COUPLED THERMODYNAMIC MODELING AND EXPERIMENTAL STUDY OF SnO₂-SnO-CaO-SiO₂ SYSTEM

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Contents

Acknowledgements	4 -
Abstract	5 -
Résumé	6 -
1 Introduction	7 -
1.1 Research Objective	7 -
1.2 Organization	7 -
2 Thermodynamic optimization and modeling	9 -
2.1 Thermodynamic optimization	9 -
2.2 Thermodynamic Models	11 -
2.2.1 Phase transitions (Melting and boiling temperature)	11 -
2.2.2 Stoichiometric compounds	12 -
2.2.3 Liquid solution phase	12 -
2.2.3.1 Modified Quasichemical Model	14 -
2.2.4 Metallic and gas phase	16 -
2.3 Extrapolation techniques in ternary liquid solution	16 -
Reference	19 -
3 Critical evaluation and thermodynamic optimization of the Sn-O system	22 -
3.1 Introduction	22 -
3.2 Phase and thermodynamic models	24 -
3.2.1 Stoichiometric compounds	24 -
3.2.2 Liquid solution (liquid SnO-SnO ₂ solution)	25 -
3.2.3 Metallic and gas phases	26 -
3.3 Critical evaluation and optimization	26 -
	- 1 -

3.3.1 Phase transitions and phase diagrams	27 -
3.3.1.1 SnO ₂	27 -
3.3.1.2 SnO	28 -
$3.3.1.3\ Sn_3O_4$ and others	31 -
3.3.1.4 Metallic Sn phase	32 -
3.3.1.5 Liquid oxide solution	33 -
3.3.2 Thermodynamic properties	34 -
3.3.2.1 SnO ₂	34 -
3.3.2.2 SnO	35 -
3.3.2.3 Sn ₃ O ₄	36 -
3.3.2.4 Gas phase	37 -
3.3.2.5 Prediction of Sn ⁴⁺ /Sn ²⁺ ratio in liquid Sn oxide solution	37 -
3.4 Summary	38 -
References	39 -
4 Coupled phase diagram experiment and thermodynamic optimization of the SnO2-	SnO-SiO ₂
system	64 -
4.1 Introduction	64 -
4.2 Key phase diagram study for the SnO ₂ -SiO ₂ system in air	64 -
4.2.1 Crucible materials and preparation	65 -
4.2.2 Experimental procedures and technique	66 -
4.2.3 Experimental results and discussion	67 -
4.3 Phase and thermodynamic models	69 -
4.3.1 Liquid phase	69 -
4.3.2 Metallic and gas phases	71 -

2	1.4 Critical evaluation and optimization of the SnO ₂ -SnO-SiO ₂ system	71 -
	4.4.1 The SnO ₂ -SiO ₂ system in air	72 -
	4.4.2 The SnO-SiO ₂ system at Sn saturation	72 -
	4.4.2.1 Phase diagrams	72 -
	4.4.2.2 Activities	73 -
2	1.5 Prediction of Sn ²⁺ /Sn ⁴⁺ ratio in liquid	74 -
2	1.6 Summary	74 -
F	Reference	76 -
5 C	critical evaluation and thermodynamic optimization of the CaO-SnO-SnO ₂ -SiO ₂ system - $\frac{1}{2}$	88 -
[5.1 Introduction	88 -
[5.2 Phase and thermodynamic models	89 -
	5.2.1 Stoichiometric Compounds	89 -
	5.2.2 Liquid phase	90 -
	5.2.3 Metallic and gas phases	92 -
ŗ	5.3 Critical evaluation and optimization of the SnO ₂ -SnO-SiO ₂ -CaO system	92 -
Į.	5.4 Summary	96 -
F	Reference	97 -
6 0	conclusion 1	05 -

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Abstract

The prediction of thermodynamic properties and phase equilibria of an oxide system can play an important role in the development and understanding of metallurgical, ceramic and geological processes. The thermodynamic databases, developed by a critical evaluation and optimization of all existing thermodynamic properties and phase diagram, can help in understanding the reaction mechanism in various industrial processes and in developing new technology for various industries.

As part of a large thermodynamic database development for glassmaking applications, all solid and liquid oxide phases of the Sn-Si-Ca-O system were critically evaluated and optimized in the present study. All the unary, binary and ternary systems have been critically evaluated and optimized based upon the available phase equilibrium and thermodynamic data. In particularly, the liquid solution was described by the Modified Quasichemical Model with consideration of both SnO and SnO₂. Due to the lack of the phase diagram data, phase diagram experiments of the SnO₂-SiO₂ system were performed for the first time using the quenching method followed by Electron Probe Micro-Analysis and X-Ray Diffraction for phase identification. The optimization results of all systems in this study is self-consistent. All the thermodynamic calculations in the present study were carried out using FactSage[™] thermodynamic software.

Résumé

La prédiction des propriétés thermodynamiques et des équilibres de phase d'un système d'oxyde peut jouer un rôle important dans le développement et la compréhension des procédés métallurgiques, céramiques et géologiques. Les bases de données thermodynamiques, développées par une évaluation critique et une optimisation de toutes les propriétés thermodynamiques existantes et diagramme de phase, peuvent aider à mieux comprendre le mécanisme de réaction dans divers procédés industriels et à développer de nouvelles technologies pour diverses industries.

Dans le cadre d'un grand développement de la base de données thermodynamique pour les applications de fabrication du verre, toutes les phases solides et liquides du système Sn-Si-Ca-O ont été évaluées et optimisées de manière critique dans la présente étude. L'optimisation de tous les systèmes dans cette étude est cohérente avec les principes thermodynamiques. Tout le système unaire, binaire et ternaire a été évalué de manière critique et optimisé en fonction de l'équilibre de phase disponible et des données thermodynamiques. Tous les modèles thermodynamiques pour chaque solution utilisée dans cette étude ont été développés sur la base de leur structure. Les expériences de diagramme de phase du système SnO₂-SiO₂ ont été effectuées pour la première fois en utilisant la méthode de trempe suivie de la Micro-analyse électronique et de la radiographie des rayons X pour l'identification de la phase. Tous les calculs thermodynamiques dans la présente étude ont été réalisés à l'aide du logiciel thermodynamique FactSageTM.

1 Introduction

1.1 Research Objective

In order to better understand the interaction between the glass and tin oxide, the reliable phase diagrams of tin oxide containing systems are required. The main goal of the present study is to develop a self-consistent thermodynamic database with high predictability for the SnO₂-SnO-SiO₂-CaO system. Unary, binary and ternary systems (including all solid and liquid phases) in the SnO₂-SnO-SiO₂-CaO system were critically evaluated and optimized during the present research. For the present FactSage database^[1] does not contain liquid SnO and SnO₂ together for the liquid slag, the present optimization should be started from the SnO, SnO₂ and SnO-SnO₂ systems. The present database is also consistent with the FactSage database for complex industrial applications.

1.2 Organization

The present thesis is composed of the following chapters:

Chapter 2 briefly presents the approach of thermodynamic optimization and all thermodynamic model used to describe solid and liquid phases present in the SnO₂-SnO-SiO₂-CaO system.

Chapter 3 shows the optimization results of the Sn-O binary system based on the critical evaluation of all available literature data for phase equilibria and thermodynamic properties.

Chapter 4 presents the key phase diagram experimental results for the SnO_2 -SiO₂ system in air. Presented are the materials preparation and experimental procedure as well as characterization technique used to measure the phase diagram of the SnO_2 -SiO₂ system in air (PO₂ = 0.21 atm). The optimization results of the SnO_2 -SnO-SiO₂ system, based on the present key experimental data on the SnO_2 -SiO₂ system in air and available literature data on the SnO-SiO₂ system, are also presented. Chapter 5 presents the thermodynamic evaluation and optimization of the SnO₂-SnO-SiO₂-CaO systems. The results of the SnO₂-SiO₂-CaO system in air and the SnO-SiO₂-CaO system in metallic Sn saturation condition are presented.

Chapter 6 summarizes all the work in this study and provides suggestions for the future work.

2 Thermodynamic optimization and modeling

2.1 Thermodynamic optimization

In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as the activity aid in the optimization of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back-calculated. In this way, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from the low-order system to high-order systems can be applied to industrial processes.

The details of the optimization procedure are as below:

1. The system of interest is defined.

2. All available literature data are collected;

a) Thermodynamic data including phase equilibria (phase diagrams, phase equilibria between solid, liquid and gas), calorimetric data (heat capacity, enthalpy of formation and enthalpy of mixing), vapor pressures (obtained by Knudsen cell, Langmuir method), chemical potentials (obtained by electromotive force measurements), activities, etc.,

b) Crystal structural data is used to estimate and predict the thermodynamic properties of pure solid and liquid.

c) Physical properties including magnetism, conductivity, molar volume, etc. might be also helpful for the evaluation of the system.

d) Data from higher order systems of which the system of interest is a sub-system may be useful. For the system without enough data, the interpolation from higher-order systems to lower-order sub-systems is used to determine thermodynamic properties of the system.

3. If data were not available for some systems of interest, it is required to conduct the phase diagram experiments or thermodynamic property measurements.

4. Reliability of data are assessed before the optimization. It happens experimental data from different sources might be different with each other by more than experimental error limits. Furthermore, different types of thermodynamic property and phase equilibrium data could be inconsistent with each other. Hence, all experimental data must be critically and simultaneously assessed according to their experimental techniques, sample preparation, and analytical methods. Sometimes, the accuracy of the experimental data is difficult to evaluate from the description of the experimental technique, and then their consistency or inconsistency can be judged during the optimization of the entire system. Moreover, the accuracy of the experimental data in lower-order systems can be evaluated from the data in higher-order systems by interpolation or extrapolation, and vice versa.

5. An appropriate thermodynamic model representing the Gibbs energy function for a phase should be selected. The model should reflect the structure of the solution phase. In this way, the prediction capacity of the database containing the parameters in low order systems can be achieved in the multicomponent systems.

6. Model parameters for each phase are optimized based on reliable experimental data. The optimized model parameters are stored to construct the thermodynamic database for a given system. At this stage, the optimization software (for example based on a least-square regression

code) may be applied for the optimization of the system. The optimization of model parameters continues until back-calculation reproduces all reliable experimental data within experimental error limits.

7. Thermodynamic property and phase equilibrium data of interest are back-calculated. Based on thermodynamic models and optimized model parameters, any type of thermodynamic calculations becomes feasible. In the present study, the FactSage (version 7.0) thermochemical software^[1] was used for thermodynamic calculations.

2.2 Thermodynamic Models

Thermodynamic model is essential to appropriately represent and predict the thermodynamic properties and phase equilibrium of the materials. In this study, the liquid solution phase was modeled based on the Modified Quasichemical Model. All solid phases in the present studied system was treated as stoichiometric compounds. That is, no solid solution was considered as there is no report on the solid solutions in the present Sn oxide containing system. It should be noted that the optimization of the CaO-SiO₂ system was done previously and the optimized results are available in the FactSage database^[1]. This result is adopted in this study without any modification.

2.2.1 Phase transitions (Melting and boiling temperature)

Figure 2.1 shows the schematic diagram of the Gibbs energies of solid, liquid and gas phases of single component system. Of course, the phase with the lowest Gibbs energy is the most stable phase at a given temperature. At the melting temperature, the Gibbs energy of the liquid phase is equal to that of solid phase. At the boiling temperature, the Gibbs energy of the gas phase is equal to that of liquid phase. Based on these basic thermodynamics, the consistency of the Gibbs energy and the phase transition temperatures of pure stoichiometric phases can be easily tested.

If the Gibbs energies of all phases are known, the transition temperatures like melting and boiling temperatures can be determined too.

2.2.2 Stoichiometric compounds

The Gibbs energy of a pure component is expressed by:

$$G_T^{\circ} = H_T^{\circ} - TS_T^{\circ}$$
(2-1)

$$H_T^{\circ} = \Delta H_{298.15}^{\circ} + \int_{298.15}^T C_p dT$$
(2-2)

$$S_T^{\circ} = S_{298.15}^{\circ} + \int_{298.15}^{T} C_p / T dT$$
(2-3)

where G_T° , ΔH_T° and ΔS_T° are respectively the standard Gibbs energy, enthalpy and entropy of a given stoichiometric compound at the absolute temperature T. $\Delta H_{298.15}^{\circ}$ is the standard enthalpy of formation of the compounds from pure elements at 298.15 K ($\Delta H_{298.15}^{\circ}$ of elemental species stable at 298.15 K and 1 atm are assumed to be 0 J/mol as reference). $S_{298.15}^{\circ}$ is the standard entropy at 298K, and C_p is the heat capacity.

In this study, the Gibbs energy of the pure components including the solid and liquid SnO, solid Sn₃O₄, and the solid and liquid SnO₂ have been optimized based on the experimental thermodynamic properties and phase equilibrium data. In the SnO-SiO₂ and SnO₂-SiO₂ system, there is no binary compounds reported. In SnO₂-CaO-SiO₂ and SnO-CaO-SiO₂ systems, the Gibbs energy of the two binary compounds CaSnO₃ and Ca₂SnO₄ and two ternary compounds CaSnSiO₅ and Ca₃Si₂SnO₉ have been optimized to reproduce the experimental phase equilibrium and activity data.

2.2.3 Liquid solution phase

The standard molar Gibbs energy of a pure component i is written as:

$$g_i^{\circ} = h_i^{\circ} - T s_i^{\circ}$$
(2-4)

where g_i° , h_i° and s_i° represent the standard Gibbs energy, enthalpy and entropy of i respectively and T is the absolute temperature.

When two components 1 and 2 are mixed, the Gibbs energy of the solution depends upon the interaction between 1 and 2. For an ideal solution where there is no interaction between 1 and 2, the solution Gibbs energy is written as:

$$G^m = \left(n_1 g_1^\circ + n_2 g_2^\circ\right) - T\Delta S^{conf}$$
(2-5)

where G^m is the Gibbs energy of solution, g_i° is the molar Gibbs energy of the component i, and ΔS^{conf} is the configurational entropy obtained by randomly mixing n_1 moles of 1 and n_2 moles of 2 on the same sublattice. It can be written as:

$$\Delta S^{conf} = -RT(n_1 \ln X_1 + n_2 \ln X_2)$$
(2-6)

For ideal solutions, interactions between 1 and 2 are zero. However, for non-ideal solution, interactions between components are not zero, which are quantified as the molar excess Gibbs energy of the solution (g^E). Therefore, the Gibbs energy of the non-ideal solution is given by:

$$G^{m} = \left(n_{1}g_{1}^{\circ} + n_{2}g_{2}^{\circ}\right) - T\Delta S^{conf} + (n_{1} + n_{2})g^{E}$$
(2-7)

 g^E can be expanded as a polynomial function of the composition:

$$g^{E} = \sum q_{12}^{ij} X_{1}^{i} X_{2}^{j}$$
(2-8)

where X_1 and X_2 are the more fractions of components 1 and 2 in the solution, and $q_{12}^{ij}(=a + bT + cT^2)$ is the excess interaction parameters. If only q_{12}^{11} is used to describe the thermodynamic properties of a solution, it is known as a "regular" solution.

2.2.3.1 Modified Quasichemical Model

When the solution deviates largely from ideal solution, the configuration entropy is not anymore close to ideal solution. In order to well describe the configurational entropy of the solution with strong short range ordering, Pelton^[2] developed the Modified Quasichemical Model (MQM). In the model, the real structure of solutions with short rang ordering is took into account and the classical quasichemical model is modified by improving the configurational entropy term of the model to adequately represent the thermodynamic properties of the liquid phase.

In the MQM, the following second-nearest-neighbor(SNN) pair exchange reaction between the cationic species A and B in the oxide melt is considered:

$$(A - A) + (B - B) = 2(A - B); \qquad \Delta g_{AB}$$
 (2-9)

where A and B are cationic species in the solution and (A-B) represents a SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the change in the non-configurational Gibbs energy due to the formation of 2 moles of (A-B) pairs. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{\circ} + n_{B}g_{B}^{\circ}\right) - T\Delta S^{conf} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(2-10)

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

$$\Delta S^{conf} = -RT(n_A \ln X_A + n_B \ln X_B) - R(n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2}\right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B}\right))$$
(2-11)

where X_A and X_B are the mole (or site) fractions, X_{AA} , X_{BB} and X_{AB} are pair fractions and Y_A and Y_B are coordination-equivalent fractions, which are given as the following:

$$X_A = \frac{n_A}{n_A + n_B} = 1 - X_B \tag{2-12}$$

$$X_{ij} = \frac{n_{ij}}{n_{AA} + n_{AB} + n_{BB}}$$
(2-13)

$$Y_A = \frac{n_A Z_A}{n_A Z_A + n_B Z_B} \tag{2-14}$$

where Z_A and Z_B are the coordination number of A and B.

 Δg_{AB} is expanded as an empirical function of composition in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{i \ge 1} g_{AB}^{0j} X_{BB}^{j}$$
(2-15)

where Δg_{AB}° , Δg_{AB}^{i0} and Δg_{AB}^{0j} are the parameters of the model which may be functions of temperature.

It should be noted that Equation (2-11) is accurate only in one-dimentional lattice (Ising Model), and it provides an approximation in three dimensional lattices, in which Z_A and Z_B are given the smaller value than the actual value.

2.2.4 Metallic and gas phase

To calculate the metallic Sn saturation condition, the solid and liquid Sn from FACT pure substance database^[1] were considered. Particularly, for the Sn saturation in the Sn-O system, the Sn solution containing oxygen (FTmisc SnLQ) was considered for more accurate phase equilibrium description. The Gibbs energies of gas species were taken from FACT pure substance database^[1].

2.3 Extrapolation techniques in ternary liquid solution

Thermodynamic properties of ternary systems can be estimated from binary model parameters using 'geometric' models. This was elaborated by Pelton^[3].

The Gibbs energy of a ternary solution can be expressed as:

$$g_{sol} = \sum g_i^0 x_i - T\Delta S^{mix} + g^E \tag{2-16}$$

where g_{sol} and g_i^0 are the molar Gibbs energies of the solution and pure component i, respectively, and ΔS^{mix} is the entropy of mixing. g^E may contain the excess Gibbs energy extrapolated from binary model parameters and ternary excess parameters.

Several "geometric" models have been proposed to predict the thermodynamic properties of a ternary system from optimized binary model parameters. Pelton^[3] presented a detail description of these models which are illustrated in Figure 2.2. The selection of geometric models depends upon the nature of relevant binary systems. In all these models, the excess Gibbs energy (g^E) of a solution at any composition p can be estimated from the binary interaction parameter or the excess Gibbs energies of the binary sub-system at points a, b and c.

The excess Gibbs energy of a ternary solution can be written as:

$$g^{E} = \frac{X_{12}\Delta g_{12}}{2} + \frac{X_{13}\Delta g_{13}}{2} + \frac{X_{23}\Delta g_{23}}{2} + (\text{ Ternary terms})$$
(2-17)

where Δg_{ij} is the Gibbs energy change for the reaction:

$$i - i + j - j = 2(i - j)$$
 (2-18)

If ternary data are available, 'ternary terms' can be used to estimate the ternary interactions. However, precautions are taken to keep these terms as small as possible, otherwise doubts are cast upon the predictive ability of the model. These ternary polynomial terms are identically zero in the three binary sub-systems. The ternary term may be introduced using the function below:

$q_{123}^{ijk}X_1^iX_2^jX_3^k$

where q_{123}^{ijk} is an empirical coefficient.

The Kohler and Muggianu models in Figure 2.2 are "symmetric" models, whereas the Kohler/Toop and Muggianu/Toop models in Figure 2.2 are "asymmetric" models. If component 2 and 3 are chemically similar while component 1 is chemically different, then asymmetric model is more physically reasonable than symmetric model. A symmetric model and an asymmetric model will give very different results, when g^E is large and Δg_{ij} depends strongly upon compositions. Pelton^[3] showed that if the models are used improperly, then it can lead to thermodynamically inconsistent and unjustifiable results.

Chartrand and Pelton^[4] gave a detailed description of the estimation of the excess Gibbs energies in a ternary solution from binary model parameters when liquid phase is modeled by MQM. If the three binary subsystems of a ternary system have been optimized and the parameters are in the form of Equation (2-15), and symmetric Kohler-type approximation is chosen for the 1-2 subsystem, then Δg_{12} can be written:

$$\Delta g_{12} = \Delta g_{12}^0 + \sum_{l \le (i+j)} g_{12}^{ij} \left(\frac{X_{11}}{X_{11} + X_{12} + X_{22}} \right)^i \left(\frac{X_{22}}{X_{11} + X_{12} + X_{22}} \right)^j$$
(2-19)

If Toop-type approximation is chosen, then Δg_{12} can be written as:

$$\Delta g_{12} = \Delta g_{12}^0 + \sum_{l \le (i+j)} g_{12}^{ij} X_{11}^i (X_{22} + X_{23} + X_{33})^j$$
(2-20)

To estimate the Gibbs energy of ternary or multicomponent solutions from the optimized lowerorder parameters, FactSage thermodynamic software^[1] allows users to use any of these "geometric models" which increases the flexibility and the ability to find out the Gibbs energy.

Reference

[1] www.FactSage.com. FactSage 7.0 version

[2] Pelton, A.D., Degterov, S.A., Eriksson, G., Robelin, C. and Dessureault, Y., 2000. The modified quasichemical model I—binary solutions. Metallurgical and Materials Transactions B, 31(4), pp.651-659.

[3] Pelton, A.D., 2001. A general "geometric" thermodynamic model for multicomponent solutions. Calphad, 25(2), pp.319-328.

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Figure 2.1 Melting and boiling temperature



Figure 2.2 Some geometric models used for estimating ternary thermodynamic properties from the optimized binary data (From Pelton^[3])

3 Critical evaluation and thermodynamic optimization of the Sn-O system

3.1 Introduction

Tin (Sn) is a desirable metal with increasing technological and economic importance. Almost all the commercial tin is extracted from Cassiterite (SnO₂)^[1]. Cassiterite is often in granites, but the phase relations of such tin-bearing granite are largely unknown. To understand more information on the Sn-O system under widely different temperature ranges and oxygen partial pressure conditions, many studies on phase equilibria ^[2-34] and thermodynamic properties^[23,32,33, 35-54] of the Sn-O system have been conducted. However, available experimental results by different authors are often inconsistent and incomplete in terms of the temperature and composition. Accurate control of the oxygen partial pressure to determine the valency of Sn oxide, the high vapor pressure of SnO₂ and the hygroscopic nature of Sn-rich components are among challenges bringing about experimental difficulties in better understanding of this system.

The phase diagram of the Sn-O system was investigated by many researchers as shown in Figure 3.1. As shown in the diagrams, there are a lot of inconsistency and contradictions in the available phase diagrams: (i) the excess solubility of oxygen (O) in the liquid metallic Sn, (ii) the boiling temperature of liquid Sn, (iii) the melting and boiling temperature of SnO, (iv) the melting and boiling temperature of SnO₂, (v) excess solubility of Sn in liquid SnO, and (iv) the different kinds of stable compounds and their thermal stability range.

In 1947, the original phase diagram of the Sn-O system in Figure 3.1 (a) was constructed by Spandau and Kohlmeyer^[2]. The first feature of the diagram is that the Sn₃O₄ coexists with Sn or SnO₂. The second feature is liquid SnO which appears above 1040 °C in equilibrium with Sn and SnO₂. In addition, the excess solubility of liquid Sn in liquid SnO and the solubility of O in liquid Sn were not clearly determined. The boiling temperature of SnO was predicted to be 1700 °C and the melting and boiling temperature of SnO₂ was estimated to be 2000 °C and 2500 °C,

respectively. Later, Spandau and Kohlmeyer^[3] modified his original phase diagram of the two liquid field in 1949, as shown in Figure 3.1 (b). The stable field of gas Sn was added to reflect more reasonable phase diagram. This phase diagram is referred by Hansen and Elliott^[4] and Massalski et al.^[5]. Drábek and Stemprok^[6] investigated the low-temperature region of the Sn-O system in 1974 and presented the phase diagram as shown in Figure 3.1 (c). In the diagram, SnO, Sn₃O₄ and SnO_2 are considered as the stable solid compounds. The solid SnO is stable from 100 °C to 270 °C, and Sn₃O₄ is stable from unknown temperature to 450 °C. This phase diagram appears also on the paper of Moh^[7]. In 1980, Kuxmann and Dobner^[8] revised the phase diagram proposed by Spandau and Kohlmeyer^[2, 3], as shown in Figure 3.1 (d). Based on their experimental measurements, the solubility of O in the liquid Sn has been changed, and the temperature for the eutectic point for liquid oxide to metallic liquid Sn and solid SnO₂ was revised to be 1045 °C. In this phase diagram, the Sn₃O₄ was eliminated because it was considered to be metastable. This phase diagram is also referred by Roth et al.^[9] Paparoni^[10] summarized the previous experimental works and constructed the revised phase diagram of the Sn-O system in 2000, as shown in Figure 3.1 (e). The melting and boiling temperature of SnO₂ was alternated to be 1625 °C and 1730 °C, respectively. The boiling temperature of SnO was proposed to be 1430 °C and the eutectic temperature of liquid oxide to metallic liquid Sn and solid SnO2 was 1127 °C. Cahen et al.^[11] performed in 2003 the thermodynamic assessment of the Sn-O system based on the phase diagram data. He also reported DSC analysis results for the thermal stability of Sn₃O₄ (stable above 137 °C) and the eutectic temperature of liquid oxide to metallic liquid Sn and solid SnO₂ at 1036 °C. However, the assessment was incomplete and many thermodynamic data and phase diagram data in the Sn-O system were not properly evaluated and not taken into account in the thermodynamic assessment. This phase diagram was referred later by Okamoto^[12].

Although the Sn-O binary system is the most fundamental system of the Sn oxide containing system, no complete and consistent thermodynamic assessment of the Sn-O system including all phase diagrams and thermodynamic properties of all phases has been performed yet. Therefore, this study focuses on the complete review, critical thermodynamic evaluation and optimization of all the reported experimental phase equilibrium and thermodynamic data on the Sn-O system.

The present study of the Sn-O system lays the foundation to study the phase equilibria of the multicomponent SnO-SnO₂-SiO₂-CaO-Al₂O₃-Fe₂O₃-FeO system which is important for various pyrometallurgical applications in glass-making, cement-making and steel-making, and geochemistry^[6, 55-57].

3.2 Phase and thermodynamic models

3.2.1 Stoichiometric compounds

The Gibbs energy of a stoichiometric component is expressed by:

$$G_T^{\circ} = H_T^{\circ} - TS_T^{\circ} \tag{3-1}$$

$$H_T^{\circ} = \Delta H_{298.15}^{\circ} + \int_{298.15}^T C_p dT$$
(3-2)

$$S_T^{\circ} = S_{298.15}^{\circ} + \int_{298.15}^{T} C_p / T dT$$
(3-3)

where G_T° , ΔH_T° and ΔS_T° are respectively the standard Gibbs energy, enthalpy and entropy of a given pure component at the absolute temperature T. $\Delta H_{298.15}^{\circ}$ is the standard enthalpy of formation of the pure component from pure elements at 298.15 K. $\Delta H_{298.15}^{\circ}$ of elemental species stable at 298.15 K and 1 atm are assumed to be 0 J/mol as reference. $S_{298.15}^{\circ}$ is the standard entropy at 298.15 K and C_p is the heat capacity as a function of the temperature. With the available information of $\Delta H_{298.15}^{\circ}$, $S_{298.15}^{\circ}$ and C_p , the one set of G_T° can be determined. Also, the available information of G_T° can be used to derive the $\Delta H_{298.15}^{\circ}$, $S_{298.15}^{\circ}$ and C_p .

In the present study, the Gibbs energies of the SnO (solid and liquid), SnO₂ (solid and liquid) and Sn₃O₄ (solid) were determined using these thermodynamic equations.

3.2.2 Liquid solution (liquid SnO-SnO₂ solution)

No solid solution is reported in the Sn-O system. The liquid solution in the Sn-O system was described using the Modified Quasi-chemical Model (MQM)^[58]. In the MQM, short range ordering (SRO) of second-nearest-neighbor (SNN) cation is taken into account in the liquid solution. This model has been extensively used for the description of liquid oxide solution, and to keep the consistent description of multicomponent slag containing Sn oxide, the MQM is used to describe liquid oxide solution in this study.

In the MQM, the following quasi-chemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B); \qquad \Delta g_{AB}$$
 (3-4)

where A and B are cationic species Sn^{2+} and Sn^{4+} in the SnO-SnO₂ solution and (A-B) represents an SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{i \ge 1} g_{AB}^{0j} X_{BB}^{j}$$
(3-5)

where Δg_{AB}° , Δg_{AB}^{i0} and Δg_{AB}^{0j} are the parameters of the model which may be functions of temperature.

Then, the Gibbs energy of the solution is given in the MQM by:

$$G^{m} = \left(n_{A}g_{A}^{\circ} + n_{B}g_{B}^{\circ}\right) - T\Delta S^{conf} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(3-6)

where n_i and g_i° are the numbers of moles and molar Gibbs energies of the pure components (that is, liquid SnO and SnO₂ in this study), n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{conf} is the configurational entropy for the random distribution of the (A – A), (B - B) and (A - B) pairs in the one dimensional Ising model^[59]. In the configuration entropy, the coordination numbers of Sn⁴⁺ and Sn²⁺ were set to be 2.7529, and 1.3774, respectively, which is the same as the same charged cations like Si⁴⁺ and Ca²⁺.

In this study, the SnO-SnO₂ is close to the ideal solution and the Gibbs energy of Sn²⁺-Sn⁴⁺ quasichemical reaction was optimized using a small temperature-independent model parameter: $\Delta g_{Sn^{2+}-Sn^{4+}} = 9000.0 \text{ J/mol}$. The details of the optimization process will be described below.

3.2.3 Metallic and gas phases

To calculate the metallic solid and liquid Sn saturation condition, solid Sn and liquid metallic Sn-O solution were taken from the previous thermodynamic assessment^[60]. In particularly, liquid Sn can dissolve considerable amount of oxygen to form liquid metallic Sn-O solution. Heuzey and Pelton^[60] already performed the critical evaluation of liquid Sn solution containing oxygen in binary and multicomponent system. This result is stored in FactSage FTmisc-SnLQ database, and FACTPS database^[61]. The Gibbs energies of gas species (O₂, Sn, SnO, SnO₂, Sn₂O₂, Sn₃O₃ and Sn₄O₄) were taken from FACT pure substance database^[61]. The $\Delta H_{298.15}^{\circ}$, $S_{298.15}^{\circ}$ and C_p of all the metallic and gas phases taken from FACT pure substance database are listed in Table 3.1.

3.3 Critical evaluation and optimization

During the optimization, at first, all the phase diagram and thermodynamic properties data reported in Sn-O system were critically evaluated and the accuracy and reliability of all the available experimental data were assessed. Then, a set of Gibbs energies of all the stoichiometric components and solution model parameters of liquid metallic Sn and liquid Sn oxide solutions were obtained to reproduce all reliable thermodynamic properties and phase diagram data within their experimental error limits.

All the available solid Sn oxides with their crystal structures were listed in Table 3.2. The phase diagram of the Sn-O system at 1atm total pressure calculated from the present models with optimized parameters was shown in Figure 3.2. Optimized invariant reactions were listed in Table 3.3-3.7 along with all available experimental data. The optimized model parameters for the stoichiometric compounds were listed in Tables 3.8 in comparison with all experimental thermodynamic properties available in literature. The details of literature reviews and optimized results are presented below.

3.3.1 Phase transitions and phase diagrams

3.3.1.1 SnO₂

In the Sn-O system, the stannic oxide (SnO₂) is the most stable in air among all the oxides. The melting and boiling behavior of SnO₂ has been investigated by many researchers and their data are summarized in Table 3.3 and Table 3.4 and presented in the Sn-O phase diagram (see Figure 3.2).

The melting temperature of SnO₂ was estimated by Spandau and Kohlmeyer^[2] to be 2000 °C, but no detail information about the estimation methods was provided. This value was used in the construction of the previous phase diagrams shown in Figure 3.1 (a), (b), (d) and (f). Ruff^[13] investigated the melting behavior of SnO₂ by heating SnO₂ in zirconia (ZrO₂) crucible under an atmosphere of nitrogen (N₂). In the experiment, it was found that SnO₂ came to melt and decomposed to liquid Sn at 1625 °C. Barczak and Insley^[14] investigated the melting temperature of SnO₂ in sealed Platinum (Pt) crucible using the differential thermal analysis (DTA) technique and comparing favorably with the quenching data. It was reported the melting temperature to be 1630 \pm 5 °C which almost agreed with the value measured by Ruff^[13]. By far, their measurement seems to be the most reliable for the melting temperature of SnO₂ and their result was taken in this study. With regarding the boiling temperature of SnO₂, Ruff^[13] reported the boiling point to be 2250 °C, where the stained tin oxide vapored to produce greenish color in the furnace. No more detail was available in his paper and the reliability of this measurement is questionable. Spandau and Kohlmeyer^[2] estimated the boiling temperature of liquid SnO₂ to be 2500 °C from their vapor pressure measurements of SnO2 and Sn at 1500 °C. As the vapor pressure of SnO₂ was slightly lower than that of Sn according to their experiments, they concluded that the boiling temperature of SnO₂ should be higher than that of Sn (2270 °C according to their work). However, their estimation has critical problem. At the experimental temperatures, the SnO₂ was in solid state rather than liquid state, while Sn was in liquid state, so their vapor pressure measurement cannot give proper estimation of the boiling temperature of liquid SnO₂. Colin et al.^[15] studied the evaporation of SnO₂ at the temperatures from 981 to 1265 °C using the mass-spectrometer. The partial pressure of gas species like SnO, Sn_2O_2 and O_2 in equilibrium with solid SnO₂ were measured. Paparoni^[10] extrapolated these partial pressure data to higher temperature and calculated the boiling temperature to be 1830 °C. However, there is one critical problem in this calculation. As the experimental data of Colin et al. was obtained from gas/solid SnO₂ equilibration, strictly speaking the results calculated by Paparoni was the sublimation point rather than boiling point. In addition, the accuracy in the temperature dependence extrapolated from the results of Colin et al. at 981 - 1265 °C to higher temperature is rather doubtable. Therefore, it can be said that the boiling temperature of SnO₂ available in literature is still not accurate. In present work, the boiling temperature was determined to be 1989 °C based on the optimized Gibbs energy of the liquid SnO₂ and available thermodynamic data of gases phase^[61]. This will be discussed below in details.

3.3.1.2 SnO

Stannous oxide (SnO) is also known as romarchite. The stability of the solid SnO has been investigated by many researchers as shown in Table 3.5. Solid SnO is decomposed to Sn and SnO₂ with increasing temperature, and then liquid SnO is produced again from Sn and SnO₂ at high

temperature^[2, 3, 6, 10, 11], as shown in Fig 3.1 (g). That is, solid SnO does not directly transform to liquid SnO at 1 atm.

Platteuw and Meyer^[16] prepared SnO sample and heated to the temperatures between 300 °C and 550 °C at 1 atm total pressure. After quenching the sample, the phase was analyzed by XRD. According to his experiments, SnO was decomposed to the mixture of Sn and SnO2 at all the experimental temperature range. That is, the decomposition temperature of SnO is lower than 300 °C. Drábek and Stemprok^[6] reported that the SnO was the stable at 200 °C and 255 °C and it is decomposed to Sn₃O₄ and Sn at 290 °C from XRD and SEM observation. Koike et al.^[17] determined the decomposition reaction at 285 °C using quenching experiments followed by XRD phase analysis. There are also some debates^[6, 16] on whether SnO is the stable at room temperature or not. Considering the natural occurrence of SnO and the stability of SnO at high pressure measured by Drábek and Stemprok^[6] and Paparoni^[10], SnO is considered to be stable below 285 °C^[24] in the present study.

The eutectic reaction of liquid metallic Sn and solid SnO₂ produces nearly a stoichiometric liquid SnO^[2, 3, 6, 10, 11]. However, there is a certain inconsistency in the eutectic temperature in literature, as listed in Table 3.6. This inconsistency was mainly caused by the contamination from the crucible materials which decreases the melting temperature of the SnO. Spandau and Kohlmeyer^[2, 3] prepared the sample of mixture of Sn and SnO in alumina crucible and determined the solidification temperature of molten SnO (cooling process) to be 1040 °C from cooling curve analysis, which was used in the phase diagrams shown in Figure 3.1 (a) and (b). Platteeuw and Meyer^[15] found the liquid Sn and solid SnO₂ were stable at 1127 °C, which meant the liquid SnO should be stable at the temperature higher than 1127 °C. Takeda et al.^[18] found the transitions at 1122 °C in heating and 1090 °C in cooling process from their DSC experiments. In their experiment, 0.78 wt.%-2.52 wt.% MgO from the crucible dissolved in these samples. Carbó-Nóver and Richardson^[19] conducted the phase stability experiment of SnO at temperature from 900 °C and 1250 °C in Al₂O₃ crucible under argon (Ar) atmosphere and reported that the liquid SnO was stable above 1100 °C from quenched samples analyzed by XRD. However, they reported

about 3.7 wt.% Al₂O₃ dissolved into the liquid at 1110 °C - 1250 °C, which indicated the melting point of pure SnO would be higher than1100 °C. Drábek and Stemprok^[6] performed quenching experiment in Al₂O₃ crucible over 200 °C to 1095 °C, and reported the melting temperature of the SnO to be 1080 °C. Although there was no analysis of the amount of Al₂O₃ dissolving into the sample, the results of Carbó-Nóver and Richardson^[19] tell that there should be contamination of Al_2O_3 which decreases the melting temperature of SnO. Using DTA and XRD phase analysis, Kuxmann and Dobner^[8] determined the melting point of SnO. They used the different crucibles in DTA. The melting temperatures were determined to be 1030 °C in MgAl₂O₄ crucible, 1034 °C in ZrO₂ crucible, and 1045 °C in Al₂O₃ crucible. Cahen et al.^[11] reported the value to be 1040 °C by DSC experiments, but the details of experiments such as crucible materials were not given. Most recently, Xu et al.^[20] determined the melting temperature of SnO to be between 1125 °C and 1130 °C by quenching experiment followed by EPMA phase analysis. In particularly, they placed the sample on the sintered SnO₂ substrate in order to eliminate the contamination from other oxide crucible. Moreover, in their experiments, the holding time of sample at a given temperature was long enough to allow the sample to reach full equilibrium state. Considering the possible change of melting temperature of SnO by crucible materials, the results by Xu et al. was considered as the most reliable data in the present study.

The conflicting results on the boiling point of SnO in literature were summarized in Table 3.7. All the available published boiling temperatures of the SnO were estimated from vapor pressure data of SnO^[2, 10, 15, 16, 21]. Spandau and Kohlmeyer^[2] roughly estimated the boiling temperature of the SnO to be about 1700 °C. They found that evaporation rate of SnO is higher than Sn and SnO₂ at the same experimental temperature and sample condition, and therefore they concluded that the boiling point of SnO (1700 °C) should be lower than that of Sn (2270 °C) and SnO₂ (2500 °C). Their result was preferred by the phase diagram in Figure 3.1 (a), (b) and (d). Later, Spandau and Ullrich^[31] determined the boiling temperature of SnO to be 1425°C by extrapolation of the vapor pressure data of SnO gas over the Sn and SnO₂ mixture at the temperature range between 1007 °C and 1127 °C. Platteeuw and Meyer^[16] calculated the boiling temperature to be 1394°C from the vapor pressure data of SnO gas over the Sn and SnO₂ mixture at the temperature to from the temperature from

1007 °C to 1127 °C. However, both results^[16,21] are unreliable because the vapor pressure of SnO measured in their experiments were not in the liquid SnO state. Moreover, both studies assumed that SnO is the only gas species, while Colin et al.^[15] found the mixture of gas species of SnO, Sn₂O₂, Sn₃O₃ and Sn₄O₄ using the mass spectrometer. Paparoni^[10] made the estimation of the boiling temperature of the SnO by extrapolation the vapor pressure measurement of Colin et al.^[15]. However, this extrapolation by Paparoni is again wrong because Colin et al.'s experiments were performed at 807°C to 921°C where no liquid SnO is stable.

In the present work, the boiling temperature of the SnO was calculated to be 1718 °C from the optimized Gibbs energy of the liquid SnO and gas phase.

3.3.1.3 Sn₃O₄ and others

The existence and its thermal stability of Sn₃O₄ have been debated by many authors. Spandau and Kohlmeyer^[2, 3] determined the Sn₃O₄ to be stable up to 1040 °C, as shown in Figure 3.1 (a) and (b). In their experiments, the SnO was heating under N₂ atmosphere between 600 °C and 1000 °C and the quenched samples were analyzed by chemical method. It was observed that at the experimental temperature the SnO decomposed into the product with the molar ratio of Sn:SnO₂:SnO=1:1:2. Lawson^[22] heated solid SnO₂ in an atmosphere of N₂ at the temperature between 427 °C and 777 °C, and the product was analyzed by XRD and Mossbauer spectroscopy. His experimental results indicated that Sn₃O₄ was metastable compound at high experimental temperature, while the Sn₃O₄ was stable compound at the low experimental temperature around 427 °C. Unfortunately, the accurate stability range of Sn₃O₄ was not determined. Drábek and Stemprok^[6] conducted experiments between 200 °C and 410 °C, and between 450 °C and 1095 °C. It was found that Sn₃O₄ was stable compound between 290 °C and 410 °C and unstable below 255 °C and above 450 °C. This work was referred to the phase diagram of Figure 3.1 (c). Yang et al.^[23] found that Sn₃O₄ was the stable at 423 °C and 458 °C using chemical analysis (coulometric titration) and XRD. Koike^[17] performed the quenching experiment followed by XRD analysis from 285 °C to 800 °C, and reported the Sn₃O₄ as a stable phase at temperature between 285 °C and

512 °C. In the present study, therefore, 512 °C was taken as the highest stable temperature of Sn_3O_4 . Cahen et al.^[11] determined that the lowest temperature for Sn_3O_4 to be stable was 137 °C. They performed the DSC experiment of the SnO and SnO_2 mixture between 50 °C to 250 °C and found the beginning of decomposition reaction of Sn_3O_4 to be 137 °C. This result was taken in the present study for the lowest stability temperature of Sn_3O_4 .

Besides the SnO, Sn_3O_4 and SnO_2 , the existence of other compounds in the Sn-O system such as Sn_2O_3 and Sn_5O_6 were reported in the literature^[6, 7, 24, 25, 26]. However, there was no strong evidence to prove Sn_2O_3 and Sn_5O_6 to be the stable compounds in the Sn-O system at 1 atm total pressure.

3.3.1.4 Metallic Sn phase

The melting temperature 231.9 °C of the Sn metal was well studied by McLarent^[27] and accepted as the standard for the international practical temperature scale of 1976^[28]. For the boiling temperature of the Sn, two different values 2270 °C and 2603 °C were reported by Spandau and Kohlmeyer^[2] and Cahen et al.^[11] respectively. With the well optimized Gibbs energy of the liquid and gas Sn from FACT pure substance database^[61], the boiling temperature of the Sn in the present study was determined to be 2603 °C.

The solubility of the oxygen in the liquid Sn in equilibrium with the liquid SnO was investigated by many researchers^[8, 19, 30, 31]. As can be seen in Figure 3.3, the experimental data are consistent at the low temperature where liquid Sn is in equilibrium with solid SnO₂, while the results are quite scattered at high temperature in equilibrium with liquid SnO. This discrepancy at high temperature results most probably from the contamination of liquid SnO by oxide crucible materials, as discussed above in section 3.3.1.2. That is, the solubility of impurity in liquid SnO can decrease the activity of liquid SnO and therefore the oxygen solubility in liquid Sn can be reduced: Sn(I) + O(I) = SnO(I). The results of Carbó-Nóver and Richardson^[19] were preferred in this study because they made the correction of oxygen solubility considering the solubility of 4 wt.% Al₂O₃ in the liquid SnO. It should be noted that the oxygen solubility measured by Carbó-Nóver and Richardson is the largest among the experimental data, which also supports our explanation for the scatters. In fact, because the optimization results of Heuzey and Pelton^[60] for the oxygen solubility in liquid Sn is accurately describe the results, as shown in Fig. 3.3, their model parameters are taken in this study without any modification.

3.3.1.5 Liquid oxide solution

Liquid oxide solution extends from liquid SnO₂ to liquid SnO composition. However, liquidus of SnO₂ in this Sn-O system is not investigated yet. Many previous phase diagrams in Fig. 3.1 indicate that there would be a noticeable excess solubility of Sn to liquid SnO (extension of liquid Sn oxide solution toward metallic Sn side), which is speculation and no experimental data at 1 atm total pressure support such excess Sn solubility. In fact, a couple of studies proved that a small amount of metallic Sn and liquid Sn oxide co-exist at a stoichiometric SnO composition. This is completely opposite to the speculated phase diagrams showing an excess Sn solubility to liquid Sn oxide. For example, Carbó-Nóver and Williamson^[29] carefully examined the composition of liquid Sn oxide using chemical analysis after the equilibration with liquid Sn. They reported that non-stoichiometric Sn oxide (SnO-SnO2) was in equilibrium with liquid Sn, and the non-stoichiometry of Sn oxide was about SnO_{1.04} even at 1250°C (that means that about 4 atomic % of SnO₂ could be dissolved in liquid SnO under liquid Sn saturation condition).

In order to reproduce general phase boundary of liquid Sn oxide solution, and the eutectic reaction of liquid Sn oxide to liquid metallic Sn and solid SnO₂, a small temperature independent term was optimized: $\Delta g_{Sn^{2+}-Sn^{4+}} = 9000.0$ J/mol. The calculated eutectic composition is 0.5016 mole fraction of oxygen, and the deficiency of Sn in liquid SnO (Sn_{1- δ}O) is δ = 0.0032 at 1125 °C.

3.3.2 Thermodynamic properties

3.3.2.1 SnO₂

The optimized thermodynamic properties such as enthalpy, entropy, heat capacity and Gibbs energy of the SnO₂ and all the relevant data from literature are summarized in Table 3.8, and also compared in Figure 3.5 and 3.6. The enthalpy of formation of solid SnO₂ was measured by Lavut et al.^[35, 36] to be -557.63 kJ/mol and Humphrey and O'Brien^[37] to be -580.82 kJ/mol using the combustion calorimetry. In the present study, it is found that the results of Lavut is more consistent with the experimental Gibbs energy of formation data. The low temperature heat capacity was determined by Zhogin et al.^[38] from 5 K to room temperature, while the results of Millar^[39] was only available from 70 K. Both results are consistent each other, and also consistent with the high temperature heat capacity data measured by Kapustinskii et al.^[47], as shown in Figure 3.5. The standard entropy at 298 K of SnO₂ (48.96 J/mol-K) calculated by Zhogin^[40] from their low temperature heat capacity data was taken in this study, and the heat capacity function of SnO₂ was determined based on all the heat capacity data in Fig. 3.5.

The Gibbs energy of solid SnO₂ was measured by many researchers^[41-45] using the electro-motive force (emf) measurement^[42-45] and gas equilibration^[41] techniques, as shown in Figure 3.6. For the gas equilibration method, Emmett and Shultz^[41] measured the partial pressure of H₂O and total pressure over the reaction SnO2(s) + 2H2(g) = Sn(I) + H2O(g). Then the equilibrium constant at the certain temperature was calculated, which was used to calculated the Gibbs energy of this reaction and Gibbs energy formation of SnO₂. In the emf measurements, the oxygen partial pressure for the chemical reaction of the Sn(I) + O2(g) = SnO2(s) was measured. It should be noted that the liquid Sn is not pure Sn, but contains oxygen impurity, as shown in Fig. 3.4. However, all the previous experimental study using the emf technique considered the liquid Sn as pure liquid Sn. Strictly speaking, therefore, the previous analyses contain a certain error in the Gibbs energy of formation of SnO₂ (0.0076 kJ/mol at 1000 K). In the present study, liquid Sn containing impurity oxygen is considered in the calculation. As can be seen in Fig. 3.6, all the experimental data are well reproduced in the present study, which means the optimized

standard enthalpy and entropy at 298 K and heat capacity of solid SnO₂ discussed above are consistent with the Gibbs energy data of SnO2.

When it comes to the liquid SnO₂, there has been no direct experimental study on the enthalpy, entropy, heat capacity and Gibbs energy of the liquid SnO₂. Therefore all the thermodynamic properties of liquid SnO₂ were determined by the following steps. For the heat capacity of the liquid SnO₂, the function reported by Gurvich and Veyts^[46] was used in present work, in which the heat capacity of the SnO₂ was estimated from that of the liquid GeO₂ and PbO₂. From the known melting temperature of SnO₂, and estimated heat of fusion (ΔH_{fusion}), then the standard enthalpy and entropy of liquid SnO₂ at 298.15 K can be calculated. There are several reported ΔH_{fusion} data of SnO₂ as listed in Table 3.9. However, no data were experimentally determined and there are big discrepancies between them. In the present study, so called limiting slope rule^[62] was first applied to estimate the ΔH_{fusion} . The limiting liquidus slope of solid SnO₂ in the Al₂O₃-SnO₂^[14], CuO-SnO₂^[63] and PbO-SnO₂^[64] phase diagrams were used in the evaluation, but the results were inconsistent with each other. In the present study, therefore, ΔH_{fusion} of the SnO₂ was estimated by assuming that the ΔS_{fusion} of SnO₂ is the same as that of TiO₂ because the entropy of fusion is of iso-prototype (structure) phase could be similar (structure of solid SnO₂ and TiO₂ are listed in Table 3.1.)

3.3.2.2 SnO

The heat capacity function of the solid SnO was optimized to reproduce the low-temperature data by Millar^[39] and high-temperature data by Veryatin et al.^[47] as listed in Table 3.8 and shown in Figure 3.7. There are two sets of enthalpy of formation data by Humphrey and O'Brien^[37] (-285.98 KJ/mol) and Lavut^[35, 36] (-280.71 KJ/mol) using combustion calorimetry method, and two set of the standard entropy at 298 K calculated from the low-temperature heat capacity data by Millar^[39] (56.74 J/mol-K) and Kostryukov et al.^[48] (57.17 J/mol-K). However, the thermal stability range of solid SnO cannot be reproduced using these original literature enthalpy and entropy data. Therefore, the standard enthalpy and entropy at 298 K of the solid SnO were optimized to
reproduce the stability range of the solid SnO, and the result are listed in Table 3.8. In this study, in order to make SnO more stable at the low temperature, the solid SnO enthalpy is optimized to be -287.9 KJ/mol, which is more negative than the experimental value^[35-37]. For the entropy, the optimized value is 52.7, which is smaller than measurements^[39, 48] in order to make SnO less stable at high temperature. Belford and Alcock^[31] and Grau and Flengas^[34] measured the Gibbs energy of the solid SnO using the emf method. Experiments of Belford and Alcock^[31] were performed between 497 °C and 707 °C and the experiments of Grau and Flengas^[34] were conducted between 777 °C and 1100 °C. The accuracy of these Gibbs energy measurements is doubtable because solid SnO is unstable at these temperature range and decomposed into Sn and SnO₂, as discussed in section 3.3.1.2.

The heat capacity of liquid SnO in the present study was taken from the results by Paquin^[49]. Using the emf method, Kozuka et al.^[50], Grau and Flenga^[34] and Karakaya and Thompson^[51] measured the oxygen partial pressure in equilibrium with liquid Sn and liquid SnO, that is for the reaction of Sn(l) + $\frac{1}{2}$ O₂(g) = SnO(l), which can be used to calculate the Gibbs energy of the liquid SnO. In the present study, the standard enthalpy and entropy at 298 K of the liquid SnO were optimized to reproduce these oxygen partial pressure data as shown in Figure 3.8. It should be noted that the liquid Sn is not pure Sn but Sn containing small amount of oxygen, which is calculated using the results by Heuzey and Pelton^[60] (FactSage FTmisc-SnLQ). In the optimization of the thermodynamic properties of liquid SnO, the eutectic temperature of SnO to metallic Sn and SnO₂ was also taken into account.

3.3.2.3 Sn₃O₄

The only thermodynamic information of Sn₃O₄ in literature is the Gibbs energy of formation of Sn₃O₄ measured by Yang et al.^[23] In their study, the equilibrium oxygen partial over Sn and Sn₃O₄ between 423 °C and 458 °C was measured by the emf technique, and the Gibbs energy of formation of Sn₃O₄ from Sn and O₂ was derived. In the present study, the heat capacity of Sn₃O₄ was firstly determined to be $157.821 + 3.826217 \times 10^{-2}T - 3.925231 \times 10^{-6}T^2 - 2.491467 \times$

 $10^{6}T^{-2}$ by mixing SnO and SnO₂ with the ratio 2:1. Then, the standard enthalpy and entropy at 298 K were determined to reproduce the thermal stability of Sn₃O₄ shown in Fig. 3.2 and the Gibbs energy of formation data in Fig. 3.9. The optimized thermodynamic values are listed in Table 3.8. The optimized Gibbs energy of formation of Sn₃O₄ was about 5 kJ/mol higher than the experimental data by Yang et al.^[33] It should be noted that the result of Yang et al.^[33] make Sn₃O₄ to be over-stable in the Sn-O system.

3.3.2.4 Gas phase

The partial pressures of various gas species in equilibration with SnO^[21] and the mixture of Sn and SnO₂^[15, 16] were measured by Spandau and Ullrich^[21], Platteeuw and Meyer^[16] and Colin et al.^[15]. The results are presented in Figure 3.4. Spandau and Ullrich^[21] and Platteeuw and Meyer^[16] ^[16, 21] assumed gas SnO was the only species in the gas phase, while Colin et al. conducted a mass-spectrometric study of the vaporization of tin oxide and found the gas phase evolved from a Sn and SnO₂ mixture was made up of SnO, Sn₂O₂, Sn₃O₃ and Sn₄O₄, which was refered by this study.

In present study, the thermodynamic properties of gas species Sn, SnO, Sn₂O₂, Sn₃O₃, Sn₄O₄ and O₂ were from the FACT pure substance database^[61] as listed in Table 3.1. Combining this gas database and the newly optimized solid SnO2 thermodynamic properties, the partial pressure of each gas phase measured by Colin^[15] can be explained very well as shown in Figure 3.4, which proved the consistency between the newly optimized solid SnO₂ thermodynamic properties and the gas database from FactSage.

3.3.2.5 Prediction of Sn⁴⁺/Sn²⁺ ratio in liquid Sn oxide solution

Iso-oxygen partial pressure trajectory in liquid Sn oxide solution is predicted in the phase diagram of the Sn-O system (Figure 3.10 (a)). This result can tell how much Sn2+ and Sn4+ can coexist at a given temperature under a certain oxygen partial pressure. At a given constant oxygen partial pressure, the Sn2+/Sn4+ increases with increasing temperature. The amount of Sn2+(SnO) in

liquid Sn oxide solution under air condition where oxygen partial pressure is 0.21 atm is calculated in Fig.3.10 (b). No experiment on the distribution of Sn2+ and Sn4+ has been conducted.

3.4 Summary

All available thermodynamic properties and phase diagram data of the Sn-O system at 1 atm total pressure were critically evaluated and optimized to obtain a set of thermodynamic functions of all stable phases. Discrepancies among existing experimental data were resolved. New phase diagram is constructed from the optimized thermodynamic functions, and consistent thermodynamic data for all phases are obtained. The optimized thermodynamic data can be used for any phase diagram calculations and thermodynamic properties calculations in the Sn-O system at 1 atm total pressure.

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Table 3.1 Thermodynamic properties of solid and liquid Sn and gas phase considered in the present study. The data are taken from the FactSage FACTPS database^[61].

Dhaco	$\Delta H^{\circ}_{298.15}$	$\Delta S^{\circ}_{298.15}$	C_p
Flidse	kJ/mol	J/mol-K	J/mol-K
Sn Solid	0.0	51.20	$21.593624 + 1.80958 \times 10^{-2}T$ (298-505K)
Spliquid	6.26	62.80	$21.539232 + 6.146296 \times 10^{-3}$ T + 1.2882536×10^{6} T ⁻² (505-800K)
Sh Liquiu	0.20	02.85	28.4512 (800-2876K)
Sn Gas	308.20	172.84	26.41776 (298-5000K)
SpO Gas	20.96	222.00	$37.96 - 2.808 \times 10^5 T^{-2} - 5.533 \times 10 T^{-0.5}$ (298-1000K)
SIIO Gas	20.80	232.00	$34.7 + 1.303 \times 10^{-3}T$ (1000-2000K)
SpO. Gas	116.01	251 50	$49.38036 + 2.288856 \times 10^{-2}T - 5.017435 \times 10^{5}T^{-2} - 1.158099 \times 10^{-5}T^{2} $ (298-800K)
51102 083	110.91	251.50	$62.165 + 7.796411 \times 10^{-5}T - 1.746351 \times 10^{6}T^{-2} - 8.130847 \times 10^{-9}T^{2} $ (800-6000K)
Sn ₂ O ₂ Gas	-249.37	313.80	$70.45856 + 2.67776 \times 10^{-3}T - 7.02912 \times 10^{5}T^{-2}$ (298-2000K)
Sn₃O₃ Gas	-525.93	379.49	105.68784 + 4.01664×10 ⁻³ T – 1.054368×10 ⁶ T ⁻² (298-2000К)
Sn ₄ O ₄ Gas	-808.35	452.29	140.91712 + 5.35552×10 ⁻³ T – 1.405824×10 ⁶ T ⁻² (298-2000К)

Table 3.2 Crystal structures of solid Sn and Sn oxides. The crystal structure information of Ti, Ge and Pb oxides is included for the comparison with SnO₂.

Phase	Composition (O mol %)	Space group	Person symbol	Prototype
α-Sn	0	Fd <u>3</u> m	cF8	C (diamond)
β-Sn	0	I4 ₁ /amd	tl4	β-Sn
SnO	50	P4/nmm	tP4	PbO
Sn_3O_4	57.1	NK	NK	Sn ₃ O ₄
SnO ₂	66.7	P4 ₂ /mnm	tP6	TiO ₂
TiO ₂	66.7	P4 ₂ /mnm	tP6	TiO ₂
GeO ₂	66.7	P4 ₂ /mnm	hP9	SiO ₂
PbO ₂	66.7	P4 ₂ /mnm	oP1	$Fe_2N_{0.94}$

Note: NK: Not known

Temperature(°C)	Technique	Crucible	Heating/Cooling	Atmosphere	Starting material	Reference	Year
1625	QM, XRD	ZrO ₂	Heating	N ₂	SnO ₂	Ruff [13]	1913
2000	Estimation					Spandau [2]	1947
1630±5	DTA, QM, XRD	Pt	Heating	SnO ₂	SnO ₂	Barczak [14]	1962
1625	Optimization					This work	

Table 3.3 Summary of the experiments related to the melting temperature of the SnO₂.

Note: QM: Quenching method, DTA: Differential thermal analysis, XRD: X-ray diffraction

Table 3.4 Summary of the experiments related to the boiling temperature of the SnO₂.

Temperature (°C)	Technique	Pressure	Atmosphere	Reference	Year
2250	Color change	1 atm	N ₂	Ruff [13]	1913
2000	Estimation	1 atm	N ₂	Spandau [2]	1947
1830	Estimation	1 atm		Paparoni [10]	2000
1989	Optimization	1 atm		This work	

Temperature range (°C)	Technique	Crucible	Atmosphere	Starting material	Time	Reference	Year
Below 300	QM, XRD	AI_2O_3	N ₂	SnO	NK	Platteeuw [16]	1956
200 ~ 255	QM, XRD, SEM	AI_2O_3	N ₂	SnO	20h ~ 1440h	Drabek [6]	1974
Uncertain ~ 285	QM, XRD	AI_2O_3	Ar	SnO	48h	Koike [17]	1997
75 ~ 285	Optimization					This work	

Table 3.5 Summary of the experiments related to the stability range of the solid SnO.

Note: NK: Not known, QM: Quenching method, XRD: X-ray diffraction, SEM: Scanning electron microscopy

Temperature	Tochniquo	Cruciblo	Heating/	Atmosphoro	Starting material	Equilibration	Poforonco	Voor
(°C)	rechnique	Crucible	Cooling	Atmosphere	(mass ratio)	time for QM	Reference	fedi
1040	DTA	AI_2O_3	Cooling	N ₂	Sn:SnO = 1:1		Spandau [2]	1947
1127	QM, XRD	AI_2O_3	Heating	N ₂	Sn+SnO ₂	NK	Platteeuw [16]	1956
1042	NK						Glassner [32]	1957
1100		AL-O-	Heating	٨٢	SnO:SnO ₂ :Cl =	1_9h	Carbó-Nóver [19]	1072
1100		A12U3	neating	AI	98.6:1:0.01	1-011		1972
1042	NK						Samsonov [33]	1973
1080	QM, XRD	AI_2O_3	Heating	NK	SnO	20-1140h	Drabek [6]	1974
1100	Emf	ZrO ₂	Heating	Ar	Sn+SnO		Grau [34]	1976
1045	DTA, QM, XRD	AI_2O_3	Cooling	Ar	Sn:SnO = 1:1	30-45min	Kuxmann [8]	1980
1034	DTA, QM, XRD	ZrO ₂	Cooling	Ar	Sn:SnO = 1:1	30-45min	Kuxmann [8]	1980
1030	DTA, QM, XRD	$MgAl_2O_4$	Cooling	Ar	Sn:SnO = 1:1	30-45min	Kuxmann [8]	1980
1122		MaO	Heating	۸r	$s_n \cdot s_n O_n = 1 \cdot 1$		Takada [19]	1000
1090	DSC	IvigO	Cooling	AI	511.51102 - 1.1		Takeua [10]	1990
1040	DSC, QM, XRD	NK	Cooling	NK	SnO	NK	Cahen [11]	2003
1125-1130	QM, EPMA	SnO ₂	Heating	Ar	Sn:SnO = 1:4	2-8h	Xu [20]	2013
1125	Optimization						This study	

Table 3.6 Summary of the experiments related to the melting temperature of the SnO.

Note: NK: not known, QM: Quenching method, XRD: X-ray diffraction, DSC: Differential scanning calorimetry, DTA: Differential thermal analysis, EPMA: Electron probe microanalysis, Emf: electro motive force measurement.

Temperature (°C)	Technique	Pressure	Atmosphere	Reference	Year
1700	Estimation	1 atm	N ₂	Spandau [2]	1947
1421	Estimation	1 atm	N ₂	Spandau [21]	1953
1394	Estimation	1 atm	N ₂	Platteeuw [16]	1956
1527	NK	1 atm	NK	Glassner [32]	1957
1425	Estimation	1 atm	N ₂	Colin [15]	1964
1527	NK	1 atm	NK	Samsonov [33]	1973
1425	Estimation	1 atm	NK	Paparoni [10]	2000
1635	Optimization	1 atm	NK	Cahen [11]	2003
1718	Optimization	1 atm		This work	

Table 3.7 Summary of the experiments related to the boiling temperature of SnO.

Note: NK: not known.

Temperature	Tashuisua	Crucible	Heating/	Atus sauk sus		Equilibration	Deference	Veer
range (°C)	rechnique	Cruciple	Cooling		Starting material	time for QM	Reference	rear
600 ~ 1000	СА	AI_2O_3	Heating	N ₂	SnO	4-70h	Spandau [2]	1947
Below 427	QM, ED,	NK	Heating	N ₂	SnO	15min-16h	Lawson [22]	1067
	XRD, MS							1907
290 ~ 410	QM, XRD, SEM	AI_2O_3	Heating	N ₂	SnO	20h-1440h	Drabek [6]	1974
423 ~ 458	QM, XRD, CA	ZrO ₂	Heating	NK	SnO	4h-6h	Yang [23]	1994
285 ~ 512	QM, XRD	AI_2O_3	Heating	Ar	SnO	48h	Koike [17]	1997
137 ~ 400	DSC, QM, XRD	NK	Cooling, Heating	NK	SnO+SnO ₂	NK	Cahen [11]	2003
137 ~ 512							This work	

Table 3.8 Summary of the experiments related to the stability range of the Sn₃O₄.

Note: NK: Not known, ED: Electron diffraction, MS: Mossbauer spectroscopy, CA: Chemical analysis, XRD: X-ray diffraction, DSC: Differential

scanning calorimetry, SEM: Scanning electron microscopy.

$\Delta H_{298.15}^{\circ}$	$\Delta S^{\circ}_{298.15}$	C_p	Tashniswa	Deference	Veer
kJ/mol J/mol-K		J/mol-K	rechnique	Reference	rear
	52.30	Points (70-290K)	AC	Millar [39]	1929
		$74.7848 + 8.0718 \times 10^{-3}T - 1.94514 \times 10^{6}T^{-2} \text{ (273-1498K)}$	MC	Kapustinskii [40]	1936
-580.82±0.33			CC	Humphrey [37]	1953
-580.74	52.30	$73.88944 + 10.0416 \times 10^{-3}T - 2.158944 \times 10^{6}T^{-2}$ (298-1500K)	NK	Campbell [52]	1956
-581.10	52.30	$73.94 + 10.05 \times 10^{-3}T - 2.16 \times 10^{6}T^{-2}$ (298-1898K)	NK	Veryatin [47]	1965
-581.13	52.34±1.26	$73.953 + 10.0502 \times 10^{-3}T - 2.1608 \times 10^{6}T^{-2}$ (298-1500K)	NK	Samsonov [33]	1973
577 62±0 16	16		CC	Lavut [35, 36]	1979
-577.05±0.10					1980
	48.96	Measurement from 5 to 300 K (No equation given)	AC	Zhogin [38]	1980
	40.00	$76.041 + 7.36217 \times 10^{-3}T + 7.69 \times 10^{-10}T^2 - 2.223867 \times 10^{6}T^{-2}$	Ontimization	This work	
-577.63	48.96	(273-1903K)	Optimization		
		04.2 (1909.22004)		Veryatin [47]	1965
		J	INIX	Samsonov [33]	1973
		92 (1903-4400)	Est	Gurvich [46]	1991
-555.41	40.65	92	Optimization	This work	1991
	56.74	Points (70-295K)	AC	Millar [39]	1929
-285.98±0.67			СС	Humphrey [37]	1953
	\H ² _{298.15} J/mol 580.82±0.33 580.74 581.10 581.13 577.63±0.16 577.63 555.41 285.98±0.67	$M_{298.15}^{\circ}$ $\Delta S_{298.15}^{\circ}$ J/mol J/mol-K 52.30 580.82±0.33 580.74 52.30 581.10 52.30 581.13 52.34±1.26 577.63±0.16 48.96 577.63 48.96 555.41 40.65 56.74 285.98±0.67	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 3.9 Summary of thermodynamic properties of the stoichiometric Sn oxide phases.

			$45.9737 + 1.4644 \times 10^{-2} T$ (273-1273K)	NK	Kelley [53]	1960
	-286.40	56.50	$39.36 + 1.516 \times 10^{-2} T$ (273-1273K)	NK	Veryatin [47]	1965
	-280 71+0 21				Lovut [25, 26]	1969
	-200.7110.21				Lavut [55, 50]	1970
	-286.38±1.26	56.52	$39.3634 + 1.51591 \times 10^{-2} T$ (273-1273K)	NK	Samsonov [33]	1973
		57.17±0.3	Measurement from 12.1 to 304.4 K (No equation given)	AC	Kostryukov [48]	1978
	-280.71	57.17		NK	Gurvich [46]	1991
	207.00	F0 7	$40.89 + 1.545 \times 10^{-2}T - 1.963 \times 10^{-6}T^2 - 1.338 \times 10^{5}T^{-2}$	Ontimization	This work	
	-287.90	52.7	(273-1453K)	Optimization		
SnO			60.7(1315-1800K)	NK	Veryatin [47]	1965
liquid	-261.35	64.63	63	NK	Paquin [49]	2003
nquiu	-261.35	63.83	63	Optimization	This work	
Sn ₃ O ₄		1=0.00	$157.821 + 3.826217 \times 10^{-2}T - 3.925231 \times 10^{-6}T^{2} - 2.491467 \times 10^{6}T^{-2}$	Ontimization	This work	
Solid	-1157.70 158.60		$2C_p(solid SnO) + 1C_p(solid SnO_2)$ (273-1453K)	optimization		

AC: Adiabatic calorimetry, CC: Combustion calorimetry, MC: Metallic calorimetry, Est: Estimation, NK: Not known.

Phase	$\Delta H_{fusion}(kJ)$	ΔS_{fusion} (J/K)	Technique	Reference	Year
	47.69	25.06	NK	Samsonov [29]	1973
	45.47	23.89	NK	SGTE [54]	1999
	23.40	12.30	NK	Fact [20]	2010
SnO ₂	150.54	79.11	LS of PbO-SnO $_2$	Urazov [61]	1957
	223.40	117.39	LS of AI_2O_3 -SnO ₂	Barczak [21]	1962
	113.81	59.80	LS of CuO-SnO $_2$	Scarlat [55]	2001
	41.12	21.61	Estimation	This work	2017
TiO ₂	46.02	21.61	NK	Fact [20]	1992

Table 3.10 The enthalpy and entropy of fusion of SnO₂.

Note: LS: Calculated according to the limiting slope theory, NK: not known



Figure 3.1 Previous phase diagrams of the Sn-O system in literature.



Figure 3.2 Optimized phase diagram of the Sn-O system in the present study.



Figure 3.3 Oxygen solubility in the liquid Sn^[8, 19, 30, 31].



Figure 3.4 Calculated partial pressure of each gas species equilibrated with solid SnO₂ in comparison with experimental data^[15, 16, 21].



Figure 3.5 Heat capacity of the solid $SnO_2^{[38, 40]}$.



Figure 3.6 The Gibbs energy of solid SnO₂ optimized in this study in comparison with experimental data^[41-45].



Fig. 3.8 Calculated oxygen partial over the liquid SnO (Sn saturation) in comparison with experimental data^[34, 50, 52].



Figure 3.9 Optimized Gibbs energy of Sn₃O₄ in comparison with experimental data by Yang et al.^[23].



Figure 3.10 Calculated iso-PO₂ (atm) contours in the liquid SnO-SnO₂ solution from the present thermodynamic modeling.

4 Coupled phase diagram experiment and thermodynamic optimization of the SnO₂-SnO-SiO₂ system

4.1 Introduction

The thermodynamic knowledge of phase diagrams and chemical reactions of materials is indispensable to optimize the existing material processes and develop new materials and associated production process. The thermodynamic knowledge of the Sn oxide containing multicomponent system SnO₂-SnO-SiO₂-CaO-Al₂O₃-Na₂O-Fe₂O₃-FeO is crucial in various industrial applications including glass, ceramics, iron and steel-making, and geochemistry ^[1-5]. However, even the phase equilibria of the SnO₂-SnO-SiO₂ system have not been well studied. Actually, no investigation is available for the phase diagram of the SnO₂-SiO₂ system in air, and inconsistency exists among previous experimental phase diagram and thermodynamic studies on the SnO-SiO₂ system at Sn saturation.

The purpose of the present study is to perform the critical evaluation and optimization of the SnO-SnO₂-SiO₂ system. Due to the lack of the phase diagram information in the SnO₂-SiO₂ system, key phase diagram experiments were also conducted in air to assist the present thermodynamic optimization.

4.2 Key phase diagram study for the SnO₂-SiO₂ system in air

For the successful phase equilibrium study of the SnO₂-SiO₂ system in air at high temperatures, the following problems should be overcome. First of all, the volatile loss of SnO₂ during the experiments should be supressed. As Leite et al.^[6] pointed out, the SnO₂ showed a peritectic decomposition according to the reaction, $SnO_2(s) \rightarrow SnO(g) + \frac{1}{2}O_2(g)$, and the decomposition/evaporation rate above 1200 °C is significant. Secondly, as Sn oxide is very corrosive, choosing the suitable crucible materials for equilibration experiments is critical for accurate phase diagram experiment. The tight control of oxygen partial pressure during the equilibration experiment is also important because Sn²⁺/Sn⁴⁺ ratio in molten Sn oxide phase changes significantly depending on oxygen partial pressure of system.

4.2.1 Crucible materials and preparation

Paparoni et al.^[7-9] evaluated various crucible materials used in the phase equilibrium experiments of Sn oxide containing system. The ideal metallic crucible should be manufactured from the metal that does not react with liquid Sn and does not reduce SnO₂ to Sn. The metals with the affinity for Sn such as Pt, Pd, Au and Fe are inadequate. Among common metals, Be, B, Mo, W, Si and C have less reaction with Sn. But, the special attention should be given to their oxide because their oxides are more stable than SnO₂ and the metals would reduce SnO₂ to Sn during phase diagram experiments. Many studies^[10-13] reported the common oxides such as Al₂O₃, ZrO₂, MgAl₂O₄ (spinel) and SiO₂ can be dissolved in molten Sn oxide, and therefore the crucible made of such oxides cannot be used in the phase diagram experiments.

Rhenium (Re) has the advantage of being malleable, having negligible solubility in liquid Sn at high temperatures, having a high melting point at atmospheric pressure (3186 °C), and not contaminating the Sn oxide charge at high temperature and pressure^[14, 15]. As mentioned above, open crucible cannot be used in the phase diagram study of Sn oxide system due to the significant evaporation of Sn oxide at high temperatures. But it is difficult to produce sealed Re capsules by welding^[7, 8].

The double closed crucibles as shown in Figure 4.1 were created in the present study to minimize the volatile loss of SnO₂. The Re capsule as the inner crucible was made of 0.0127mm Re foil, coiled three times to give cylindrical containers of about 3.5mm in length and 2.5mm in diameter with a wall thickness of 0.0381 mm. The Re capsules were sealed by folding up the end of Re cylinders as shown in Figure 4.2 or by gently turning both edges to the middle and joining along the seam by arc welding. The sealed platinum (Pt) capsules with 15 mm in length, 2.873 mm in inner diameter, and 3 mm in outer diameter were prepared as the outer crucibles by arc welding. Molybdenum (Mo) capsules and lids machined from 99.97% molybdenum rods were also used

as the inner crucibles in some of the experiments. However, Rhenium capsules were preferred over molybdenum capsules because the latter slightly contaminate the Sn oxide charge.

4.2.2 Experimental procedures and technique

The starting materials were made from SiO_2 and SnO_2 powers (99.99 wt.% purity). The powers for each sample were weighted and mixed with an agate pestle and mortar filled with 2-propanol alcohol for 1 h. The starting material powders were kept in a drying oven at 110 °C prior to use. About 10 mg of starting mixture was tightly packed into Re crucible. After sealing the double crucibles, samples were brought to the furnace at target temperatures in air for 7 min to 12 h, and then quenched rapidly in cold water. The quenched samples were encapsulated and cast in epoxy resin, polished for metallographic and microanalysis by using oil-based diamond 1 μ m to minimize the water absorption. The phase characterization of quenched samples was carried out by X-ray diffraction (XRD). The composition of various phases and surface condition of samples were obtained by electron probe microanalysis (EPMA).

All the equilibration experiments were conducted in a Deltech DT-31-VTOS vertical tube furnace equipped with an alumina tube (67 mm inner diameter) and MoSi heating elements. B-type thermocouple (Pt30Rh-Pt6Rh) was located at about 10 mm away from the sample. The temperature of the furnace was controlled within ± 1 °C by a PID controller connected to the thermocouple. The temperature of the furnace was periodically calibrated by melting diopside mineral samples (CaMgSi₂O₆, melting point at 1392 °C^[16]). All the crucibles placed in a porous Al₂O₃ holder were suspended by Pt wire within reaction tube inside the furnace.

All the details on experimental composition, temperature and holding time are listed in Table 4.1. The key experimental temperatures and compositions were deliberately selected to determine the eutectic temperature and the size of miscibility gap based on preliminary phase diagram calculated in the course of the present study. The sample was kept at the target temperature for the minimum time required to achieve equilibrium in order to minimize the volatile loss of SnO₂.

The times for the equilibration were planned individually for each particular sample by taking the particular melting behavior into account.

After the equilibration experiment, EPMA analyses were conducted for the phase analysis with the JEOL 8900 probe at McGill University using Wavelength-Dispersive Spectrometry (WDS). An accelerating voltage of 15 kV was used with a 20 nA beam current and counting times of 20 s on peaks and 10 s on backgrounds. Raw data were reduced with the ZAF correction using cassiterite (Sn) and quartz (Si) standards. XRD patterns of quenched samples were obtained using the Bruker Discover D8 X-ray diffractometer equipped with VANTEC detector and CuKα radiation at McGill University. All XRD profiles were identified with the powder diffraction files of the International Centre for Diffraction Data using the DIFFRAC.EVA software package (Bruker AXS, Karlsruhe, Germany, 2000).

4.2.3 Experimental results and discussion

The back-scattered electron (BSE) images of some samples are shown in Figure 4.3. Experimental conditions and results are summarized in Table 4.1 and the results are compared in Figure 4.4 with the optimized phase diagram from the thermodynamic modeling.

In spite of all efforts to prevent the evaporation of SnO₂ during the experiments, it always happened in all samples. This does not mean that the double closed crucibles were leaked. In the most times, the evaporation of SnO₂ happened and it condensated in other part of crucibles. For example, as shown in Figure 4.3 (a), the SnO₂ appears only in the center of the sample (sample II; 1h equilibration time) because the SnO₂ within periphery was evaporated. After holding the sample for longer time 12h, all the SnO₂ in the sample (sample III) was completely evaporated as shown in Figure 4.3 (b). Of course, the evaporation rate of the SnO₂ became higher with the increasing experimental temperature, and thus the samples for high-temperature experiments were always kept for the short time.

The particular attention was paid to ensure the achievement of equilibrium. As mentioned above, due to the evaporation of SnO_2 , it is hard to obtain fully equilibrium state in the entire sample. If there was a chemical reaction between SnO_2 and SiO_2 before the compete evaporation of SnO_2 , there would be a certain change in the original SiO_2 powder particles. Therefore, a few grains (the original starting material powder particles) were usually selected in the different regions of quenched sample and we analyzed the composition at the rim and core of the particle using EPMA. If the analyses were identical (within 0.5 cation %) and if the stoichiometry was acceptable (i.e. cation proportions were within 0.5% of the expected values), the phase was considered to be equilibrated. If there were quenched crystals which formed during the quenching process, their morphology would be different from that of stable crystalline phase at given equilibrium conditions. In this way, the equilibrium phase assemblage could be identified. Due to the continuous volatile loss of the SnO_2 in samples during the experiment, SnO_2 content in the liquid phase that is remained in the quenched sample would readily be less than original equilibrium content. Therefore, EPMA results were not directly used for the equilibrium phase composition. Instead, EPMA results were used for phase identifications of SnO_2 , SiO_2 and liquid.

Although some samples would not be fully in equilibrium state, the experimental results can still be helpful to determine the general feature of the SnO₂-SiO₂ system in air. The overall phase diagram is presented in Fig. 4.4 along with the experimental data. In the experiments, the liquid phase appeared in the samples IV to sample XIII at the experimental temperature above 1510 °C. The solid SnO₂ and SiO₂ phases were only stable phases in the samples I, II and III at the experimental temperature below 1500 °C. Therefore, the eutectic temperature of this system should be between 1500 °C and 1510 °C. For the samples between 1510 °C and 1625 °C, both solid and liquid phase coexisted. Liquid phase was found in the sample with $X_{SiO2} = 0.5$ at 1625 °C. Moreover, the experimental results indicated the strong possibility of the presence of the liquid miscibility gap. As can be seen in Fig. 4.4, the samples with $X_{SiO2} = 0.5$ and 0.6 at 1650°C show liquid phase without stable solid phases. In order to have such condition, thermodynamically it would form a liquid miscibility gap. No liquid phase separation was detected for the sample with $X_{SiO2} = 0.5$ and 0.6 at 1650°C most probably because of the short experimental time. In sample X,

the color of glass was yellow and according to the EPMA analysis, the glass composition was closer to SnO instead of SnO₂. This would happen because of the reduction of SnO₂ to SnO by Mo from crucible materials. In some cases, quartz was detected instead of cristobalite, although cristobalite is thermodynamically more stable SiO₂ crystal. This might happen due to the phase transition of SiO₂ during the quenching.

In summary, present phase diagram experiments determined that the phase diagram of the SnO₂-SiO₂ system in air should have a liquid miscibility gap in the SnO₂-rich region and eutectics of SnO₂ and SiO₂ in the SiO₂-rich region. The eutectic and monotectic temperatures should be about 1500~1510 °C and 1625~1650 °C, respectively. No intermediate solid phase between SnO₂ and SiO₂ was detected. No mutual solubility between solid SnO₂ and SiO₂ was detected.

4.3 Phase and thermodynamic models

The standard Gibbs energies of the solid and liquid SnO₂ and SnO were taken from the previous optimization in chapter 3 and the standard Gibbs energies of the solid and liquid SiO₂ were taken from FACT pure substance database^[17].

4.3.1 Liquid phase

In the present work, the liquid oxide phase in the SnO₂-SnO-SiO₂ system was described using the Modified Quasi-chemical Model (MQM)^[18]. In the MQM, short range ordering (SRO) of second-nearest-neighbor (SNN) cation is taken into account in the liquid solution. The cationic species considered in the present solution are Sn⁴⁺, Sn²⁺ and Si⁴⁺.

In MQM, the following quasi-chemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B); \qquad \Delta g_{AB}$$
 (4-1)

- 69 -

where A and B are cationic species in the solution and (A-B) represents an SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{i \ge 1} g_{AB}^{0j} X_{BB}^{j}$$
(4-2)

where Δg_{AB}° , Δg_{AB}^{i0} and Δg_{AB}^{0j} are the parameters of the model which may be functions of temperature. X_{AB} is the mole fraction of (A-B) bonds in the liquid solution.

The Gibbs energy of the solution is then given by:

$$G^{m} = \left(n_{A}g_{A}^{\circ} + n_{B}g_{B}^{\circ}\right) - T\Delta S^{conf} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$

$$\tag{4-3}$$

where n_i and g_i° are the numbers of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{conf} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising model^[19].

The SRO behavior in the liquid solution can be well described by setting the coordination numbers of cations. In the present study, the coordination numbers of Sn⁴⁺, Sn²⁺ and Si⁴⁺ were set to be 2.7529, 1.3774 and 2.7549, respectively. Among the three binary quasi-chemical reactions, the Gibbs energy parameter (Δg_{AB}) of the Sn²⁺-Sn⁴⁺ reaction for the SnO-SnO₂ solution was taken from the previous optimization in Chapter 3. The Gibbs energies of Sn⁴⁺-Si⁴⁺ and Sn²⁺-Si⁴⁺ reactions were optimized in this study to describe the binary SnO₂-SiO₂ and SnO-SiO₂ solutions, respectively.

$$\Delta g_{Si^{4+}-Sn^{4+}} = 8000 + 6500X_{Sn^{4+}-Sn^{4+}}^{1} \tag{4-4}$$

$$\Delta g_{Si^{4+}-Sn^{2+}} = 1500 + 6400X_{Si^{4+}-Si^{4+}}^3 + 1000X_{Si^{4+}-Si^{4+}}^6$$
(4-5)

The two set of model parameters were optimized to reproduce the phase diagram and thermodynamic properties of the SnO₂-SiO₂ system in air and the SnO-SiO₂ system in Sn saturation, respectively.

The Gibbs energy of the ternary SnO_2 -SnO- SiO_2 liquid solution was calculated from the binary parameters using the 'Toop-type' geometric model with SiO_2 as the 'asymmetric component'. In this way, Sn^{2+}/Sn^{4+} ratio in the ternary solution can be better described. No ternary interaction parameters were introduced in the present study.

4.3.2 Metallic and gas phases

To calculate the metallic saturation condition, a stoichiometric solid Sn and the liquid Sn solution (containing oxygen and Si as dilute elements) from FACT database^[17] were considered. The Gibbs energies of gas species were taken from FACT pure substance database^[17].

4.4 Critical evaluation and optimization of the SnO₂-SnO-SiO₂ system

All experimental data from the present work and literature under oxygen partial pressures ranging from metallic saturation to air were critically evaluated and optimized to obtain one set of optimized thermodynamic model parameters. With these optimized parameters, all the reliable thermodynamic properties and phase diagram data could be reproduced within the experimental error limits. Strictly speaking, there is a certain amount of SnO₂ (up to about 0.5 mol % of total Sn oxides) in the molten oxide even at metallic Sn saturation. However, for the sake of simplicity, the notations of the SnO₂-SiO₂ and SnO-SiO₂ systems were used below to represent oxidizing (in air) and reducing (in Sn saturation) conditions, respectively.
4.4.1 The SnO₂-SiO₂ system in air

The optimized phase diagram of the SnO₂-SiO₂ system is plotted in Figure 4.4 along with all present key experimental data. To reproduce such experimental data, liquid parameters were optimized as shown in Eq. (4-4). The calculated eutectic point is at 1500 °C and 84.9 mol% SiO₂, which is in good agreement with experimental data. The liquid miscibility gap is calcualted between 0.02 mol% SiO₂ and 75 mol% SiO₂ at 1650 °C, and the consolute temperature is calculated at about 2016 °C, which almost agrees with the estimated miscibility gap (miscibility width up to 70 mol% SiO₂ and the consolute temperature at 2327 °C) by Hudon and Baker^[20-23] based on ionic radii of cation in SnO₂-SiO₂ solution.

4.4.2 The SnO-SiO₂ system at Sn saturation

4.4.2.1 Phase diagrams

Many phase diagram studies have been conducted in the SnO-SiO₂ system at Sn saturation. All the experimental studies are summarized in Table 4.2. The SnO-SiO₂ system is a simple eutectic system. Keysselitz and Kohlmeyer^[24] investigated this system by thermal analysis (TA), and Slonimilii and Tseidler^[25] and Koike et al.^[26] studied the phase equilibrium by quenching method followed by XRD phase analysis. Paparoni^[7], Ilyushechkin et al.^[27] and Xu et al.^[28] conducted quenching experiments and analyzed the compositions of solid and liquid phase using EPMA. Grau and Flengas^[29] conducted electro motive force measurement (emf) of the SnO-SiO₂ system. The change in emf profile can provide the liquidus and activity data. The contamination from oxide crucibles exists in the experiments^[24-26]. Paparoni^[7] did not apply protective gas in the experiments, so his experimental results might be out of Sn saturation. Xu et al.^[28] put special care to minimize the contamination from crucible, and kept longer reaction time to achieve equilibrium state. So the experimental results by Xu et al.^[28] were considered as the most accurate data. The experimental liquidus measured by Grau and Flengas^[29] and Ilyushechkin et al.^[27] are well consistent with the results by Xu^[30].

The optimized phase diagram of the SnO-SiO₂ system at Sn saturation are plotted in Figure 4.5 along with all the experimental data. The optimized diagram calculated from the present study is in good agreement with the experimental data by Xu et al.^[28]. The optimized eutectic in the present study is 905 °C and 0.46 mol fraction of SiO₂. It should be noted that Risbud^[32] proposed the miscibility gap of the SnO-SiO₂ system in the SnO-rich side at the temperatures below 630 °C. They observed phase separation of glass into tin oxide and silica glass after quenching. *However, strictly speaking, the miscibility observed in this study may not occur in the binary SnO-SiO₂ system, but rather in a ternary system containing SnO, SiO₂ and small amounts of SnO₂^[32]. Because this experiment is not conducted with Sn saturation and SnO has the tendency to be oxidized to be SnO₂.*

The MQM parameter of liquid SnO-SiO₂ is optimized to reproduce the phase diagram in Figure 4.5. As there is no mutual solubility between SnO and SiO₂, both solids were considered as stoichiometric compounds. As will be discussed below, there are too much scatters in the activity data, the MQM parameters were mainly determined from the phase diagram information.

4.4.2.2 Activities

The activity of liquid SnO in the SnO-SiO₂ melt at Sn saturation was determined by several researchers. Chizhikov et al.^[33], Kozuka et al.^[34], Grau and Flengas^[29] and Koike et al.^[35] investigated the activity of SnO using electro motive force measurements (emf). The activity of SnO measured by Chizhikov et al.^[33] shows very negative deviation from ideal solution. Grau and Flengas^[29] mentioned that the inaccuracy of Chizhikov's measurements would be caused by Al₂O₃ electrode which does not behave as a purely oxide-ion conducting membrane. Grau and Flengas^[29], Kozuka et al.^[34] and Koike et al.^[35] used the CaO-stabilized ZrO₂ electrode. Flengas^[36] pointed out the problem of the open cell used by Kozuka^[34] and Koike^[35]. In the open cell, the continuous diffusion of the gaseous phase can cause the oxygen partial pressures in the two electrode compartments are not at their equilibrium values, and therefore the emf results can be incorrect. Data from Grau and Flengas^[29] were considered to be unreliable by Koike et al.^[35]

because the equilibration time for emf measurement by Grau and Flengas^[29] was too short to allow samples to reach equilibrium. All of the emf measurements also have the problem of the electrode corrosion by SnO, which can contaminate the composition of liquid phase. Carbó-Nóver and Richardson^[37] calculated the activities of SnO from the oxygen content in liquid tin metal, which was in equilibrium with the SnO-SiO₂ melt. However, about 10 mol% Al₂O₃ can be dissolved in liquid SnO-SiO₂ melt due ot the contamination from Al₂O₃ crucible. More details on the experimental measurements can be found in Table 4.3.

All the experimental data are plotted in Fig. 4.6. As can be seen, the scatter between experimental data is relatively large. In the present work, the calculated activity of liquid SnO in the present study is close to ideal solution.

4.5 Prediction of Sn²⁺/Sn⁴⁺ ratio in liquid

Crau and Flengas^[29] and Carbó-Nóver and Richardson^[37] investigated the variations of the Sn^{4+}/Sn^{2+} ratio in the SnO-SiO₂ melts saturated with Sn by wet chemical analysis. Although the experimental data are quite scattered as depicted in Figure 4.8, the experimental results^[29, 37] clearly show that the amount of Sn⁴⁺ is less than 1 % of total Sn, and the molar ratio of Sn²⁺/Sn⁴⁺ increases significantly with increasing the molar ratio of SiO₂. During the quenching, the disproportionation of SnO in the SnO-rich side causes the measured concentration of Sn²⁺ is somewhat lower than the actual equilibrium value, which also explains why our model can predict the Sn²⁺/Sn⁴⁺ ratio better in SiO₂ rich side than the SnO rich side. The calculated result of Sn²⁺/Sn⁴⁺ from the present thermodynamic modeling is generally consistent with experimental data as shown in Figure 4.8.

4.6 Summary

Coupled key phase diagram study and thermodynamic modeling of the SnO-SnO₂-SiO₂ system was carried out in the present study to obtain one set of Gibbs energy functions to describe the

phase equilibria and thermodynamic properties in this ternary system. In particular, the phase diagram of the SnO₂-SiO₂ system in air was investigated for the first time using the quenching method followed by EPMA and XRD phase analysis. General features of the phase diagram such as the size of a liquid miscibility gap, monotectic temperature and eutectic temperatures of the binary system were well determined with the help of key phase diagram study and thermodynamic modeling. The present models and optimized model parameters can be used along with thermodynamic software such as FactSage to calculate any phase diagram and thermodynamic property of this system under various oxygen partial pressures from Sn saturation to 1 atm.

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Sample	Starting composition (mol% SiO2)	Crucible	Temperature (°C)	Duration (minutes)	Phase
I	0.70	Re folding	1350	60	Cst+Crs
П	0.70	Re folding	1500	60	Cst+Crs
III	0.70	Re folding	1250	720	Cst+Crs
IV	0.50	Re folding	1650	10	Glass
V	0.50	Re folding	1600	7	Cst+Glass
VI	0.95	Re folding	1550	10	Cst+Crs+Glass
VII	0.60	Re folding	1625	4	Cst+Qz+Glass
VIII	0.70	Mo welding	1530	28	Cst+Crs+Glass
IX	0.70	Re folding	1520	30	Cst+Crs+Glass
Х	0.70	Mo wielding	1510	30	Cst+Crs+Glass(SnO)
XI	0.80	Re wielding	1625	15	Glass
XII	0.60	Re folding	1650	15	Glass
XIII	0.95	Re welding	1558	20	Cst+Crs+Glass

Table 4.1 Equilibration Experimental Results for the SnO_2 -SiO₂ System

Cst: Cassiterite (SnO₂), Crs: Cristobalite (SiO₂), Qz: Quartz (SiO₂)

Technique	Crucible	Heating/Cooling	Atmosphere	Starting material	Time	Reference	Year
ТА	AI_2O_3	Heating	N ₂	SnO/SnC ₂ O ₄ +SiO ₂	NK	Keysselitz[24]	1933
QM&XRD	AI_2O_3	Heating	N ₂	SnO + Natural quartz	1h	Slonimilii[25]	1959
emf	ZrO ₂	NA	Ar	$SnO+H_2SiO_3$		Grau[29]	1976
QM&XRD	ZrO ₂	Heating	Ar	SnCl ₂ +SiO ₂	48h	Koike[35]	1997
QM&EPMA	SiO ₂	Heating	Air	Sn+SnO+SiO ₂	4-2400h	Paparoni[7]	2000
QM&EPMA	NK	NK	NK	NK	NK	llyushechkin[27]	2004
QM&EPMA	SnO ₂ /SiO ₂	Heating	Ar	Sn+SnO ₂ +SiO ₂	2-8h	Xu[28]	2013

Table 4.2 Summary of phase diagram study on the SnO-SiO₂ system at S saturation.

Table 4.3 Summary of the experimental activity data of liquid SnO in the SnO-SiO₂ system at Sn saturation.

Technique	Electrolyte / (Electrode)	Atmosphere	Temperature range (°C)	Reference	Year
emf	Sn, SnO-SiO₂/ (Al₂O₃) /Sn, SnO	NK	1000-1150	Chizhikov[33]	1963
emf	Sn, SnO-SiO2/ (ZrO2-CaO) /Sn, SnO	Ar	1050-1150	Kozuka[34]	1968
OIN	Al₂O₃ crucible		1000-1250	Carbó-Nóver[37]	1972
emf	Sn, SnO-SiO2/ (ZrO2-CaO) /Ni, NiO	Ar	800-1200	Grau[29]	1976
emf	Sn, SnO-SiO ₂ / (ZrO ₂ -CaO) /Ni, NiO	Ar	994-1170	Koike[35]	1997
NK: not known	OIN: overgon in tin				

NK: not known OIN: oxygen in tin



Figure 4.1 The double crucibles used in the present study.



Figure 4.2 The method to fold the Re capsule.



Figure 4.3 Backscattered SEM micrographs of several representative samples. The compositions of samples and experimental conditions are listed in Table 4.1.



Figure 4.4 Calculated optimized phase diagram of the SnO₂-SiO₂ system in air from this study along with the present key phase diagram data. For the details of the exprimental conditions, please see Table 4.1.



Figure 4.5 Calculated optimized phase diagram of the SnO-SiO₂ system at Sn saturation in this study along with the phase diagram data in literature^[7, 24, 25, 27, 28, 29, 35].



Fig. 4.6 Activity of liquid SnO in the SnO-SiO₂ melt saturated with liquid Sn at 1150 °C^[29, 33, 34, 35, 37]. Line is calculated from the thermodynamic model parameters in this study.



Figure 4.8 Calculated Sn²⁺/Sn⁴⁺ ratio in the SnO-SiO₂ liquid at Sn saturation at 1150°C.

5 Critical evaluation and thermodynamic optimization of the CaO-SnO-SnO₂-SiO₂ system

5.1 Introduction

The SnO₂-SnO-SiO₂-CaO-FeO_x system forms the basis of a number of metallurgical slags used in tin smelting and recycling^[1-7]. Although this system was widely used in industrial practices, the phase equilibria and thermodynamic properties of the whole system have not been fully characterized.

Within the SnO₂-SnO-SiO₂-CaO system, the binary system CaO-SiO₂ has been well established^[8] and stored in the FactSage FACT Oxide (FToxid) database^[9]. The thermodynamic modeling of the binary systems, SnO₂-SiO₂ in air and SnO-SiO₂ at Sn saturation, have been constructed in Chapter 4. In this study, the critical evaluation and optimization of the SnO₂-SnO-CaO-SiO₂ system was carried out based on the previously optimized binary system. For the binary SnO₂-CaO system in air and SnO-CaO system at Sn saturation, no phase equilibria or thermodynamic property information is available. The liquidus surface in the ternary SnO₂-SiO₂-CaO system in air and the SnO-SiO₂-CaO system in equilibrium with tin metal was investigated by Xu et al.^[10, 11], which provided information required to characterize the phase relations and thermodynamics over a wide range of compositions.

In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for the Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the evaluation of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back-calculated. In this way, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are

made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from low order to high order systems can be applied to industrial processes.

The purpose of the present study is to critically evaluate and optimize thermodynamic properties and phase diagrams of the SnO₂-SiO₂-CaO system in air and the SnO-SiO₂-CaO system at Sn saturation. This work is part of a wide database development project for the multicomponent system SnO₂-SnO-SiO₂-CaO-Al₂O₃-Na₂O-Fe₂O₃-FeO.

5.2 Phase and thermodynamic models

5.2.1 Stoichiometric Compounds

The Gibbs energy of a stoichiometric compound is expressed by:

$$G_T^{\circ} = H_T^{\circ} - TS_T^{\circ}$$
(5-1)

$$H_T^{\circ} = \Delta H_{298.15}^{\circ} + \int_{298.15}^T C_p dT$$
(5-2)

$$S_T^{\circ} = S_{298.15}^{\circ} + \int_{298.15}^{T} C_p / T dT$$
(5-3)

where G_T° , ΔH_T° and ΔS_T° are respectively the standard Gibbs energy, enthalpy and entropy of a given stoichiometric compound at the absolute temperature T. $\Delta H_{298.15}^{\circ}$ is the standard enthalpy of formation of the compounds from pure elements at 298.15 K. $\Delta H_{298.15}^{\circ}$ of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference. $S_{298.15}^{\circ}$ is the standard entropy at 298K, and C_p is the heat capacity.

The standard Gibbs energies of solid and liquid SnO₂ and SnO were taken from the previous optimization in chapter 3 without any modification and the standard Gibbs energies of solid and liquid SiO₂ and CaO were taken from FACT pure substance database^[9]. The optimized phase diagram of the CaO-SiO₂ system indicates the following compounds, wollastonite (CaSiO₃),

rankinite ($Ca_3Si_2O_7$), dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5). The Gibbs energies of all these binary compounds were taken from FACT pure substance database^[9].

For the SnO₂-SiO₂ system, two binary compounds CaSnO₃ and Ca₂SnO₄, which have been predicted to be stable in the SnO-SiO₂ system at Sn saturation, were optimized in this study. For the ternary SnO₂-SiO₂-CaO system in air and SnO-SiO₂-CaO system at Sn saturation, two stable ternary compounds, CaSiSnO₅ and Ca₃Si₂SnO₉ were considered. In this study, the heat capacities of CaSnO₃ and Ca₂SnO₄ were optimized by mixing the corresponding amount of the SnO₂ and CaO. The heat capacity of CaSiSnO₅ was determined by mixing CaSiO₃ and SnO₂, and the heat capacity of Ca₃Si₂SnO₉ was prepared by mixing Ca₃Si₂O₇ and SnO₂. Then, $\Delta H^{\circ}_{298.15}$ and $S^{\circ}_{298.15}$ of these compounds were optimized based on the experimental thermodynamic property and phase equilibrium data. The optimized thermodynamic properties of these compounds are listed in Table 5.1.

5.2.2 Liquid phase

In the present work, the liquid oxide phase in the SnO₂-SnO-SiO₂-CaO system was described using the Modified Quasi-chemical Model (MQM)^[15]. In the MQM, short range ordering (SRO) of second-nearest-neighbor (SNN) cation is taken into account in the liquid solution. The cationic species in the present study is Sn⁴⁺, Sn²⁺, Si⁴⁺ and Ca²⁺.

In MQM, the following quasi-chemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B); \qquad \Delta g_{AB}$$
 (5-4)

where A and B are cationic species in the solution and (A-B) represents an SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{i \ge 1} g_{AB}^{0j} X_{BB}^{j}$$
(5-5)

where Δg_{AB}° , Δg_{AB}^{i0} and Δg_{AB}^{0j} are the parameters of the model which may be functions of temperature.

The Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{\circ} + n_{B}g_{B}^{\circ}\right) - T\Delta S^{conf} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(5-6)

where n_i and g_i° are the numbers of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{conf} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional lsing model^[16]. The coordination numbers of Sn⁴⁺, Sn²⁺, Si⁴⁺ and Ca²⁺ were set to be 2.7529, 1.3774, 2.7549 and 1.3774, respectively, to keep the consistency of the thermodynamic modeling. Among the six quasi-chemical reactions in the SnO₂-SnO-CaO-SiO₂ system, the model parameters of the SiO₂-CaO solution were taken from the previous study^[8]. The Gibbs energy parameters (Δg_{AB}) of the Sn²⁺-Sn⁴⁺ reaction for the SnO-SnO₂ solution, the Sn⁴⁺-Si⁴⁺ reaction for the SnO₂-SiO₂ solution and the Sn²⁺-Si⁴⁺ reaction for the SnO-SiO₂ solution were taken from the previous optimization in Chapters 3 and 4. The SnO-CaO system at Sn saturation was considered as the ideal solution and the model parameter for the Sn²⁺-Ca²⁺ was set to be zero. The Gibbs energy parameters (Δg_{AB}) of Sn⁴⁺-Ca²⁺ reaction were optimized in this study to better describe the liquidus of the SnO₂-SiO₂-CaO system in air and the phase diagram of the SnO₂-CaO system:

$$\Delta g_{Ca^{2+}-Sn^{4+}} = -19000 - 3000X_{Sn^{4+}-Sn^{4+}}^{1}$$
(5-7)

There are four ternary liquid solutions in the SnO₂-SnO-SiO₂-CaO system. For the ternary liquid solutions of liquid SnO₂-SiO₂-CaO solution in air and liquid SnO-SiO₂-CaO solution at Sn saturation, the Gibbs energies of each solution were first predicted from binary model parameters using a

specific geometric model, and then ternary model parameters were introduced for a more accurate description of the liquidus surface of the ternary systems:

$$q_{Ca^{2+}-Si^{4+}-Sn^{4+}}^{001} = -1000, q_{Ca^{2+}-Si^{4+}-Sn^{4+}}^{012} = 30000$$
(5-8)

$$q_{Ca^{2+}-Si^{4+}-Sn^{2+}}^{001} = 1700, q_{Ca^{2+}-Si^{4+}-Sn^{2+}}^{001} = -17000$$
(5-9)

The mathematical expressions of the ternary excess parameters can be found in Chapter 2.

Regarding geometric interpolation techniques for ternary liquid systems, the SnO₂-SiO₂-CaO system was treated using the 'Toop-type' model with CaO as the 'asymmetric component' because the CaO can behave differently (basic component) from the other two components (acidic component) in this ternary solution: the CaO-SiO₂ system and CaO-SnO₂ system shows the similar negative deviation from the ideal solution, while the SiO₂-SnO₂ system shows the positive deviation from the ideal solutions. The ternary SnO-SiO₂-CaO system was treated using 'Toop-type' approximation with SiO₂ as the 'asymmetric component'.

5.2.3 Metallic and gas phases

To calculate the metallic saturation condition, a stoichiometric solid Sn and the liquid Sn solution (containing oxygen and Si as dilute elements) from FACT database^[9] were considered. The Gibbs energies of gas species were taken from FACT pure substance database^[9].

5.3 Critical evaluation and optimization of the SnO₂-SnO-SiO₂-CaO system

All experimental data in the literature were critically reviewed, and one set of optimized thermodynamic model parameters were obtained to reproduce all reliable experimental phase diagram data as much as possible within experimental error limits. Phase diagrams of the Sn oxide containing systems were determined either at Sn saturation or in air condition. Strictly speaking, there are always a certain amount of Sn⁴⁺ oxide even at metallic Sn saturation, and also Sn²⁺ oxide in air. However, for the sake of convenience, the notations SnO₂-CaO-SiO₂ and SnO-CaO-SiO₂ are used to represent oxidizing and reducing conditions, respectively, in this study. In the thermodynamic optimization, the previous results on the SnO-SnO2-SiO2 system with its subbinary SnO-SnO2, SnO-SiO2 and SnO2-SiO2 systems (see Chapters 3 and 4) were used without any modification.

There have been no phase diagram data in the CaO-SnO₂ system. However, the existence of two binary compounds, CaSnO₃ and Ca₂SnO₄, have been confirmed^[11]. No thermodynamic data for the compounds and liquid phase have been investigated. In the case of the CaO-SnO system, no phase diagram is available. No binary compound has been reported for this binary system.

In the SnO₂-SiO₂-CaO system, the primary phase fields of two binary compounds CaSnO₃ and Ca₂SnO₄, and two ternary compounds CaSiSnO₅ and Ca₃Si₂SnO₉ have been identified^[17-19]. It has been reported that CaSiSnO₅^[17], Ca₃Si₂SnO₉^[18] and CaSnO₃^[19] are stable at 1400 °C. The melting point of Ca₂SnO₄ is over 1480 °C. Xu et al.^[11] investigated the liquidus of the SnO₂-CaO-SiO₂ in air using the quenching method followed by the electron probe microanalysis (EPMA). Experiments were performed in Al₂O₃ crucibles and the samples were held for 2 to 24 h at fixed temperature to ensure the achievement of equilibrium. The atmosphere within the reaction tube was maintained by a flowing air stream. The achievement of equilibrium was tested by checking the composition homogeneity of phases in all samples by EPMA. And the contamination from crucible was also checked by EPMA. Experimental phase diagram data available for the SnO₂-CaO-SiO₂ system in air were limited to the CaO-SiO₂-rich side because of the difficulty in obtaining the accurate chemical equilibrium data for SnO₂-rich slag due to the volatile loss of the SnO₂.

Xu et al.^[10] also studied phase equilibria of the SnO-CaO-SiO₂ system at Sn saturation using the similar technique. The experiments were performed under Ar atmosphere using SiO₂ or SnO₂ as the substrate of the crucible to avoid the crucible contamination. The samples were held for 2 to 8h to ensure the achievement of the equilibria. The primary crystalline phase fields of SnO₂, SiO₂,

CaSiO₃ and CaSiSnO₅ were observed in this system. Koike et al.^[20] investigated the liquidus of the SnO-CaO-SiO₂ system by keeping the constant composition 5mol% CaO using the quenching method and XRD analysis. The results of Koike et al. are in good agreement with those of Xu et al.

The predicted phase diagram of the CaO-SnO₂ system is presented in Figure 5.1. In the prediction of the CaO-SnO₂ system, we considered the phase diagram data in the ternary SnO₂-SiO₂-CaO system. That is, in order to reproduce the phase stability of binary compounds CaSnO₃ and Ca_2SnO_4 in the ternary SnO₂-SiO₂-CaO system in air, the Gibbs energies of these two compounds could be reasonably constrained. Then, for reproducing the estimated melting temperatures of two binary compounds, the model parameters of liquid CaO-SnO₂ solution was determined. In fact, there are no melting temperature data for the CaSnO₃ and Ca₂SnO₄ compounds in air. According to Xu et al.^[11], CaSnO₃ is still stable at 1600 °C. Therefore, in the present modeling, the melting temperature of CaSnO₃ was assumed to be about 1700 °C, and that of Ca₂SnO₄ about 1900°C; Usually, orthosilicate compound in binary silicate system has higher melting temperature than that of metasilicate compound, so similar trend can be expected in the CaO-SnO₂ system. As mentioned earlier, there is no phase diagram information for the binary SnO-CaO system. As both SnO and CaO would have similar thermodynamic behavior, the liquid CaO-SnO solution was assumed to be ideal solution, and no binary compounds were considered in this study. The predicted phase diagram of the CaO-SnO in Sn saturation is given in Figure 5.2. As CaSnO₃ and Ca₂SnO₄ compounds are very stable, they are even shown up in the CaO-SnO system in Sn saturation condition. In the future, the experimental study on the CaO-SnO-SnO₂ system over a wide range of the oxygen partial pressure is necessary to confirm and improve the accuracy of the predicted phase diagrams in Figure 5.1 and 5.2.

The calculated phase diagrams of the SnO₂-CaO-SiO₂ system in air at 1600 °C and 1500 °C are presented in Figure 5.3 along with the experimental data by Xu et al.^[11]. Overall, the experimental data of the liquidus of binary and ternary compounds were well reproduced at both temperatures. In order to reproduce these experimental data, two ternary parameters in the

liquid phase were optimized (see section 5.2.2). The Gibbs energies of ternary stoichiometric compounds $CaSiSnO_5$ and $Ca_3Si_2SnO_9$ were optimized simultaneously, as listed in the Table. 5.1. As seen in Figure 5.4, the ternary compounds $CaSiSnO_5$ and $Ca_3Si_2SnO_9$ are only stable at 1500 °C and destabilized at 1600 °C. The binary compound $CaSnO_3$ is stable over 1600 °C.

The phase diagrams of the SnO-CaO-SiO₂ system at Sn saturation at 1400 °C, 1350 °C, 1300 °C and 1250 °C are calculated in Figure 5.4 and compared with all available experimental data. Overall, the experimental data are well described at each temperature. For this optimization, two ternary model parameters were introduced for the liquid SnO-CaO-SiO₂ solution (see section 5.2.2). It should be noted that ternary compounds CaSiSnO₅ and Ca₃Si₂SnO₉ where Sn is Sn⁴⁺ state which are stable even in the Sn saturation condition, as shown in Figure 5.4. The optimized Gibbs energy of the ternary compounds CaSiSnO₅ and Ca₃Si₂SnO₉ in the SnO₂-CaO-SiO₂ system in air can reproduce the primary phase field of the ternary compounds at Sn saturation. This demonstrates the consistency of Gibbs energy data of ternary compounds and liquid solution between the SnO₂-SiO₂-CaO system in air and SnO-SiO₂-CaO system at Sn saturation. In addition, this also support the possibility of appearance of CaSnO₃ and Ca₂SnO₄ compounds where Sn is Sn⁴⁺ in the CaO-SnO system at Sn saturation, as presented in Figure 5.2.

The calculated activity of the SnO liquid in the SnO-CaO-SiO₂ slag at Sn saturation at 1150 °C is shown in Figure 5.5. The activities of SnO in the ternary liquid phase containing 8.2 mol% CaO and 11.2 mol% CaO under Ar atmosphere were measured by Koike et al.^[21] using emf method. Unfortunately, the present model cannot reproduce the experimental data accurately, but the trend of the activity is well reproduced. It should be noted that the accurate measurement of activity of SnO using emf seems to be difficult, as demonstrated in the SnO-SiO₂ system (see Figure 4.6).

5.4 Summary

A critical assessment and thermodynamic optimization of the phase diagrams of the SnO-SnO₂-CaO-SiO₂ system were carried out in air and at Sn saturation. Binary phase diagram of the CaO-SnO and CaO-SnO2 systems were predicted as part of the optimization of this quaternary system. The complex phase relations of the quaternary system were well reproduced from the thermodynamic models with the optimized model parameters within 5 mol% in composition and 50 K in temperature. The phase diagrams of the SnO-SnO₂-CaO-SiO₂ system important for various industrial processes can be predicted, from the present model with optimized parameters, at any temperature and composition range under a given oxygen partial pressures from Sn saturation to 1 atm pressure.

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Phase	$\Delta H_{298.15K}^{\circ}$	$\Delta S_{298.15K}^{\circ}$	C _p
riidse	(kJ/mol)	(J/mol⋅K)	(J/mol·K)
CaSnO₃	-1276.819	87.76	$1C_p(SnO_2) + 1C_p(CaO)$
Ca_2SnO_4	-1937.809	124.51	$1C_p(SnO_2) + 2C_p(CaO)$
CaSiSnO₅	-2207.136	135.95	$1C_p(SnO_2) + 1C_p(CaSiO_3)$
$Ca_3Si_2SnO_9$	-4540.062	254.57	$1C_p(SnO_2) + 1C_p(Ca_3Si_2O_7)$

Table 5.1 Optimized thermodynamic properties of the Stoichiometric compounds in the SnO₂-SnO-CaO-SiO₂ system



Figure 5.1 Predicted phase diagram of the CaO-SnO₂ system in air.



Figure 5.2 Predicted phase diagram of the CaO-SnO system at Sn saturation.



Figure 5.3 Calculated phase diagrams of the SnO₂-CaO-SiO₂ system in air at 1 atm at (a) 1600 °C and (b) 1500 °C.



Figure 5.4 Calculated phase diagrams of the SnO-CaO-SiO₂ system at Sn saturation at 1 atm at (a) 1400 °C, (b) 1300 °C, (c) 1200 °C, and (d) 1100 °C.



Figure 5.5 Calculated activity of the SnO liquid in the SnO-CaO-SiO_2 slag at Sn saturation at 1150 $^{\circ}$ C.

6 Conclusion

All the thermodynamic properties and phase diagrams of the binaries, ternaries, and quaternary in the SnO-SnO₂-CaO-SiO₂ system (SnO-SnO₂, SnO-SiO₂, SnO₂-SiO₂, CaO-SnO, CaO-SnO₂, Ca CaO-SnO-SiO₂, and CaO-SnO₂-SiO₂ systems) were critically evaluated and optimized in the present study to obtain one set of optimized model parameters representing the Gibbs energies of all the phases in this quaternary system. In order to assist the optimization, the high-temperature phase equilibrium experiments were conducted for the SnO₂-SiO₂ system. The thermodynamic models with optimized model parameters can reproduce the phase diagram of the system within 5 mol % and 50 K under the oxygen partial pressure from Sn saturation to 1 atm pressure. The present results can be conjugated with the existing database in the FactSage to perform the thermodynamic calculations of multicomponent system for the better understanding of industrial process.

Although the optimization of all thermodynamic properties of solid and liquid phases was performed reasonably well in comparison with available experimental data, there are still certain limitations in terms of modeling and experiments. In the future, the experimentations in the following areas can contribute to the thermodynamic modeling of the present Sn oxide systems:

- Further phase diagram experiments in the SnO₂-SiO₂ are necessary to determine the size
 of miscibility gap and the eutectics in the system. For this, new methodology to suppress
 the volatility of SnO₂ at high temperature should be developed.
- No experimental phase diagrams of the SnO₂-CaO system in air and SnO-CaO system at Sn saturation are available. The new experimental study on these phase diagrams are expected to improve the quality of thermodynamic modeling.

 Thermodynamic data for several binary SnO₂-CaO stoichiometric compounds and ternary stoichiometric compounds in the SnO₂-CaO-SiO₂ system are needed to better constrain the Gibbs energy of the systems.