)$, whether measured over solid or liquid sodium metaborate, will yield information for the sublimation reaction at $T = 298.15$ K and make the comparison easier and uniform. It is evident from Table 6 that, while the third-law values of enthalpies of sublimation obtained in different studies (column 7) are reasonably consistent, the second-law enthalpies of sublimation (column 6) differ significantly, and so are the second-law entropies of sublimation (column 8). The value of $\Delta_{sub}S^{\circ}_m$ (298.15 K) = (210.2 ± 6.8) J K^{-1} mol^{-1}, recommended in the present study, is in excellent agreement with the value (213.7 ± 4.2) J K^{-1} mol^{-1}, deducible from JANAF.[17] The results of the present study showing the best agreement between second- and third-law evaluations, we sought to deduce the enthalpy of formation of $NaBO_2(g)$ by combining $\Delta_{sub}H^{\circ}_m$ (298.15 K) = (346.3 ± 9.4) kJ mol^{-1} recommended in the present study with the enthalpy of formation of $NaBO_2(s)$ $(-(975.7 \pm 2.1)$ kJ mol$^{-1})$ recommended in JANAF.[17] The resulting value, $\Delta_f H^{\circ}_m$ ($NaBO_2$, g, 298.15 K) = $-(629.4 \pm 9.6)$ kJ mol^{-1} is in reasonable accord with that $(-(648.5 \pm 12.6)$ kJ mol$^{-1})$ adopted in JANAF.[17] These aspects together with the consistency of results from experiments based on two established techniques (TTG and KEMS) permit us to state that the present study represents one that is both comprehensive and reliable.

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■ REFERENCES

(1) Balasubramanian, R.; Lakshmi Narasimhan, T. S.; Viswanathan, R.; Nalini, S. *J. Phys. Chem. B* **2008**, *112*, 13873–13884.

(2) Bonnell, D. W.; Plante, E. R.; Hastie, J. W. *J. Non-Cryst. Solids* **1986**, *84*, 268–275.

(3) Spear, K. E.; Besmann, T. M.; Beahm, E. C. *MRS Bull.* **1999**, *24*, 37–44.

(4) Wu, C.; Zhang, H.; Yi, B. *Catal. Today* **2004**, *93–95*, 477–483.

(5) Demirci, U. B.; Akdim, O.; Andrieux, J.; Hannauer, J.; Chamoun, R.; Miele, P. *Fuel Cells* **2010**, *10*, 335–350.

(6) Büchler, A.; Berkowitz-Mattuck, J. B. *J. Chem. Phys.* **1963**, *39*, 286–291.

(7) Gorokhov, L. N.; Gusarov, A. V.; Makarov, A. V.; Nikitin, O. T. *Teplofizika Vysokikh Temperatur* **1971**, *9*, 1173–1176(English Translation p 1082–1084; To be consistent with the Russian paper, the title of Column 2 of Table 3 should read Temp. range K and not °C)..

(8) Yasue, Y.; Asano, M. *Bull. Atom. Energy Res. Inst. Kyoto Univ.* **1985**, *67*, 47–48.

(9) Asano, M.; Yasue, Y. *J. Nucl. Mater.* **1986**, *138*, 65–72.

(10) Cole, S. S.; Taylor, N. W. *J. Am. Ceram. Soc.* **1935**, *18*, 82–85.

(11) Kröger, C.; Sörström, W. *Glastech. Ber.* **1965**, *38*, 313–322.

(12) Akishin, P. A.; Gorokhov, L. N.; Khodeev, Yu. S. *J. Struct. Chem.* **1961**, *2*, 197–198(translated from *Zh. Strukt. Khim.*, **1961**, *2*, 209–210).

(13) Viswanathan, R.; Lakshmi Narasimhan, T. S.; Nalini, S. *J. Phys. Chem. B* **2009**, *113*, 8362–8368.

(14) Viswanathan, R.; Lakshmi Narasimhan, T. S.; Nalini, S. *J. Chem. Eng. Data* **2010**, *55*, 3779–3785.

(15) Lakshmi Narasimhan, T. S.; Sai Baba, M.; Viswanathan, R. *Thermochim. Acta* **2005**, *427*, 137–147.

(16) Figen, A. K.; Pişkin, S. *Adv. Powder Technol.* **2010**, *21*, 513–520.

(17) Chase M. W., Jr.; Davies, C. A.; Downey, J. R.; Jr.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data.* **1985**, *14*. Supplement No. 1, p 248, for $NaBO_2(s)$, p 250 for $NaBO_2(s,l)$ and p 251 for $NaBO_2(g)$.

(18) Mann, J. B. *Recent Developments in Mass spectrometry*. Proceedings of the International Conference on Mass Spectrometry. Ogata, K.; Hayakawa, T., Eds.; Univ. of Tokyo Press: Japan, 1970, 814−819. (Tables of ionization cross sections as a function of electron energy were obtained on request).

(19) The NBS tables of chemical thermodynamic properties: *J. Phys. Chem. Ref. Data.* **1982**, *11*, Supplement No. 2. p 160. for Ag.

(20) IUPAC Technical Report. *Pure Appl. Chem.* **2002**, *74*, 1987−2017.

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