A thermodynamic investigation of evaporation of oxide melts containing titanium dioxide

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The problem of definition of oxide melt composition varied during evaporation is urgent and is in a basis of fundamental representations of origin and the composition of meteorites. Thereupon the CaO–TiO$_2$–SiO$_2$ system melts are interesting, the compounds of this system – perovskite and titanite (sphene) are in the substance of white inclusions (CAI). The purpose of the present study was the determination of melt thermodynamic properties for calculation of melt concentration changing during evaporation in the temperatures range 1600-2300 K.

The information on the structure and thermodynamic properties as well as on the phase relations in the CaO–TiO$_2$–SiO$_2$ system is not so extensive and it was not considered in details. The results of mass-spectrometric investigations obtained in [*Stolyarova et al.*, 2004; *Stolyarova and Plotnikov*, 2005] are contradicted to other experimental data [*Xirouchakis et al.*, 1997; *DeCapitani and Kirschen*, 1998; *Shornikov et al.*, 2000; *Shornikov and Archakov*, 2003; *Shornikov*, 2005].

The first part of the present study was the calculation of the thermodynamic properties of melts of CaO–TiO$_2$–SiO$_2$ system at temperatures from 1600 to 2300 K within the framework of the ideal associated solutions theory.

The simplified lattice model used like it was before for the CaO–Al$_2$O$_3$–SiO$_2$ [*Shornikov*, 2007], MgO–Al$_2$O$_3$–SiO$_2$ [*Shornikov*, 2008], CaO–MgO–Al$_2$O$_3$–SiO$_2$ [*Shornikov*, 2009] and CaO–MgO–Al$_2$O$_3$–FeO–SiO$_2$ [*Shornikov*, 2009] systems. It accounts for the intermolecular interactions using the semi-phenomenological energy parameters calculated on the experimental [*Xirouchakis et al.*, 1997; *DeCapitani and Kirschen*, 1998; *Shornikov et al.*, 2000; *Shornikov and Archakov*, 2003] and reference [*Glushko et al.*, 1978–1982] values. The source thermodynamic data took into account 18 condensed phases (11 solid and 7 liquid) and 14 gas phase components, listed in the Table below.

Table. The Gibbs energy of formation (from elements) of condensed phases and vapor species over the melts of the CaO–TiO$_2$–SiO$_2$ system at 2050 K calculated in the present study

Condensed phases				Gas phase	
Solid phases	$\Delta_f G°_{2050}$, kJ/mole	Liquid phases	$\Delta_f G°_{2050}$, kJ/mole	Vapor species	$\Delta_f G°_{2050}$, kJ/mole
CaO	–416.099	CaO	–404.461	Ca	–25.442
CaTiO$_3$	–1071.809	CaTiO$_3$	–1055.171	CaO	–76.385
Ca$_3$Ti$_2$O$_7$	–2563.232			O	118.320
Ca$_4$Ti$_3$O$_{10}$	–3660.494			O$_2$	0.000
CaTiSiO$_5$	–1665.569	CaTiSiO$_5$	–1697.195	O$_3$	276.725
CaSiO$_3$	–1043.621	CaSiO$_3$	–1050.971	Ti	185.495
Ca$_2$SiO$_4$	–1511.832	Ca$_2$SiO$_4$	–1503.841	TiO	–128.510
Ca$_3$SiO$_5$	–1921.320			TiO$_2$	–336.523
Ca$_3$Si$_2$O$_7$	–2540.999			Si	161.631
TiO$_2$	–574.148	TiO$_2$	–569.996	SiO	–257.183
SiO$_2$	–540.626	SiO$_2$	–541.222	SiO$_2$	–313.278
				Si$_2$	189.307
				Si$_2$O$_2$	–552.779
				Si$_3$	261.005

The Table gives the calculated values of the Gibbs energies for the compounds and the gas phase components over the $CaO–TiO_2–SiO_2$ system. They were used for calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the total Gibbs energy for the system studied was found by the Gibbs energy minimization method.

The oxide activities $a(i)$ and the Gibbs energy of melt formation (from oxides) in the $CaO–TiO_2–SiO_2$ system ($\Delta_f G_T$) were calculated for two more interesting system sections: $CaSiO_3–CaTiO_3$ (at fixed concentration of $x(CaO)$, equal to 50 mole %) and $CaTiO_3–SiO_2$ (at fixed ratio of mole fractions of $x(CaO) / x(TiO_2)$, equal to 1). The obtained results are shown in the Fig. 1 in comparison with the experimental data [*Shornikov et al.*, 2000; *Shornikov and Archakov*, 2003].
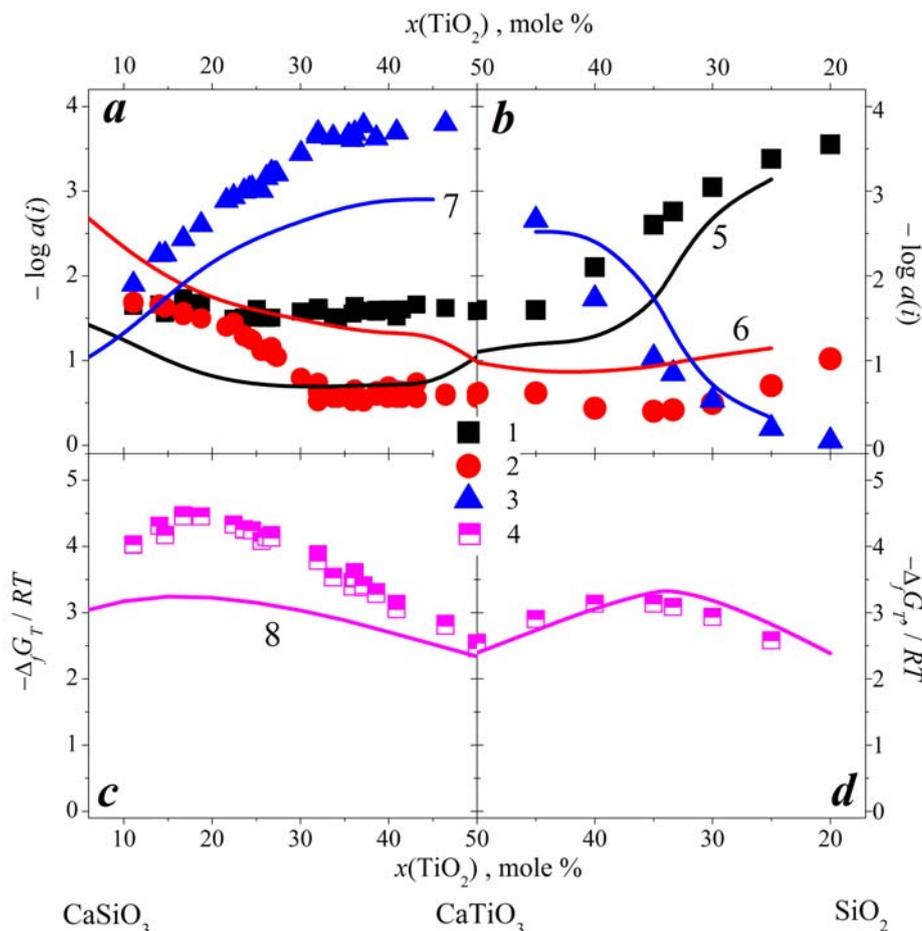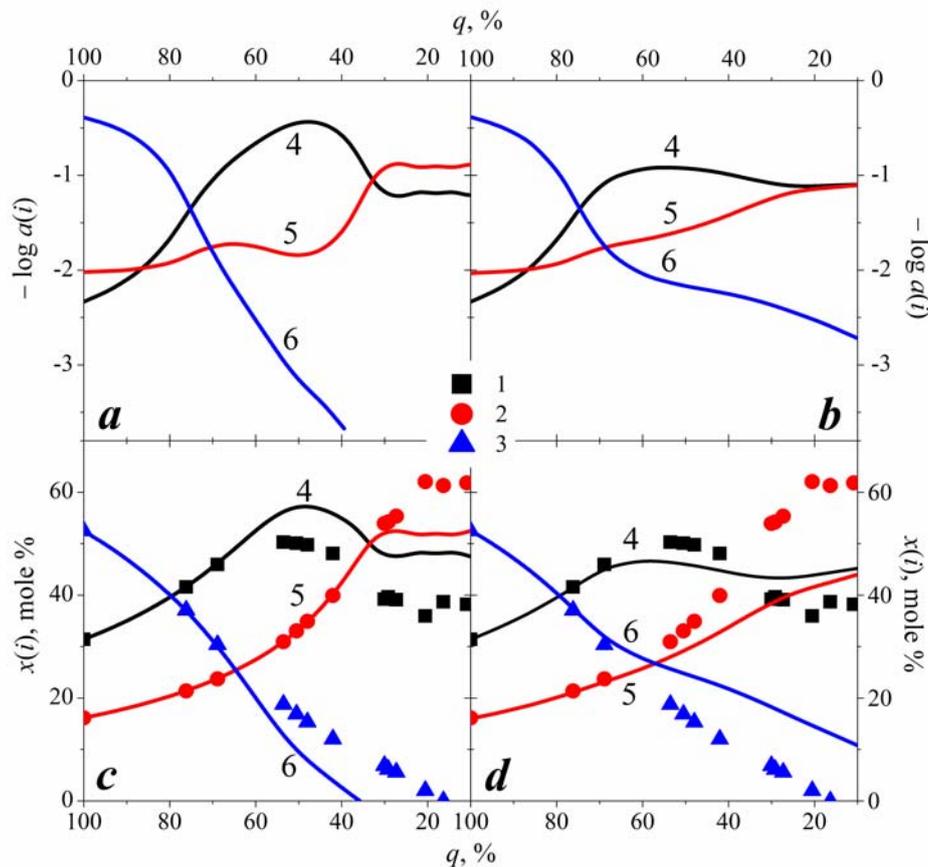

Fig. 1. The oxide activities (*a*, *b*) of calcium (1, 5), titanium (2, 6), silicon (3, 7) and the Gibbs energies of melt formation from oxides (*c*, *d*) in the $CaSiO_3–CaTiO_3$ system (*a*, *c*) and $CaTiO_3–SiO_2$ system (*b*, *d*) at the temperature 2050 K: 1–4 – obtained by the mass-spectrometric Knudsen effusion method [*Shornikov et al.*, 2000; *Shornikov and Archakov*, 2003], 5–8 – calculated in the present study.

As seen from the Fig. 1, the calculated oxide activities and the Gibbs energy of melt formation (from oxides) in the $CaO–TiO_2–SiO_2$ system melts obtained at present study well correspond to experimental data. Observable deviations of the calculated oxide activity values from experimental data are insignificant – approximately in 2 times. The minimal value of the Gibbs energy of melt formation (from oxides) in the $CaO–TiO_2–SiO_2$ sytem is large ($\Delta_f G_{2050} = -53.4$ kJ/mole). It corresponds to the titanite ($CaTiSiO_5$) concentration.

The second part of present study is calculations of the concentration changing in the condensed phase of the $CaO–TiO_2–SiO_2$ system melts during evaporation based on obtained thermodynamic information.

The approach to calculations of concentration changing during evaporation was described earlier in detail [*Shornikov*, 2009]. As the gaseous complex oxides are present in insignificant amounts in the case of evaporation of the $CaO–TiO_2–SiO_2$ system melts [*Archakov et al.*, 2000], the evaporation process of melt can be presented as the evaporation of combination of simple oxides. The studied earlier experimentally composition of the $CaO–TiO_2–SiO_2$ system [*Archakov et al.*, 2000] has been

chosen for the calculations of concentration changing during evaporation. It consist of 31.4 mole % CaO, 16 mole % TiO_2 and 52.6 mole % SiO_2. The calculation has been executed as for a case of conditions of external chemical influence absence (in chemically neutral conditions) and for a case of the reducing conditions typical for experimental investigations. These conditions have been set the constant fixed partial pressure of molecular oxygen of $p(O_2) = 5.0 \cdot 10^{-5}$ atm.

Fig. 2. The activities (*a*, *b*) of calcium oxide (4), titanium dioxide (5) and silicon dioxide (6) and the concentration changing in the condensed phase (*c*, *d*) of calcium oxide (1, 4), titanium dioxide (2, 5) and silicon dioxide (3, 6) *vs.* the $CaO–TiO_2–SiO_2$ system melt weight loss during evaporation at the temperature 2300 K in various redox conditions: (*a*, *c*) – in chemical neutral conditions and (*b*, *d*) – in reducing conditions ($p(O_2) = 5.0 \cdot 10^{-5}$ atm). The experimental data obtained by mass-spectrometric Knudsen effusion method in [*Shornikov et al.*, 2000] are denoted by symbols (1-3). The calculation results obtained in present study are indicated by lines (4-6).

According to Fig. 2 the considered melt loses SiO_2 at evaporation, moving to the calcium oxide field. At the weight reduction of initial melt to 50 % due to melt evaporation, the SiO_2 concentration has decreased from 52 to 15 mole % (i. e. it has decreased almost in 4 times). The maximum concentration of CaO in melt is observed. Then the melt loses SiO_2 completely, evaporating in the form of perovskite $CaTiO_3$. This rule is characteristic as for a case of melt evaporation in chemically neutral conditions, and for a case of melt evaporation in reducing conditions (Fig. 2*c* and 2*d*).

We may observe also on Fig. 2*c* and 2*d* the differences in the concentration dependences caused by various redox conditions of melt evaporation. So, in case of melt evaporation in chemically neutral conditions, the melt loses SiO_2 completely at the weight loss smaller, than in experimental conditions (Fig. 2*c*). In case of melt evaporation in the fixed reducing conditions it occurs differently – at more melt weight loss (Fig. 2*d*). Thus, experimental data are in an interval between the calculated values corresponding to the chemically neutral conditions and the fixed reducing conditions.

It is easy to notice (Fig. 2*a* and *c*, Fig. 2*b* and *d*) that the concentration changes of considered melt condensed phase during evaporation are proportional to changes of logarithms of activity values (to chemical potentials) of oxides in the melt in various redox conditions. It shows interrelation of melt evaporation processes and the melt thermodynamic properties (in particular, chemical potentials of melt components).

Thus, thermodynamic properties of silicate melts containing a titanium dioxide were investigated within the framework of the developed theoretical approach based on the experimental thermodynamic data [*Shornikov*, 2009]. The interrelation of melt thermodynamic properties with the melt evaporation processes and the melt concentration changing due to evaporation in the field of high temperatures (1600-2300 K) is shown.

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