ALKALI VAPOR PRESSURES OVER SOME SIMPLE SILICATE MELTS

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Mass spectrometric analysis of gaseous phase above $Na_2O.4 SiO_2$; $K_2O.4 SiO_2$ and Na_2O $.K_2O.8 SiO_2$ melts was used to identify the species observed and to determine their partial pressure values. The principal species observed were the corresponding alkaline species and oxygen.

The temperature dependence of sodium and kalium partial pressures was established and corresponding vaporization enthalpy values were calculated by second law treatment of those vapor data. The average value of sodium vaporization enthalpy in binary melt amounts of $\Delta H_T^0 = 315 \pm 10$ kJ mol^{-1} being in a good agreement with the data published previously. The vaporization enthalpy of potassium $\Delta H_T^0 = 142 \pm 8$ kJ mol^{-1} is considerably lower with comparison to sodium and does not change if potassium evaporates from binary $K_2O.4 SiO_2$ or ternary $Na_2O.K_2O.8 SiO_2$ melts respectively.

Thermodynamic data on high temperature vaporization of some elements and their simple compounds have been measured very frequently. However, only few data have been published about vaporization of more complicated compounds and especially of silicate vitreous materials. Preston and Turner[1] calculated vapor pressures of some binary systems Na_2O—SiO_2 from experimental data on weight losses due to evaporation by high temperatures. Kröger and Sörström[2] used similar method to determine vapor pressures over some binary and multicomponent silicate melts. High temperature mass spectrometry[3,4] and atomic absorption[5] were used to detect chemical composition of gaseous phase and to measure partial pressures of single compounds. Recently, Kassis and Frischat[6] used Kundsen-cell thermobalance combination to determine weight loss by evaporation and to calculate partial and total pressures over $(Na_2O + Rb_2O).3 SiO_2$ system.

This study has the aim to contribute to the present knowledge on evaporation from Na_2O—SiO_2, K_2O—SiO_2 and Na_2O—K_2O—SiO_2 melts respectively.

EXPERIMENTAL

The glass samples were prepared in laboratory by mixing and fusion of T13 sand with sodium carbonate A.R. and potassium carbonate A.R. respectively. A platinum crucible placed in an electrical furnace was used for glass fusion. Chemical composition of glasses was checked by determination of alkali content using flame photometry.

The vaporization of $Na_2O.4 SiO_2$ (glass I), $K_2O.4 SiO_2$ (glass II) and $Na_2O.K_2O. 8 SiO_2$ (glass III) was studied by using high temperature mass-spectrometry in the temperature range of $1\,260-1\,567$ K, e.g. evaporation of all samples proceeds from corresponding melts. The reliability of the whole experimental procedure was checked in the case of glass I starting from mixing and fusion of glass sample. Therefore, two glass samples of the same composition I_a, I_b were used.

A Bendix Time of Flight mass-spectrometer (mod 3 015) coupled with a high temperature Knudsen source, was employed for mass spectrometry investigation. Details of the apparatus and the experimental procedure were described previously[7,8]. The glass samples were vaporized from a conventional graphite crucible with an effusion hole 1 mm in diameter heated by electron bombardment. Stainless-steel wool was put under and on the sample in order to prevent its overflow the effusion hole because of its wettability. The temperatures were measured by a Leeds and Northrup optical pyrometer sighting the effusion hole. At each temperature (T), the absolute vapor pressures of the observed species were calculated from the measured ion-intensities (I^+) by using the well-known relation[7]: $P = I^+ T(K/a_i\sigma_i)$, where K is the instrument sensitivity factor previously determined by a quantitative vaporization of silver[9]; σ_i is the ionization cross section taken from Mann[10], and a_i the isotopic abundance of the observed species respectively.

RESULTS AND DISCUSSION

The principal species observed during the vaporization of the glasses I, II and III, were the corresponding alkaline species and oxygen. The least squares treatment of vapor pressure data yielded following equations (pressure P in Pa):

$$\text{glass } I_a \quad \log P_{Na} = 10.58 \pm 0.21 - (16\,597 \pm 311)/T$$

$$\text{glass } I_b \quad \log P_{Na} = 10.38 \pm 0.18 - (16\,310 \pm 255)/T$$

$$\text{glass II} \quad \log P_K = 4.79 \pm 0.09 - (7\,415 \pm 134)/T$$

$$\text{glass III} \quad \log P_{Na} = 8.01 \pm 0.23 - (13\,137 \pm 278)/T$$

$$\log P_K = 4.45 \pm 0.12 - (7\,134 \pm 171)/T$$

The slopes and the intercepts were calculated by weighting proportionally to the number of corresponding values determined in each run. The associated errors are the standard deviations. The mass-spectrometric technique used does not permit a reliable measurements of oxygen intensity owing to the scarce shutterability of its species.

A very good agreement has been observed between measurements of sodium partial pressures over two $Na_2O.4 SiO_2$ samples prepared independently (glass I_a, I_b) indicating a good reliability and reproducibility of the procedure used in the preparation. A comparison of $Na_2O.4 SiO_2$ and $K_2O.4 SiO_2$ system respectively shows different evaporation behaviour of those melts especially in low temperature range, where potassium exhibits higher partial pressure comparing to sodium. The difference between sodium and potassium partial pressures values diminishes with rising temperature. Also data on evaporation of three component system Na_2O.

.$K_2O.8\,SiO_2$ indicate higher partial pressures of potassium in the whole temperature range followed. By higher temperatures the sodium and potassium partial pressure values become closer.

Evaporation data in three component $Na_2O.K_2O.8\,SiO_2$ melt allow to draw some conclusions on the mixed alkali effect. A comparison of the temperature dependence of potassium partial pressures over two component and three component melts, (glass II and glass III respectively) shows the practically independent evaporation of potassium and sodium. Moreover the potassium vaporization enthalpies determined by second law treatment of the partial pressure measured over the glasses II and III, ΔH_T^0 (glass II) = 142 ± 3 kJ mol^{-1} and ΔH_T^0 (glass III) = 136 ± 3 kJ mol^{-1} are within their standard deviations.

On the contrary sodium exhibits a little lower partial pressure in the glass III with comparison to the $Na_2O.4\,SiO_2$ melt. Also the vaporization enthalpy of this element from three component melt ΔH_T^0 = 251 ± 5 kJ mol^{-1} is lower than that found on the two component melts ΔH_T^0 = 317 ± 6 kJ mol^{-1} and 312 ± 5 kJ mol^{-1} for glass I$_a$ and I$_b$ respectively.

The evaluation of binary sodium oxide–silicium oxide melts has been studied for systems of different Na_2O/SiO_2 ratio. The total vapor pressures reported in literature[2,3,6] were compared with those derived from mass spectrometric partial pressure data of sodium considering the dissociative vaporization process:

$$Na_2O\,(melt) \rightarrow 2\,Na\,(g) + \tfrac{1}{2}O_2\,(g)$$
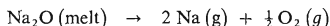
which gives $P_{tot} = \tfrac{5}{4}P_{Na}$. The slopes reported in Fig. 1 indicate no significant difference in vaporization enthalpies for systems with different $Na_2O : SiO_2$ ratio. The only exception ($Na_2O.3\,SiO_2$ melt) has been not proved by Kassis and Frischat[6]. Although the pressure data of those authors seem to be a little lower (Fig. 1), the
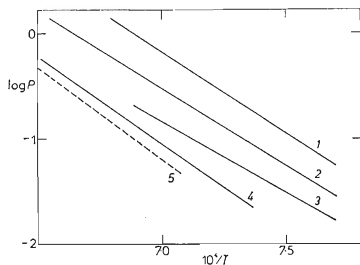

Fig. 1

Total vapor pressure P/Pa, over the systems at different Na_2O/SiO_2 ratio: *1* 1 : 1, ref.[2]; *2* 1 : 2, ref.[3]; *3* 1 : 3, ref.[2]; *4* 1 : 6; this paper; *5* 1 : 3, ref.[6]).

corresponding vaporization enthalpy $\Delta H_T^0 = 316 \text{ kJ mol}^{-1}$ is in excellent agreement with the average value $\Delta H_T^0 = 315 \pm 6 \text{ kJ mol}^{-1}$ found in this work. Also the value $299 \cdot 35 \text{ kJ mol}^{-1}$, reported by Altemose and Tong[4], is in a satisfactory agreement with the above data.

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