Thermodynamic properties of minerals and fluids

Shornikov S. I.¹, Ivanova M. A.¹, Minaeva M. S.² Thermodynamic properties of the MgO – FeO – SiO₂ melts

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Abstract. Within the framework of the developed semiempirical model, the calculations of thermodynamic properties of the MgO–FeO–SiO₂ melts in the temperature region 1800–2400 K were made. The calculated values of the oxide activities and the mixing energies of melts are compared with available information. Keywords: thermodynamic properties of oxide melts, the MgO–FeO–SiO $_{\rm 2}$ system

The physico-chemical properties of the MgO– FeO–SiO₂ system are important for understanding of geological and cosmochemical processes, as well as for metallurgy and the production of electro-ceramics and magnesite refractories. Information on the phase diagram of the MgO–FeO–SiO₂ system is based on the results obtained by Bowen & Schairer (1935). The MgSiO₃–FeSiO₃ and Mg₂SiO₂–Fe₂SiO₄ cross sections are shown in Fig. 1.



Fig. 1. The phase diagrams of the MgSiO₃–FeSiO₃ (**a**) and Mg₂SiO₂–Fe₂SiO₄ (**b**) system determined by Bowen & Schairer (1935). Symbols: 1 – olivine + liquid; 2 – olivine + clinopyroxene + liquid; 3 – clinopyroxene + liquid; 4 – clinopyroxene + tridymite + liquid; 5 – clinopyroxene; 6 – rhombic pyroxene; 7 – clinopyroxene + olivine + tridymite; 8 – olivine + tridymite; 9 – olivine + tridymite + liquid; 10 – tridymite + liquid; 11 – cristobalite + liquid; 12 – liquid; 13 – olivine.



Fig. 2. The FeO activity in the FeO–MgSiO₃ melts at 1873 K: **1** (Kojima et al., 1969), **2** (Ban-ya & Shim, 1982), **3** (Plante et al., 1992) and calculated in the present study (**4**).

Experimental determinations of the iron oxide activity (a_{FeO}) in the MgO–FeO–SiO₂ melts were performed in a wide temperature range (1577–2173

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K) by various approaches (Kitayama & Katsura, 1968; Kojima et al., 1969; Sakawa et al., 1976; Banya & Shim, 1982), including the Knudsen effusion mass spectrometric method (Plante et al., 1992; Costa et al., 2017). Some results for the FeO– MgSiO₃ system cross section are presented in Fig. 2. As it can see from Fig. 2 discrepancies exist between the obtained results. There are also no satisfactory agreements between the experimental values of the oxide activities in the ternary melts obtained in (Kojima et al., 1969; Sakawa et al., 1976; Ban-ya & Shim, 1982; Plante et al., 1992) and those in the boundary melts – MgO–SiO₂ (Kambayashi & Kato, 1983) and FeO–SiO₂ (Distin et al., 1971).

The thermodynamic properties of the MgO–SiO₂, FeO–SiO₂, and MgO–FeO binary melts were considered earlier (Shornikov, 2006; Shornikov, 2015; Shornikov et al., 2020). The aim of the present study was theoretical calculations of the values of oxide activities and mixing energies (ΔG^m) in the



Fig. 3. The activities of MgO (a, e), FeO (b, f), SiO₂ (c, g) and mixing energy (d, h) in the MgSiO₃–FeSiO₃ (a–d) and Mg₂SiO₂–Fe₂SiO₄ (e–h) melts at 1873 (1–4, 6) and 2273 K (5, 7), obtained experimentally: 1 (Kojima et al., 1969), 2 (Sakawa et al., 1976), 3 (Costa et al., 2017); and calculated: 4 (Bjorkvall et al., 2000), 5 (Wu et al., 1993), as well as in the present study (6, 7).

MgO–FeO–SiO₂ melts at 1800–2400 K using a semiempirical model (Shornikov, 2019) in order to refine its parameters. The model parameters were calculated from experimental and theoretical data of the standard Gibbs energies (ΔG°) of formation of simple oxides (MgO, FeO, and SiO₂) and their binary compounds

(no ternary compounds were found in the MgO– FeO–SiO₂ system), as well as vapor species (Mg, Mg₂, MgO, Fe, Fe₂, FeO, FeO₂, Si, Si₂, SiO, SiO₂, Si₂O₂, O, O₂, O₃, and O₄). The ΔG° values of the condensed phases and vapor species over the melt were used to find the equilibrium conditions for given melt composition and temperature. The similar detailed calculations of the oxide activities and mixing energies in the MgO–FeO–SiO₂ melts were performed by Bjorkvall et al. (2000) and Wu et al. (1993) at 1873 and 2273 K, respectively.

The experimental data obtained in (Kojima et al., 1969; Sakawa et al., 1976; Costa et al., 2017) and the results of calculations performed in (Wu et al., 1993; Bjorkvall et al., 2000) and in the present study are presented in Fig. 3. The available thermodynamic information is varied. Calculations of the MgO activity in the MgSiO₃-FeSiO₃ and in the Mg₂SiO₂-Fe₂SiO₄ melts at a significant FeO concentration performed in the present study correspond satisfactorily to those obtained in (Wu et al., 1993; Bjorkvall et al., 2000; Costa et al., 2017), but large discrepancies are observed in the forsterite region (Fig. 3e). In the case of FeO activities, the presented experimental and theoretical data correspond to each other, with the exception of the results of calculations by Bjorkvall et al. (2000), which show significant positive deviations from ideality (Fig. 3b, f). The SiO₂ activities in the presented cross sections (Fig. 3c, g) and calculated in this study differ approximately 3 times from those obtained in (Wu et al., 1993; Bjorkvall et al., 2000), which, however, do not quite correspond to the accepted values for the boundary melts (Distin et al., 1971; Kambayashi & Kato, 1983). The observed discrepancies are probably due to the low mixing energy values in the MgSiO₃-FeSiO₃ and in the Mg₂SiO₂-Fe₂SiO₄ melts (Fig. 3d, h). They are in the range from -10 to -25kJ/mol, and practically unchanged at 1873-2273 K, that indicates the melt behavior is close to ideal.

Thus, the oxide activities calculated in the present study in the MgO–FeO–SiO₂ melts at 1800-2400 K satisfactorily correspond to the available physicochemical experimental and theoretical data.

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