
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

ISOMÄKI, Iikka; ZHANG, Rui; XIA, Long gong; HELLSTEN, Niko; TASKINEN, Pekka A.
Thermodynamic assessment of ZnO-SiO₂ system

Published in:
Transactions of Nonferrous Metals Society of China (English Edition)

DOI:
[10.1016/S1003-6326\(18\)64832-0](https://doi.org/10.1016/S1003-6326(18)64832-0)

Published: 01/09/2018

Document Version
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Published under the following license:
CC BY-NC-ND

Please cite the original version:
ISOMÄKI, I., ZHANG, R., XIA, L. G., HELLSTEN, N., & TASKINEN, P. A. (2018). Thermodynamic assessment of ZnO-SiO₂ system. *Transactions of Nonferrous Metals Society of China (English Edition)*, 28(9), 1869-1877. [https://doi.org/10.1016/S1003-6326\(18\)64832-0](https://doi.org/10.1016/S1003-6326(18)64832-0)

A thermodynamic assessment of the ZnO-SiO₂ system

Ilkka Isomäki, Rui Zhang, Longgong Xia¹, Niko Hellstén, Pekka A. Taskinen*

Aalto University, School of Chemical Technology,

Department of Materials Science and Engineering, Thermodynamics and Modelling research group

P.O. Box 16200, FI-00076 Aalto (Finland)

¹) *permanent address*: Central South University, School of Metallurgy and Environment, 410083 Changsha, Hunan, P.R. China

Abstract

A complete literature review, critical evaluation of the available data and thermodynamic optimization of the phase equilibria and thermodynamic properties of oxide phases in SiO₂-ZnO system at 1 atm pressure are presented. The molten oxide phase is described with an associate solution model. A set of optimised model parameters of all phases was obtained which reproduces all available and reliable thermodynamic and phase equilibrium data within their experimental error limits from 298 K to above the liquidus temperatures over the entire composition range. The created database of the model parameters can be used in the Gibbs energy minimization software to calculate the thermodynamic properties and the phase diagram sections of interest.

Key words: Phase diagram, willemite, silicate, Gibbs energy, enthalpy of formation

1. Introduction

Considerable interest has been directed towards the development of advanced materials based on zinc oxide over the years [1-4]. Zinc silicate is one of the most promising new systems due to its unique

* corresponding author; e-mail: pekka.taskinen@aalto.fi; cell: +358 40 501 7411; fax: +358 9 470 22798

electrical and physical properties [5-7]. Zinc is a common impurity element in copper ores and thus its detailed chemistry in silicate systems is of interest [8].

The purpose of this paper is to present a critical review of the available experimental thermodynamic and phase equilibrium data for the binary SiO_2 -ZnO system, and to obtain a set of self-consistent thermodynamic parameters to describe the system properties.

2. Literature on the ZnO-SiO₂ system

The binary SiO_2 -ZnO system has been experimentally studied [9-13,16,17] and thermodynamically assessed [14,15] by a few researchers. Bunting [9] measured the SiO_2 -ZnO phase diagram features using an equilibration-quenching-optical microscopy analysis technique and found a large liquid immiscibility region in the SiO_2 rich side at elevated temperatures, one compound (willemite or zinc orthosilicate Zn_2SiO_4), and two eutectic reactions ($\text{L} \rightarrow \text{SiO}_2 + \text{Zn}_2\text{SiO}_4$ and $\text{L} \rightarrow \text{ZnO} + \text{Zn}_2\text{SiO}_4$). A monotectic equilibrium of two immiscible liquids in equilibrium with cristobalite was reported to extend from 0.02 to 0.35 mole fraction of ZnO, and the compound to melt congruently at 1785 ± 3 K. Eutectic points were determined to be at 1705 K and 0.491 mole fraction of ZnO at SiO_2 saturation side and at 1780 K and 0.775 mole fraction of ZnO at ZnO saturation. However, the compositions of the liquidus line in the paper of Bunting were estimated from the initial compositions of the samples prior to equilibration. Impurities in the starting materials as well as evaporation of ZnO at elevated temperatures [18] did bring unpredictable errors to his results.

Williamson & Glasser [10] and Weber et al. [11-12] re-investigated experimentally the SiO_2 -ZnO system. Their data agreed well with the findings of Bunting [9] on the eutectic point at the silica-rich region. The eutectic point between Zn_2SiO_4 and ZnO, however, was much lower than the value proposed by Bunting, and the location of the liquidus was not well explained in their studies. Ringwood & Major [19], Syono et al. [21], Akaogi et al. [21] and Liu et al. [22] used high-temperature X-ray techniques for measuring the (P,T) - phase diagrams of zinc silicates.

Reyes & Gaskell [13] measured the activity of ZnO in the SiO_2 -ZnO melts at 1833 K using a transpiration technique with CO-CO₂ mixtures as the carrier gas. The measured Gibbs energies of formation of SiO_2 -ZnO melts were significantly more negative than the estimated value [9, 11-12], indicating that ZnO is a

relatively basic oxide. Itoh & Azakami [23] conducted EMF measurements in the solid mixtures of the system using oxygen concentration cells. Calorimetric measurements are also available on the zinc orthosilicate-metasilicate transition pressure [24].

Björkman [14] initially assessed the SiO_2 -ZnO system by treating the liquid oxide mixture as an ideal solution but he considered the formation of Zn_2SiO_4 as an associated species which reduces the concentration and thus activity of ZnO. The calculated phase relations as well as the activity of ZnO were found to be in a good agreement with the available data. Jak et al. [15, 25] optimised the SiO_2 -ZnO system by employing the quasi-chemical model and least-squares optimisation module of the F*A*C*T software package [26]. The thermodynamic properties of SiO_2 were taken from the F*A*C*T database, and the properties of ZnO from Barin [27]. Thermodynamic information about Zn_2SiO_4 was insufficient in the literature [28-32]. Therefore, Jak et al. [15] adopted the standard entropy of Zn_2SiO_4 from the compilation of Barin [27], and optimized the other thermodynamic properties of Zn_2SiO_4 . The experimental phase diagram points used in the optimisation [9-12] were well re-produced by the assessed parameters in their study.

The development of advanced experimental apparatus and analytical techniques makes it possible for the researchers to control the experimental conditions and achieve results efficiently and in more reliable way. Hansson et al. [16] studied experimentally the phase equilibria and liquidus temperatures of the SiO_2 -ZnO system using an equilibration-quenching-EPMA (Electron Probe X-ray MicroAnalysis) technique [33]. Two binary eutectics involving congruently melting willemite (m.p. 1785 ± 3 K) were ascertained at 1721 ± 5 K and 0.52 ± 0.01 mole fraction ZnO, and at 1775 ± 5 K and 0.71 ± 0.01 mole fraction ZnO, respectively. Xia et al. [17] studied the SiO_2 -ZnO system using an equilibration and quenching technique in a wide temperature range from 1703 to 1963 K. Their results obtained by EPMA confirmed the findings reported by Hansson et al. [16] and expanded the experimental data range.

A few experimental attempts have also been made on re-determining the thermodynamic properties of Zn_2SiO_4 [23-24, 34]. Also a first principles study about the stability of zinc silicates in high pressures has

been carried out [35]. Bekturganov et al. [36] calculated the low-temperature c_p function of willemite by *ab initio* techniques.

3. Review of Experimental Data

The experimental phase diagram measurements of the $\text{SiO}_2\text{-ZnO}$ system and the available thermodynamic data of Zn_2SiO_4 were compiled from the literature and evaluated critically. The recent phase diagram studies [16, 17] deviate systematically from the older observations [9-12] which involve systematical errors and uncertainties. An additional problem with the experimental phase diagram and liquidus data is that the measurements have been made at relatively low temperatures. No experimental data about the critical point of the molten-state miscibility gap at silica-rich compositions could be found. The zinc oxide activity data by Reyes & Gaskell [13] obtained by vapor pressure transpiration measurements seem too low at small zinc oxide concentrations, i.e. in the silica-rich compositions obviously due to systematic errors in their experimental method. Due to the large differences between the recent experimental points and the computational phase diagrams from the 20th century and those from Hansson et al. [16] and Xia et al. [17], the system was found to require reassessment.

4. Thermodynamic Modelling

The thermodynamic modelling and the model parameter optimization was carried out using the Calphad technique in the Thermo-Calc software environment [37].

4.1 Unary phases

The Gibbs energy of a component i in phase φ , ${}^0G_i^\varphi = G_i^\varphi(T) - H_i^{SER}$ ($i = \text{ZnO}$ and SiO_2) was expressed by equation:

$${}^0G_i^\varphi(T) = a + b \cdot T + c \cdot T \ln T + d \cdot T^2 + e \cdot T^{-1} + f \cdot T^3 + g \cdot T^7 + h \cdot T^9 \quad (1)$$

H_i^{SER} is the sum of enthalpies of the elements at 298.15 K and 1 atm in their stable states (Stable Element Reference, denoted as SER); T is the absolute temperature (K) and a-h are substance specific coefficients. In this work, the Gibbs energy functions used for pure ZnO are consistent with MTDATA [38] and the Mtox

oxide database [39]. The Gibbs energy expression for pure SiO₂ was taken from MTDATA SGTE SUB database [40].

4.2. Solution phases

An associate solution model was employed to describe the liquid oxide phase [41] which was assumed to consist of three species: ZnO, Zn₂SiO₄ and SiO₂. The molar Gibbs energy of liquid oxide solution can thus be expressed as follows:

$$G_m^{Liq} - H^{SER} = y_{ZnO} {}^0G_{ZnO}^{Liq} + y_{SiO_2} {}^0G_{SiO_2}^{Liq} + y {}^0G_{Zn_2SiO_4}^{Liq} + RT(y_{ZnO} \ln y_{ZnO} + y_{SiO_2} \ln y_{SiO_2}) + RT(y_{Zn_2SiO_4} \ln y_{Zn_2SiO_4}) + {}^E G_m \quad (2)$$

where y represents the mole fraction of an associate ZnO, SiO₂ and Zn₂SiO₄ in the liquid oxide solution. The symbol y was used for the associate concentrations in order to distinguish from the macroscopic component concentrations in figures denoted as x . The Gibbs energy of molten zinc orthosilicate associate

${}^0G_{Zn_2SiO_4}^{Liq}$ was described as:

$${}^0G_{Zn_2SiO_4}^{Liq} = 2 \cdot {}^0G_{ZnO}^{Liq} + {}^0G_{SiO_2}^{Liq} + a + b \cdot T + c \cdot T \cdot \ln(T) \quad (3)$$

where ${}^0G_{ZnO}^{Liq}$ and ${}^0G_{SiO_2}^{Liq}$ are Gibbs energies of liquid ZnO and SiO₂ and a as well as b are the enthalpy and entropy of formation of zinc orthosilicate (Zn₂SiO₄) associate, respectively.

In eq. (2), ${}^E G_m$ is excess Gibbs energy of the liquid oxide phase which was described in this study by Redlich-Kister polynomials [42], as:

$$\begin{aligned} {}^E G_m = & y_{ZnO} y_{SiO_2} [{}^0L_{ZnO, SiO_2} + {}^1L_{ZnO, SiO_2} (y_{ZnO} - y_{SiO_2})] \\ & + y_{ZnO} y_{Zn_2SiO_4} [{}^0L_{ZnO, Zn_2SiO_4} + {}^1L_{ZnO, Zn_2SiO_4} (y_{ZnO} - y_{Zn_2SiO_4}) + {}^2L_{ZnO, Zn_2SiO_4} (y_{ZnO} - y_{Zn_2SiO_4})^2] \\ & + y_{SiO_2} y_{Zn_2SiO_4} [{}^0L_{SiO_2, Zn_2SiO_4} + {}^1L_{SiO_2, Zn_2SiO_4} (y_{SiO_2} - y_{Zn_2SiO_4}) + {}^2L_{SiO_2, Zn_2SiO_4} (y_{SiO_2} - y_{Zn_2SiO_4})^2 + {}^3L_{SiO_2, Zn_2SiO_4} (y_{SiO_2} - y_{Zn_2SiO_4})^3] + [{}^{ex}L_{ZnO, Zn_2SiO_4, SiO_2}] \end{aligned} \quad (4)$$

In eq. (4), ${}^lL_{ZnO, SiO_2}$, ${}^lL_{ZnO, Zn_2SiO_4}$ and ${}^lL_{SiO_2, Zn_2SiO_4}$ ($l = 0, 1, 2, 3$) are the interaction parameters between different species to be optimized in the present work. A general temperature dependent form of the interaction parameters ${}^lL_{i,j} = c + d \cdot T$ was used. The ternary parameter in eq. (4) will be expressed using the Muggianu formalism [43-46] as:

$${}^{ex}L_{ZnO, Zn_2SiO_4, SiO_2} = y_{ZnO} y_{Zn_2SiO_4} y_{SiO_2} [y_{ZnO} \cdot {}^0L_{ZnO, Zn_2SiO_4, SiO_2} + y_{Zn_2SiO_4} \cdot {}^1L_{ZnO, Zn_2SiO_4, SiO_2} + y_{SiO_2} \cdot {}^2L_{ZnO, Zn_2SiO_4, SiO_2}] \quad (5)$$

It should be pointed out on the basis of the literature review summarized above that no experimental data could be found on the mutual solubilities between the solid ZnO (wurtzite) and SiO₂ (tridymite, cristobalite) phases. Therefore, in the present work, the terminal (solid) solutions (ZnO-based and SiO₂-based solutions) in the ZnO-SiO₂ system have been treated as pure oxides in the parameter optimisation.

4.3. Compounds

Based on the literature review, a solid orthosilicate compound willemite (Zn₂SiO₄) has been confirmed to exist in the ZnO-SiO₂ system under ambient pressure [24]. The molar Gibbs energy function of this olivine type stoichiometric compound [20] was expressed as:

$${}^0G_{Zn_2SiO_4} - 2H_{Zn}^{SER} - H_{Si}^{SER} - 4H_O^{SER} = A + B \cdot T + C \cdot T \ln T + D \cdot T^2 + F \cdot T^{-1} \quad (6)$$

where A to F are coefficients specific to Zn₂SiO₄. The thermodynamic coefficients retrieved from the Mtox oxide database [39] were employed to describe initially the properties of solid and liquid Zn₂SiO₄. The zinc metasilicate ZnSiO₃ crystallising as pyroxene or ilmenite structure is stable at elevated pressures only [20, 24, 47] and thus it was not included in the present optimisation.

Optimization of the thermodynamic parameters was performed manually using the CALPHAD technique [48] and the Thermo-Calc 4.1 [37] software package. A step-by-step optimization procedure was adopted and the data of new experiments [17] as well as selected literature data were employed. First, the binary parameters ${}^lL_{SiO_2, Zn_2SiO_4}$ and ${}^lL_{ZnO, Zn_2SiO_4}$ were evaluated. Then the three ternary parameters

according to eq. (5) were assessed. After achieving a good fit with the experimental data for the liquid oxide phase, the enthalpy parameter for solid Zn_2SiO_4 , see eq. (6), was calculated. Only the enthalpy of solid willemite was reassessed, for adjusting the liquidus line within the willemite primary phase field according to the recent liquidus measurements [16, 17] and the melting point of willemite. The heat capacity parameters were taken from Mtox database as such.

5. Results and Discussion

Since the Mtox oxide database [38, 39] has been well developed and widely applied in many industrial fields, the thermodynamic data in the present work were based on this database. With the newly published experimental observations of the molten phase in the ZnO-SiO_2 system [16, 17], the improvement was made on the description of the liquid phase. The thermodynamic assessment of the ZnO-SiO_2 system was conducted manually using the earlier work completed with MTDATA software [49] and its assessment module as the starting point. The system was treated as a true binary ZnO-SiO_2 system, even though it really is a quasi-binary section of the ternary Si-O-Zn . In order to maintain compatibility with the Mtox database, the liquid oxide phase was modelled with species ZnO , SiO_2 and Zn_2SiO_4 , which is a flexible model for liquid multicomponent silicates [49] compared for instance to ionic liquid model [41]. No adjustments to the primary data were made and they were taken from the original literature sources with appropriate inaccuracies.

Fig. 1 shows the calculated phase diagram for the ZnO-SiO_2 system. The experimental points reproduced in the graph were taken from Xia et al. [17], Williamson & Glasser [10], Weber et al. [11, 12] and Hansson et al. [16]. There are no experimental data available concerning the critical point or tie-lines of the silica-rich miscibility gap, except the monotectic equilibrium. Monotectic temperature according to Bunting [9] is 1968 K. The calculated monotectic temperature of this work is 1975 K. The resulting critical temperature is 2345 K and its composition $x_{\text{ZnO}}=0.141$. The miscibility gap was assessed according to the existing data at much lower temperatures than the critical point. The liquidus curve on the ZnO rich side is S-shaped, suggesting that there is a metastable miscibility gap [50]. There is a possible submerged metastable miscibility

gap with a critical temperature just below the inflection point on the liquidus curve. Often the immiscibility domain is entirely metastable and is not present on the equilibrium diagram [51].

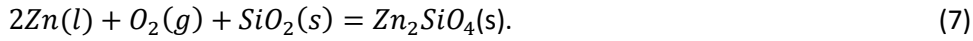
Fig. 2 shows a magnified phase diagram section around the willemite composition and its congruent melting point. The assessed melting point of willemite is 1512 °C (1785 K) and the experimental values of Bunting [9] and Segnit [52] are 1785 K and 1784.5 K, respectively. The calculated silica-rich eutectic point 1 is located at $x_{\text{ZnO}}=0.52$ and $T=1729$ K. The experimental value by Xia et al. [17] is $x_{\text{ZnO}} = 0.52$ and $T = 1718$ K. The value obtained by Hansson et al. [16] is $x_{\text{ZnO}} = 0.519$ and $T = 1734$ K. The obtained fit is thus good between the experimental and assessed phase diagram values. The calculated zinc-oxide-rich eutectic point 2 is located at $x_{\text{ZnO}} = 0.71$ and $T = 1771$ K. Xia et al. [17] obtained the value of $x_{\text{ZnO}} = 0.716$ and $T = 1773$ K. Hansson et al. [16] reported the values $x_{\text{ZnO}} = 0.72$ and $T = 1779$ K. The obtained agreement of the assessed value with the 2nd eutectic point is very good, and the experimental values of Hanson et al. [16] and Xia et al. [17] are reproduced well by the optimized solution properties.

Fig. 3 shows the calculated liquid oxide enthalpy plot as a function of composition at 2400 K. The curve obtained is compatible with the formation of miscibility gap in silica-rich compositions. No experimental data were available for comparison of the mixing enthalpy.

Fig. 4 shows the assessed component activities of ZnO and SiO₂ as a function of zinc oxide mole fraction at 1833 K. The standard states used in the graph were pure, solid ZnO(s) and pure, solid SiO₂(s). Fig. 5 shows the activities of ZnO and SiO₂ as a function of zinc oxide mole fraction at 1833 K. Standard states were solid ZnO and cristobalite for SiO₂. The graph indicates that the ZnO activity values of Reyes & Gaskell [13] measured at 1833 K were much too low in the low ZnO concentration region. When system was assessed according to the existing literature data, the zinc oxide activity data of Reyes & Gaskell [13] seems to be too low compared to calculated data. It seems to be incorrect if the other literature data are correct. The first three points of Björkman [14] agree well with the calculated curve of this study, but his two last points not so well. Barin's data [53] were from 1773 K, because at 1833 K willemite is molten. Two experimental points by Itoh & Azakami at 973 and 1073 K [23] agree well with the assessed ZnO activity values of this study.

Fig. 6 displays the assessed activity plots of ZnO, with liquid ZnO as the standard state, as a function of composition at five temperatures from 1823 to 2023 K with steps of 50 K. The previously assessed values by Jak et al. [15] are in good agreement with this study. When the calculated activity of zinc oxide at 973 and 1073 K at silica saturation according to this work was compared with the experimental values of Itoh & Azakami [23], it was found that the values are well in line with each other. The data were not used in the assessment. The EMF data by Itoh & Azakami [23] shows a slightly more negative enthalpy of formation of Zn_2SiO_4 from the component oxides than the other authors [29, 31-32].

The solid line in Fig. 7 shows the assessed $RT \ln (P_{O_2})$ for the equilibrium reaction (7) between willemite, silica and liquid zinc with pure gaseous 1 atm oxygen as standard state:



Itoh & Azakami [23] measured the partial pressures of oxygen for equilibrium (7) by an EMF technique in the temperature range 973 to 1073 K. Their experimental results agree well with the calculated values of this study. This figure represents a straightforward validation for the current assessed data of the ZnO-SiO₂ system, as the experimental values by Itoh & Azakami [23] were not used as experimental points in the parameter optimisation.

Table 1 presents the assessed thermodynamic parameters for the liquid phase and Gibbs energy of solid willemite obtained in this study. Table 2. shows the available literature data for the Gibbs energy of formation of solid Zn_2SiO_4 .

Table 1. The assessed model parameters of the ZnO-SiO₂ system obtained in this study (T/K).

Liquid oxide:	
${}^0L_{ZnO, SiO_2}$	$= +8183.41521$
${}^1L_{ZnO, SiO_2}$	$= +70897.9728$
${}^0L_{SiO_2, Zn_2SiO_4}$	$= +295000 - 162.5T$
${}^1L_{SiO_2, Zn_2SiO_4}$	$= +23000$
${}^2L_{SiO_2, Zn_2SiO_4}$	$= +25541.0194$
${}^3L_{SiO_2, Zn_2SiO_4}$	$= +24926.48$

$${}^0L_{Zn_2SiO_4,ZnO} = +14000$$

$${}^1L_{Zn_2SiO_4,ZnO} = -4000$$

$${}^2L_{Zn_2SiO_4,ZnO} = +29000 - 2T$$

$${}^0L_{SiO_2,Zn_2SiO_4,ZnO} = +75000 - 55T$$

$${}^1L_{SiO_2,Zn_2SiO_4,ZnO} = +75000 - 55T$$

$${}^2L_{SiO_2,Zn_2SiO_4,ZnO} = +150000 - 110T$$

Willemite $Zn_2SiO_4(s)$:

$${}^0G_{Zn_2SiO_4} - 2H_{Zn}^{SER} - H_{Si}^{SER} - 4H_O^{SER} =$$

$$-1698000 + 867.065702672T - 144.89T \ln T - 0.01847T^2 + 151\,4500T^{-1}$$

$Zn_2SiO_4(l)$:

$$-1666364.73 + 1347.6291 \cdot T - 215 \cdot T \cdot \ln(T)$$

When results from this work were compared with the available literature data, it was found that enthalpy of formation of Zn_2SiO_4 obtained at 298 K is near the calorimetric values of King [28] and Todd [30]. The enthalpy value is almost exactly the same as adopted by Barin [27].

When obtained entropy of formation at 298 K is compared to the experimental value of Todd [30], it can be found that results are close to each other. This entropy value is almost exactly the same as compiled by Barin [27].

When results from this work are compared to literature, it was found that enthalpy of formation of Zn_2SiO_4 from oxides at 298 K obtained in this work is near the value of Kubaschewski [54], King [28], Todd [30] and Navrotsky [31]. Entropy for formation from oxides at 298 K obtained in this work is close the value given by Todd [30].

When enthalpy values obtained by Kitchener & Ignatowicz [29] for formation of Zn_2SiO_4 from oxides at elevated temperatures are compared with the values of Kozłowska-Rog & Rog [32] and Navrotsky [31], it was found that they vary from -29.3 to -34.7 kJ/mol. The deviating value by Itoh & Azakami [23] is -46.6 kJ/mol and it was obtained by EMF techniques over a narrow temperature interval. Value of this work at 298 K is -31.4 kJ/mol, which is very well in the range of the experimental literature data.

Table 2. Gibbs energy of formation of solid Zn_2SiO_4 by different experimental reactions and authors (T/K).

Reference	Reaction	Temperature region K	$\Delta_R H$ kJ/mol	$\Delta_R S$ J/(mol*deg)
Tanaka et al. [34]	$Zn_2SiO_4 + 2CO(g)$	1423-1573	491	-273
	$= 2Zn(g) + 2CO_2(g) + SiO_2(s)$			
	$2Zn(g) + Si + 2O_2(g) = Zn_2SiO_4$	1423-1573	-1951	-613
Kitchener & Ignatowicz [29]	$Zn_2SiO_4 + 2H_2(g)$	1073-1275	495.3856	321.2057
	$= 2Zn(g) + 2H_2O(g) + SiO_2(s)$			
	$2ZnO + SiO_2 = Zn_2SiO_4$	1073-1275	-29.82774	-0.96232
Itoh & Azakami [23]	$2ZnO + SiO_2 = Zn_2SiO_4$	900-1100	-758.470	-233.85
	$2ZnO + SiO_2 = Zn_2SiO_4$	973-1073	-46.590	-16.79
Kozłowska-Rog & Rog [32]	$2ZnO + SiO_2 = Zn_2SiO_4$	953-1273	-34.6854	-5.8576
Navrotsky [31]	$2ZnO + SiO_2 = Zn_2SiO_4$	298	-29.288	
		965	-32.6352	
		965	-32.7607	
		1000	No data	-3.7656
		1173	-29.7064	
King [28]	$2Zn + Si + 2O_2(g) = Zn_2SiO_4$	298	-1584.481	n.a.
	$2ZnO + SiO_2 = Zn_2SiO_4$	298	-29.2462	
Todd [30]	$2Zn + Si + 2O_2(g) = Zn_2SiO_4$	298	-1584.481	-380.744
	$2ZnO + SiO_2 = Zn_2SiO_4$	298	-29.2462	2.092
This work	$2Zn + Si + 2O_2(g) = Zn_2SiO_4$	298	-1642.9999	-380.97
	$2ZnO + SiO_2 = Zn_2SiO_4$	298	-31.3799	2.6398
Kubaschewski [54]	$2ZnO + SiO_2 = Zn_2SiO_4$	298	-32.6352	n.a.
Barin [27]	$2Zn(s) + Si + O_2(g) = Zn_2SiO_4$	298	-1644.412	-380.996
	$2Zn(g) + Si + 2O_2(g) = Zn_2SiO_4$	1400	-1866.57	-573.931
		1500	-1861.13	-570.181

When entropy values from Kitchener & Ignatowicz [29] for formation of Zn_2SiO_4 from oxides at elevated temperatures are compared to Kozłowska-Rog & Rog [32] and Navrotsky [31], it was found that all values are from -5.86 to -0.96 J/(K·mol). Itoh & Azakami [23] obtained a much more negative value of -16.79 J/(K·mol). Value from this work at 298 K is 2.66 J/(K·mol) which is not far from the literature values, but has opposite sign.

6. Conclusions

In this study, the ZnO-SiO₂ system was reassessed using the description of Mtox oxide database as the starting point. SiO₂ pure substance values were taken from the SGTE SUB pure substance database [40].

The properties of liquid oxide phase were reassessed totally and also the enthalpy term of the Gibbs energy

of solid Zn_2SiO_4 . The new thermodynamic modelling agrees well with the recent experimental data and it can be used for predicting e.g. areas of the phase diagram without experimental points, like the critical point of the liquid miscibility gap, with better accuracy than using the previous assessments [15, 49].

A thermodynamic re-assessment of the binary ZnO-SiO_2 system was conducted using new experimental data about the liquidus lines in the silica, zinc oxide and willemite primary phase fields. Experimental oxygen activity data for willemite and zinc oxide data at 973 and 1073 K at silica saturation were used to validate the assessment. The oxygen potential $RT\ln(P_{\text{O}_2})$ for the invariant reaction between metallic zinc, willemite and silica was calculated from the optimized set of thermodynamic parameters, and agreement with the experimental values of Itoh & Azakami [23] was good. The assessed data also reproduces well the Gibbs energy of formation of willemite measured by Kitchener & Ignatowicz [29]. The obtained fit between the recent experimental data and assessed phase boundaries was good. Also, the experimental ZnO activity data from the literature were compared with the calculated results and agreement was good, except for the vapour pressure measurements by Reyes & Gaskell [13]. Their experimental ZnO activities were too low at low ZnO concentrations of the ZnO-SiO_2 system. The present assessed activities in the liquid oxide phase are in good agreement with the calculated values from the optimisation by Jak et al. [15]. Mixing enthalpies of the liquid oxide phase were calculated at three temperatures and the results seem reasonable, but no experimental observations are available for validation of the results.

4.2 Acknowledgements

The authors like to acknowledge the financial support of Tekes, Fimecc Oy (SIMP program), Finnish Metals Producers Fund and CIMO (Centre for International Movement, an agency of Finnish Ministry of Education and Culture).

List of references

[1] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V.C. Avrutin, S.J. Cho, & H. Morkoc, A comprehensive review of ZnO materials and devices. J. Appl. Phys., 98 (2005) (4) 041301.

- [2] C. Klingshirn, ZnO: From basics towards applications. *Physica Status Solidi (b)*, 244 (2007) (9) 3027-73.
- [3] R. Kumar, G. Kumar, O. Al-Dossary & A. Umar, ZnO nanostructured thin films: Depositions, properties and applications—A review. *Materials Express.*, 5 (2015) (1) 3-23.
- [4] H. Ma, P.L. Williams & S.A. Diamond, Ecotoxicity of manufactured ZnO nanoparticles—A review. *Environmental Pollution*, 172 (2013) (1) 76-85.
- [5] F. Iskandar, Nanoparticle processing for optical applications—A review. *Advanced Powder Technology*, 20 (2009) (4) 283-92.
- [6] M.M. Viitanen, W.P. Jansen, R.G. van Welzenis, H.H. Brongersma, D.S. Brands, E.K. Poels & A. Blik, Cu/ZnO and Cu/ZnO/SiO₂ catalysts studied by low-energy ion scattering. *J. Phys. Chem. B*, 103 (1999) (29) 6025-9.
- [7] G. Gao, S. Reibstein, M. Peng & L. Wondraczek, Tunable dual-mode photoluminescence from nanocrystalline Eu-doped Li₂ZnSiO₄ glass ceramic phosphors. *J. Mater. Chem.*, 21 (2011) (9) 3156-61.
- [8] F. Habashi, Recent trends in extractive metallurgy. *J. Min. Metall. B*, 45B (2009) (1) 1-13.
- [9] E.N. Bunting, Phase Equilibria in the System SiO₂-ZnO. *J. Res. Natl. Bur. Stand.*, 13 (1930) (4) 131-36.
- [10] J. Williamson & F.P. Glasser, Crystallisation of zinc silicate liquids and glasses. *Phys. Chem. Glasses*, 5 (1964) 52-59.
- [11] L. Weber & E. Grauer-Carstensen, The solidification behaviour of melts in the system Zn₂SiO₄-Mg₂SiO₄. *J. Mater. Sci.*, 12 (1977) (10) 1988-1993.
- [12] L. Weber & H.R. Oswald, Investigation of phase intergrowth morphologies in the system Zn₂SiO₄-SiO₂ by photo-emission electron microscopy. *J. Mater. Sci.*, 10 (1975) (6) 973-982.
- [13] R.A. Reyes & D.R. Gaskell, Thermodynamic activity of ZnO in silicate melts. *Metall. Mater. Trans. B*, 14B (1983) (4) 725-731.
- [14] B. Björkman, An Assessment of Cu, Ni, and Zn Silicate Systems: 1. The binary systems CuO_{0.5}-SiO₂, NiO-SiO₂ and ZnO-SiO₂. *Scand. J. Metall.*, 15 (1986) 185-190.
- [15] E. Jak, S. Degterov, P. Wu, P.C. Hayes & A. Pelton, Thermodynamic optimization of the systems PbO-SiO₂, PbO-ZnO, ZnO-SiO₂ and PbO-ZnO-SiO₂. *Metall. Mater. Trans. B*, 28B (1997) (6) 1011-1018.
- [16] R. Hansson, B.J. Zhao, P.C. Hayes & E.A. Jak, A reinvestigation of phase equilibria in the system Al₂O₃-SiO₂-ZnO. *Metall. Mater. Trans. B*, 36B (2005) (2) 187-193.
- [17] L. Xia, Z. Liu & P.A. Taskinen, Experimental Determination of the Liquidus Temperatures of the Binary (SiO₂-ZnO) System in Equilibrium with Air. *J. Eur. Ceram. Soc.*, 35 (2015) (14) 4005-4010.

- [18] H.A. Wriedt, The O-Zn (Oxygen-Zinc) System. *Bull. Alloy Phase Diagr.*, 8 (1987) (2) 166-76.
- [19] A.E. Ringwood & A. Major, High Pressure Transformations in Zinc Germanates and Silicates. *Nature*, 215 (1967) (Sept. 23) 1367-68.
- [20] Y. Syono, S. Akimoto & Y. Matsui, High pressure transformations in zinc silicates. *J. Solid St. Chem.*, 3 (1971) (3) 369-380.
- [21] M. Akaogi, H. Yusa, E. Ito, T. Yagi, K. Suito & J.T. Iiyama, The ZnSiO_3 Clinopyroxene-Ilmenite Transition: Heat capacity, Enthalpy of Transition, and Phase Equilibria. *Phys. Chem. Miner.*, 17 (1990) (1) 17-23.
- [22] X. Liu, M. Kanzaki & X. Xue, Crystal structures of Zn_2SiO_4 III and IV synthesized at 6.5-8 GPa and 1273 K. *Phys. Chem. Minerals*, 40 (2013) (6) 467-478.
- [23] S. Itoh & T. Azakami, Thermodynamic Studies of ZnO in Solids Zinc Silicate—Fundamental studies of zinc extraction by the iron-reduction distillation process (4th report). *Shigen-to-Sozai*, 105 (1989) (9) 685-692.
- [24] K. Leinenweber, A. Navrotsky, P. McMillan & E. Ito, Transition enthalpies and entropies of high pressure zinc metasilicates and zinc metagermanates. *Phys. Chem. Minerals*, 16 (1989) (8) 799-808.
- [25] E. Jak, N. Liu, H.G. Lee, P. Wu, A.D. Pelton & P. Hayes, "Phase Equilibria in the System PbO-ZnO-SiO_2 ". In: *Proc. 6th AusIMM Extractive Metallurgy Conference*, Brisbane 3-6 July, 1994, Aus. IMM, Victoria (Australia), pp. 253-255.
- [26] C.W. Bale, P. Chartrand, S. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melancon, A.D. Pelton & P. Petersen, FactSage Thermochemical Software and Databases. *Calphad*, 26 (2002) (2) 189-228.
- [27] I. Barin, *Thermochemical Data of Pure Substances*, 1st Ed. VCH, Weinheim, 1989.
- [28] E.G. King, Heats of formation of crystalline calcium orthosilicate, tricalcium silicate and zinc orthosilicate. *J. Am. Chem. Soc.*, 73 (1951) (2) 656-658.
- [29] J.A. Kitchener & S. Ignatowicz, The reduction equilibria of zinc oxide and zinc silicate with hydrogen. *Trans. Faraday Soc.*, 47 (1951) 1278-86.
- [30] S.S. Todd, Low-temperature heat capacities and entropies at 298.15 K of crystalline calcium orthosilicate, zinc orthosilicate and tricalcium silicate. *J. Am. Chem. Soc.*, 73 (1951) (7) 3277-78.
- [31] A. Navrotsky, Thermodynamics of formation of the silicates and germanates of some divalent transition metals and of magnesium. *J. Inorg. Nucl. Chem.*, 33 (1971) 4035-50.
- [32] A. Kozłowska-Róg & G. Róg, Thermodynamics of zinc and cobalt silicates. *Polish J. Chemistry*, 53 (1979) 2083-86.

- [33] E. Jak & P. Hayes, Phase equilibria determination in complex slag systems. *Miner. Process. Extr. Metall.*, 117 (2008) (1) 1-17.
- [34] N. Tanaka, T. Iseki, L. Ling, R. Shimpo & O. Ogawa, Standard Gibbs energy of formation of Zn_2SiO_4 . *Shigen-to-Sozai*, 114 (1998) (8) 567-72.
- [35] S. Zh. Karazhanov, P. Ravindran, P. Vajeeston, A.G. Ulyashin, H. Fjellvåg & B.G. Svensson, Phase stability and pressure-induced structural transitions at zero temperature in ZnSiO_3 and Zn_2SiO_4 . *J. Phys: Condens. Mater.*, 21 (2009) 485801.
- [36] N.S. Bekturganov, M.R. Bissengaliyeva & D.B. Gogol, Calculation of vibrational spectra and thermodynamic functions of a natural zinc silicate – willemite. *Euras. Chem-Technol. J.*, 15 (2013) 227-232.
- [37] J.O. Andersson, T. Helander, L. Höglund, P. Shi & B. Sundman, Thermo-Calc & DICTRA, computational tools for materials science. *Calphad*, 26 (2002) (2) 273-312.
- [38] R.H. Davies, A.T. Dinsdale, J.A. Gisby, J. A. J. Robinson & S. M. Martin, MTDATA-thermodynamic and phase equilibrium software from the National Physical Laboratory. *Calphad*, 26 (2002) (2) 229-271.
- [39] MTOX, Release Notes for Version 7.0 of Mtox Database, National Physical Laboratory, Teddington, UK, 2011.
- [40] SGTE Database for Pure Substances, Scientific Group Thermodata Europe (<http://www.sgte.org/>)
- [41] T. Barry, A. Dinsdale & J. Gisby, Predictive thermochemistry and phase equilibria of slags. *JOM*, 45 (1993) (4) 32-38.
- [42] O. Redlich & A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.*, 40 (1948) (2) 345-348.
- [43] H. Rannikko, A Thermodynamic Assessment for Cu-O-CaO-SiO₂ System. PhD Thesis, Helsinki University of Technology, Espoo, 1995, p. 12.
- [44] Thermo-Calc S, User's Guide, Thermo-Calc Software AB, 2008, p. 11-9.
- [45] M. Hillert, Empirical methods for predicting and representing thermodynamic properties of ternary solution phases. *Calphad*, 4 (1980) (1) 1-12.
- [46] Y-M. Muggianu, M. Gambino & J-P. Bros, Enthalpies de Formation des Alliages Liquides Bismuth-Etain-Gallium a 723 K. *J. Chim. Phys.*, 72 (1975) (1) 83-88.
- [47] V. Galkin, G. Kuznetsov & A. Turkin, Thermal expansion of ZnSiO_3 high-pressure phases. *Phys. Chem. Minerals*, 34 (2007) (6) 377-381.

- [48] N. Saunders & A.P. Miodownik, CALPHAD Calculation of Phase Diagrams: A Comprehensive Guide. Pergamon Materials Series, Elsevier Science Ltd., Oxford, 1998.
- [49] J. Gisby, A. Dinsdale, I. Barton-Jones, A. Gibbon & P. Taskinen, "Predicting Phase Equilibria in Oxide and Sulphide Systems". In: Proc. Sulfide Smelting 2002 (Ed. R. Stephens & H. Sohn), TMS; Warrendale (PA), pp. 533-545.
- [50] E.M. Levin, Liquid Immiscibility in Oxide Systems. In: Phase Diagrams, Materials Science and Technology, Vol 3 (Ed. Alper A.M.), Academic Press, London, 1970, 145-146.
- [51] A.R. West, Solid State Chemistry and Its Applications. John Wiley & Sons, Chichester, 1987, p. 391.
- [52] E.R. Segnit & A.E. Holland, The system MgO-ZnO-SiO₂. J. Am. Ceram. Soc., 48 (1965) (8) 409-412.
- [53] I. Barin, Thermochemical Data of Pure Substances, 2nd Ed. VCH, Weinheim, 1993.
- [54] O. Kubaschewski & C.B. Alcock, Metallurgical Thermochemistry, 5th Ed. Pergamon Press, Oxford, 1979, p. 322, 338-339 & 355.

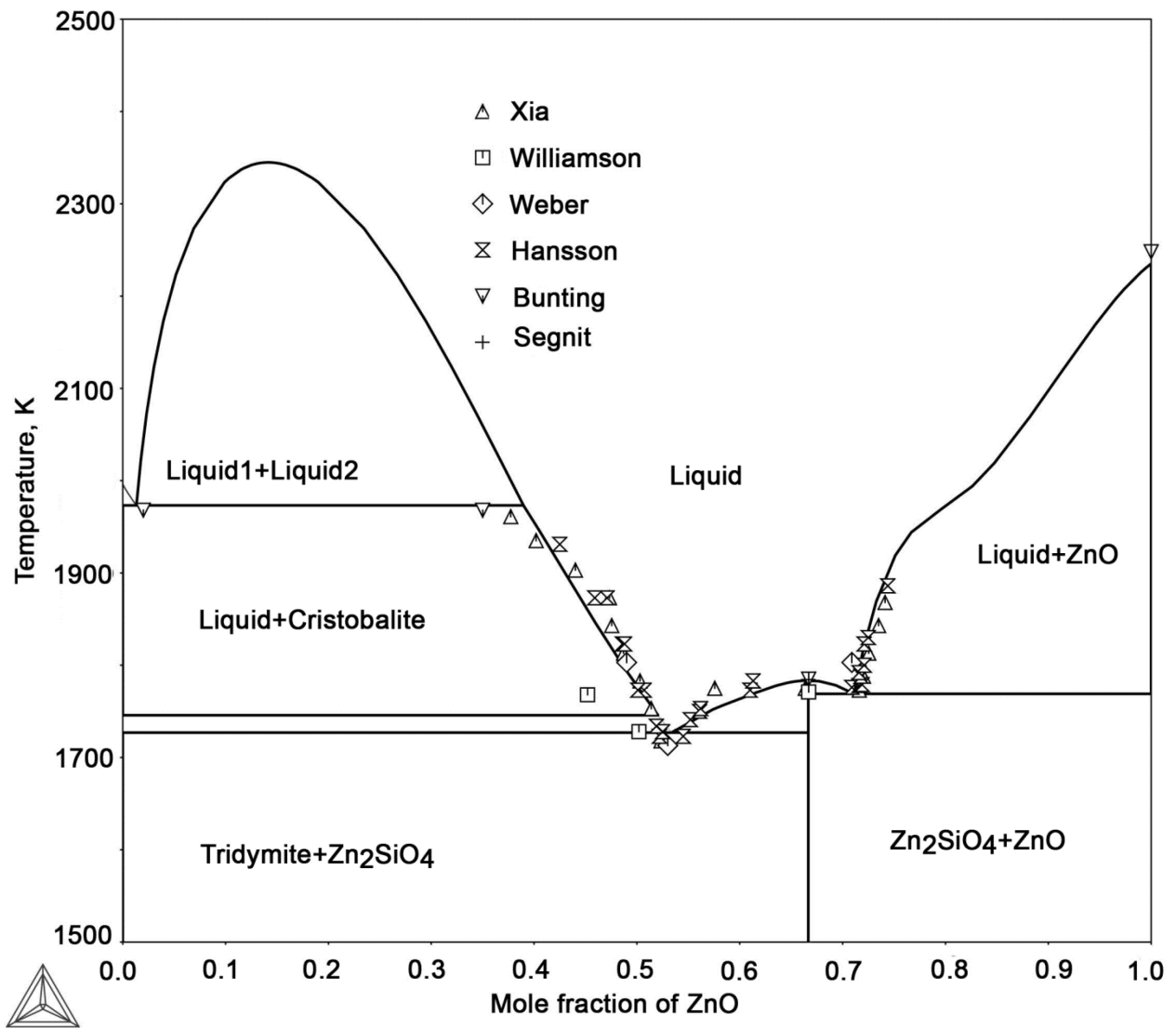


Figure 1. The assessed binary phase diagram ZnO-SiO₂ with the experimental data on the liquidus lines superimposed.

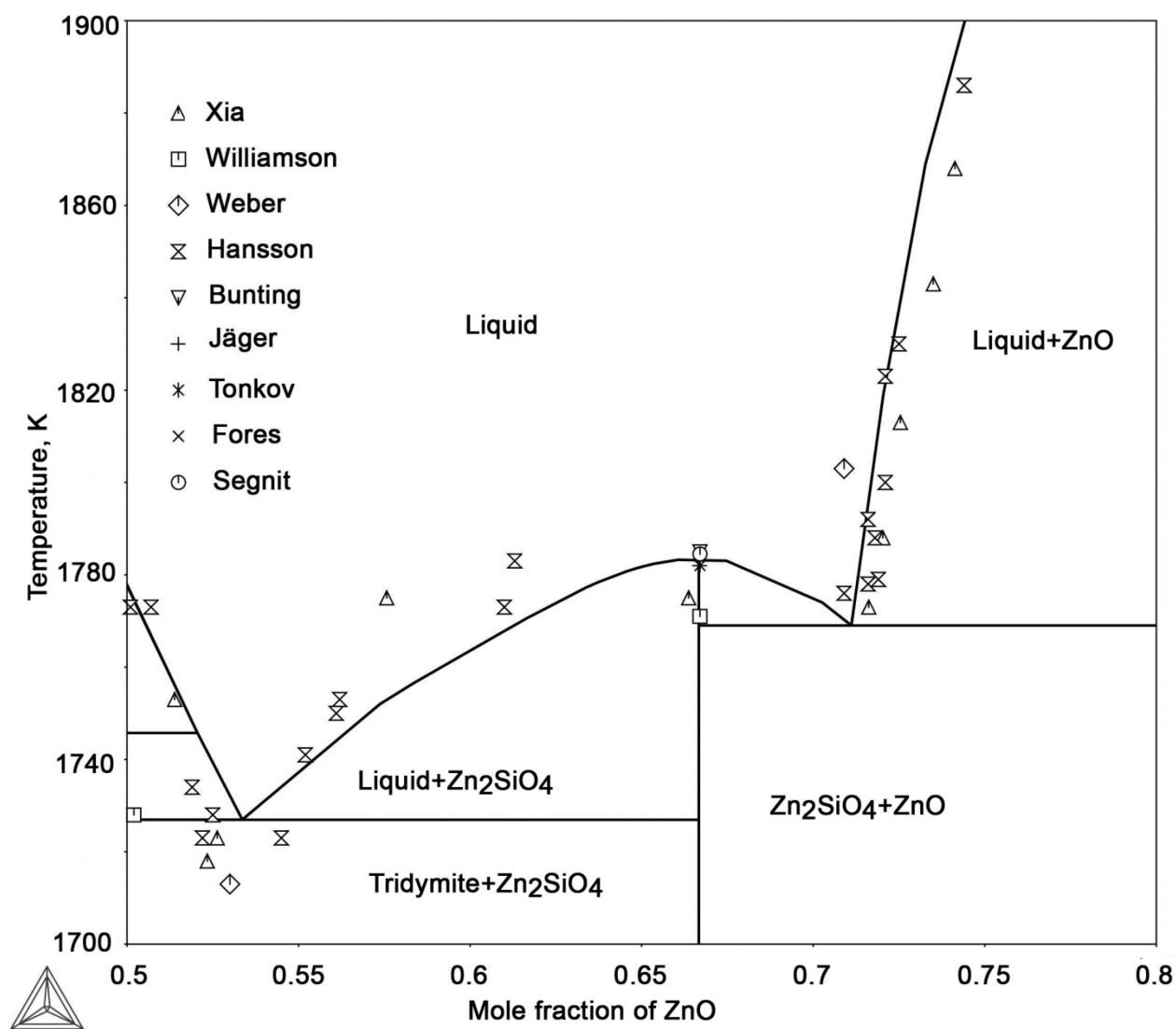


Figure 2. A detail of the assessed binary phase diagram around the willemite Zn₂SiO₄ primary phase field.

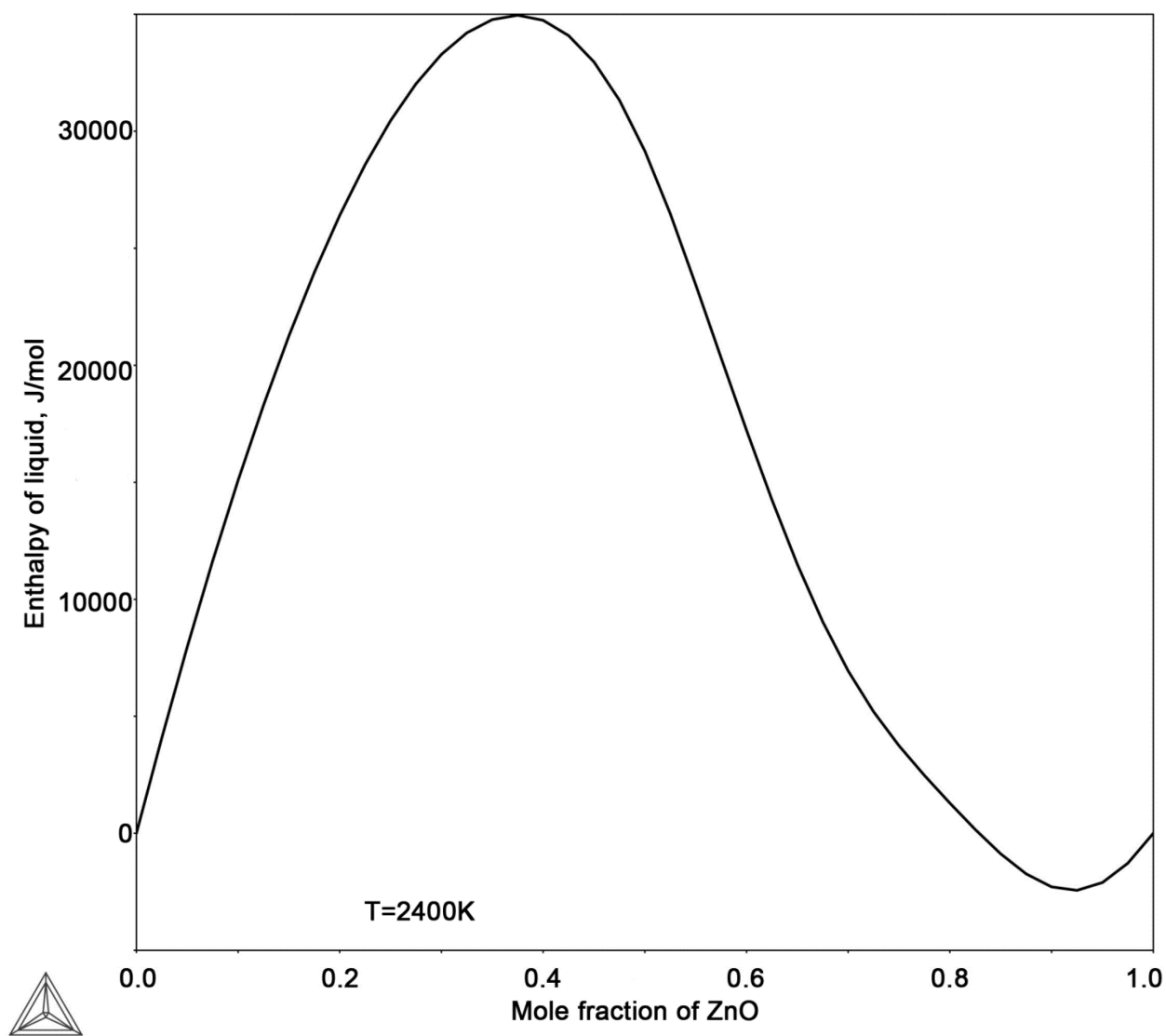


Figure 3. The assessed enthalpy of mixing of liquid ZnO-SiO₂ solution at 2400 K; standard states ZnO(l) and SiO₂(l).

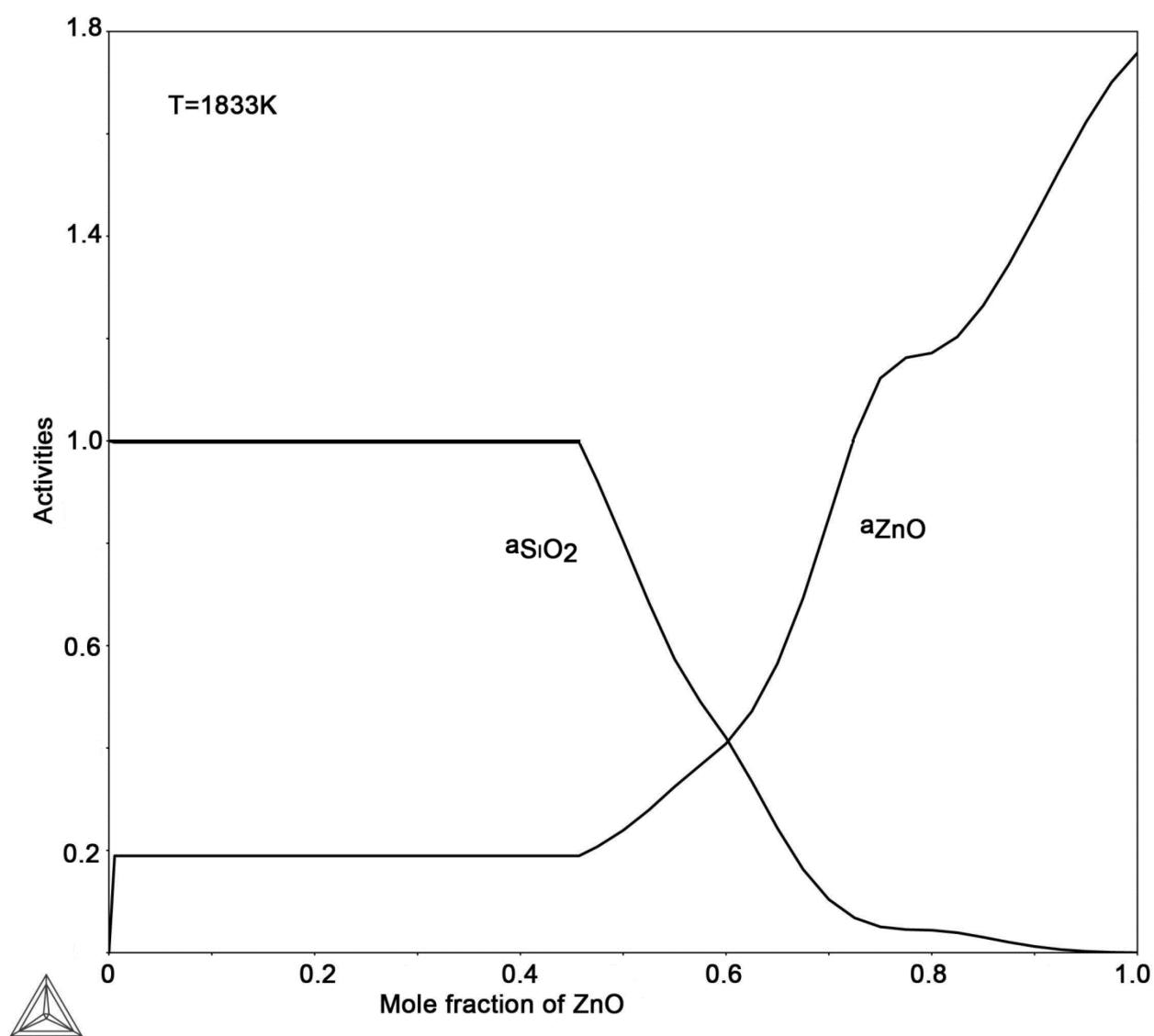


Figure 4. The assessed activities of ZnO and SiO₂ in the system at 1833 K; standard states ZnO(s) and SiO₂(s).

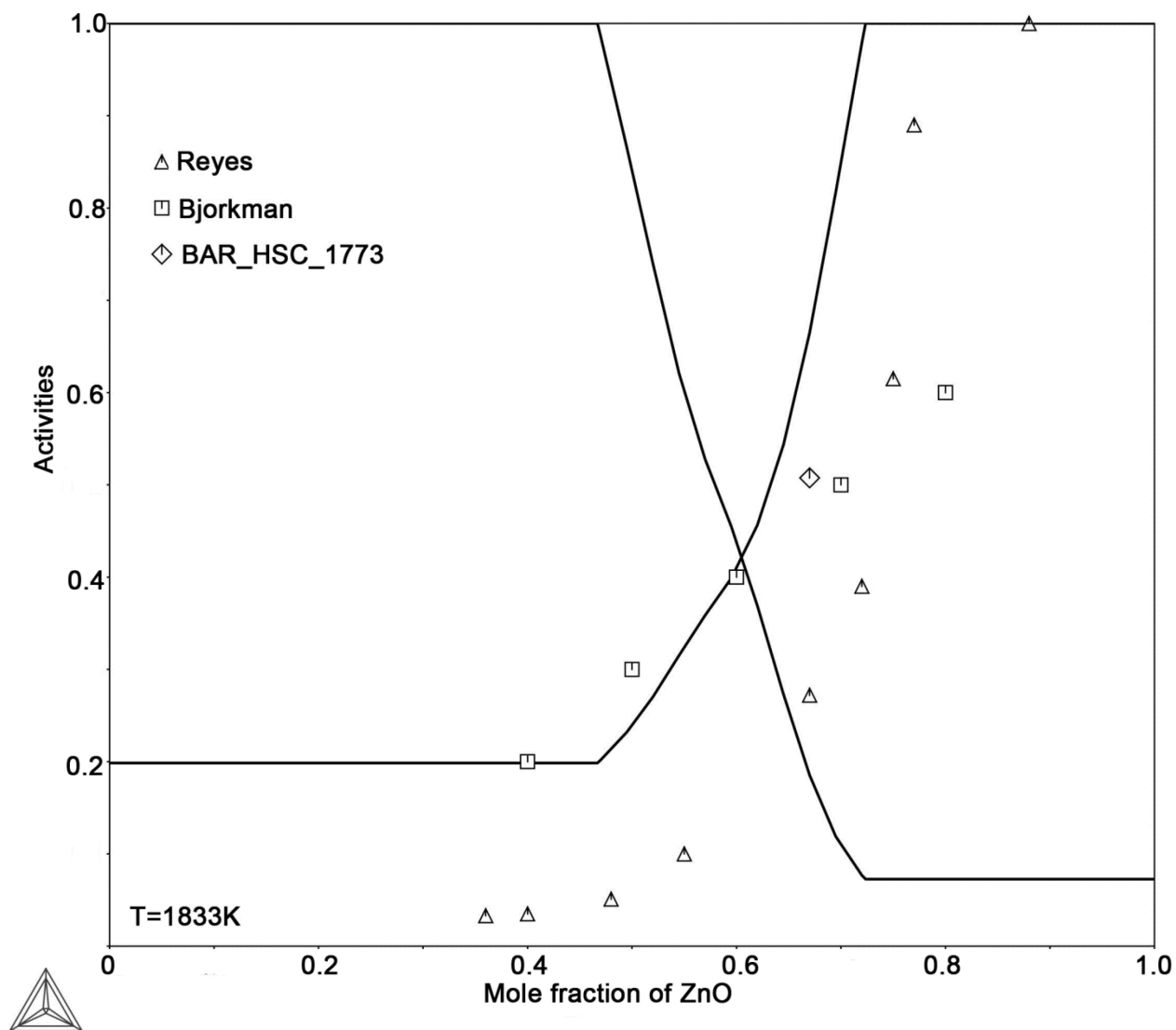


Figure 5. The assessed activities of ZnO and SiO₂ in the system at 1833 K with the literature data; standard states ZnO(s) and SiO₂(s, cristobalite).

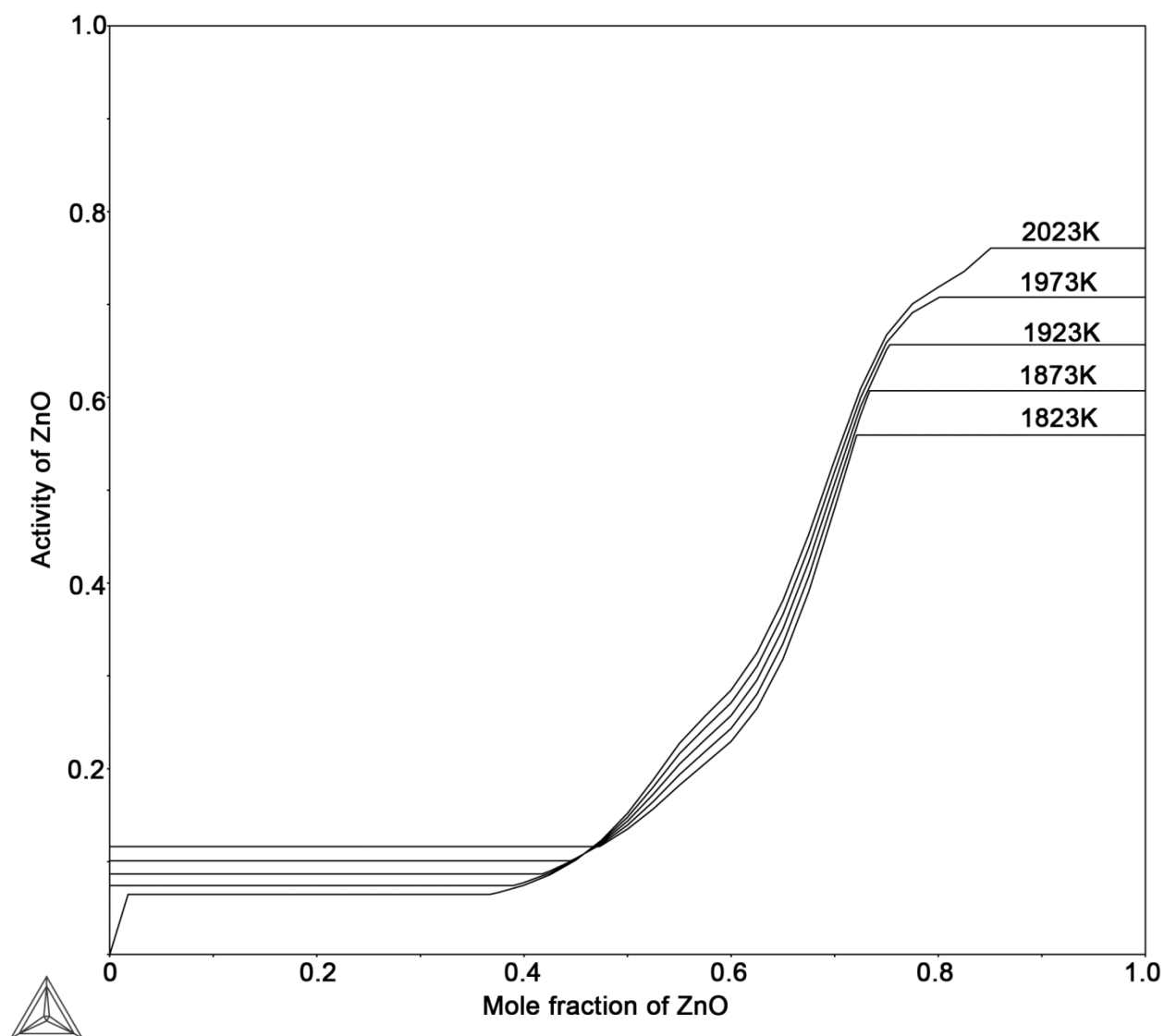


Figure 6. The assessed activities of ZnO in the ZnO-SiO₂ system from 1823 K to 2023 K at 50 K intervals; standard state ZnO(s).

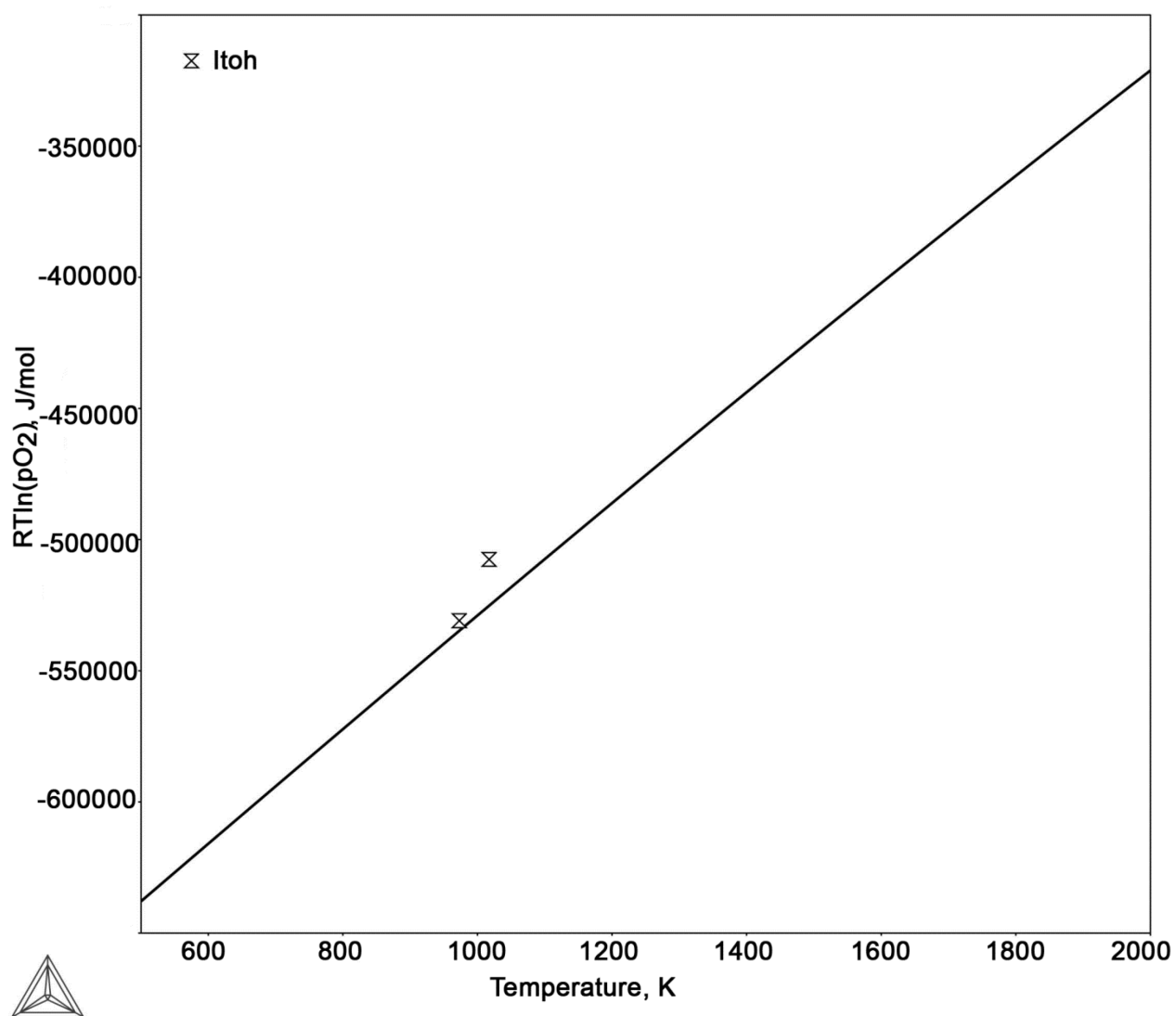


Figure 7. Oxygen potential of Zn-SiO₂-Zn₂SiO₄ equilibrium according to EMF data by Itoh & Azakami [23] and the present assessment (—); standard states Zn(l), SiO₂(s), Zn₂SiO₄(s).