INTRODUCTION: The only magnesium aluminate in the MgO–Al₂O₃ system is MgAl₂O₄. Spinel represents a great interest in cosmochemical studies as a main mineral of the Ca–Al–inclusions (CAIs) substance found in carbonaceous chondrites. It is the earliest object of the Solar system with unusual isotopic characteristics [1]. Fig. 1 shows the phase diagram of the MgO–Al₂O₃ system [2], where you can see a wide area of spinel solid solutions with MgO and Al₂O₃.

![Phase diagram of MgO–Al₂O₃ system](image)

**Fig. 1.** The phase diagram of the MgO–Al₂O₃ system [2]: 1 – MgO (solid solution); 2 – MgO + liquid; 3 – MgO (solid solution) + MgAl₂O₄ (solid solution); 4 – MgAl₂O₄ (solid solution); 5, 6 – MgAl₂O₄ + liquid; 7 – MgAl₂O₄ + Al₂O₃; 8 – Al₂O₃ + liquid; 9 – liquid.

During the formation of usual CAIs and especially unusual FUN CAIs at a certain stage of their evolution undergone of chemical and isotopic fractionation at evaporation. The evaporation process took place from the melt and, apparently, its crystallization occurred simultaneously with evaporation [3–5]. At the same time at the high-temperature stage of crystallization, the first crystallizing phase from the melt was spinel according to the high temperature melting point of spinel (Fig. 1). Thus, it can be assumed that the evaporation occurred from the developing heterogeneous system of crystal–melt. In this case, information about the spinel evaporation becomes particularly important. Here we present experimental data on the spinel evaporation, which can clarify the questions about the composition of the crystallizing mineral at evaporating conditions.

RESULTS AND DISCUSSIONS: We studied evaporation of stoichiometric spinel in the temperature range 1851–2089 K [2, 6] and spinel solid solutions in the temperature range 2000–2200 K [7] from the Knudsen molybdenum effusion cell by the mass spectrometric method.

We observed the change in stoichiometric spinel composition at temperatures exceeding 2000 K due to the predominant evaporation of the components of the gas phase belonging to the magnesium oxide. It led to a shift in the spinel composition in an area with a higher content of Al₂O₃. This fact limited the temperature range where the study of stoichiometric spinel was carried out. On the other hand, this circumstance made it possible to study the evaporation of solid spinel solutions up to the corundum field, choosing the temperature conditions of experiments.

The established molecular composition of the gas phase over spinel and their solid solution region shows to evaporation according to reactions typical for the evaporation of individual oxides:

\[ [\text{MgO}] = (\text{Mg}) + (\text{O}) \]  \hspace{1cm} (1)
\[ [\text{MgO}] = (\text{MgO}) \]  \hspace{1cm} (2)
\[ [\text{Al₂O₃}] = 2(\text{Al}) + 3(\text{O}) \]  \hspace{1cm} (3)
\[ [\text{Al₂O₃}] = 2(\text{AlO}) + (\text{O}) \]  \hspace{1cm} (4)
\[ [\text{Al₂O₃}] = (\text{Al₂O}) + 2(\text{O}) \]  \hspace{1cm} (5)

(here and further square brackets denote the condensed phase, round brackets denote the gas phase).

The (MgAlO) presence in minor amounts in the gas phase testified to the occurrence of the following heterogeneous reactions:

\[ [\text{MgAl₂O₄}] = (\text{MgAlO}) + (\text{Al}) + 3(\text{O}) \]  \hspace{1cm} (6)

The values of partial pressures of vapor species \( (p_i) \) over spinel (Fig. 2) and their solid solution region (Fig. 3) were determined by the Hertz–Knudsen equation.

The oxide activities \( (a_i) \) were calculated from the partial pressures values and presented in Fig. 4. They allowed to determine the values of mixing energy \( (\Delta G) \), as well as the enthalpy and entropy of spinel equal to \(-12.02\pm1.14 \text{ kJ/mol} \) and \(5.03\pm0.56 \text{ J/(mol}\times\text{K}) \), respectively, and the melting enthalpy of spinel at \(2420\pm25 \text{ K} \), equal to \(55.81\pm4.62 \text{ kJ/mol} \) (per 1 mol compound).

The mixing energy in the MgO–Al₂O₃ system at 2200 K shows a slightly lower value compared to the Al₂O₃–SiO₂ system [8], which is due to the weak chemical interaction in the Al₂O₃–SiO₂ melts. At the same time a greater ordering of the spinel solid solution compared to the CaO–Al₂O₃ system [9] is manifested in higher values of mixing energy (Fig. 5).
Fig. 2. The partial pressure values of vapor species over spinel [6]: 1 – Mg; 2 – MgO; 3 – Al; 4 – AlO; 5 – Al₂O₃; 6 – O; 7 – O₂; 8 – MgAlO.

Fig. 3. The partial pressure values of vapor species over spinel solid solutions at 2100 K [7]: 1 – Mg; 2 – MgO; 3 – Al; 4 – AlO; 5 – Al₂O₃; 6 – O; 7 – O₂; 8 – MgAlO.

Fig. 4. The activities of MgO (1) and Al₂O₃ (2) in the MgO–Al₂O₃ system at 2200 K [7].

Fig. 5. The mixing energies in the MgO–Al₂O₃ (1), Al₂O₃–SiO₂ (2) and CaO–Al₂O₃ (3) systems determined by the Knudsen mass spectrometric effusion method at 2200 K, obtained at the present study and in [8, 9], respectively. Dotted lines correspond to heterogeneous areas.

Summary: The presented data shows that the evaporation of stoichiometric spinel without changing of its composition is possible at temperatures not exceeding 2000 K, or briefly at temperatures not exceeding 2100 K (Fig. 2). Otherwise, the stoichiometric spinel chemical composition will change with enrichment in Al₂O₃ (Fig. 3–5), which will lead to a different spinel evaporation behavior comparer to evaporation of the stoichiometric spinel.

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