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Feature article

Critical evaluation and thermodynamic optimization of the Li-O, and Li_2O-SiO_2 systems

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ABSTRACT

A critical evaluation and thermodynamic optimization of all available experimental data of the Li-O and Li_2O-SiO_2 systems were performed to obtain one set of consistent Gibbs energy functions for all phases in the systems. The obtained Gibbs energy functions can reproduce all available and reliable experimental data from 298 K to above liquidus temperatures at one atm total pressure. It is the first time, to the best of our knowledge that the Gibbs energy of stoichiometric phases like Li_2O, Li_4SiO_4, Li_2SiO_3, and $Li_2Si_2O_5$ was comprehensively evaluated and optimized. The liquid oxide solution was modeled using the Modified Quasichemical Model to describe its thermodynamic behavior accurately considering the short range ordering. Discrepancies observed in the metastable liquid immiscibility and the liquidus in the SiO_2-rich region of the Li_2O-SiO_2 system was resolved. The phase diagram and thermodynamic data of all the solid and liquid phases were well reproduced within experimental error limits.

1. Introduction

The Li_2O-containing oxide systems are important for numerous industrial applications such as the metallurgical, ceramics, and glass industries. In the steel industry, Li_2O is gaining interest as a substitute of CaF_2 in the mold flux for the continuous casting process [1]. The applicability as a CaF_2 alternative stems from strong fluxing ability and environment friendliness. The lithium silicate glasses are extensively applied as dental prosthetics owing to its crystallization behavior [2], biocompatibility [3] and mechanical and thermal stability [4]. The fast conducting Li^+ ion in the glass, compounds, and solid solutions make it important for electrode manufacturing. [5–7] The superior thermal stability and good tritium release characteristic qualify compounds like Li_4SiO_4 for a promising solid breeding material and has been considered in International Thermonuclear Experimental Reactor (ITER) test blanket module [8,9].

Inspite of the technological importance, the thermodynamic and phase stability experiments in the Li_2O containing systems are limited. The experimental investigations of Li_2O containing systems are constrained by the volatilization of Li_2O at high temperatures, hydration of Li_2O- rich phases, and high viscosity of lithium silicate melts leading to glassy transitions and intrinsic crystallization problems. Thus, all the phase stabilities and thermodynamic properties are not experimentally well determined or have discrepancies; hence, the literature data are needed to be critically evaluated and thermodynamically optimized.

Keeping in mind the huge industrial application of Li_2O containing oxide systems, a thermodynamically consistent database for the Li_2O-Na_2O-CaO-MgO-Al_2O_3-SiO_2 system is being developed at McGill University. The present publication is the primary paper in a series of publications that will elaborate this effort. In this study, the available thermodynamic and phase equilibria in the Li-O and Li_2O-SiO_2 systems are critically evaluated and optimized.

Thermodynamic "optimization" of a chemical system comprises of critical assessment of all available thermodynamic and phase equilibrium data and formulation of a set of Gibbs energy equations for of all phases as a function of temperature and composition. With the help of these Gibbs energy functions, one can back-calculate not only the thermodynamic properties but also the phase diagrams. In the thermodynamic optimization process, all the data are rendered self-consistent and experimental discrepancies can be easily resolved. This also leads to correct thermodynamic interpolations and extrapolations in the regions where experiments have not been conducted.

The Li-O system was assessed by Sangster and Pelton [10] and recently by Chang and Hallstedt [11]. The binary Li_2O-SiO_2 system was assessed in a limited way by Romero-Serrano et al. [12] using a Gibbs energy polynomial model supposed to take the structure of silica based slag into consideration. Romero-Serrano et al. [12] were

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able to reproduce the activity data at 1673 K (1400 °C) and 1473 K (1200 °C), however, the optimization did not include the stoichiometric phases. In the present assessment, the liquid Gibbs energy is described by the Modified Quasichemical Model [13,14] (MQM). The MQM enables in replicating the strong short-range ordering (SRO) and network forming and breaking behaviours seen in the alkali silicate melts. Subsequently, systematic assessment of unary, binary and multicomponent systems helps in reducing the thermodynamic inconsistencies and ease in extrapolating the Gibbs energy functions to ternary and multicomponent systems.

2. Thermodynamic model

2.1. Stoichiometric phase

In the present work, several stoichiometric phases are evaluated in the Li-O, and binary Li_2O-SiO_2 system, namely, Li_2O, Li_2O_2, Li_8SiO_6, Li_4SiO_4, Li_2SiO_3, and $Li_2Si_2O_5$ (LT: low temperature, and HT: high-temperature polymorph). A summary of structural data is given in Table 1 while transition temperatures are tabulated in Table 2. The thermodynamic properties of Li_2O are optimized in the present work and are presented in Table 3, and SiO_2 was obtained from the previous study by Wu et al. [15].

All the non-standard space groups were converted into standard notation according to the International Union for Crystallography [45].

The Gibbs energy of a stoichiometric phase is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{1}$$

$$H_T^o = \Delta H_{298\ \mathrm{K}}^o + \int_{298\ \mathrm{K}}^{T} C_P\ \mathrm{dT} \tag{2}$$

$$S_T^o = S_{298\ \mathrm{K}}^o + \int_{298\ \mathrm{K}}^{T} \left(C_P/T\right)\ \mathrm{dT} \tag{3}$$

where ΔH_{298K}^o is the standard enthalpy of formation of a given compound from pure elements at 298.15 K (ΔH_{298K}^o of elemental species stable at 298.15 K and 1 atm are assumed to be 0 J mol^{-1} as reference), S_{298K}^o is the standard entropy at 298.15 K, and C_p is the heat capacity of a compound.

The Gibbs energies of all stoichiometric solid, liquid and gas species were described using these equations. In the present study, when the experimental C_p of a compound is unavailable, it was estimated from the stoichiometric amount of constituent oxide phases using the Neumann-Kopp (N-K) rule. If no data available, S_{298K}^o was also estimated using the N-K rule. If necessary, ΔH_{298K}^o and S_{298K}^o were adjusted to reproduce phase diagram or other experimental data.

2.2. Liquid oxide phase

In the present study, the molten oxide phase was described using the MQM. The SRO phenomenon in liquid oxide solution is taken into account by considering second-nearest-neighbor (SNN) pair exchange reactions of cationic species in molten oxide phase, oxygen being the common anionic species. Therefore, liquid components considered in the MQM model in the present study were $LiO_{0.5}$, and SiO_2, because cations like Li^+ and Si^{4+} were considered in pair exchange reaction given below.

In the MQM model, the following quasichemical reaction in liquid oxide phase is considered:

$$(\mathrm{A-A}) + (\mathrm{B-B}) = 2(\mathrm{A-B}) : \Delta g_{AB} \tag{4}$$

where A and B are cationic species in the solution and (A–B) represents a second-nearest-neighbour A–B pair containing oxygen anion in-between. This reaction is identical to the classical silicate network forming/breaking reaction [46], where O^{2-}, O^0, and O^-, respectively. The Gibbs energy of the above reaction Δg_{AB} is the model parameter, which can be expanded as an empirical function of composition. The Gibbs energy of the solution, G^m is given by:

$$G^m = \left(n_A g_A{}^o + n_B g_B{}^o\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB} \tag{5}$$

where n_i and $g_i{}^o$ are the number of moles and molar Gibbs energies of the pure components, respectively, and n_{AB} is the number of moles of (A–B) bonds at equilibrium. ΔS^{config} is the configurational entropy of mixing of random distribution of the (A–A), (B–B) and (A–B) pairs in the one-dimensional Ising approximation:

$$\Delta S^{config} = -R(n_A \ln X_A + n_B \ln X_B) - R\left[n_{AA}\ln\left(\frac{X_{AA}}{Y_A{}^2}\right) + n_{BB}\ln\left(\frac{X_{BB}}{Y_B{}^2}\right) + n_{AB}\ln\left(\frac{X_{AB}}{2Y_AY_B}\right)\right] \tag{6}$$

Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^o{}_{AB} + \sum_{i\geq 1} g_{AB}^{i0} X_{AA}^i + \sum_{j\geq 1} g_{AB}^{0j} X_{BB}^j \tag{7}$$

where $\Delta g^o{}_{AB}$, g_{AB}^{i0} and g_{AB}^{0j} are the model parameters which may be functions of temperature.

In the present study, cationic species (A or B in Eq. (5)–(7)) are Li^+ and Si^{4+}. Therefore, the possible quasichemical reaction represented by Eq. (4), comprises of A nd B as Li^+ and Si^{4+}, respectively. The Gibbs energies of the liquid $LiO_{0.5}$ (1/2 Li_2O) and SiO_2 were taken from the FACT pure substance database [47]. In order to adopt $SiO_4{}^{4-}$ as a network forming unit of SiO_2 in the MQM, Si^{4+} is used as the cationic species which is surrounded by four broken oxygen. On addition of Li_2O, Li^+ cation serves as the $SiO_4{}^{4-}$ network breaker, and pairs with the free oxygen. To reproduce the short range ordering at 0.33 mol fraction SiO_2 the coordination numbers of the cations were set in the model to be 0.688722 for Li^+ and 2.75488 for Si^{4+}. This assumption was based on the position of the minima of the enthalpy of mixing of liquid similar to the Na_2O-SiO_2 system [48] and the Li_4SiO_4 composition with the highest melting point. The SNN coordination numbers (Z) of the species (Li^+ and Si^{4+}) were kept the same as Na^+ and Si^{4+} in the Na_2O-SiO_2 system [48]. The Gibbs energy parameters (Δg_{AB}) of the Li^+-Si^{4+} reactions for the Li_2O-SiO_2 were optimized in the present study. The binary liquid Li_2O-SiO_2 solution ($LiO_{0.5}$-SiO_2 was the actual model species considered in modeling) was described using Eqs. (4)–(7).

2.3. Metallic phase and gas phases

The Gibbs energies of metallic Li and all gas species were taken from FACT pure substance database [47]. As the solubility of oxygen in liquid Li is very small [11], liquid Li was treated as a stoichiometric phase in this study.

3. Critical evaluation and optimization

The unary Li-O is discussed first and the transitions of the compounds and optimized thermodynamic properties are presented in Table 2 and 3, respectively.