HIGH TEMPERATURE STUDY OF VAPORIZATION PROCESSES AND THERMODYNAMIC PROPERTIES OF K₂O-GeO₂ MELTS

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The vaporization processes of K₂O-GeO₂ melts from molybdenum and platinum effusion cells in the temperature range 630-1540 K were studied using MI 1201 commercial mass spectrometer provided with the ion source modified for high temperature measurements (1).

The $(K)^+$, $(GeO)^+$, $(KO)^+$, $(O_2)^+$, and $(Ge)^+$ ions were detected in the mass spectra of vapor over the K₂O-GeO₂ melts at temperatures studied at ionizing energy 20 eV. The special search showed the absence of associated forms corresponding to the $(K_iGe_jO_k)^+$ ions. The obtained data showed that the main processes of the K₂O-GeO₂ melt evaporation are the same as in the case of K₂O and GeO₂ and may be described by the following reactions

$$[K_2O] = 2(K) + \tfrac{1}{2}(O_2) \qquad [1]$$
$$[GeO_2] = (GeO) + \tfrac{1}{2}(O_2) \qquad [2]$$
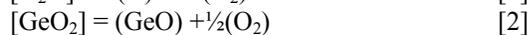
(the square and round brackets denote the components of the condensed and gas phases, respectively).

The K₂O and GeO₂ activities ($a(i)$) and the Gibbs energies of melt formation ($\Delta_f G_T$) were calculated using the values of partial pressures of vapor species over studied melts determined by the Hertz-Knudsen equation and the equilibrium constant data (2) for the reactions [1, 2].

The results of the present study were considered in the comparison with the same data on similar alkali-glass Na₂O-SiO₂ (3), Na₂O-GeO₂ (4) and K₂O-SiO₂ (5) melts in order to interpret the nature of alkali-germanate melts.

At the present study a special attention was devoted to the choice of the reliable thermodynamic data on the Na₂O-SiO₂, Na₂O-GeO₂ and K₂O-SiO₂ melts.

The determined thermodynamic properties of the K₂O-GeO₂ melts clarified the significant negative deviations from the ideality, which is typical for the other alkali-glass melts (Figures). The values of deviations increase in the following order: Na₂O-SiO₂ → Na₂O-GeO₂ → K₂O-SiO₂ → K₂O-GeO₂. The same increase is observed for the consideration of negative deviations in the orders: silicate → germanate melts and Na₂O-(SiO₂, GeO₂) → K₂O-(SiO₂, GeO₂) melts.

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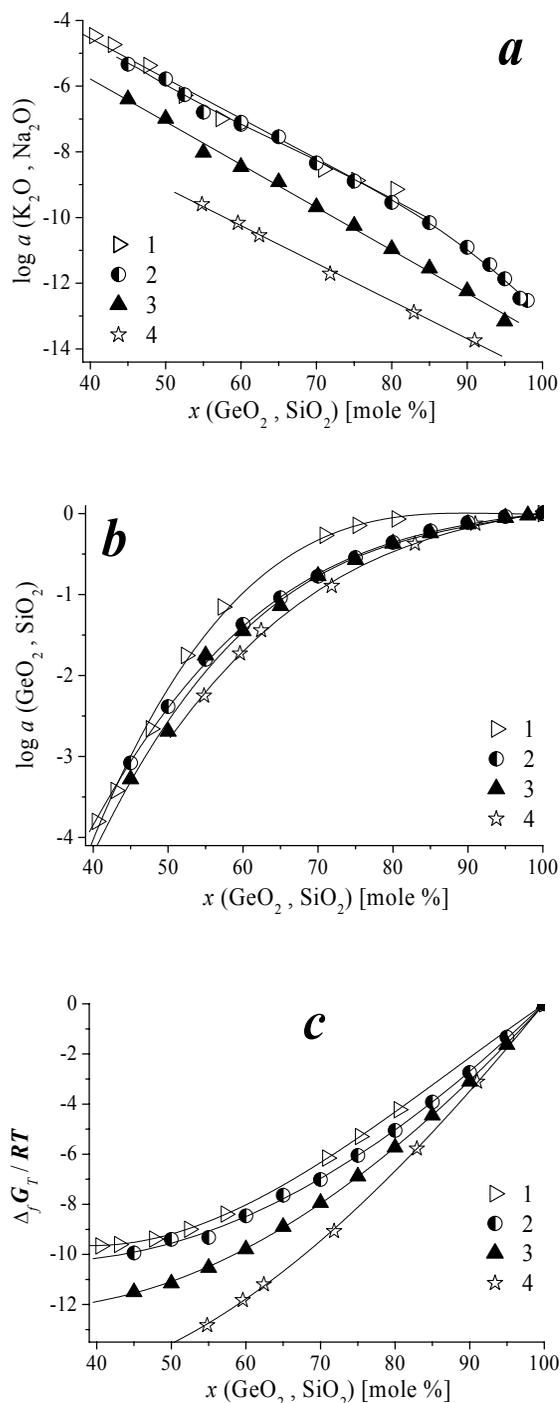
Figures. The oxide activities (*a*, *b*) and the Gibbs energies (*c*) of alkali-glass melt formation (1 – Na₂O-SiO₂, 2 – Na₂O-GeO₂, 3 – K₂O-SiO₂ and 4 – K₂O-GeO₂) determined by mass spectrometric Knudsen effusion techniques (1 – at 1473 K (3) and 4 – at 1300 K at the present study) and by e. m. f. techniques (2 – at 1450 K (4) and 3 – at 1300 K (5)).