

VAPORIZATION OF ALKALI BOROSILICATE GLASSES

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The vaporization behavior of glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$, $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ and $0.85Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ systems has been studied by a mass-spectrometric Knudsen effusion method in the temperature range 806-1172 K. Here, R is an alkali metal and R' an alkali metal other than Na. Vapor species of $RBO_2(g)$ and $R_2(BO_2)_2(g)$ have been identified over the glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$ system and those of $NaBO_2(g)$, $R'BO_2(g)$, $Na_2(BO_2)_2(g)$ and $NaR'(BO_2)_2(g)$, except for $NaLi(BO_2)_2(g)$, over the glasses in the other two systems. The vapor of Na(g) has been further observed in the initial stage of heating over the glasses in the $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system, while no vaporization of R'(g) occurs. Chemical activities of RBO_2 and $R_2(BO_2)_2$ pseudo components in the glasses become small on going Li to Cs, that is, the vaporization of $CsBO_2(g)$ and $Cs_2(BO_2)_2(g)$ is most suppressed thermochemically from the glasses. Enthalpies of formation and dissociation energies for $R_2(BO_2)_2(g)$ and $NaR'(BO_2)_2(g)$ are not so different from one another, except for $D_0^\circ(Li_2(BO_2)_2)$.

1. Introduction

Borosilicate glasses will be used as matrix materials for the storage and then the disposal of high-level radioactive wastes. Hence, thermochemical properties of components in borosilicate glasses in both condensed and gaseous phases at

high temperatures are very important to predict the vaporization behavior of borosilicate glasses containing actual high-level radioactive wastes. Many studies have been made of the vaporization of simulated high-level radioactive wastes incorporated into borosilicate glasses [1]. From these studies, alkali metals and boron are found to vaporize significantly from borosilicate glasses, but the description of the chemical form of the vapors is very inadequate.

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Table 1
 Oxide compositions of glasses used in the present work and previous works [2-5]

Glass	Ref.	Oxide composition						
		Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	B ₂ O ₃	SiO ₂
1	[2]	-	1	-	-	-	1	3
4	[3,4]	-	1	-	-	0.15	1	3
8	[4]	-	0.85	-	-	0.15	1	3
9	[4]	-	-	-	-	1	1	3
10	[5]	-	1	-	0.15	-	1	3
11	[5]	-	0.85	-	0.15	-	1	3
12	[5]	-	-	-	1	-	1	3
13	-	-	1	0.15	-	-	1	3
14	-	-	0.85	0.15	-	-	1	3
15	-	-	-	1	-	-	1	3
16	-	0.15	1	-	-	-	1	3
17	-	0.15	0.85	-	-	-	1	3
18	-	1	-	-	-	-	1	3

Recently, the present authors have studied the vaporization of sodium [2], cesium [3,4] and rubidium [5] from borosilicate glasses by a mass-spectrometric Knudsen effusion method and they have reported vapor species in detail. In the present paper, vapor species and their partial pressures in equilibrium with glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$, $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ and $0.85Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ systems have been reported together with previous data [2–5]. Here, R is an alkali metal and R' an alkali metal other than Na. The compositions of the glasses are listed in table 1. In the glasses in the $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system, the molar ratio of Na_2O plus R'_2O to B_2O_3 is slightly larger than unity, while in those in the $0.85Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system the ratio is equal to unity by reducing the Na_2O content. By this selection, a comparison of the vaporization behavior of both systems has been made.

Chemical activities of components in the glasses, enthalpies of formation and dissociation energies for $R_2(BO_2)_2(g)$ and $NaR'(BO_2)_2(g)$ have been determined from the partial pressure data.

2. Experimental

The glass samples were prepared in a manner similar to that described in the previous work [5]. The mass spectrometer equipped with a platinum Knudsen cell and the experimental procedure used in the present work have been reported elsewhere [4].

3. Results and discussion

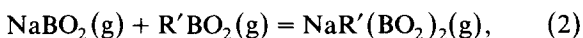
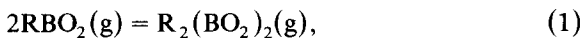
The identified ion species are R^+ , RBO^+ , RBO_2^+ , $R_2BO_2^+$, RO^+ , RB^+ and B^+ over the glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$ system and additionally $NaR'BO_2^+$ over those in the other two systems. From these ion species [6], the vapor species over the glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$ system are determined to be $RBO_2(g)$ and $R_2(BO_2)_2(g)$, and those over the other two systems to be $NaBO_2(g)$, $R'BO_2(g)$, $Na_2(BO_2)_2(g)$ and $NaR'(BO_2)_2(g)$ except for $NaLi(BO_2)_2(g)$.

The identification of $R'_2(BO_2)_2(g)$ over the latter glasses was very difficult.

For the glasses in the $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system, in which the molar ratio of Na_2O plus R'_2O to B_2O_3 is slightly larger than unity, that is, the total amount of Na_2O and R'_2O is in excess of that needed to form imaginary $NaBO_2$ and $R'BO_2$ compounds in the glasses, the shape of the ionization efficiency curve for the Na^+ ion varied with the lapse of time in the initial stage of heating. This indicates that $Na(g)$ vaporizes in the initial stage of heating. However, the shape of the curve of the R'^+ ion did not vary with time, indicating that no vaporization of $R'(g)$ occurs. The preferential vaporization of $Na(g)$ may be explained from the thermochemical trend that the dissociation energy of the bond between Na and BO_2 in $NaBO_2(g)$ is the smallest among those in $RBO_2(g)$ [4]. For the glasses in the $0.85Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system, in which the molar ratio is equal to unity, neither $Na(g)$ nor $R'(g)$ is identified.

Measured ion intensities were converted into corresponding partial pressures by the silver reference method [4]. Figure 1 shows the partial pressures of $RBO_2(g)$ and $R_2(BO_2)_2(g)$ over the glasses in the $R_2O \cdot B_2O_3 \cdot 3SiO_2$ system. The order of the partial pressures of $RBO_2(g)$ is as follows: $LiBO_2(g) < NaBO_2(g) < KBO_2(g) < RbBO_2(g) < CsBO_2(g)$. The result corresponds just to the order of those over $RBO_2(s)$ [7]. The partial pressures of $NaBO_2(g)$, $KBO_2(g)$, $Na_2(BO_2)_2(g)$ and $NaK(BO_2)_2(g)$ over glass 14 and those of $NaBO_2(g)$, $LiBO_2(g)$ and $Na_2(BO_2)_2(g)$ over glass 17 in the $0.85Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system are shown in fig. 2. The partial pressures over glasses 13 and 16 in the $Na_2O \cdot 0.15R'_2O \cdot B_2O_3 \cdot 3SiO_2$ system are almost equal to those over glasses 14 and 17, respectively.

From the partial pressure data, free energies and third-law enthalpies of dimerization were evaluated for the following equations:



as shown in table 2. Here, free energy functions for $RBO_2(g)$ and $R_2(BO_2)_2(g)$ were taken from

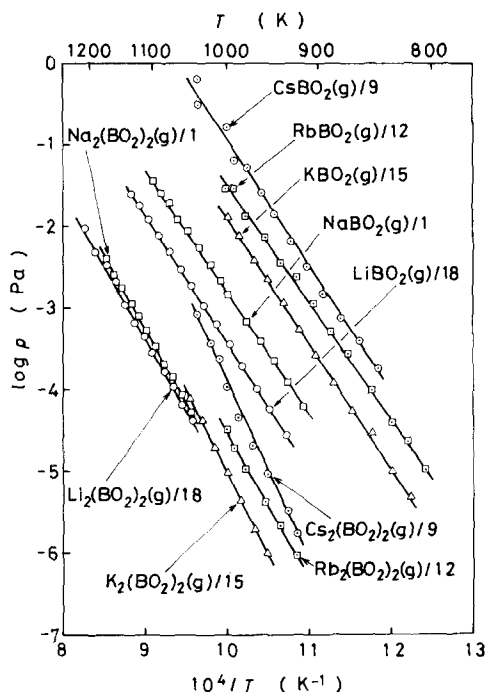


Fig. 1. Partial pressures of $\text{RBO}_2(\text{g})$ and $\text{R}_2(\text{BO}_2)_2(\text{g})$ over glasses 1, 9, 12, 15 and 18 in the $\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 3\text{SiO}_2$ system. Lines are drawn by least-squares fitting.

the literature [8–10] and those for $\text{NaR}'(\text{BO}_2)_2(\text{g})$ were estimated by averaging those for $\text{Na}_2(\text{BO}_2)_2(\text{g})$ [10] and $\text{R}'_2(\text{BO}_2)_2(\text{g})$ [10]. The values of $\Delta G_{r,1000}^\circ$ for eq. (1) for K, Rb and Cs are much smaller than those for eq. (2), respectively. From these results, it can be understood that $\text{NaR}'(\text{BO}_2)_2(\text{g})$ is easily identified and the observation of $\text{R}'_2(\text{BO}_2)_2(\text{g})$ is very difficult over glasses 13 and 14, 10 and 11, and 4 and 8. Over glasses 16 and 17, the vapors of $\text{Li}_2(\text{BO}_2)_2(\text{g})$ and $\text{NaLi}(\text{BO}_2)_2(\text{g})$ could not be distinctly measured

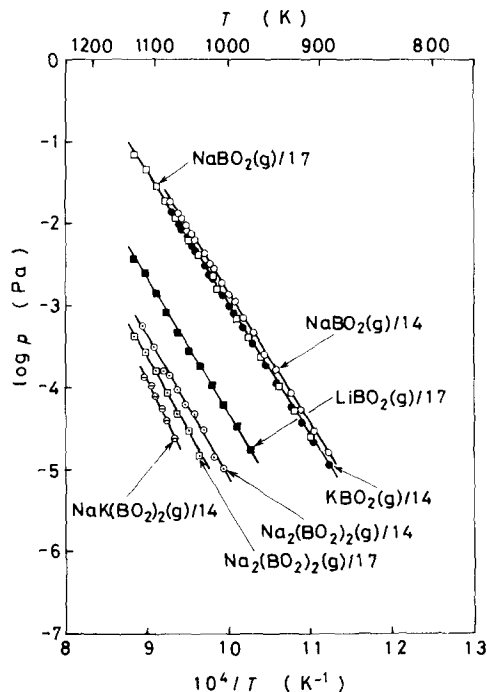


Fig. 2. Partial pressures of $\text{NaBO}_2(\text{g})$, $\text{KBO}_2(\text{g})$, $\text{Na}_2(\text{BO}_2)_2(\text{g})$ and $\text{NaK}(\text{BO}_2)_2(\text{g})$ over glass 14 and those of $\text{NaBO}_2(\text{g})$, $\text{LiBO}_2(\text{g})$ and $\text{Na}_2(\text{BO}_2)_2(\text{g})$ over glass 17 in the $0.85\text{Na}_2\text{O} \cdot 0.15\text{R}'_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 3\text{SiO}_2$ system. Lines are drawn by least-squares fitting.

owing to low partial pressure of $\text{LiBO}_2(\text{g})$. The partial pressure of $\text{NaLi}(\text{BO}_2)_2(\text{g})$ is estimated to be 4×10^{-5} Pa at 1100 K from the trend in thermochemical quantities in table 2. The value is just on the sensitivity limit of the mass spectrometer.

According to Wenzel and Sanders [11], the same chemical formulas as those of the vapor species were taken as the pseudo components in

Table 2
Free energies at 1000 K and third-law enthalpies at 0 K for dimerization reaction

Reaction	Glass	$\Delta G_{r,1000}^\circ$ (kJ mol ⁻¹)	$\Delta H_{r,0}^\circ$ (kJ mol ⁻¹)
$2\text{LiBO}_2(\text{g}) = \text{Li}_2(\text{BO}_2)_2(\text{g})$	18	-128.4 ± 7.1	-293.5 ± 9.0
$2\text{NaBO}_2(\text{g}) = \text{Na}_2(\text{BO}_2)_2(\text{g})$	1	-105.6 ± 7.1	-277.0 ± 9.0
$2\text{KBO}_2(\text{g}) = \text{K}_2(\text{BO}_2)_2(\text{g})$	15	-72.2 ± 7.1	-236.0 ± 9.0
$2\text{RbBO}_2(\text{g}) = \text{Rb}_2(\text{BO}_2)_2(\text{g})$	12	-65.7 ± 7.1	-220.4 ± 9.0
$2\text{CsBO}_2(\text{g}) = \text{Cs}_2(\text{BO}_2)_2(\text{g})$	9	-53.5 ± 7.1	-210.0 ± 9.0
$\text{NaBO}_2(\text{g}) + \text{KBO}_2(\text{g}) = \text{NaK}(\text{BO}_2)_2(\text{g})$	14	-94.5 ± 5.9	-260.7 ± 8.1
$\text{NaBO}_2(\text{g}) + \text{RbBO}_2(\text{g}) = \text{NaRb}(\text{BO}_2)_2(\text{g})$	11	-98.7 ± 5.9	-261.3 ± 8.1
$\text{NaBO}_2(\text{g}) + \text{CsBO}_2(\text{g}) = \text{NaCs}(\text{BO}_2)_2(\text{g})$	8	-92.2 ± 5.9	-248.9 ± 8.1

Table 3
Chemical activities, molar fractions and activity coefficients of pseudo components with underlines in glasses at 1000 K

Glass	Pseudo component	<i>a</i>	<i>x</i>	γ
18	2LiBO ₂ ·3SiO ₂	0.23	0.40	0.58
1	2NaBO ₂ ·3SiO ₂	9.5×10 ⁻²	0.40	0.24
15	2KBO ₂ ·3SiO ₂	5.9×10 ⁻²	0.40	0.15
12	2RbBO ₂ ·3SiO ₂	1.7×10 ⁻¹	0.40	4.3×10 ⁻²
9	2CsBO ₂ ·3SiO ₂	8.3×10 ⁻³	0.40	2.1×10 ⁻²
18	<u>Li₂(BO₂)₂</u> ·3SiO ₂	5.8×10 ⁻²	0.25	0.23
1	<u>Na₂(BO₂)₂</u> ·3SiO ₂	3.5×10 ⁻²	0.25	0.14
15	<u>K₂(BO₂)₂</u> ·3SiO ₂	3.1×10 ⁻³	0.25	1.2×10 ⁻²
12	<u>Rb₂(BO₂)₂</u> ·3SiO ₂	9.1×10 ⁻⁴	0.25	3.6×10 ⁻³
9	<u>Cs₂(BO₂)₂</u> ·3SiO ₂	8.6×10 ⁻⁵	0.25	3.4×10 ⁻⁴
17	1.7NaBO ₂ ·0.3LiBO ₂ ·3SiO ₂	3.0×10 ⁻²	0.06	0.50
14	1.7NaBO ₂ ·0.3KBO ₂ ·3SiO ₂	4.9×10 ⁻³	0.06	8.2×10 ⁻²
11	1.7NaBO ₂ ·0.3RbBO ₂ ·3SiO ₂	3.8×10 ⁻⁴	0.06	6.3×10 ⁻³
8	1.7NaBO ₂ ·0.3CsBO ₂ ·3SiO ₂	9.1×10 ⁻⁵	0.06	1.5×10 ⁻³

the glasses instead of the oxide components. In this case, the chemical activity of a given pseudo component can be determined from the ratio between the partial pressure of the corresponding vapor over the glass and that over RBO₂(s) [7]. The results are shown in table 3. The chemical activities and activity coefficients for the RBO₂ and R₂(BO₂)₂ pseudo components become small on going from Li to Cs, respectively, that is, the results indicate that the vaporization of CsBO₂(g)

Table 4
Third-law enthalpies of formation and dissociation energies for R₂(BO₂)₂(g) and NaR'(BO₂)₂(g)

Vapor	Glass	$\Delta H_{f,0}^{\circ}$ (kJ mol ⁻¹)	D_0° (kJ mol ⁻¹)
Li ₂ (BO ₂) ₂ (g)	18	-1589.7±11.0	1342.1±20.4
Na ₂ (BO ₂) ₂ (g)	1	-1550.2±13.6	1197.2±21.6
K ₂ (BO ₂) ₂ (g)	15	-1585.2±20.1	1194.6±26.2
Rb ₂ (BO ₂) ₂ (g)	12	-1576.4±41.6	1171.8±44.9
Cs ₂ (BO ₂) ₂ (g)	9	-1584.0±41.6	1171.4±45.1
NaK(BO ₂) ₂ (g)	14	-1571.8±13.4	1200.0±21.5
NaRb(BO ₂) ₂ (g)	11	-1575.9±22.4	1197.1±28.1
NaCs(BO ₂) ₂ (g)	8	-1572.5±22.4	1189.1±28.1

and Cs₂(BO₂)₂(g) is most suppressed thermochemically from the glasses.

The combination of $\Delta H_{r,0}^{\circ}$ in table 2 with the enthalpies of formation for RBO₂(g) [12] yields the enthalpies of formation for R₂(BO₂)₂(g) and NaR'(BO₂)₂(g), and further combination with the enthalpies of formation for R(g) [8] and BO₂(g) [8] gives the dissociation energies for bonds between R and BO₂ in R₂(BO₂)₂(g) and NaR'(BO₂)₂(g). As can be seen in table 4, the enthalpies of formation and the dissociation energies are not so different from one another, respectively, except for $D_0^{\circ}(\text{Li}_2(\text{BO}_2)_2)$.

4. Conclusion

A mass-spectrometric Knudsen effusion method was used for the study of the vaporization behavior of alkali borosilicate glasses. The vapor species, their thermochemical quantities and the chemical activities of the components in the glass were determined. The results are very useful for the prediction of the vaporization behavior of alkali metals and boron from actual high-level radioactive waste borosilicate glasses.

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