

**Thermodynamic study of regularities in vapor composition over oxide compounds
(the CaO–MgO–Al₂O₃–FeO–SiO₂ system)**

S. I. Shornikov

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow

sergey.shornikov@gmail.com

On the basis of the experimental data obtained by the Knudsen effusion mass spectrometry method, we have considered dissociation regularities of complex gaseous oxides contained in the gas phase over the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds. The thermodynamic calculations took into account the effect of redox conditions on the compounds' evaporation and possible changes in the composition of the condensed phase at evaporation.

Key words: thermodynamics of evaporation, the CaO–MgO–Al₂O₃–FeO–SiO₂ system, gaseous oxides

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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 studies into the origin and composition of meteorites, in particular, the substance of CAI white inclusions formed mostly by the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds.

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

As known [Semenov *et al.*, 1976], 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_jZ_kO_l) formed in accordance with the following reactions:



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.

In case of the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds, 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), (CaSiO), (CaSiO₃), (MgAlO), (AlSiO) [Shornikov, 2003]. 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), (Fe), (FeO), (SiO).

Let us consider the evaporation regularities of the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds 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.

Fig. 1 shows the vapor species partial pressures of the gas phase $p(i)$ and changes in the of the gas phase composition $x(i)$ over the alumosilicate melt depending on the condensed phase composition $x(\text{SiO}_2)$ at 2200 K. As follows from Fig. 1, the complex gaseous oxide (AlSiO) quantity in the gas phase increases as the silicon dioxide [SiO₂] content in the condensed phase decreases.

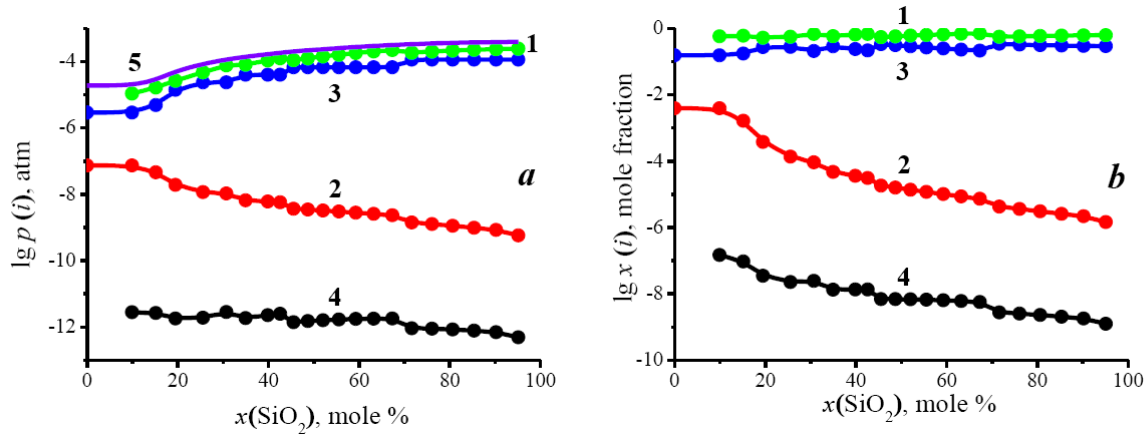


Fig. 1. The calculated dependencies of the vapor species partial pressures (a) and the gas phase compositions (b) over the Al₂O₃–SiO₂ system melts at 2200 K. The calculations based on the experimental data [Shornikov, 2002].

Table of symbols: 1 – (SiO), 2 – (Al), 3 – (O₂), 4 – (AlSiO), 5 – the total vapor pressure over melt.

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

$$p(\text{X}_i\text{Y}_j\text{O}_k) = \frac{p(\text{X}_i\text{O}_{k-m})p(\text{Y}_j\text{O}_m)}{K_{r5}}, \quad (6)$$

which in this case can be written as:

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

where K_r is the reaction equilibrium constant. Calculation of the concentration dependences $p(i)$ and $x(i)$ was executed, as before, within the framework of the thermodynamic approach developed [Shornikov, 2009].

Thus, an increase in the gaseous alumosilicate content in the gas phase is proportional to the $p(\text{Al})$ and $p(\text{SiO})$ product increase, which corresponds, in its turn, to reduction of partial oxygen pressure of according to equilibrium (1).

Typical temperature dependences of the vapor species partial pressures in the gas phase above oxide compounds for mullite Al₆Si₂O₁₃ and magnesium spinel MgAl₂O₄ are shown in Fig. 2. From Fig. 2 it is seen that the complex gaseous oxides' (AlSiO and MgAlO) content in the gas phase above the oxide compounds increases along with temperature growth in the temperature interval under study in advance of the partial pressure increase of simple gas phase components: (Al) and (SiO) in case of mullite (Fig. 2a) and (Mg) and (AlO) in case of spinel (Fig. 2b). 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.

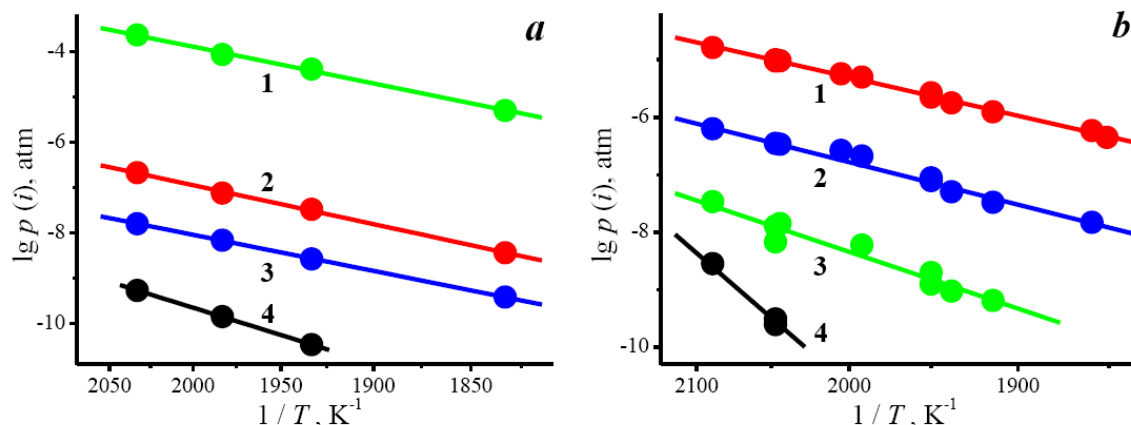


Fig. 2. The experimental temperature partial pressures dependencies of vapor species over oxide compounds:

a – mullite: 1 – (SiO), 2 – (Al), 3 – (O), 4 – (AlSiO);

b – spinel: 1 – (Mg), 2 – (O), 3 – (AlO), 4 – (MgAlO).

The data obtained by the Knudsen effusion mass spectrometric method [Shornikov, 2002; Shornikov, 2001].

The influence of redox conditions during evaporation of the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds on the complex gaseous oxides' content in the gas phase can be illustrated by Fig. 3. Fig. 3 shows two typical high-temperature dependences for mullite:

1) dependence of the partial pressures of components in the gas phase above the oxide melt on the partial pressure of molecular oxygen (Fig. 3a) and

2) dependence of the composition of the gas phase above the oxide depending on the molecular oxygen content in the gas phase (Fig. 3b). Both dependences are calculated, as above, within the framework of the thermodynamic approach. Calculation of the concentration dependences $p(i)$ and $x(i)$ was executed, as before, within the framework of the thermodynamic approach developed and described in details in [Shornikov, 2009].

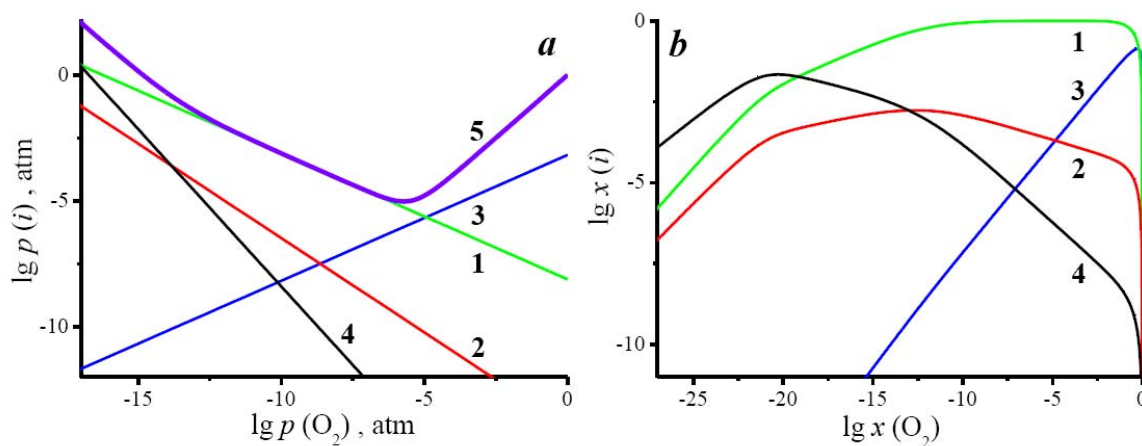


Fig. 3. The calculated partial pressures of vapor species of gas phase over mullite vs the molecular oxygen partial pressure (*a*) and the gas phase compositions over mullite (*b*) at 2200 K. The calculations based on the experimental data [Shornikov, 2002].

Table of symbols: 1 – (SiO), 2 – (Al), 3 – (O), 4 – (AlSiO), 5 – the total vapor pressure over melt.

As follows from Fig. 3a, the partial pressure of the complex gaseous oxide (AlSiO), 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. At the same time, one observes a sharp increase in the content of the gaseous (AlSiO) at a low molecular oxygen content in the gas phase above the melt (Fig. 3b). These regularities are probably also conditioned, as well as in case of dependences of the complex gaseous oxides' content 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 equilibriums (1) and (5).

Thus, on the basis of the completed study into the evaporation regularities of the CaO–MgO–Al₂O₃–FeO–SiO₂ system compounds 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 complex gaseous oxides' (X_iY_jO_k) content in the gas phase above oxide compounds is low, which is apparently related to their considerable dissociation.

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

3. The complex gaseous oxides' (X_iY_jO_k) content 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 complex gaseous oxides' (X_iY_jO_k) content 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' (X_iY_jO_k) content of in the gas phase above the compounds

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