

THERMODYNAMICS OF MOLECULAR OXYGEN DISSOCIATION IN VAPOR OVER ALKALI SILICATES AND GERMANATES

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The process of successive condensation of any matter is assumed to be characterized by temperature dependencies of the total pressure of the gas phase over the compounds. Recently in the investigation of regularities of evaporation processes of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ compounds [1] we observed the linear dependence of logarithm of vapor total pressure over the compounds *vs.* the molecular oxygen content in vapor (or the degree of its dissociation). It points to the fact that there is a relationship between the red-ox reactions in the gaseous substance and the condensation processes. In this connection it seems to be useful to consider the observed regularities on example of other oxide compounds [2].

Particular theoretical and practical interest causes doubtless similarity on properties of silicates and its germanate analogues. The germanates have a lot of essential differences which are defined by an opportunity of existence of 4-fold and 6-fold coordination germanium with oxygen in contrast to a silicon of only 4-fold coordination.

Alkali-germanate systems ($\text{Na}_2\text{O-GeO}_2$ and $\text{K}_2\text{O-GeO}_2$) are the low-temperature analogues for alkali-silicate system ($\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$). These silicate system are particular in respect to many multi-component systems, important both for study of nature and technical application.

The present work focuses on obtaining and analyzing thermodynamic data describing the $\text{K}_2\text{O-GeO}_2$ system in a wide temperature and concentration range. Comparing this thermodynamic information with the same on systems with similar properties ($\text{Na}_2\text{O-GeO}_2$, $\text{Na}_2\text{O-SiO}_2$, $\text{K}_2\text{O-SiO}_2$) was of particular interest. This approach based on complete thermodynamic data comparison was expected to be used for establishing evaluation criteria of accuracy and reliability data on these systems. The most accurate data used in further thermodynamic calculations of equilibrium partial pressures of vapor species over these systems. The analysis of dissociation processes of molecular oxygen in vapor over alkali germanates and silicates based on these results.

One of the most modern and informative experimental methods, representing a combination of the Knudsen effusion method and the mass spectrometric analysis of a gas phase over the substance, allowing, in particular, to define the values of equilibrium partial pressure of vapor species and also to establish the field borders on the phase diagram were used in the present study for investigation of vaporization processes and thermodynamic properties of potassium germanates.

Measurements were performed on an MI-1201 commercial mass spectrometer equipped with an ion source adapted for high-temperature studies. $\text{K}_2\text{O-GeO}_2$ samples containing 54.80, 59.59, 62.41, 66.40, 71.83, 82.93, 91.00, and 100.00 mole % GeO_2 were evaporated from molybdenum and platinum effusion cells in the range 950-1550 K.

The vapor composition over the $\text{K}_2\text{O-GeO}_2$ system indicates that their vaporization behavior is governed by reactions characteristic of oxides that dissociate in the vapor phase into atoms, lower oxides, and molecular oxygen and is consistent with the general rules in other alkali-glass-forming systems.

Fig. 1 shows typical composition dependences obtained in this work for the partial pressures $p(\text{K})$, $p(\text{GeO})$, and $p(\text{O}_2)$ over $\text{K}_2\text{O-GeO}_2$ melts at 1300 K. With decreasing $x(\text{K}_2\text{O})$ in the melt, $p(\text{K})$ drops sharply, while $p(\text{GeO})$ and $p(\text{O}_2)$ increase. The total vapor pressure over the melt passes through a minimum near 55 mole % GeO_2 , which may correspond to the congruently melting compound $10\text{K}_2\text{O} \cdot 11\text{GeO}_2$.

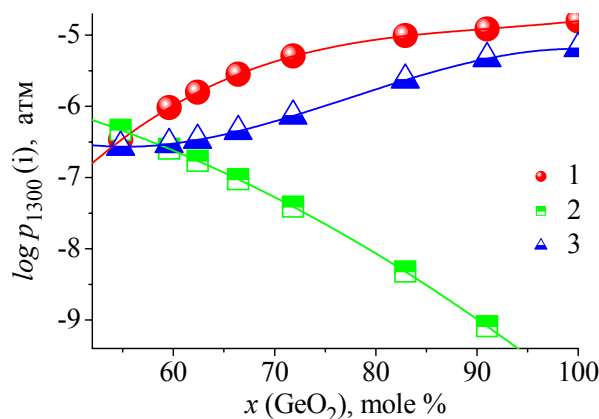


Fig.1. Composition dependences of (1) $p(\text{GeO})$, (2) $p(\text{K})$, and (3) $p(\text{O}_2)$ over $\text{K}_2\text{O}-\text{GeO}_2$ melts at 1300 K

Particular attention was paid in this study to the selection of thermodynamic data for the $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{GeO}_2$, and $\text{K}_2\text{O}-\text{SiO}_2$ systems to be compared with potassium germanates. In the case of the $\text{Na}_2\text{O}-\text{SiO}_2$ system, we gave preference to the more accurate data obtained by Zaitsev et al. [3] using Knudsen cell mass spectrometry in a broad temperature range (942-1719 K).

In the case of the $\text{Na}_2\text{O}-\text{GeO}_2$ system we gave preference to the most systematic data reported by Kohsaka et al. [4].

Thermodynamic data for the $\text{K}_2\text{O}-\text{SiO}_2$ system are rather difficult to select. The EMF data reported by Kozhina [5] agree to some extent, as to the composition dependences of total and partial thermodynamic functions, with the results obtained by Zaitsev et al. [6] in the range 869-1730 K using mass spectrometry but differ markedly in absolute values.

The thermodynamic properties of $\text{K}_2\text{O}-\text{GeO}_2$ melts exhibit significant deviations from ideality, characteristic of alkali glass-forming systems. The deviation from ideality increases in the order $\text{Na}_2\text{O}-\text{SiO}_2 \rightarrow \text{Na}_2\text{O}-\text{GeO}_2 \rightarrow \text{K}_2\text{O}-\text{SiO}_2 \rightarrow \text{K}_2\text{O}-\text{GeO}_2$. The negative deviation from ideality also increases in going from silicates to germanates and in going from $\text{Na}_2\text{O}-(\text{SiO}_2, \text{GeO}_2) \rightarrow \text{K}_2\text{O}-(\text{SiO}_2, \text{GeO}_2)$.

The composition dependences of the K_2O and Na_2O activities in the systems in question show a linear variation and the values of $a(\text{Na}_2\text{O})$ and $a(\text{K}_2\text{O})$ in the silicate melts coincide at 1473 K. This behavior of glass-forming systems is of both theoretical and practical interest.

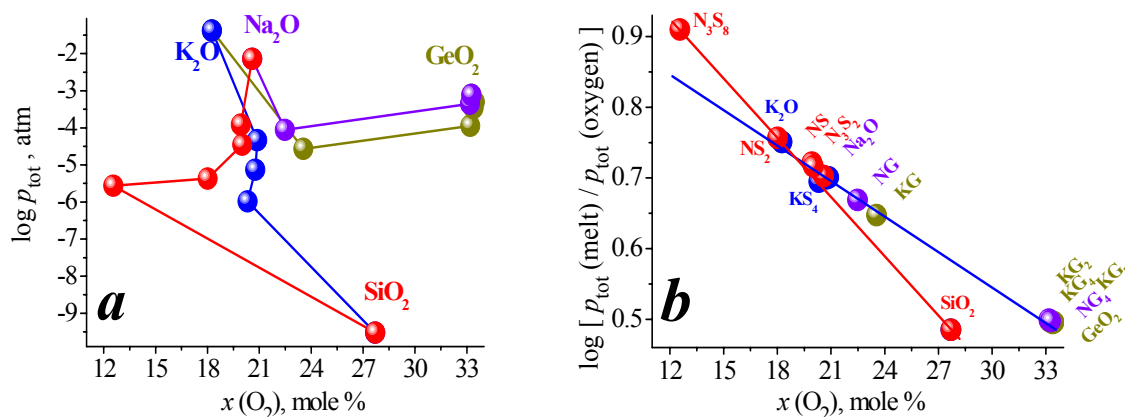


Fig.2. The total vapor pressure over alkali silicates and germanates (a) and ratio of total vapor pressures over the melt compounds and oxygen itself (b) vs. molecular oxygen mole fraction in vapor at 1473 K (table of symbols: K= K_2O , N= Na_2O , G= GeO_2 , S= SiO_2).

The determined values of oxide activities in potassium germanates and reference data on sodium germanates and potassium and sodium silicates and the information on the constants of gas-phase and heterogeneous equilibria were used in the thermodynamic calculations of the composition and

partial pressures of vapor species for the wide temperature range. The total vapor pressures over compounds (fig. 2a) were calculated by summing the proper partial pressures of the vapor species taken for the case of chemically neutral conditions according to the approach described earlier [7].

As may be seen from fig. 2b one can subdivide compounds into two linear dependencies of ratio logarithm of total vapor pressure over the melt compounds and over oxygen itself vs. the molecular oxygen mole fraction in vapor $x(\text{O}_2)$. This ratio is characterized the difference of total vapor pressure over the melts from the same corresponding to oxygen. The last was calculated with the same molecular oxygen content as for the corresponding compound. According to fig. 2b, there are two tendencies in these dependencies – silicate and germanate.

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