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Prediction of the thermodynamic functions of mixing of binary oxide melts in the $PbO–SiO_2$, $Al_2O_3–SiO_2$ and $CaO–Al_2O_3$ systems by structure-based modification of the quasi-chemical model

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ABSTRACT

A structure-based modification of the Guggenheim's quasi-chemical model for the prediction of the thermodynamic functions of mixing in binary silicate and aluminate melts is presented and the extension of this approach to ternary systems is discussed. Based on the "anionic" point of view on the oxide melts structure, the novel method for determination of the interchange energy (a principal parameter of the quasi-chemical theory) was proposed along with a simple and general set of the equations. The activity calculations of the end-member components and integral and partial enthalpies and Gibbs free of mixing along with the whole range of compositions for $PbO–SiO_2$ and $Al_2O_3–SiO_2$ systems as well as the model calculations of components in $CaO–Al_2O_3$ melts were made. The reasonable agreement between results of model calculations and experimental data showed the reliability of this approach in predicting of the thermodynamic functions of mixing in binary and aluminate systems. This approach has the advantage that prior knowledge of the experimental mixing properties of liquid oxide systems is not required.

1. Introduction

Modeling of the thermodynamic properties of silicate and aluminosilicate melts is necessary for understanding of the geochemical processes in magmas [1]. If the activities of melt species could be calculated it would be possible to model crystallization processes, and to calculate the solubility of volatile and trace element in melts. Such information is necessary to model magma dynamics and rheology, to predict geochemical trends during magma evolution, and to calculate ore-forming processes in magmatic systems. The information on the structure of oxide melts is widely used in the development of thermodynamic models. The geometry of the coordination sphere, the interatomic distances, number of cations involved in the medium range organization of the silicate network, and their relationships with it are determined by different diffraction and spectroscopic methods. It has been shown that the cations are surrounded by cages formed of bridging and non-bridging oxygen atoms [2–4]. When a cation enters a cage, depolymerization of polymer silicate anions takes place and some bridging oxygen atoms are converted into non-bridging atoms in order to maintain the overall charge balance. One of the reasons for phase separation in silicate melts is the coulombic repulsions between poorly screened cations. To neutralize such repulsions, metal cations occupy the less polymerized domains of the melt by forming bonds with non-bridging oxygen atoms.

Numerous mixing models of silicate melts, which take in consideration polymeric reactions, have been developed [5–10]. In the polymeric models, it is postulated that at each composition, at given pressure and temperature, the melt is characterized by an equilibrium distribution of the ionic species of oxygen, ionic polymers of monomer units $SiO_4^{4-}S$, and metal cations. The polymeric approach to silicate melts has been extended to ternary systems [9]. The adopted expression for the Gibbs free energy of mixing is composed of a chemical interaction term, a cationic mixing term and an elastic strain energy contribution, linearly related to composition. The model reproduces adequately the experimentally observed thermodynamic activities of the components along the limiting binary and within the ternary system. The coupling a generalized polymeric approach with an improved generalized convex-hull procedure proposed in [10] permit to depict the topology of the liquidus for a n-component system at various pressures and temperatures.

The association models [11–15] present another approach to

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the thermodynamic modeling of liquid metallic and silicate systems. These models usually adopt a step-wise series of reactions between the end-member components to form a series of associates. The association models assume that the thermodynamic properties of the liquid depend predominantly on the Gibbs free energy of formation of the associates. For example, Sommer [11,12] proposes that the Gibbs free energy of mixing, ΔG_m^{ex}, of the components of the system A-B with a single associate A_mB_n is given by following general equation:

$$\Delta G_m^{ex} = \Delta G_{ass} + \Delta G_{reg} \tag{1.1}$$

The Gibbs free energy due to the formation of the associate, ΔG_{ass}, is defined as follows:

$$\Delta G_{ass} = n(\Delta G_f^o,\ A_mB_n) \tag{1.2}$$

where n and ΔG_f^o, A_mB_n are the number of moles of the associate and the Gibbs free energy of formation of one mole of the associate. ΔG_{reg} is the Gibbs free energy due to the interactions between the components A and B between themselves and with the associate A_mB_n. The thermodynamic properties of liquid then assumed to depend predominantly on the Gibbs free energy of formation of these associates rather than by interactions between the associates. One the main drawback of such associate formalism comes from the discrepancy between the model implications that the associates are distinct molecules; whereas, most likely such molecules do not exist in reality [16]. The ion-association model of ideal mixing of Nesbitt and Fleet [13] reproduces fairly well the thermodynamic properties in binary silicate systems. It considers the association reactions:

$$2A^{melt} + B^{melt} = (A_2B)^{melt} \tag{1.3}$$

$$2(MO)^{melt} + (SiO_2)^{melt} = (M_2SiO_4)^{melt} \tag{1.4}$$

where $(MO)^{melt}$ corresponds to bivalent cation oxide in the melt (e.g., CaO, PbO). The equilibrium constant for reaction (1.3) can be written:

$$K_{(1.5)} = \frac{n_{A2B}(n_T)^2}{\left(n_A - 2n_{A_2B}\right)^2(n_B - n_{A_2B})} \tag{1.5}$$

where n_A, n_B and n_{A2B} are the total number of moles of A and B and A_2B in equilibrium; and n_T is total number of moles in the system.

The modified quasi-chemical model has been successfully applied to liquid oxide systems [16–19]. The modifications, introduced by Pelton et al. [16–19], enhance the reliability of the interpolations and extrapolations of the thermodynamic properties of ordered liquid oxide systems and allow setting the composition of maximum ordering so as to comply with the experimental data. The modifications are: the polynomial expansion of interchange energy (a parameter of the model) and molar non-configurational entropy change in the equivalent fraction; fixing of the composition of maximum ordering; selection of the coordination numbers. The modified quasi-chemical model is a principal part of FactSage thermochemical software and databases for optimization of the thermodynamic functions of mixing in binary and multicomponent systems and for phase diagrams calculation [20].

The Cell model was introduced by Kapoor and Frohberg [21], extended by Gaye and Welfringer [22] and generalized for metallurgical slags and high alloyed steel grades by Lehmann and Zhang [23] in the Generalized Central Atom model (GCA model). In the Cell model oxide melts are considered to consist of symmetric cells like [Ca–O–Ca] and [Si–O–Si], representing SiO_2 and CaO, respectively, and asymmetric cells of the type [Ca–O–Si], etc. Model parameters are the cell formation energy, W_{ij}, and the cell interaction energy, E_{ij}, which can be expanded as linear function of composition and temperature. In the GCA model the structure of liquids is described in terms of cells composed of a central atom and its shell of the nearest neighbors. One of the main differences in comparison with the Cell model is that the number of nearest neighbors can depend on the nature of the central atom. In particular, in the case of slags the number of the nearest anions of a given cation is equal to its valence state and is also the number of the nearest anions. The developed GCA model has permitted to greatly improve the predictions given by the Cell model for slags and it is the new approach for the predictions of the thermodynamic properties of high alloyed liquid steels.

Electrical conductivity measurements on silicate melts indicate that ionic conductivity is unipolar: the charge transfer is fulfilled by cations, whereas anionic groupings are essentially stationary [13,24]. Coulombic forces between charges of opposite signs lead to an ordering of ions, so the melt can be considered as a quasi-lattice with two distinct reticular sites from a statistical point of view. Hence, the concept of two (cation and anion) sub-lattices, earlier proposed by Temkin [25] for molten salts with random mixing in the sub-lattices, can be applied to silicate melts. Temkin obtained an expression of activity for molten salts in terms of ion activities. Subsequently, this model was extended for solid phases with more than two sub-lattices, and also for partially ionic liquids [26,27].

The aim of this paper is the development of a structural based approach for prediction of the thermodynamic functions of mixing for binary silicate and aluminate melts, based on the Guggenheim's quasi-chemical model, with an emphasis on the methods for independent determination of the model's parameters. We present methods to calculate these parameters using available structural and thermochemical data for crystal oxides, oxygen-containing molecules and ions.

2. Consideration of silicate melts in the frame of Guggenheim's quasi-chemical theory

The information regarding the short and medium range ordering in silicate, aluminate and aluminosilicate melts can be used as the basis for the development of realistic thermodynamic models for binary and higher order liquid oxide systems. The ^{17}O nuclear magnetic resonance spectroscopy (^{17}O NMR) has provided new information on structure of melts and glasses from an “anionic” viewpoint, related to the oxygen coordination environment [3,4]. The peaks for bridging oxygen linking Si, Al, and B atoms as well as non-bridging oxygen have been resolved and distinguished using the ^{17}O NMR techniques [3,4]. The consideration of silicate melts as a matrix of oxygen ions with different cations, including silicon cations, was originally used by Lumsden [28] for a modeling of the thermodynamic properties of oxide melts. In principle, the general solution of the problem of the calculation of the thermodynamic functions of mixing should be based on a detailed knowledge of the statistics and energetics of all the mixture's constituent atoms. In line with a new view about the structure of oxide melts the quasi-chemical treatment of oxide melts is of the interest because, as we believe, the resulting equations for the calculation of thermodynamic functions of mixing could be a basis for further structure-based modifications to obtain an approach for more realistic predictions of the thermodynamic properties of silicate and aluminate melts. From anionic view point on structure of silicate melts, the reactions between metal oxides and silica can be modeled as substitution of silicon atoms (ions) by metal atoms (ions), and *vice versa*, in the oxygen coordination polyhedra (Fig. 1). In Fig. 1, the oxygen species refer to the following structural linkages of oxygen coordination polyhedra (the second-