

**THERMODYNAMICS OF COMPLEX MOLECULAR SPECIES IN THE GAS PHASE
OVER THE CaO–MgO–Al₂O₃–TiO₂–SiO₂ SYSTEM.**

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Studies of high-temperature evaporation of meteoritic matters are important for understanding geochemical phenomena at early stages of Solar system. Special attention is for studies of origin and composition of the CAIs substance formed mostly by the CaO–MgO–Al₂O₃–TiO₂–SiO₂ system compounds. The goal of our work was to consider evaporation regularities of this system melts related to presence of complex gaseous oxides in the gas phase over them.

Experimental data obtained by the Knudsen effusion mass spectrometry were used to analyze principal tendencies in the formation of complex oxides contained in the gas phase. Dependencies are derived for concentrations of the complex molecular species in the gas at the vaporization of mullite Al₆Si₂O₁₃, wollastonite CaSiO₃, spinel MgAl₂O₄, perovskite CaTiO₃, and the Al₂O₃–SiO₂ and CaO–SiO₂ binary boundary systems on temperature, melt composition, and oxygen partial pressure. Experimental data obtained in the 1500–2500 K temperature range. The following complex gaseous oxides were detected: CaAlO, CaSiO₃, MgAlO, AlSiO, CaTiO₃ [1–5]. Their quantity in the gas phase is inappreciable and does not exceed 1 % in the total concentration. Predominant gas phase components being atomic and monoxide gaseous compounds are – Ca, Mg, Al, AlO, TiO, SiO.

In the case of evaporation of Al₂O₃–SiO₂ and CaO–SiO₂ melts, it is shown that AlSiO and CaSiO₃ are present in the gas phase. Their molar fractions increase with decreasing SiO₂ content in the melt [1, 3]. The content of complex molecules increases by more than an order of magnitude. The regularity of the observed trend is that the increase in the content of complex molecules in the gas phase directly correlates with the increase in the activity of refractory melt components (Al₂O₃ and CaO).

It is shown that the content of complex molecules depends on the oxygen partial pressure in the gas phase over the compound. At the same time, the dependence extends only to complex molecules, which are "scarce" in oxygen, or, better to say, molecules that lost oxygen during dissociation. In particular, in the case of evaporation of the Al₂O₃–SiO₂ and MgO–Al₂O₃ systems [1, 5] the AlSiO and MgAlO partial pressure decrease with oxygen partial pressure increase, and the CaTiO₃ partial pressure does not depend on the oxygen pressure in the CaO–TiO₂ system [4].

According to the temperature dependences of partial pressures and contents of the components of the gas phase over the Al₆Si₂O₁₃, MgAl₂O₄, and CaTiO₃ [1, 4, 5], it follows that at the compounds evaporation the content of the AlSiO, MgAlO and CaTiO₃ complex gaseous molecules increases with increasing temperature. This can be explained by the values of the thermal effects of evaporation reactions, from which it follows that the enthalpy of formation $\Delta H_f(T)$ of complex molecules from condensed phases are positive and exceed those for reactions of their formation from gaseous atoms and simple molecules in absolute value. The experiment dependencies are determined by the van't Hoff isobar equation:

$$d \ln K_r(T) / d(1/T) = -\Delta H_f(T) / R.$$

It shows in general that the change of equilibrium constant in dependence on the inverse temperature is determined by the sign and value of $\Delta H_f(T)$. $\Delta H_f(T)$ is negative for exothermic reaction and positive for endothermic reaction. A negative value means that the $\ln K_r(T)$ value and therefore the $K_r(T)$ value itself becomes larger as the temperature increases, which in turn means a shift in equilibrium to the reaction products. In the case of an exothermic reaction, the situation is the opposite. Thus, the $\Delta H_f(T)$ positive value should be reflected in the $\ln K_r(T) - 1/T$ diagram by lines with a negative slope. The sign of enthalpy of reaction reveals the mechanism of formation of complex molecules. If complex molecules forms in the gas phase reactions, then due to the exothermicity of such reactions in the $\ln K_r(T) - 1/T$ diagram, the lines would have a positive slope, which is not observed in the experiment. Therefore we can conclude that the formation of AlSiO, MgAlO and CaTiO₃ complex molecules occurs as a result of heterogeneous reactions, and not in reactions in the gas phase.

References: [1] Shornikov S. I. et al. (1994) *Rapid Commun. Mass Spectr.* 8:478–480. [2] Shornikov S. I. et al. (1997) *Russ. J. Phys. Chem.* 71:19–22. [3] Shornikov S. I. and Archakov I. Yu. (2000) *Glastech. Ber. Glass. Sci. Technol.* 73C2:51–57. [4] Shornikov S. I. and Yakovlev O. I. (2015) *Geochem. Int.* 53:690–699. [5] Shornikov S. I. (2017) *Russ. J. Phys. Chem. A* 91:10–16.