Thermodynamics of Na$_2$O–SiO$_2$ Melts

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Abstract—The thermodynamic properties of Na$_2$O–SiO$_2$ solid (942–1285 K) and liquid (1103–1719 K, 19.5–61.8 mol % Na$_2$O) silicates were studied by Knudsen cell mass spectrometry. To determine the activities of the constituent oxides, these were reduced to volatile suboxides directly in effusion cells. Mass spectra of the saturated vapor over Na$_2$O–SiO$_2$ showed the presence of the Na$^+$, Na$_2$O$^+$, NaO$^+$, O$_2^+$, TaO$^+$, TaO$_2^+$, NbO$^+$, NbO$_2^+$, MoO$^+$, MoO$_2^+$, MoO$_3^+$, and NiO$^+$ ions resulting from the ionization of the Na, Na$_2$O, NaO, NaO$_2$, O$_2$, TaO, TaO$_2$, NbO, NbO$_2$, MoO, MoO$_2$, MoO$_3$, and NiO molecules. The activities calculated by two different procedures were found to coincide within the experimental error. The enthalpies and Gibbs energies of formation of sodium silicates were shown to be extremely low. The formation of solid ortho- and metasilicates is accompanied by a decrease in entropy, in contrast to the other sodium silicates. Sodium orthosilicate has the lowest enthalpy and Gibbs energy. A thermodynamic model for Na$_2$O–SiO$_2$ melts is proposed which relies on associated solution theory and takes into account silica polymerization. The model describes the composition and temperature dependences of the activities of the constituent oxides in the melt with an accuracy no worse than the experimental error (2–3%). The model, in combination with the thermodynamic functions of formation of all the intermediate solid phases, was used to calculate phase equilibria in the Na$_2$O–SiO$_2$ system. The results agree well with the experimental data obtained by physicochemical methods.

INTRODUCTION

Sodium silicates enter into the composition of many minerals and are therefore of immense importance in chemistry, geochemistry, and petrology. They are widely used in the production of glass and ceramics, in civil engineering, etc. The unique ability of silica to form polymeric molecules of arbitrary dimensions and orientation engenders considerable theoretical interest in sodium silicates.

In earlier studies [1–5], we developed an approach which allowed us to significantly extend the composition and temperature ranges of Knudsen cell mass spectrometry and provided the theoretical basis for modeling the thermodynamic behavior of silicate melts. The objective of this work was to obtain reliable data on the thermodynamic properties of phases in the Na$_2$O–SiO$_2$ system and to apply the thermodynamic model of liquid silicates [1, 5, 6] to Na$_2$O–SiO$_2$ melts, characterized by strong interaction between the constituent oxides.

EXPERIMENTAL

The thermodynamic properties of the melts were studied by Knudsen cell mass spectrometry. As in earlier studies [1–5], the constituent oxides were reduced to volatile suboxides directly in effusion cells:

\[ n\text{Na}_2\text{O}(cr) + R(cr) = RO_n(g) + 2n\text{Na}(g), \] (1)
\[ n\text{SiO}_2(cr) + R(cr) = ROn(g) + n\text{SiO}(g), \] (2)

where R is the reducing agent (cell material: Nb, Ta, Mo, or Ni). In a few experiments, powders of reducing agents were added to the mixtures to be studied. Thermodynamic calculations and measurements show that, in the Na$_2$O–SiO$_2$ system, only reaction (1) takes place. Since the activity of the reductant was in all cases unity, the equilibrium constant of this reaction is given by

\[ K_p(1) = \frac{p(RO_n)[p(\text{Na})]^{2n}}{[a(\text{Na}_2\text{O})]^n}, \] (3)

where the pressures labeled 0 refer to mixtures in which the activity of Na$_2$O is unity. Therefore, studying mixtures with high and low Na$_2$O contents, one can determine Na$_2$O activity as

\[ [a(\text{Na}_2\text{O})]^n = \frac{p(RO_n)[p(\text{Na})]^{2n}}{p^0(RO_n)[p^0(\text{Na})]^{2n}}, \] (4)

\[ = \frac{I(RO_n^+)[I(\text{Na}^+)]^{2n}}{I^0(RO_n^+)[I^0(\text{Na}^+)]^{2n}}. \]
Here, $I$ and $I_0$ are the corresponding ion intensities—either the sums of the ion currents produced by ionization of particular molecules or those parts of the total ion currents corresponding to molecular ions. In both cases, in going from partial pressures to ion intensities, the total or partial ionization cross sections of the corresponding molecules canceled. This notably improves the accuracy in the activity of the constituent oxides [1, 4]. Because of the high volatility of Na$_2$O, mixtures with a high Na$_2$O content could not be studied at high temperatures, and $\alpha$(Na$_2$O) values were calculated by equation (3) using reference data [7] for determining $K_p$ in (1).

Samples for this investigation were prepared from extra-pure-grade SiO$_2$ dried in vacuum and Na$_2$O obtained by thermal dissociation of extra-pure-grade Na$_2$CO$_3$. Some of the samples were synthesized directly in effusion cells, the others were prepared by reacting the constituent oxides in closed Ni crucibles under a vacuum of $10^{-4}$ Pa or better. Chemical and x-ray diffraction analyses of solidified samples showed that the dissolution of Ta, Nb, Mo, and Ni oxides in the samples was insignificant and the oxygen stoichiometry of the constituent oxides remained virtually unchanged. In other words, the representative point of the sample composition remained on the Na$_2$O–SiO$_2$ pseudobinary join of the Na–O–Si system. The x-ray patterns contained only lines corresponding to equilibrium phase relations in the Na$_2$O–SiO$_2$ system.

In our experiments, we used double effusion cells. The sample was placed in one compartment and the reference standard in the other. As reference materials, we used Ag (99.99% purity), Ni (99.98%), and Cu (99.999%). To verify that a nearly equilibrium state was reached in the effusion cell, we varied the effusion area, all other dimensions being the same, and used cells from different materials. Under the conditions of our measurements, changes in sample composition were negligible. The procedure of high-temperature mass spectrometric measurements was described in detail elsewhere [8, 9].

Mass spectra of the saturated vapor over Na$_2$O–SiO$_2$ showed the presence of the Na$^+$, Na$_2$O$^+$, NaO$^+$, O$_2^-$, TaO$^+$, TaO$_2^+$, NbO$^+$, NbO$_2^+$, MoO$^+$, MoO$_2^+$, MoO$_3^+$, and NiO$^+$ ions resulting from the ionization of the Na, Na$_2$O, NaO, Na$_2$O$_2$, O$_2$, TaO, TaO$_2$, NbO, NbO$_2$, MoO, MoO$_2$, MoO$_3$, and NiO molecules. The strongest signals were those from Na$^+$, TaO$^+$, NbO$_2^+$, and MoO$_2^+$. O$_2^-$ ions were detected only in experiments with Ni and Mo cells. The peaks from the species produced by ionization of Mo, Nb, and Ta oxides were identified using earlier results [2–5]. The origin of the Na$^+$, Na$_2$O$^+$, NaO$^+$, and O$_2^-$ ions can be understood only if the mechanism of Na$_2$O vaporization is known. Na$_2$O was reported to vaporize congruently [10, 11] by the reaction

$$2Na_2O(cr) = 4Na(g) + O_2(g). \quad (5)$$

Therefore, Na and O$_2$ would be expected to be the major components of the saturated vapor over Na$_2$O, with $p(Na) = 4p(O_2)$. The concentrations of Na$_2$O, NaO, NaO$_2$, and NaO$_2$ molecules were assumed to be much lower, by three and more orders of magnitude [10, 11]. However, according to a recent detailed study [12], NaO$_2$ molecules are quite stable in the gas phase and their concentration in the vapor over Na$_2$O is relatively high. This implies that Na$_2$O may vaporize not only by reaction (5) but also according to the equation

$$2Na_2O(cr) = 3Na(g) + NaO_2(g) \quad (6)$$

with $p(Na) = 3p(NaO_2)$. Thus, the ion current $I(Na^+)$ may comprise two contributions, one due to the ionization of Na atoms and the other to the ionization of Na$_2$O molecules. The formation of O$_2^+$ ions is due mainly to the dissociative ionization of Na$_2$O molecules, which is unlikely to yield NaO$^+$ ions. The absence of the O$_2^+$ signal in the mass spectrum of the saturated vapor over Na$_2$O–SiO$_2$ in Nb and Ta cells testifies to low concentrations of NaO$_2$ and O$_2$. Therefore, Na atoms are the only source of Na$^+$ ions. In contrast, the presence of the O$_2^+$ signal in experiments with Ni and Mo cells indicates that there is a second source of Na$^+$ ions—Na$_2$O molecules—clearly, if there is a second mechanism of vaporization. To check this assumption, we carried out measurements in Nb, Ta, Mo, and Ni cells for pure Na$_2$O, Na$_2$O–SiO$_2$ melts of a particular composition, and mixed-phase samples with compositions falling in the same two-phase region. The Na partial pressures measured with Nb and Ta cells differed markedly, by a factor of 1.6–1.7, whereas the activities calculated by equations (3) and (4) coincided within the experimental error (1–3%). The Na$_2$O activities determined with Mo and Ni cells were substantially higher, obviously because the second mechanism—dissociative ionization of Na$_2$O molecules—came into play, contributing to the Na$^+$ signal. To evaluate this contribution, we carried out experiments in which the residual oxygen in the spectrometer chamber was frozen out using a liquid-nitrogen trap situated in the source region or by cooling the jacket of the Knudsen unit with liquid nitrogen. This enabled us to eliminate the corresponding systematic error in the O$_2^+$ signal and to determine the