

Shornikov S.I., Archakov I.Yu. Vaporization and phase relations in the system CaO-SiO₂

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Numerous publications concerning the study of physico-chemical properties of the binary system CaO-SiO₂ are inspired by the practical application of compounds of this system in diverse technological processes, in production of cement and ceramic materials, in metallurgy and geochemistry. According to [1], two calcium silicates, i.e. pseudowollastonite α -CaSiO₃ and bi-calcium silicate α -Ca₂SiO₄ fuse congruently at temperatures 1817±2 K and 2403±15 K, respectively. Rankinite Ca₃Si₂O₇ dissociates at temperature 1737±5 K, Ca₃SiO₅ is stable in the temperature interval 1523-2423 K and fuses incongruently (Fig. 1). According to [2], the latter compound fuses congruently at temperature 2448 K. A temperature of the phase transition for wollastonite β -CaSiO₃ is 1473±2 K, for α' -Ca₂SiO₄, 1723±15 K [1].

Despite the numerous studies of thermodynamic properties of the system CaO-SiO₂, differences in estimated chemical potentials of components ($\Delta\mu(i)$) in the case of the most studied pseudowollastonite are significant (about 20 and 80 kJ/mol for $\Delta\mu(\text{SiO}_2)$ and $\Delta\mu(\text{CaO})$, respectively). The most precise studies fulfilled with the methods of high-temperature calorimetry [3, 4] are confined by temperature 1700 K.

The purpose of the present study is to solve the above discrepancies, specification of the information on the system CaO-SiO₂, and addition of data for temperatures above 2000 K.

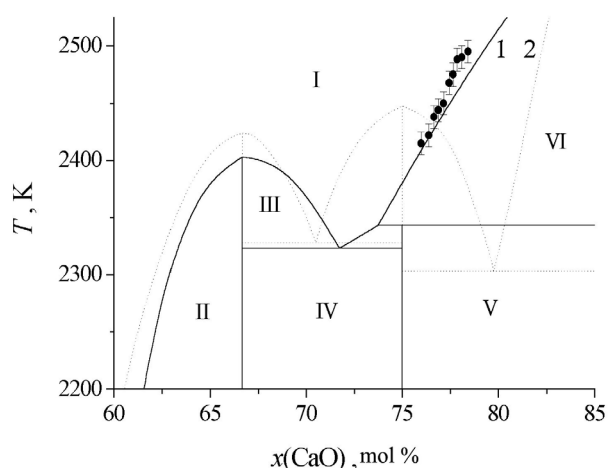


Fig. 1. Melting diagram of the system CaO-SiO₂ near Ca₃SiO₅ composition (1 – according to [1], 2 – [4]). Fields: I – liquid, II and III – α -Ca₂SiO₄ + liquid, IV – α -Ca₂SiO₄+Ca₃SiO₅, V – Ca₃SiO₅+CaO, VI – CaO + liquid. Results of the present study are shown by points. 1. $x(\text{CaO})$, mol. %

Vaporization and phase relations in the system CaO-SiO₂ within the range 1700-2600 K were studied using the earlier approach [5, 6] based on the results, obtained with the Knudsen mass-spectrometry. Vaporization of the sam-

ples in the system CaO-SiO₂ was carried out from the molybdenum chambers with a ratio of a vaporization area and an effusive hole above 250 cm using a high-temperature ion source, designed on the basis of the MI 1201T spectrometer [2]. In order to diminish an influence of the dissociative ionization of a vapor, the energy of 20.0±0.1 eV was used.

The mass-spectra of a vapor over the studied samples in the system CaO-SiO₂ were characterized by predominance of molecular ions (SiO)⁺ and (Ca)⁺. A total intensity of other lines did not exceed 10 % of the intensity of the (SiO)⁺ and (Ca)⁺ lines.

The observed incongruent vaporization of melts in the system CaO-SiO₂, determined by different rates of a vaporization of different components, results in changing of a composition of the condensed phase during the vaporization. It allows determination of thermodynamic properties of the liquid phase within the wide range of concentration at constant run conditions using the approaches, which are based on the Gibbs-Duhem equation. In particular, a chemical potential of SiO₂ within the Belton-Fruehan method [7] can be defined by the following relation

$$\mu(\text{SiO}_2) = -RT \int_{x(\text{SiO}_2)=1}^{x(\text{SiO}_2)} (1-x(\text{SiO}_2)) d \ln \frac{I(\text{Ca})^+}{I(\text{SiO})^+}, \quad (1)$$

whereas a chemical potential of CaO can be found from the Gibbs-Duhem equation

$$\mu(\text{CaO}) = - \int_{x(\text{SiO}_2)=x^*(\text{SiO}_2)}^{x(\text{SiO}_2)} \frac{x(\text{SiO}_2)}{1-x(\text{SiO}_2)} d\mu(\text{SiO}_2), \quad (2)$$

where $x^*(\text{SiO}_2)$ – inferior limit of integration, defined from the position of the liquidus line at given temperature. A value $x^*(\text{SiO}_2)$ was deduced from the dependence of intensities of ionic fluxes of (SiO)⁺ and (Ca)⁺ on the time of vaporization by the Hertz-Knudsen equation [6].

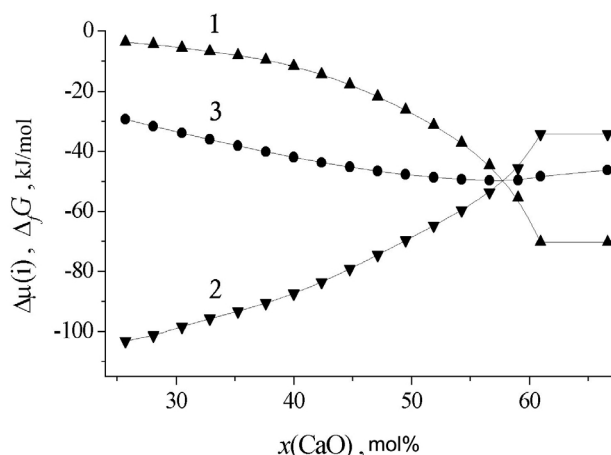


Fig. 2. Chemical potentials of SiO₂ (1), CaO (2), and the Gibbs energy of melt formation in the system CaO-SiO₂ (3), calculated in the present study at temperature 2100 K.

The Gibbs energy of melt formation in the system CaO-SiO₂ (Fig. 2) was calculated from the relation

$$\Delta_f G = \sum_i x(i) \mu(i) \quad (3)$$

The obtained value correlates with earlier results at lower temperatures [8, 9].

An interpretation of a character of melt vaporization within the compositional range $\text{Ca}_2\text{SiO}_4\text{-CaO}$ and temperatures 2400-2500 K allows determination of position of the liquidus in the given portion of the diagram CaO-SiO_2 . Figure 1 shows that the obtained position of the liquidus corresponds to an absence of the eutectic between Ca_3SiO_5 and CaO [2], as well as contradicts the proposed congruent melting of Ca_3SiO_5 [2].

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