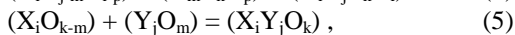
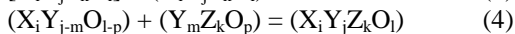
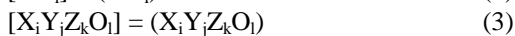
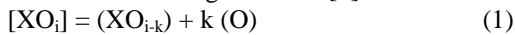


A STUDY OF COMPLEX GASEOUS OXIDES OVER THE CaO–MgO–Al₂O₃–TiO₂–SiO₂ MELTS. S. I. Shornikov and O. I. Yakovlev, Vernadsky Institute of Geochemistry & Analytical Chemistry of RAS, Kosygin st., 19, Moscow, 119991, Russia; e-mail: sergey.shornikov@gmail.com.

Introduction: Studies of substances' high-temperature evaporation are of topical importance for both understanding geochemical and cosmochemical phenomena, and their practical application in various fields of engineering. They acquire special importance in the studies into the origin and composition of meteorites, in particular, the CAI substance formed mostly by the CaO–MgO–Al₂O₃–TiO₂–SiO₂ system compounds.

As known in the gas phase over oxide compounds there can be both simple gaseous oxides consisting of a single element with oxygen compound (X_iO_j) and complex gaseous oxides (X_iY_jO_k) formed in accordance with the following reactions [1]:



where X and Y are elements, round brackets designate the gas phase, and square brackets – condensed phase. Their content in the gas phase is usually insignificant. However cases are known where the gas phase above an oxide compound consisted mostly of complex gaseous oxides.

The goal of this work was to consider evaporation regularities of the CaO–MgO–Al₂O₃–TiO₂–SiO₂ melts related to presence of complex gaseous oxides in the gas phase over them.

Results and Discussion: In case of the CaO–MgO–Al₂O₃–TiO₂–SiO₂ melts, as follows from the experimental data obtained by the Knudsen effusion mass spectrometry method, in the 1500–2500 K temperature range in the gas phase above these melts the following complex gaseous oxides were detected: (CaAlO), (CaSiO₃), (MgAlO), (AlSiO), (CaTiO₃) [2–5]. Their quantity in the gas phase is inappreciable and does not exceed 1% in the total concentration, the predominant gas phase components being atomic and monoxide gaseous compounds – (Ca), (Mg), (Al), (AlO), (TiO), (SiO).

Let us consider the evaporation regularities of the CaO–MgO–Al₂O₃–TiO₂–SiO₂ melts from the viewpoint of changes in the content of these complex gaseous oxides in the gas phase above oxide compounds depending on 1) condensed phase composition, 2) temperature and 3) redox conditions of evaporation of compounds in this multicomponent system.

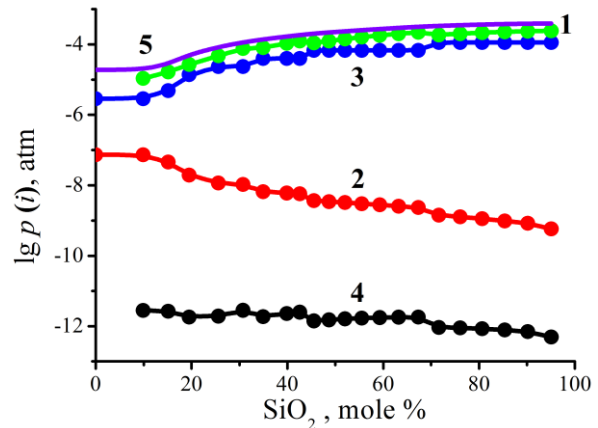


Figure 1: The calculated dependencies of the vapor species partial pressures over the Al₂O₃–SiO₂ system melts at 2200 K. The calculations based on the experimental data [2, 3]. Table of symbols: 1 – (SiO), 2 – (Al), 3 – (O₂), 4 – (AlSiO), 5 – the total vapor pressure over melt.

Fig. 1 shows the vapor species partial pressures of the gas phase $p(i)$ over the aluminosilicate melt depending on the condensed phase composition at 2200 K. As follows from Fig. 1, the (AlSiO) complex gaseous oxide quantity in the gas phase increases as the silicon dioxide content in the condensed phase decreases. Calculation of the concentration dependences $p(i)$ was executed, as before, within the framework of the thermodynamic approach developed [6].

The observed increase in the (AlSiO) content in the gas phase over the melt follows from the expression conditioned by equilibrium similar to (5):

$$p(\text{X}_i\text{Y}_j\text{O}_k) = p(\text{X}_i\text{O}_{k-m})p(\text{Y}_j\text{O}_m) / K_r, \quad (6)$$

which in this case can be written as:

$$p(\text{AlSiO}) = p(\text{Al})p(\text{SiO}) / K_r, \quad (7)$$

where K_r is the reaction equilibrium constant; and accordingly using oxide activities $a(i)$ it can be written as:

$$p(\text{AlSiO}) \sim a^{1/2}(\text{Al}_2\text{O}_3)a(\text{SiO}_2) / p^{5/2}(\text{O}). \quad (8)$$

Thus, an increase in the gaseous aluminosilicate content in the gas phase is proportional to the $a^{1/2}(\text{Al}_2\text{O}_3)$ and $a(\text{SiO}_2)$ product increase, which corresponds to the condensed phase composition.

Typical temperature dependences of the vapor species partial pressures in the gas phase above oxide compounds for magnesium spinel MgAl₂O₄ are shown in Fig. 2. It is seen that the content of (MgAlO) complex gaseous oxides in the gas phase above the spinel increases along with temperature growth in the temperature interval under study in advance of the partial

pressure increase of simple gas phase components – (Mg) and (AlO). This increase, like in the case considered above, is apparently caused by equilibrium (5), according to which the complex gaseous oxide partial pressure is proportional to the product of the corresponding partial pressures of simple gas phase components.

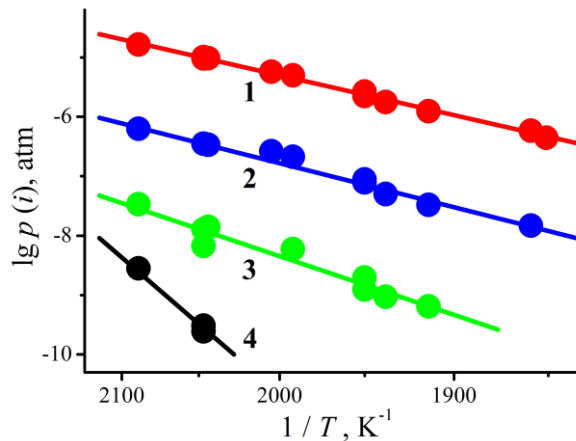


Figure 2: The experimental temperature partial pressures dependencies of vapor species over spinel: 1 – (Mg), 2 – (O), 3 – (AlO), 4 – (MgAlO). The data obtained by the Knudsen effusion mass spectrometric method [4].

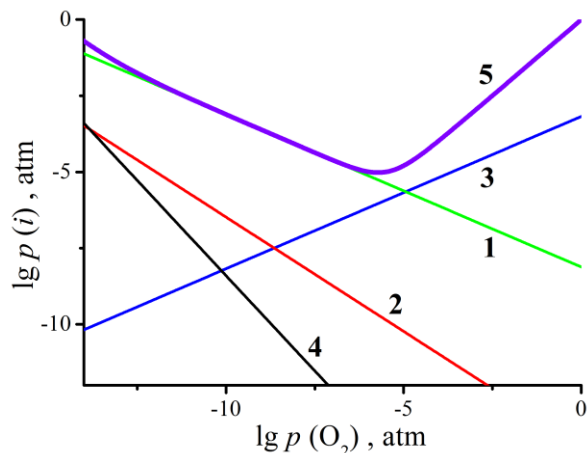


Figure 3: The calculated partial pressures of vapor species of gas phase over mullite vs the molecular oxygen partial pressure over mullite at 2200 K. The calculations based on the experimental data [2, 3]. Table of symbols: 1 – (SiO), 2 – (Al), 3 – (O), 4 – (AlSiO), 5 – the total vapor pressure over melt.

The influence of redox conditions during evaporation of the CaO–MgO–Al₂O₃–TiO₂–SiO₂ melts on the content of complex gaseous oxides in the gas phase can be illustrated by Fig. 3. The dependences are calculat-

ed, as above, within the framework of the thermodynamic approach described in details in [6, 7].

As follows from Fig. 3, the partial pressure of the complex gaseous oxide (AlSiO) over mullite Al₆Si₂O₁₃, as well as partial pressures of simple gas phase components (Al) and (SiO), increase with as the partial pressure of the molecular oxygen over a melt decreases. These regularities are probably also conditioned, as well as in case of dependences of the content of complex gaseous oxides in the gas phase above the melts under study, on the condensed phase composition (Fig. 1) and temperatures (Fig. 2), by their dissociation processes, according to equilibria (1) and (5).

Conclusions: Thus, on the basis of the completed study into the evaporation regularities of the CaO–MgO–Al₂O₃–TiO₂–SiO₂ melts related to the presence of complex gaseous oxides in the gas phase above them, it is possible to draw the following conclusions:

1. For the case of oxide compounds of the system under consideration, the content of complex gaseous oxides in the gas phase above oxide compounds is low, which is apparently related to their considerable dissociation.

2. The content of complex gaseous oxides in the gas phase over the oxide compounds under consideration depends on the condensed phase composition, which conditions the course of dissociation processes.

3. The content of complex gaseous oxides in the gas phase over the oxide compounds under consideration increases as the temperature grows in accordance with equilibrium in the gas phase (5).

4. The content of complex gaseous oxides in the gas phase over the oxide compounds under consideration depends on the redox conditions of condensed phase evaporation. Typical for evaporation in reduction environments is a substantial increase in the complex gaseous oxides' content of in the gas phase above the compounds.

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