

## MASS SPECTROMETRIC STUDY OF VAPORIZATION OF CESIUM-CONTAINING BOROSILICATE GLASSES

Mitsuru ASANO, Tomoyuki KOU and Yoshihiko YASUE \*

*Institute of Atomic Energy, Kyoto University, Uji, Kyoto 611, Japan*

Received 8 December 1986

Revised manuscript received 4 March 1987

A mass-spectrometric Knudsen effusion method has been applied to study the vaporization behavior of three cesium-containing borosilicate glasses in the temperature range 845–1150 K. Vapor species of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  have been identified for the glass containing  $\text{Cs}_2\text{O}$ , and  $\text{NaBO}_2(\text{g})$ ,  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  have been identified in addition to  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  for glasses containing  $\text{Na}_2\text{O}$  and  $\text{Cs}_2\text{O}$ . The vapor species of  $\text{Na}(\text{g})$  has been further observed in the initial stage of heating to 1000 K for the glass in which the mole ratio of  $\text{Na}_2\text{O}$  plus  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is larger than unity, while no vaporization of  $\text{Na}(\text{g})$  occurs for the glass in which the ratio is equal to unity. Enthalpies of vaporization, enthalpies of formation and dissociation energies for the vapors and chemical activities of pseudo components in the glasses have been determined from the measured partial pressures and discussed by comparing with those for sodium borosilicate glasses,  $\text{NaBO}_2(\text{s})$  and  $\text{CsBO}_2(\text{s})$ .

### 1. Introduction

In the near future, high-level radioactive wastes will be stored after solidification by incorporating most likely into borosilicate glasses. Among radioactive elements in high-level radioactive wastes, cesium is the most hazardous and its vaporization during vitrification treatments and in possible fire accidents in storage may be a serious problem. Many studies have been done on the vaporization of cesium from borosilicate glasses containing simulated high-level radioactive wastes [1–10]. However, only a few studies have been done on the chemical forms of cesium-containing vapors. Hastie, Plante and Donnell [8] detected  $\text{CsBO}_2(\text{g})$  by the mass spectrometric method. Yamanaka, Terai and Hara [9] determined the mole ratio of  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  in the volatilized products as almost unity. The presence of  $\text{Cs}(\text{g})$  [1,5] and  $\text{CsO}(\text{g})$  [1,5] in the vapor was postulated from the consideration of their partial pressures over  $\text{Cs}_2\text{O}(\text{l})$ .

In the present work, a mass-spectrometric Knudsen effusion method has been applied to the determination of the chemical forms of vapors and their partial pressures for three cesium-containing borosilicate glasses. The composi-

\* Present address: Technical Research Center, Nippon Kokan K.K., Kawasaki 210, Japan.

Table 1  
Compositions of glasses used in the experiments

Glass	Composition
Glass-1 <sup>a)</sup>	1Na <sub>2</sub> O-1B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub>
Glass-2 <sup>a)</sup>	1Na <sub>2</sub> O-1.5B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub>
Glass-3 <sup>a)</sup>	1.5Na <sub>2</sub> O-1B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub>
Glass-4	1Na <sub>2</sub> O-1B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub> -0.15Cs <sub>2</sub> O
Glass-8	0.85Na <sub>2</sub> O-1B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub> -0.15Cs <sub>2</sub> O
Glass-9	1Cs <sub>2</sub> O-1B <sub>2</sub> O <sub>3</sub> -3SiO <sub>2</sub>

<sup>a)</sup> Used in previous work [11].

tions of the glasses used in the present work are shown in table 1 along with those used in previous work [11]. Glass-4 has a composition in which 0.15 mole Cs<sub>2</sub>O is added to Glass-1. The mole ratio of Na<sub>2</sub>O plus Cs<sub>2</sub>O to B<sub>2</sub>O<sub>3</sub> in Glass-4 is slightly larger than unity, while it is adjusted just equal to unity in Glass-8. Glass-9 replaces Na<sub>2</sub>O in Glass-1 by Cs<sub>2</sub>O.

Very recently, the present authors have briefly reported the vapor species over Glass-4 [12] to be NaBO<sub>2</sub>(g), Na<sub>2</sub>(BO<sub>2</sub>)<sub>2</sub>(g), CsBO<sub>2</sub>(g), Cs<sub>2</sub>(BO<sub>2</sub>)<sub>2</sub>(g) and NaCs(BO<sub>2</sub>)<sub>2</sub>(g). The vapor of Na(g) has also been observed in addition to the above species in the initial stage of heating to 1000 K. The influence of the excess alkali content on the vaporization of Na(g) will be discussed in the present work in detail. Furthermore, enthalpies of vaporization, enthalpies of formation and dissociation energies for vapors and chemical activities of pseudo components in the glasses have been determined on the basis of measured partial pressures of vapor species and discussed by comparing those with the data for Glass-1 [11], Glass-2 [11], Glass-3 [11], NaBO<sub>2</sub>(s) [13,14] and CsBO<sub>2</sub>(s) [13,14].

## 2. Experimental

Experiments were carried out with a 0.2 m radius of curvature, 90° sector single focusing Hitachi RM-6K mass spectrometer equipped with a platinum Knudsen cell in a tungsten holder. The cell has an inside diameter of 7 mm and an inside height of 9 mm. The diameter of the effusion orifice is 0.5 mm.

Glasses were prepared by melting mixtures of sodium carbonate, boric acid, silicon dioxide and cesium carbonate in platinum crucibles for 1.5 h at 1200°C. All chemicals were of reagent grade available from Ventron-Alfa. The samples showed no X-ray diffraction lines before and after vaporization experiments, indicating that no crystallization took place.

About 50 mg glass was put in the Knudsen cell and heated by radiation under a background pressure of less than  $4 \times 10^{-5}$  Pa. The temperature of the sample was measured with a well calibrated W5Re/W26Re thermocouple inserted into a hole at the bottom of the cell holder.

Vapors effusing from the cell were ionized by electron impact. Ion species were identified from the peak distances between ions of interest and background ions of known masses for all the ions and further from isotopic abundance ratios for boron-containing ions. Appearance energies for the identified ions were determined by a linear extrapolation method. Ion intensities were measured by raising and lowering step by step the sample temperature to obtain the temperature dependence of corresponding partial pressures.

The resolution of the mass spectrometer was kept at about 1200 based on the 50% valley definition, in order to avoid the interference of background ions at the same nominal mass numbers. For the  $\text{Na}_2\text{BO}_2^+$ ,  $\text{NaO}^+$  and  $\text{CsO}^+$  ions among the ions of interest, however, the resolution was raised to about 2700 to obtain better mass separation.

The measured ion intensity  $I_i$  of the vapor species  $i$  was converted into the corresponding partial pressure  $p_i$  at the sample temperature  $T$  by the relation  $p_i = kI_iT/\sigma_i g_i n_i$ , where  $k$  is the pressure calibration constant,  $\sigma_i$  is the relative ionization cross-section,  $g_i$  is the gain of the electron multiplier and  $n_i$  is the isotopic abundance ratio. The value of  $k$  was obtained by the silver reference method. Ionization cross-sections for  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  were estimated by the method described by Kordis and Gingerich [15] under the assumption that the cross-sections for simple ionization and dissociative ionization from molecules are equal. The cross-section for  $\text{CsBO}_2(\text{g})$ , however, was assumed approximately equal to the atomic ionization cross-section for  $\text{Cs}(\text{g})$ , because the value calculated by the above method is smaller than that for  $\sigma_{\text{Cs}}$ . The values for  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  were estimated by the relations of  $\sigma_{\text{Cs}_2(\text{BO}_2)_2} = 1.5 \sigma_{\text{Cs}}$  and  $\sigma_{\text{NaCs}(\text{BO}_2)_2} = 0.75 (\sigma_{\text{NaBO}_2} + \sigma_{\text{Cs}})$ , respectively. Here, atomic ionization cross-sections were taken from the literature [16]. Multiplier gains for individual ions were measured by the pulse counting method [17]. Isotopic abundance ratios for  $^{11}\text{B}$  and  $^{16}\text{O}$  were taken from the literature [18].

### 3. Results and discussion

#### 3.1. Determination of vapor species

The search for ion species was made at 1100 K by impacting vapors with electrons having an energy of 53 eV, where the maximum ion intensity is obtained. Ion species identified in the present work are shown in table 2 together with appearance energies and corresponding vapor species. It is known that the vapor species containing alkali metal elements for borosilicate glasses may be similar to those for alkali metal metaborates [4]. The vapor species determined from the comparison of the ionization behavior for the borosilicate glasses with those for  $\text{NaBO}_2(\text{s})$  [19] and  $\text{CsBO}_2(\text{s})$  [20] are listed in table 2.

Table 2  
Appearance energies and vapor species for identified ions over NaBO<sub>2</sub>(s), CsBO<sub>2</sub>(s) and glasses

Ion species	Appearance energy (eV) <sup>a)</sup>						Vapor species
	NaBO <sub>2</sub> (s) <sup>b)</sup>	CsBO <sub>2</sub> (s) <sup>c)</sup>	Glass-1 <sup>d)</sup>	Glass-4 <sup>e)</sup>	Glass-8	Glass-9	
Na <sup>+</sup>	-	-	-	5.1	-	-	Na(g)
Na <sup>+</sup>	4.7; 10.1	-	5.0; 10.0	4.7; 10.1	4.7; 10.1	-	NaBO <sub>2</sub> (g)
NaBO <sub>2</sub> <sup>+</sup>	9.2	-	9.2	9.5	9.4	-	NaBO <sub>2</sub> (g)
Na <sub>2</sub> BO <sub>2</sub> <sup>+</sup>	9.6	-	10.2	10.2	10.2	-	Na <sub>2</sub> (BO <sub>2</sub> ) <sub>2</sub> (g)
NaO <sup>+</sup>	16.8	-	ND <sup>f)</sup>	ND	ND	-	NaBO <sub>2</sub> (g)
B <sup>+</sup>	21.2; 32.5	24.5; 30.0	ND	ND	ND	ND	NaBO <sub>2</sub> (g) and/or CsBO <sub>2</sub> (g)
Cs <sup>+</sup>	-	3.9; 9.3	-	3.9; 9.3	3.9; 9.3	3.9; 9.3	CsBO <sub>2</sub> (g)
Cs <sub>2</sub> <sup>+</sup>	-	34.0; 41.0	-	ND	ND	ND	CsBO <sub>2</sub> (g)
CsBO <sup>+</sup>	-	14.0; 18.9	-	ND	ND	ND	CsBO <sub>2</sub> (g)
CsBO <sub>2</sub> <sup>+</sup>	-	8.6	-	8.8	9.0	8.8	CsBO <sub>2</sub> (g)
Cs <sub>2</sub> BO <sub>2</sub> <sup>+</sup>	-	10.2	-	ND	ND	ND	Cs <sub>2</sub> (BO <sub>2</sub> ) <sub>2</sub> (g)
CsO <sup>+</sup>	-	14.8; 19.3	-	ND	ND	ND	CsBO <sub>2</sub> (g)
CsB <sup>+</sup>	-	23.0	-	-	-	ND	CsBO <sub>2</sub> (g)
NaCsBO <sub>2</sub> <sup>+</sup>	-	-	-	9.9	10.0	-	NaCs(BO <sub>2</sub> ) <sub>2</sub> (g)

<sup>a)</sup> Estimated error is  $\pm 0.5$  eV. <sup>b)</sup> Ref. [19]. <sup>c)</sup> Ref. [20]. <sup>d)</sup> Ref. [11]. <sup>e)</sup> Ref. [12]. <sup>f)</sup> No determination.

Appearance energies for the  $\text{Na}^+$  (except for  $A(\text{Na}^+) = 5.1 \pm 0.5$  eV),  $\text{NaBO}_2^+$ ,  $\text{Na}_2\text{BO}_2^+$ ,  $\text{Cs}^+$  and  $\text{CsBO}_2^+$  ions are in good agreement with those for  $\text{NaBO}_2(\text{s})$  and  $\text{CsBO}_2(\text{s})$ , respectively, indicating that the  $\text{Na}^+$  and  $\text{Cs}^+$  ions are formed by both dissociative ionization and positive-negative ion pair formation from  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$ , respectively, the  $\text{NaBO}_2^+$  and  $\text{CsBO}_2^+$  ions by the simple ionization of  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$ , respectively, and the  $\text{Na}_2\text{BO}_2^+$  ion by the dissociative ionization from  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ . The values of appearance energies for the  $\text{NaCsBO}_2^+$  ion for Glass-4 and Glass-8 are comparable with  $A(\text{Na}_2\text{BO}_2^+)$  for  $\text{NaBO}_2(\text{s})$  and  $A(\text{Cs}_2\text{BO}_2^+)$  for  $\text{CsBO}_2(\text{s})$ , indicating that the  $\text{NaCsBO}_2^+$  ion is formed by the dissociative ionization from  $\text{NaCs}(\text{BO}_2)_2(\text{g})$ .

The appearance energies of the  $\text{NaO}^+$ ,  $\text{B}^+$ ,  $\text{Cs}^{2+}$ ,  $\text{CsBO}^+$  and  $\text{CsO}^+$  ions could not be determined owing to very weak intensities. From the similarity of ionization processes of vapors for the glasses to those for  $\text{NaBO}_2(\text{s})$  and  $\text{CsBO}_2(\text{s})$ , however, it is assumed most likely that the  $\text{NaO}^+$  ion is formed by the dissociative ionization from  $\text{NaBO}_2(\text{g})$ , the  $\text{Cs}^{2+}$ ,  $\text{CsBO}^+$  and  $\text{CsO}^+$  ions by the dissociative ionization from  $\text{CsBO}_2(\text{g})$ , and the  $\text{B}^+$  ion by the dissociative ionization from  $\text{NaBO}_2(\text{g})$  and/or  $\text{CsBO}_2(\text{g})$ . The vapor species corresponding to the  $\text{Na}_2\text{BO}_2^+$  ion and the  $\text{Cs}^+$  and  $\text{CsO}^+$  ions are not  $\text{Na}_2\text{BO}_2(\text{g})$  reported by Wilds [5] and  $\text{Cs}(\text{g})$  and  $\text{CsO}(\text{g})$  reported by Albrethsen and Schwendiman [1] and Wilds [5], respectively. Very weak intensity of the  $\text{Cs}_2\text{BO}_2^+$  ion, which is probably formed by the dissociative ionization from  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$ , was detected for Glass-4 and Glass-8 above about 1150 K and for Glass-9 above about 1000 K.

In the initial stage of heating, Glass-4, in which the mole ratio of  $\text{Na}_2\text{O}$  plus  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is slightly larger than unity, shows the ionization efficiency curve for the  $\text{Na}^+$  ion varying with the lapse of time. Just after the sample temperature was raised to 1000 K, a clear bend cannot be observed in the curve and the only value of  $A(\text{Na}^+) = 5.1 \pm 0.5$  eV is obtained as shown in fig. 1. However, in the case of the  $\text{Na}^+$  ion for  $\text{NaBO}_2(\text{s})$  [19], the ionization efficiency curve, which is also illustrated in fig. 1, shows a distinct bend at about 10.1 eV energy of impact electrons, and the shape of the curve is quite similar to that of the  $\text{Na}^+$  ion for Glass-4 after 180 min at 1000 K. It is well known that for  $\text{NaBO}_2(\text{s})$  [19] the  $\text{Na}^+$  ion with  $A(\text{Na}^+) = 10.1 \pm 0.5$  eV is formed by the dissociative ionization from  $\text{NaBO}_2(\text{g})$  and the  $\text{Na}^+$  ion with  $A(\text{Na}^+) = 4.7 \pm 0.5$  eV is formed by the positive-negative ion pair formation from  $\text{NaBO}_2(\text{g})$ . These indicate that after 180 min at 1000 K the vapor species corresponding to the  $\text{Na}^+$  ion for Glass-4 is concluded to be  $\text{NaBO}_2(\text{g})$  as described already. However, in the initial stage of heating the shape of the ionization efficiency curve for the  $\text{Na}^+$  ion differs from that after 180 min at 1000 K as well as that for  $\text{NaBO}_2(\text{s})$  [19], indicating that the vapor species may not be a single species. The value of the ionization energy of  $\text{Na}(\text{g})$ ,  $I(\text{Na}^+)$  of 5.139 eV [21] suggests that the vapor species corresponding to the  $\text{Na}^+$  ion in the initial stage of heating may be a mixture of  $\text{Na}(\text{g})$  and  $\text{NaBO}_2(\text{g})$ .

In contrast to Glass-4, the shape of the ionization efficiency curve of the

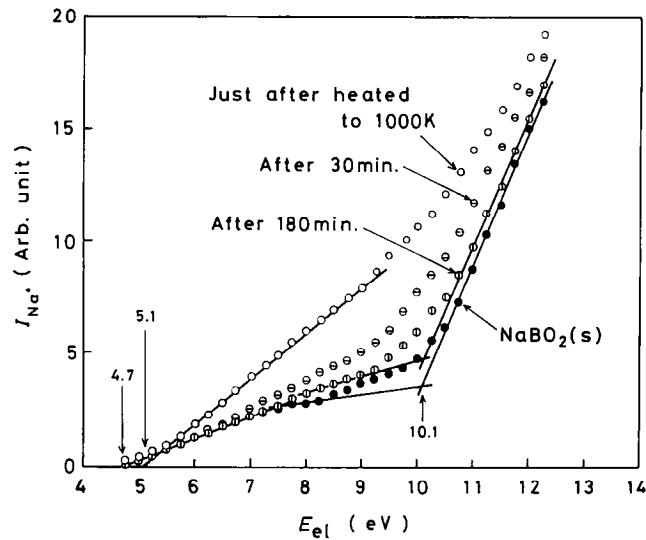


Fig. 1. Variation of ionization efficiency curves of  $\text{Na}^+$  ion for Glass-4 with heating time at 1000 K; the curve for  $\text{NaBO}_2(\text{s})$  is given as a reference.

$\text{Na}^+$  ion for Glass-8 is quite similar to that for  $\text{NaBO}_2(\text{s})$  [19] even just after heating to 1000 K as shown in fig. 2. This means that  $\text{Na}(\text{g})$  does not vaporize over Glass-8, in which the mole ratio of  $\text{Na}_2\text{O}$  plus  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is equal to

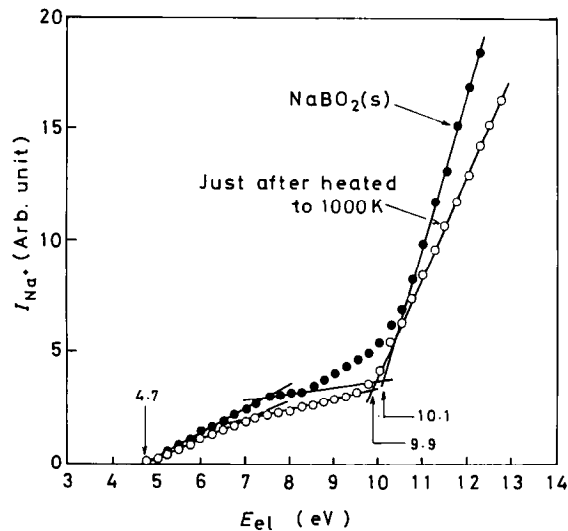


Fig. 2. Ionization efficiency curves of  $\text{Na}^+$  ion for Glass-8 just after heating to 1000 K; the curve for  $\text{NaBO}_2(\text{s})$  is given as a reference.

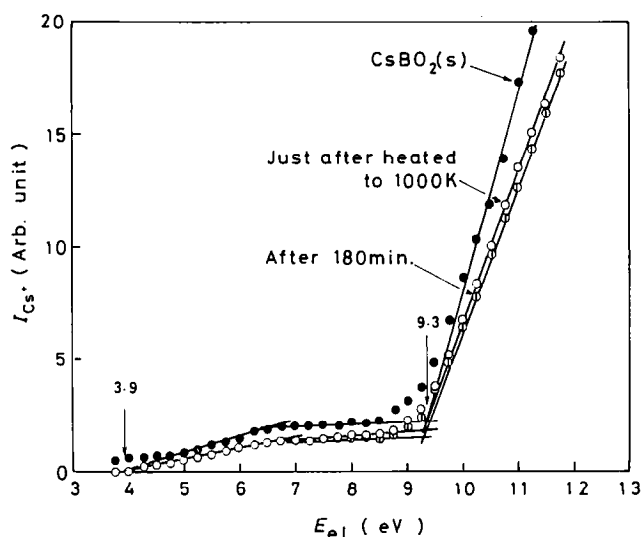


Fig. 3. Ionization efficiency curves of  $\text{Cs}^+$  ion for Glass-4 just after heating to 1000 K and after 180 min at 1000 K; the curve for  $\text{CsBO}_2(\text{s})$  is given as a reference.

unity, and that the corresponding vapor species of the  $\text{Na}^+$  ion is only  $\text{NaBO}_2(\text{g})$ .

For the  $\text{Cs}^+$  ion for Glass-4, the shape of the ionization efficiency curves at 1000 K in all heating times including the initial stage is quite similar to that for the  $\text{Cs}^+$  ion for  $\text{CsBO}_2(\text{s})$  [20], showing a bend at about 9.3 eV energy in fig. 3. This indicates that the vapor species corresponding to the  $\text{Cs}^+$  ion is only  $\text{CsBO}_2(\text{g})$  and that no vaporization of  $\text{Cs}(\text{g})$  occurs over Glass-4. The shape of the ionization efficiency curves for the  $\text{Cs}^+$  ions for Glass-8 and Glass-9 is also similar to that over Glass-4 and  $\text{CsBO}_2(\text{s})$ , indicating that the vapor species corresponding to the  $\text{Cs}^+$  ions is not  $\text{Cs}(\text{g})$  but  $\text{CsBO}_2(\text{g})$ .

The present authors [11] have studied the vapor species for three sodium borosilicate glasses Glass-1, Glass-2 and Glass-3, and showed that the vapor species are  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  for Glass-1 and Glass-2 in which the mole ratios of  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  are equal to unity and less than unity, respectively. For Glass-3 in which the ratio is larger than unity, however, the vaporization of  $\text{Na}(\text{g})$  is observed in addition to  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ . Schultz, Stolyanova and Semenov [22] have studied the vapor species for sodium borogermanate glasses. Similarly to the vaporization trend in sodium borosilicate glasses [11], they have observed the vaporization of  $\text{Na}(\text{g})$ ,  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  for the borogermanate glasses in which the mole ratio of  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is larger than unity and did not observe  $\text{Na}(\text{g})$  for the borogermanate glasses in which the ratio is less than unity. The vaporization behavior of  $\text{Na}(\text{g})$  is quite similar to the case of Glass-4 and Glass-8 in which

the ratios of  $\text{Na}_2\text{O}$  plus  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  are slightly larger than unity and equal to unity, respectively.

Furukawa and White [23] have studied the variation of Raman spectra of sodium borosilicate glasses to interpret the distribution of the  $\text{Na}^+$  ions between silicate and borate units in the glasses, and they have reported that in the glasses with the mole ratio of  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  being less than unity all  $\text{Na}^+$  ions are associated with borate units. A similar conclusion has been reached from an NMR study [24]. The preferential association of the  $\text{Na}^+$  ions with borate units may be confirmed by the fact that the free energy of formation for  $\text{NaBO}_2(\text{s})$  is larger than half of that for  $\text{Na}_2\text{SiO}_3(\text{s})$  [25,26]. Consequently, in the present glasses all  $\text{Na}^+$  and  $\text{Cs}^+$  ions are associated with borate units, except for Glass-4, in which a small portion of  $\text{Na}^+$  and  $\text{Cs}^+$  ions might be shared with silicate units.

Since vapor pressures over alkali metal metaborates are much higher than those over corresponding alkali metal metasilicates [13,27,28], the vaporization over the present glasses must occur from the  $\text{Na}^+$  and/or  $\text{Cs}^+$  ions associated

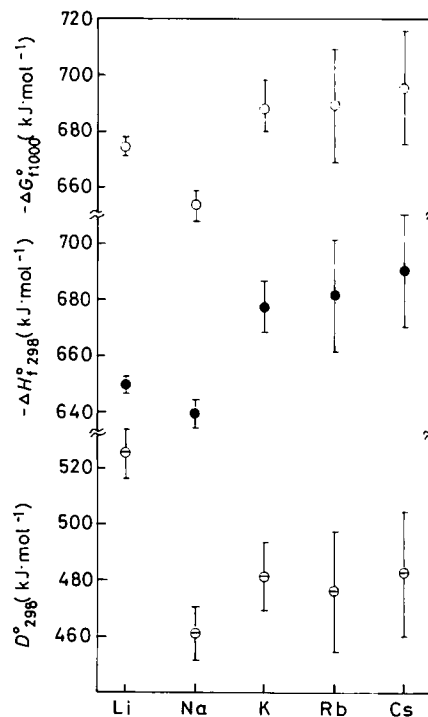


Fig. 4. Free energies of formation, enthalpies of formation and dissociation energies for alkali metal metaborate vapors.



with borate units. As shown in fig. 4, the free energy of formation for  $\text{NaBO}_2(\text{g})$  as well as the enthalpy of formation and the dissociation energy to  $\text{Na}(\text{g})$  and  $\text{BO}_2(\text{g})$  is smallest among alkali metal metaborate vapors. This indicates that the dissociation of  $\text{NaBO}_2(\text{g})$  is preferential to that of  $\text{CsBO}_2(\text{g})$ . Then, it can be explained from this thermochemical trend that the vaporization of  $\text{Na}(\text{g})$  occurs but not vaporization of  $\text{Cs}(\text{g})$  is observed over Glass-4 in which the amount of Na plus Cs is in excess for forming  $\text{NaBO}_2$  and  $\text{CsBO}_2$  imaginary compounds in this glass.

### 3.2. Partial pressures of vapor species

The partial pressure of  $\text{NaBO}_2(\text{g})$  was calculated from the measured intensities of the  $\text{Na}^+$  and  $\text{NaBO}_2^+$  ions. The contribution of the  $\text{NaO}^+$  and  $\text{B}^+$  ions to the pressure was negligibly small. Similarly, the intensities of the  $\text{Cs}^+$  and  $\text{CsBO}_2^+$  ions were used for the determination of the partial pressure of  $\text{CsBO}_2(\text{g})$ . The partial pressures of  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ ,  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  were obtained from the intensities of the  $\text{Na}_2\text{BO}_2^+$ ,  $\text{Cs}_2\text{BO}_2^+$  and  $\text{NaCsBO}_2^+$  ions, respectively.

Logarithmic values of the determined partial pressures of  $\text{NaBO}_2(\text{g})$ ,  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ ,  $\text{CsBO}_2(\text{g})$ ,  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  over the present glasses are shown as a function of reciprocal temperature in fig. 5, where the unit of pressure is Pascal. The partial pressures of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  over Glass-9 are fairly higher than those of  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  over Glass-1, respectively. The result corresponds to the fact that the partial pressures of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  over  $\text{CsBO}_2(\text{s})$  [13] are evidently high as compared with those of  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  over  $\text{NaBO}_2(\text{s})$  [13], respectively. For the same reason, over Glass-4 and Glass-8 the partial pressures of  $\text{CsBO}_2(\text{g})$  are slightly higher than those of  $\text{NaBO}_2(\text{g})$ , although the mole fraction of the  $\text{Cs}_2\text{O}$  component is smaller than that of  $\text{Na}_2\text{O}$  in these glasses. The partial pressures of  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  over Glass-4 and Glass-8 are lower than those of  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  over Glass-1, Glass-4 and Glass-8. The ratio of the partial pressures of  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  to those of  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  is about 0.16, being nearly equal to the mole ratio of  $\text{Cs}_2\text{O}$  to  $\text{Na}_2\text{O}$  in these glasses.

The partial pressure of  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  could not be measured over Glass-4 and Glass-8 because of the too weak intensity of the  $\text{Cs}_2\text{BO}_2^+$  ion. At 1150 K, the intensity ratio of the  $\text{Cs}_2\text{BO}_2^+$  ion to the  $\text{Cs}^+$  ion was below  $1 \times 10^{-4}$ . In the following section the thermochemical reason why both  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  are easily identified but  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  is not over Glass-4 and Glass-8 will be described.

The lines drawn by the least-squares treatment of data in fig. 5 are given by the equations in table 3 together with the temperature range. The errors quoted in the equations are the standard deviations of slopes and intercepts. Uncertainties in the partial pressures arise from errors in measurements of ion intensities and also conversions of ion intensities to partial pressures. From

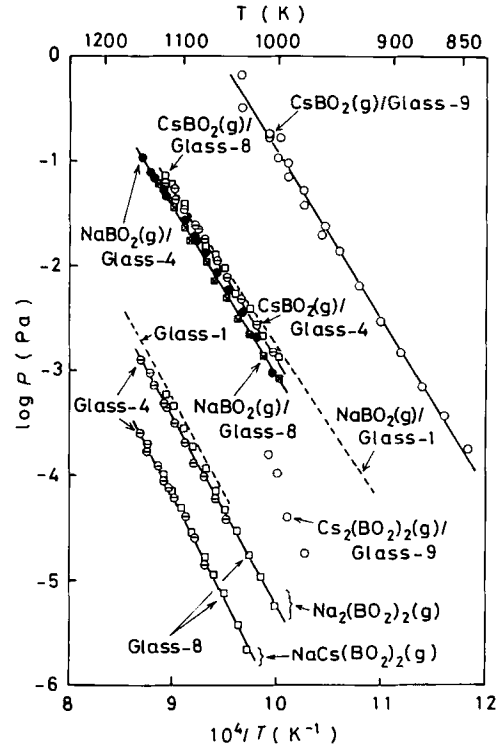


Fig. 5. Partial pressures of  $\text{NaBO}_2(\text{g})$ ,  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ ,  $\text{CsBO}_2(\text{g})$ ,  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  over Glass-1, Glass-4, Glass-8 and Glass-9.

Table 3

Least-squares equations for partial pressures of vapor species over Glass-1, Glass-4, Glass-8 and Glass-9

Glass	Vapor species	Temperature range (K)	$\log p = A - (B \times 10^3)/T$ <sup>a)</sup>	
			A	B
Glass-1	$\text{NaBO}_2(\text{g})$	915–1100	$12.28 \pm 0.08$	$15.06 \pm 0.08$
	$\text{Na}_2(\text{BO}_2)_2(\text{g})$	1045–1172	$12.83 \pm 0.15$	$17.88 \pm 0.16$
Glass-4	$\text{NaBO}_2(\text{g})$	1005–1150	$12.78 \pm 0.31$	$15.87 \pm 0.33$
	$\text{Na}_2(\text{BO}_2)_2(\text{g})$	1036–1150	$13.38 \pm 0.23$	$18.78 \pm 0.25$
	$\text{CsBO}_2(\text{g})$	1005–1120	$13.22 \pm 0.25$	$16.11 \pm 0.27$
	$\text{NaCs}(\text{BO}_2)_2(\text{g})$	1074–1150	$13.41 \pm 0.57$	$19.68 \pm 0.63$
Glass-8	$\text{NaBO}_2(\text{g})$	1002–1122	$13.43 \pm 0.27$	$16.55 \pm 0.28$
	$\text{Na}_2(\text{BO}_2)_2(\text{g})$	1002–1122	$13.44 \pm 0.14$	$18.70 \pm 0.15$
	$\text{CsBO}_2(\text{g})$	1002–1122	$12.78 \pm 0.35$	$15.65 \pm 0.37$
	$\text{NaCs}(\text{BO}_2)_2(\text{g})$	1028–1122	$13.85 \pm 0.74$	$20.03 \pm 0.80$
Glass-9	$\text{CsBO}_2(\text{g})$	845–1036	$14.91 \pm 0.31$	$15.83 \pm 0.33$

<sup>a)</sup> Unit of pressure is Pascal.

experimental and probable errors, the uncertainties in the partial pressures are estimated to be  $\Delta \log p_i = \pm 0.2$ .

### 3.3 Thermochemical quantities for vaporization

Usually, second-law enthalpies of vaporization can be derived from the slopes in the equations of the partial pressures in table 3. However, the enthalpies of vaporization for  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$  were obtained from the slopes of the relation of  $\log I_i T = a - b/T$  by the use of the intensities of the  $\text{NaBO}_2^+$  and  $\text{CsBO}_2^+$  ions, respectively. The  $\text{Na}^+$  and  $\text{Cs}^+$  ions would have kinetic energies when these ions are formed by the dissociative ionization from  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$ , respectively. It is known that the kinetic energies give rise to some spurious temperature dependences of the intensities of the  $\text{Na}^+$  and  $\text{Cs}^+$  ions [29–31]. For this reason, the second-law enthalpies of vaporization for  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$  cannot be yielded from the slopes in the partial pressure equations influenced mainly by the  $\text{Na}^+$  and  $\text{Cs}^+$  ions, respectively.

The slopes in the partial pressure equations for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$ , however, were used for the determination of the second-law enthalpies of vaporization for them. Here, the partial pressures of  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  have been calculated from the intensities of the  $\text{Na}_2\text{BO}_2^+$  and  $\text{NaCsBO}_2^+$  ions, respectively. The enthalpy of vaporization for  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  over Glass-9 could not be evaluated, because only a few measurements of the partial pressures were made.

The second-law enthalpies of dimerization reaction in the vapor phase were calculated on the basis of the second-law enthalpies of vaporization for  $\text{NaBO}_2(\text{g})$ ,  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ ,  $\text{CsBO}_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$ .

Table 4 shows the values for the present glasses together with those for Glass-1 [11],  $\text{NaBO}_2(\text{s})$  [14] and  $\text{CsBO}_2(\text{s})$  [14]. The enthalpy of vaporization becomes large when going from  $\text{NaBO}_2(\text{g})$  through  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  to  $\text{Na}_3(\text{BO}_2)_3(\text{g})$ . A similar trend is seen between  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$ . These trends can be easily understood from the partial pressures being of the order  $\text{NaBO}_2(\text{g}) > \text{Na}_2(\text{BO}_2)_2(\text{g}) > \text{Na}_3(\text{BO}_2)_3(\text{g})$  and  $\text{CsBO}_2(\text{g}) > \text{Cs}_2(\text{BO}_2)_2(\text{g})$ . The enthalpies of vaporization for  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  over Glass-4 and Glass-8 are slightly higher than those for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  as predicted from lower partial pressures of  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  than  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ .

The enthalpies of dimerization reaction yield the enthalpies of formation for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  when combined with the enthalpies of formation for  $\text{NaBO}_2(\text{g})$  [14] and  $\text{CsBO}_2(\text{g})$  [14], and the dissociation energies between Na (or Cs) and  $\text{BO}_2$  bonds for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  when combined with the enthalpies of formation for  $\text{Na}(\text{g})$ ,  $\text{Cs}(\text{g})$  and  $\text{BO}_2(\text{g})$ , respectively [25]. The values obtained are shown in table 5. The enthalpies of formation and the dissociation energies for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  determined from the vaporization of Glass-1, Glass-4 and Glass-8 are in agreement with those

Table 4  
Second-law enthalpies ( $\text{kJ} \cdot \text{mol}^{-1}$ ) of vaporization and gaseous reaction over  $\text{NaBO}_2(\text{s})$ ,  $\text{CaBO}_2(\text{s})$  and glasses

	$\text{NaBO}_2(\text{s})^{\text{a)}}$	$\text{CsBO}_2(\text{s})^{\text{a)}}$	Glass-1 <sup>b)</sup>	Glass-4	Glass-8	Glass-9
$\Delta H_v^\circ(\text{NaBO}_2\text{(g)})$	$286.1 \pm 4.8$	-	$290.1 \pm 5.6$	$305.4 \pm 14.9$	$308.7 \pm 2.1$	-
$\Delta H_v^\circ(\text{Na}_2(\text{BO}_2)_2\text{(g)})$	$360.2 \pm 3.3$	-	$342.3 \pm 3.1$	$358.8 \pm 4.8$	$358.1 \pm 2.9$	-
$\Delta H_v^\circ(\text{Na}_3(\text{BO}_2)_3\text{(g)})$	$425.5 \pm 19.0$	-	-	-	-	-
$\Delta H_v^\circ(2\text{NaBO}_2(\text{g}) = \text{Na}_2(\text{BO}_2)_2\text{(g)})$	$-212.1 \pm 10.2$	-	$-237.9 \pm 7.8$	$-252.0 \pm 30.2$	$-259.3 \pm 5.1$	-
$\Delta H_v^\circ(3\text{NaBO}_2(\text{g}) = \text{Na}_3(\text{BO}_2)_3\text{(g)})$	$-423.5 \pm 23.8$	-	-	-	-	-
$\Delta H_v^\circ(\text{CsBO}_2\text{(g)})$	-	$248.4 \pm 2.9$	-	$313.2 \pm 6.8$	$329.5 \pm 4.0$	$312.7 \pm 13.4$
$\Delta H_v^\circ(\text{Cs}_2(\text{BO}_2)_2\text{(g)})$	-	$319.3 \pm 3.1$	-	-	-	-
$\Delta H_v^\circ(2\text{CsBO}_2(\text{g}) = \text{Cs}_2(\text{BO}_2)_2\text{(g)})$	-	$-176.2 \pm 6.6$	-	-	-	-
$\Delta H_v^\circ(\text{NaCs}(\text{BO}_2)_2\text{(g)})$	-	-	-	$374.9 \pm 12.1$	$383.5 \pm 15.3$	-
$\Delta H_v^\circ{}^{\text{c)}}$	-	-	-	$-243.7 \pm 20.4$	$-254.7 \pm 16.0$	-

<sup>a)</sup> Ref. [14].

<sup>b)</sup> Ref. [11].

<sup>c)</sup>  $\text{NaBO}_2(\text{g}) + \text{CsBO}_2(\text{g}) = \text{NaCs}(\text{BO}_2)_2(\text{g})$ .

Table 5  
Second-law enthalpies of formation ( $\text{kJ} \cdot \text{mol}^{-1}$ ) and dissociation energies ( $\text{kJ} \cdot \text{mol}^{-1}$ ) for gaseous species

	$\text{NaBO}_2(\text{s})^{\text{a)}$	$\text{CsBO}_2(\text{s})^{\text{a)}$	Glass-1 <sup>b)</sup>	Glass-4	Glass-8
$\Delta H_f^\circ(\text{NaBO}_2, \text{g})$	$-639.2 \pm 5.1$	—	—	—	—
$\Delta H_f^\circ(\text{Na}_2(\text{BO}_2)_2, \text{g})$	$-1509.5 \pm 14.4$	—	$-1536.9 \pm 12.8$	$-1549.6 \pm 31.9$	$-1556.9 \pm 11.4$
$\Delta H_f^\circ(\text{Na}_3(\text{BO}_2)_3, \text{g})$	$-2373.5 \pm 28.3$	—	—	—	—
$D^\circ(\text{Na} - \text{BO}_2)$	$462.5 \pm 9.8$	—	—	—	—
$D^\circ(\text{Na}_2(\text{BO}_2)_2)$	$1137.5 \pm 22.1$	—	$1164.1 \pm 21.1$	$1177.0 \pm 36.1$	$1184.9 \pm 20.3$
$D^\circ(\text{Na}_3(\text{BO}_2)_3)$	$1812.8 \pm 37.9$	—	—	—	—
$\Delta H_f^\circ(\text{CsBO}_2, \text{g})$	—	$-690.1 \pm 20.3$	—	—	—
$\Delta H_f^\circ(\text{Cs}_2(\text{BO}_2)_2, \text{g})$	—	$-1577.8 \pm 41.1$	—	—	—
$D^\circ(\text{Cs} - \text{BO}_2)$	—	$482.3 \pm 22.1$	—	—	—
$D^\circ(\text{Cs}_2(\text{BO}_2)_2)$	—	$1147.3 \pm 44.6$	—	—	—
$\Delta H_f^\circ(\text{NaCs}(\text{BO}_2)_2, \text{g})$	—	—	—	$-1599.3 \pm 29.2$	$-1608.8 \pm 26.3$
$D^\circ(\text{NaCs}(\text{BO}_2)_2)$	—	—	—	$1191.8 \pm 33.8$	$1204.3 \pm 31.3$

a). Ref. [14]. b) Ref. [11].

Table 6  
Free energies of dimerization reaction at 1000 K

Reaction	$\Delta G^\circ$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )				
	$\text{NaBO}_2(\text{s})$	$\text{CsBO}_2(\text{s})$	Glass-1	Glass-4	Glass-9
$2\text{NaBO}_2(\text{g}) = \text{Na}_2(\text{BO}_2)_2(\text{g})$	$-94.3 \pm 7.1$	—	$-105.6 \pm 7.1$	$-108.3 \pm 7.1$	$-114.6 \pm 7.1$
$2\text{CsBO}_2(\text{g}) = \text{Cs}_2(\text{BO}_2)_2(\text{g})$	—	$-52.8 \pm 7.1$	—	—	$-53.5 \pm 7.1$
$\text{NaBO}_2(\text{g}) + \text{CsBO}_2(\text{g}) = \text{NaCs}(\text{BO}_2)_2(\text{g})$	—	—	—	$-90.5 \pm 5.9$	$-92.2 \pm 5.9$

from  $\text{NaBO}_2(\text{s})$  [14], respectively, and the agreement between the values for  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  obtained from Glass-4 and Glass-8 is good.

The dissociation energy for  $\text{Na}_3(\text{BO}_2)_3(\text{g})$  is about 1.5 times as large as that for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ , indicating that an additivity rule is held between the dissociation energies, since the number of the bonds between Na and  $\text{BO}_2$  is six in a cyclic  $\text{Na}_3(\text{BO}_2)_3(\text{g})$  molecule and four in  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ . The enthalpy of formation and the dissociation energy for  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  are not largely different from those for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$ , respectively.

The partial pressures in table 3 give free energies for dimerization reaction at 1000 K as shown in table 6. As can be seen in this table, the value for  $2\text{CsBO}_2(\text{g}) = \text{Cs}_2(\text{BO}_2)_2(\text{g})$  is significantly small. This means that when the partial pressures of  $\text{NaBO}_2(\text{g})$  and  $\text{CsBO}_2(\text{g})$  are equal, the partial pressure of  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  is fairly lower than those of  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$ . In fact, the partial pressure of  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  could not be experimentally measured over Glass-4 and Glass-8.

### 3.4. Chemical activities of components in glasses

The pseudo components obtained from the consideration of the vapor species over the glasses are shown in table 7. According to Wenzel and Sanders [32], the same chemical compositions as the vapor species were selected as the pseudo components.

The chemical activity of a given pseudo component in the glass was determined from the ratio between the partial pressure of the corresponding vapor species for the glass and that for a pure compound of the same chemical composition as the vapor species. For example, the activity and the activity coefficient for the  $\text{CsBO}_2$  pseudo component in Glass-9 were calculated by the following equation:

$$\gamma_{\text{CsBO}_2} = a_{\text{CsBO}_2} \times \frac{1}{0.4} = \frac{p_{\text{CsBO}_2}}{p_{\text{CsBO}_2}^0} \times \frac{1}{0.4}. \quad (1)$$

Table 7

Chemical activities, mole fractions and activity coefficients of pseudo components in glasses at 1000 K

Glass	Pseudo composition	$a^{\text{a)}}$	$X^{\text{a)}}$	$\gamma^{\text{a)}}$
Glass-1	$2\text{NaBO}_2-3\text{SiO}_2$	0.095	0.40	0.24
	$1\text{Na}_2(\text{BO}_2)_2-3\text{SiO}$	0.035	0.25	0.14
Glass-8	$1.7\text{NaBO}_2-3\text{SiO}_2-0.3\text{CsBO}_2$	0.044	0.34	0.13
	$1.7\text{NaBO}_2-3\text{SiO}_2-0.3\text{CsBO}_2$	$9.1 \times 10^{-5}$	0.06	$1.5 \times 10^{-3}$
Glass-9	$2\text{CsBO}_2-3\text{SiO}_2$	$8.3 \times 10^{-3}$	0.40	0.021
	$1\text{Cs}_2(\text{BO}_2)_2-3\text{SiO}_2$	$8.6 \times 10^{-5}$	0.25	$3.4 \times 10^{-4}$

<sup>a)</sup> Value of component underlined.

It was assumed that Glass-9 consists of the  $2\text{CsBO}_2\text{-}3\text{SiO}_2$  pseudo binary system. Those for the  $\text{Cs}_2(\text{BO}_2)_2$  component in Glass-9 were calculated by

$$\gamma_{\text{Cs}_2(\text{BO}_2)_2} = a_{\text{Cs}_2(\text{BO}_2)_2} \times \frac{1}{0.25} = \frac{p_{\text{Cs}_2(\text{BO}_2)_2}}{p_{\text{Cs}_2(\text{BO}_2)_2}^\circ} \times \frac{1}{0.25}, \quad (2)$$

under the assumption that Glass-9 consists of the  $1\text{Cs}_2(\text{BO}_2)_2\text{-}3\text{SiO}_2$  system. Here,  $p$  is the partial pressure over Glass-9,  $p^\circ$  is the partial pressure over  $\text{CsBO}_2(\text{s})$  [13],  $a$  is the chemical activity,  $\gamma$  is the activity coefficient and 0.4 and 0.25 in the equations are the mole fractions of  $\text{CsBO}_2$  and  $\text{Cs}_2(\text{BO}_2)_2$  in Glass-9, respectively.

In the calculations for the pseudo components with underlines in Glass-1 and Glass-8 in table 7, the partial pressures of  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  over  $\text{NaBO}_2(\text{s})$  [13] were also used. Since the  $\text{Na}_2\text{O}$  and  $\text{Cs}_2\text{O}$  contents in Glass-4 are in excess for forming the imaginary compounds  $\text{NaBO}_2$  and  $\text{CsBO}_2$ , it is impossible to rewrite the composition by the use of  $\text{NaBO}_2$  and  $\text{CsBO}_2$  pseudo components. Therefore, the result for Glass-4 is not included in table 7.

The chemical activities and the activity coefficients for the  $\text{CsBO}_2$  and  $\text{Cs}_2(\text{BO}_2)_2$  components in Glass-9 are smaller than those for  $\text{NaBO}_2$  and  $\text{Na}_2(\text{BO}_2)_2$  in Glass-1, respectively. From these results it can be concluded that the vaporization of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  is thermochemically suppressed much more than that of  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ , respectively.

As described above, the chemical activities of the components in the glasses permit to study the degree of the suppression of the vaporization of individual vapor species.

#### 4. Conclusion

The vaporization behavior of three cesium-containing borosilicate glasses was studied by a mass-spectrometric Knudsen effusion method in the temperature range 845–1150 K.

Vapor species of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  were identified over the glass containing  $\text{Cs}_2\text{O}$ , and the identification of  $\text{NaBO}_2(\text{g})$ ,  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  was made in addition to  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  over glasses containing  $\text{Na}_2\text{O}$  and  $\text{Cs}_2\text{O}$ . In the initial stage of heating the glass, in which the mole ratio of  $\text{Na}_2\text{O}$  plus  $\text{Cs}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is slightly larger than unity, the vapor species of  $\text{Na}(\text{g})$  was still observed at 1000 K, while no vaporization of  $\text{Na}(\text{g})$  took place over the glass, in which the ratio is equal to unity. Regarding the vaporization of  $\text{Cs}(\text{g})$ , it cannot be found over all of the glasses in all heating times.

The enthalpy of vaporization became large when going from  $\text{NaBO}_2(\text{g})$  through  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  to  $\text{Na}_3(\text{BO}_2)_3(\text{g})$  and similarly from  $\text{CsBO}_2(\text{g})$  to

$\text{Cs}_2(\text{BO}_2)_2(\text{g})$ . The enthalpy of formation as well as the dissociation energy for  $\text{NaCs}(\text{BO}_2)_2(\text{g})$  was not largely different from those for  $\text{Na}_2(\text{BO}_2)_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$ . The chemical activities of  $\text{CsBO}_2$  and  $\text{Cs}_2(\text{BO}_2)_2$  pseudo components were smaller than those of  $\text{NaBO}_2$  and  $\text{Na}_2(\text{BO}_2)_2$  in the glasses, respectively. This gave evidence that the vaporization of  $\text{CsBO}_2(\text{g})$  and  $\text{Cs}_2(\text{BO}_2)_2(\text{g})$  was thermochemically suppressed much more than that of  $\text{NaBO}_2(\text{g})$  and  $\text{Na}_2(\text{BO}_2)_2(\text{g})$ , respectively.

This study was partially supported by the Grants-in-Aid for Scientific Research and for Installation from the Ministry of Education, Science and Culture, Japan.

## References

- [1] A.E. Albrethsen and L.C. Schwendiman, BNWL-338 (1967).
- [2] D. Walmsley, B.A. Sammons and J.R. Grover, AERE-R-5777 (1969).
- [3] W.J. Gray, BNWL-2111 (1976); *Radioactive Waste Manag.* 1 (1980) 147.
- [4] R. Terai and E. Kosaka, *Osaka Kogyo Gijutsu Shikenjo Kiho, Bull. Govt. Ind. Res. Inst., Osaka* 27 (1976) 150.
- [5] G.W. Wilds, DP-1504 (1978).
- [6] G.B. Woolsey et al., DP-MS-79-92 (1980).
- [7] J.E. Mendel et al., PNL-3802 (1981).
- [8] J.W. Hastie, E.R. Plante and D.W. Donnell, NBSIR-83-2731 (1983).
- [9] H. Yamanaka, R. Terai and S. Hara, *Osaka Kogyo Gijutsu Shikenjo Kiho, Bull. Govt. Ind. Res. Inst., Osaka* 34 (1983) 228.
- [10] H. Yamanaka, R. Terai and S. Hara, *ibid.* 34 (1983) 261.
- [11] M. Asano and Y. Yasue, *J. Nucl. Mater.* 138 (1986) 65.
- [12] M. Asano and Y. Yasue, *J. Nucl. Sci. Technol.* 22 (1985) 1029.
- [13] Y. Yasue and M. Asano, *Bull. Inst. Atom. Energy (Kyoto Univ.)* 67 (1985) 47.
- [14] Y. Yasue and M. Asano, *ibid.* 67 (1985) 48.
- [15] J. Kordis and K.A. Gingerich, *J. Chem. Phys.* 58 (1973) 5141.
- [16] J.B. Mann, in: *Recent Developments in Mass Spectroscopy*, eds. K. Ogata and T. Hayakawa (Univ. of Tokyo Press, Tokyo, 1970) p. 814.
- [17] M. Asano, H. Kimura and K. Kubo, *Mass Spectr.* 27 (1979) 157.
- [18] *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972) 7-6.
- [19] M. Asano, Y. Yasue and K. Kubo, *Bull. Inst. Atom. Energy (Kyoto Univ.)* 66 (1984) 39.
- [20] M. Asano, Y. Yasue and K. Kubo, *J. Nucl. Sci. Technol.* 21 (1984) 614.
- [21] See ref. [18] pp. 7-10.
- [22] M.M. Schultz, V.L. Stolyanova and G.A. Semenov, *J. Non-Cryst. Solids* 38&39 (1980) 581.
- [23] T. Furukawa and W.B. White, *J. Mater. Sci.* 16 (1981) 2689.
- [24] Y.H. Yun and P.T. Bray, *J. Non-Cryst. Solids* 27 (1978) 363.
- [25] R.D. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd. ed., NSRDS-NBS-37 (Dow Chemical, Midland, 1971).
- [26] M.W. Chase et al., *J. Phys. Chem. Ref. Data* 3 (1974) 311.
- [27] V.C. Kroger and L.S. Aachen, *Glastechn. Ber.* 38 (1965) 313.
- [28] H. Nakagawa, M. Asano and K. Kubo, *J. Nucl. Mater.* 102 (1981) 292.
- [29] J. Berkowitz, H.A. Tasman and W.A. Chupka, *J. Chem. Phys.* 36 (1962) 2170.
- [30] J. Berkowitz and J.R. Marquat, *J. Chem. Phys.* 37 (1962) 1853.
- [31] A. Buchler and J.B. Berkowitz-Mattuck, *J. Chem. Phys.* 39 (1963) 286.
- [32] J.T. Wenzel and D.M. Sanders, *J. Phys. Chem. Glasses* 23 (1982) 47.