Application of the Modified Quasichemical Model to Solutions with Strong Short-Range Ordering

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Abstract

The present study is concerned with analysis of a specific feature of the modified quasichemical solution model (MQSM). The analised feature is typical for binary solutions with very strong short-range ordering. As demonstrated, a solid compound whose composition coincides with that of maximum ordering in the liquid is required for reasonable representation of phase equilibria in such a system. The limiting slopes of the liquidus curve of the compound are calculated.

As a demonstrational example, the thermodynamic model for the system K_2O-SiO_2 with the MQSM for the liquid phase is re-optimised. The new parameters of the thermodynamic model fit the available experimental data and represents reasonable phase relations for the entire compositional range.

Key words: Modified Quasichemical model, Strong short-range ordering, The system K_2O-SiO_2.

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1. Introduction

According to Pelton et al. [1], the modified quasichemical solution model (MQSM) has been applied to critical evaluation and thermodynamic optimisation of several hundred liquid oxide, salt and alloy solutions. Many of the oxide systems have been optimised by Wu [2]. Analysis of Wu's experience demonstrates that the most difficult liquid binary oxide solutions to optimise are those, in which one mixed component is a basic oxide, while the other is an acidic oxide. Liquids in such systems are usually characterised by very strong short-range ordering. Large negative values of the Gibbs free energy of the quasichemical reaction are usually required to fit available experimental data in such systems. Furthermore, strong compositional dependencies of the Gibbs free energy of the quasichemical reactions are usually used. For example, Wu [2] used polynomials up to the 7th power to express both enthalpy and entropy of the quasichemical reaction in many such systems.

An enlightening example of a binary system with very strong short-range ordering is the system K_2O-SiO_2. This system has been previously optimised by Wu et al. [3], using the MQSM for the liquid phase. Zaitsev et al. [4] used the theory of associated solutions to describe the phase relations in this system, presuming the formation of silicon-oxygen groups of arbitrary sizes and spatial configurations [5]. Romero-Serrano et al. [6] employed the structural model [7, 8] for the liquid. Recently, the system has been optimised by Yazhenskikh et al. [9] with the modified associate species model [10].

Yazhenskikh et al. reported the set of model parameters that reproduce the available experimental data and enable representing reasonable phase relations for the entire phase diagram. In contrast, Wu et al., Zaitsev et al. and Romero-Serrano et al. reported the calculated phase diagram only for the compositional range with high silica content. Following Yazhenskikh et al., the parameters of the thermodynamic model reported by Wu et al. [3] were used to calculate the phase diagram for the entire compositional range. The phase diagram calculated with the FactSage computer package [11] and the experimental liquidus data mostly reported by Kracek et al. [12] are presented in Fig. 1. As is seen from Fig. 1, the experimental liquidus data that are available mostly in the composition range from K_2SiO_3 to SiO_2 are fitted well. However, as pointed out by Yazhenskikh et al., the complimentary range, which is characterised by a lack of experimental data, contains the following discrepancies:

(i) The liquid of the orthosilicate ($2K_2O{\cdot}SiO_2$) composition is predicted to be stable even at room temperature. Clearly, such a prediction seems to be unrealistic.
(ii) The miscibility gap is predicted. This gap also seems to be unreasonable, at least by analogies with similar systems.

On the other hand, the value of the Gibbs free energy of the quasichemical reaction in ternary and multicomponent systems is determined by projecting the multicomponent compo-

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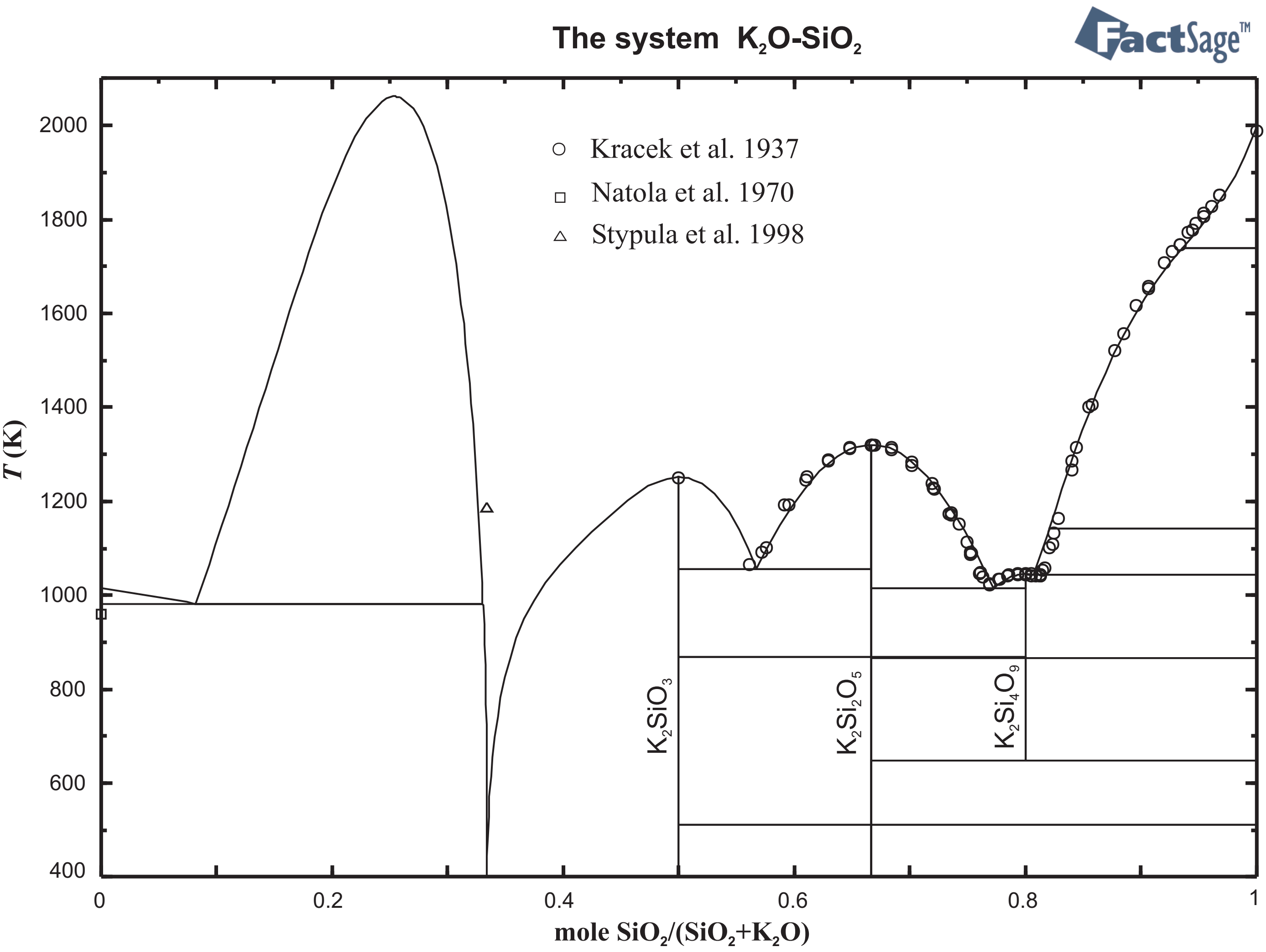

Fig. 1. Phase diagram of the system K_2O-SiO_2 calculated with the FactSage computer package, using the set of phases and the optimised parameters of the thermodynamic model reported by Wu et al. [3]

sition onto the corresponding binary line. In such projections, the values that correspond to high concentrations of K_2O in the binary system K_2O-SiO_2 can be used, even if the multicomponent compositions are dilute in K_2O. From this standpoint, it is desirable to have the parameters of the MQSM that represent reasonable phase relations for the entire compositional range. As demonstrated in [13], it is especially important in the case of using the disputable asymmetric projection methods.

Clearly, the parameters of the MQSM reported by Wu et al. result in an inflection point of the molar Gibbs free energy of mixing in the region of low silica concentration. The non-convexity of the molar Gibbs free energy of mixing leads to the prediction of the miscibility gap. As demonstrated in Section 4 of the present study, the appropriate adjustment of the parameters of the MQSM enables avoiding the prediction of the miscibility gap.

At the same time, the reasons why the orthosilicate liquid is predicted to be stable at low temperatures are not self-evident. The analysis of this discrepancy constitutes the core of the present study and is described in the next section. The analysis demonstrates that the discrepancy is originated from the specific feature of the MQSM and the feature is typical for the systems with strong short-range ordering. The feature manifests itself as well-known “V” shaped enthalpy and inverted “W” shaped entropy of mixing (see, for example, the work by Ganguly [14] and references therein). However, no detailed discussions on the impact of this feature on phase equilibrium predictions have been found in the literature.

2. Predicted stability of the liquid of the composition of maximum ordering at low temperatures

Consider a binary system $A_1 - A_2$, in which the liquid phase is modelled by the MQSM described by Pelton et al. [1]. The total Gibbs free energy of the solution of n_1 mole of A_1 and n_2 mole of A_2 is given by

$$
\begin{aligned}
&G_{A_1A_2}(T,n_1,n_2) = n_1 g_1(T) + n_2 g_2(T) + RT(n_1 \ln x_1 + n_2 \ln x_2)\\
&+RT\left[n_{11}\ln\left(\frac{x_{11}}{y_1^2}\right) + n_{22}\ln\left(\frac{x_{22}}{y_2^2}\right) + n_{12}\ln\left(\frac{x_{12}}{2y_1y_2}\right)\right]\\
&+\frac{n_{12}\Delta g_{12}}{2}\ .
\end{aligned}
\tag{1}
$$

Here, Δg_{12} is the Gibbs free energy change on forming of 2 moles of $(A_1 - A_2)$ pairs in the quasichemical reaction $(A_1 - A_1) + (A_2 - A_2) = 2(A_1 - A_2)$. x_1 and x_2 are the mole fractions of the components A_1 and A_2 . The equivalent fractions y_1 and y_2 are defined as $y_1 = z_1n_1/(z_1n_1 + z_2n_2)$ and $y_2 = z_2n_2/(z_1n_1 + z_2n_2)$, where z_1 and z_2 are the coordination numbers of the solution components A_1 and A_2, respectively. The pair mole fractions x_{ij} are defined as $x_{ij} = n_{ij}/(n_{11} + n_{22} + n_{12})$, where n_{ij} are the mole numbers of the $(A_i - A_j)$ pairs. g_1 and g_2 are the molar Gibbs free energies of the pure solution components A_1 and A_2, respectively. T is the absolute temperature and R is the universal gas constant.

In general, the composition of maximum ordering, which is determined by the ratio of the coordination numbers, is set to comply with the experimental data. For simplicity of considerations and without loss of generality, the system can be transformed so that to shift the composition of maximum ordering to the centre of the composition range. Now consider the system $A_1/z_1 - A_2/z_2 \equiv \tilde{A}_1 - \tilde{A}_2$. Since it is still the same system, merely expressed in other variables, $G_{A_1A_2}(T,n_1,n_2) = G_{\tilde{A}_1\tilde{A}_2}(T,m_1,m_2)$, where m_1 and m_2 are the transformed mole numbers of the components $\tilde{A}_1$ and $\tilde{A}_2$, respectively, so that $m_i = z_in_i$. Eq. (1) can be equivalently rewritten as follows:

$$
\begin{aligned}
&G_{\tilde{A}_1\tilde{A}_2}(T,m_1,m_2) = \frac{m_1g_1(T)}{z_1} + \frac{m_2g_2(T)}{z_2}\\
&+RT\left[\frac{m_1}{z_1}\ln(\frac{z_2y_1}{z_2y_1+z_1y_2}) + \frac{m_2}{z_2}\ln\left(\frac{z_1y_2}{z_2y_1+z_1y_2}\right)\right]\\
&+RT\left[n_{11}\ln\left(\frac{x_{11}}{y_1^2}\right) + n_{22}\ln\left(\frac{x_{22}}{y_2^2}\right) + n_{12}\ln\left(\frac{x_{12}}{2y_1y_2}\right)\right]\\
&+n_{12}\frac{\Delta g_{12}}{2}
\end{aligned}
\tag{2}
$$

The coordination-equivalent mole fractions y_i defined for the system $A_1 - A_2$ are expressed in terms of m_1 and m_2 as follows: $y_2 = m_2/(m_1 + m_2) = 1 - y_1$. Clearly, y_i are the mole fractions for the transformed system $\tilde{A}_1 - \tilde{A}_2$.

Let $g_{\tilde{A}_1\tilde{A}_2}$ be the molar Gibbs free energy of the liquid in the system $\tilde{A}_1 - \tilde{A}_2$. $g_{\tilde{A}_1\tilde{A}_2}$ is given by the following equation

$$
\begin{aligned}
&g_{\tilde{A}_1\tilde{A}_2}(T,y_1,y_2) = y_1\frac{g_1(T)}{z_1} + y_2\frac{g_2(T)}{z_2}\\
&+RT\left[\frac{y_1}{z_1}\ln\left(\frac{z_2y_1}{z_2y_1+z_1y_2}\right) + \frac{y_2}{z_2}\ln\left(\frac{z_1y_2}{z_2y_1+z_1y_2}\right)\right]\\
&+\frac{RT}{2}\left[x_{11}\ln\left(\frac{x_{11}}{y_1^2}\right) + x_{22}\ln\left(\frac{x_{22}}{y_2^2}\right) + x_{12}\ln\left(\frac{x_{12}}{2y_1y_2}\right)\right]\\
&+x_{12}\frac{\Delta g_{12}}{4}\ .
\end{aligned}
\tag{3}
$$

To simplify the subsequent formulae, assume that the Gibbs free energy of the quasichemical reaction, Δg_{12}, is a large negative constant and introduce the following notation: $g_{\tilde{A}_1\tilde{A}_2}(T,y,\xi) \equiv g(T,y,\xi)$, $y_2 \equiv y$, $g_1/z_1 \equiv \tilde{g}_1$, $g_2/z_2 \equiv \tilde{g}_2$ and $x_{12}/2 \equiv \xi$, where $\xi = \xi(y)$ is a function of the mole fraction y. In addition, define the functions $f_1(y)$ and $f_2(T,y,\xi)$ as follows:

$$
f_1(y) \equiv \frac{1-y}{z_1}\ln\left(\frac{z_2(1-y)}{z_2(1-y)+z_1y}\right) + \frac{y}{z_2}\ln\left(\frac{z_1y}{z_2(1-y)+z_1y}\right),
\tag{4}
$$

$$
\begin{aligned}
&f_2(T,y,\xi) \equiv (1-y-\xi)\ln\left(\frac{1-y-\xi}{(1-y)^2}\right) +\\
&+(y-\xi)\ln\left(\frac{y-\xi}{y^2}\right) + 2\xi\ln\left(\frac{\xi}{(1-y)y}\right) + \xi\frac{\Delta g_{12}}{RT}\ .
\end{aligned}
\tag{5}
$$

Then, Eq. (3) takes the form

$$
g(T,y,\xi) = (1-y)\tilde{g}_1(T) + y\tilde{g}_2(T) + RTf_1(y) + \frac{RT}{2}f_2(T,y,\xi).
\tag{6}
$$

The sum of the first two terms in Eq. (6) is the Gibbs free energy of a mechanical mixture of y moles of the component $\tilde{A}_2$ and $(1-y)$ moles of the component $\tilde{A}_1$. The third term corresponds to the ideal entropy of mixing in the system $A_1 - A_2$. The fourth term is the combined term that accounts for the entropy of mixing of different pairs (or bonds) and the Gibbs free energy of the quasichemical reaction. The third and the fourth terms add up to the molar Gibbs free energy of mixing $g_{\mathtt{mix}}$ in the system $\tilde{A}_1 - \tilde{A}_2$:

$$
g_{\mathtt{mix}}(T,y,\xi) = RTf_1(y) + \frac{RT}{2}f_2(T,y,\xi).
\tag{7}
$$

The equilibrium value of ξ is determined from the following equation

$$
\frac{\partial f_2(y,\xi)}{\partial \xi} = 0\ ,
\tag{8}
$$

which gives

$$
\frac{\xi^2}{(1-y-\xi)(y-\xi)} = \exp\left(-\frac{\Delta g_{12}}{RT}\right).
\tag{9}
$$

Using the notation $w \equiv \exp(-\Delta g_{12}/RT)$, Eq. (9) takes the form

$$
\xi^2(1-1/w) - \xi + y(1-y) = 0.
\tag{10}
$$

If Δg_{12} approaches $-\infty$, then the value of $1/w$ tends to zero and ξ as a function of y approaches the following limiting function $\xi_{\lim}(y)$:

$$
\xi_{\lim}(y) = \begin{cases} y; & y \le 1/2 \\ 1-y; & y > 1/2 \end{cases}\ .
\tag{11}
$$

The convergence of ξ to the limiting function $\xi_{\lim}(y)$ specified by Eq. (11) is exponentially fast in Δg_{12}. For example, in the double precision floating-point computer arithmetic, the smallest positive number ε, such that $\varepsilon + 1.0$ is distinguishable from 1.0, is approximately $2.22\mathrm{E} - 016$. Therefore, if $\Delta g_{12}/RT < -36.05$ (or, approximately, $\Delta g_{12} < -300$kJ/mol at $T = 1000$ K), the calculated ξ is not distinguishable from $\xi_{\lim}$ in double precision. Such large negative values of Δg_{12} are not unusual in the thermodynamic optimisation of the systems with strong short range ordering. For example, in the previously mentioned thermodynamic optimisation of the system $K_2O{-}SiO_2$ reported by Wu et al. [3], the value of Δg_{12} at the orthosilicate composition is -365kJ/mol. Even smaller negative values of Δg_{12} lead to the same result in the case of using the single precision floating-point arithmetic. In this case, ξ is undistinguishable from $\xi_{\lim}$ if $\Delta g_{12} < -133$kJ/mol at 1000 K.

Now consider the limiting ($\xi = \xi_{\lim}$) behaviour of the first derivative of the molar Gibbs free energy of mixing given by Eq. (7) with respect to y in the vicinity of the point $y = 1/2$. The function $f_1(y)$ defined by Eq. (4) predictably causes no difficulties, since it is originated from the ideal entropy of mixing. This function is continuously differentiable with respect to y in the interval of interest for any finite positive z_1 and z_2 with

$$\frac{df_1(y)}{dy} = \frac{1}{z_1 z_2} \, [z_1 \ln(z_1 y) - z_2 \ln(z_2(1-y)) + (z_2 - z_1)\ln(z_2(1-y) + z_1 y)] \tag{12}$$

and

$$\lim_{y \to 1/2} \frac{df_1(y)}{dy} = \frac{z_1}{z_1 z_2} \ln\left(\frac{z_1}{z_1 + z_2}\right) - \frac{z_2}{z_1 z_2} \ln\left(\frac{z_2}{z_1 + z_2}\right) . \tag{13}$$

Using the chain rule and Eq. (8) gives

$$\frac{\partial f_2(T,y,\xi)}{\partial y} = \frac{\partial f_2(T,y,\xi)}{\partial y} + \frac{\partial f_2(T,y,\xi)}{\partial \xi}\frac{\partial \xi}{\partial y} = \frac{\partial f_2(T,y,\xi)}{\partial y} . \tag{14}$$

Substituting $\xi_{\lim}(y)$ from Eq. (11) to Eq. (5), the required derivative takes the form:

$$\frac{\partial f_2(T,y,\xi)}{\partial y} = \begin{cases} 2\ln\left(\dfrac{1-y}{1-2y}\right) + \dfrac{\Delta g_{12}}{RT}; \; y < 1/2 \\ 2\ln\left(\dfrac{2y-1}{y}\right) - \dfrac{\Delta g_{12}}{RT}; \; y > 1/2 \end{cases} . \tag{15}$$

As follows from Eq.(15),

$$\lim_{y \to 1/2-0} \frac{\partial f_2(T,y,\xi)}{\partial y} = \infty \tag{16}$$

and

$$\lim_{y \to 1/2+0} \frac{\partial f_2(T,y,\xi)}{\partial y} = -\infty , \tag{17}$$

where $y \to 1/2 - 0$ and $y \to 1/2 + 0$ mean that y approaches 1/2 from the left and from the right, respectively.

Consider an arbitrary compound $\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}$. Using the well-known equation for the chemical potential of the solution components (see, for example, the book by Hillert [15]), the chemical potential, $\mu^{\mathtt{liq}}_{\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}}$, of the liquid of the composition $\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}$ in the liquid of the arbitrary composition y is expressed as follows:

$$\mu^{\mathtt{liq}}_{\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}}(T,y) = \alpha_1 \tilde{g}_1(T) + \alpha_2 \tilde{g}_2(T) + (\alpha_1 + \alpha_2) g_{\mathrm{mix}}(T,y) + [\alpha_2(1-x) - \alpha_1 x]\frac{\partial g_{\mathrm{mix}}(T,y)}{\partial y} . \tag{18}$$

Now assume that $\alpha_1 > \alpha_2$, which means that the compound is in the left part of the system $\tilde{A}_1 - \tilde{A}_2$. Substituting Eq. (7) to Eq. (18) and using the limits (13) and (16), one verifies that

$$\lim_{y \to 1/2-0} \mu^{\mathtt{liq}}_{\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}}(T,y) = -\infty. \tag{19}$$

Similarly, for any compound in the right part of the system ($\alpha_1 < \alpha_2$,)

$$\lim_{y \to 1/2+0} \mu^{\mathtt{liq}}_{\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}}(T,y) = -\infty . \tag{20}$$

Here, Eq. (17) is used instead of Eq. (16).

Therefore, in the case where the available experimental data dictate large negative values of Δg_{12}, for any compound $\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}$ with $\alpha_1 \neq \alpha_2$ and for any finite temperature there exists a compositional interval in the vicinity of the point $y = 1/2$, for which liquid is predicted to be more stable than the solid compound $\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}$.

This conclusion, however, is no longer true in the presence of a solid compound whose composition coincides with that of maximum ordering ($\alpha_1 = \alpha_2$). In this case, the chemical potential, $\mu^{\mathtt{liq}}_{\tilde{A}_{1\alpha_1}\tilde{A}_{2\alpha_2}}(T,y)$, does not depend on the derivative of the molar Gibbs free energy of mixing, $\partial g_{\mathrm{mix}}(T,y)/\partial y$, at the composition of maximum ordering. Clearly, the compound is congruently melting.

3. Shape of the liquidus curve of the compound of the composition of maximum ordering

Another interesting feature that arises from the above described "computational" discontinuity is the specific shape of the liquidus curve of the compound. As demonstrated, for example, by Hillert [15], the liquidus curve of a congruently melting compound has zero slope at the composition of the compound, provided that the molar Gibbs free energy of mixing is twice differentiable. However, if the last condition does not hold, thereby giving rise to the discontinuity, the slope of the liquidus curve is not defined at $y = 1/2$. This leads to the problem of computing the limiting ($y \to 1/2 - 0$ and $y \to 1/2 + 0$) slopes of the liquidus curve.

The slope of the liquidus $dT_{\mathtt{liq}}/dy$ of the compound $\tilde{A}_1\tilde{A}_2$ ($\alpha_1 = \alpha_2 = 1$) is expressed by the following Clyperon-type equation

$$\frac{dT_{\mathtt{liq}}}{dy} = -\frac{\partial F(T,y)/\partial y}{\partial F(T,y)/\partial T} , \tag{21}$$

where the function $F(T,y)$ is defined as

$$F(T,y) \equiv \mu^{\mathtt{liq}}_{\tilde{A}_1\tilde{A}_2}(T,y) - g^{\mathtt{sol}}_{\tilde{A}_1\tilde{A}_2}(T) . \tag{22}$$

Here, $g^{\mathtt{sol}}_{\tilde{A}_1\tilde{A}_2}$ is the molar Gibbs free energy of pure solid $\tilde{A}_1\tilde{A}_2$ and $\mu^{\mathtt{liq}}_{\tilde{A}_1\tilde{A}_2}$ is the chemical potential of the liquid of the composition $\tilde{A}_1\tilde{A}_2$ in the liquid of the composition y. The equation $F(T_{\mathtt{liq}}, y) = 0$ gives an implicit functional relation between the liquidus temperature $T_{\mathtt{liq}}$ and the composition of the liquid in the primary phase field of the compound $\tilde{A}_1\tilde{A}_2$.

The limiting slope of the liquidus curve of the compound $\tilde{A}_1\tilde{A}_2$, as $y \to 1/2 - 0$, can now be computed. The case $y \to 1/2 + 0$ can be treated in a similar way. Using Eqs. (6), (15) and (18), one verifies that

$$F(T,y) = -g^{\mathtt{sol}}_{\tilde{A}_1\tilde{A}_2}(T) + \tilde{g}_1(T) + \tilde{g}_2(T) + 2g_{\mathrm{mix}}(T,y) + (1-2y)RT\frac{df_1(y)}{dy} + (1-2y)RT\left(\ln\left(\frac{1-y}{1-2y}\right) + \frac{\Delta g_{12}}{2}\right) . \tag{23}$$

Differentiating Eq. (23) with respect to T gives

$$
\begin{aligned}
\frac{\partial F(T,y)}{\partial T} &= \frac{\partial}{\partial T}\left(-g^{\mathtt{sol}}_{\tilde{A}_1\tilde{A}_2}(T)+\tilde{g}_1(T)+\tilde{g}_2(T)+2g_{\mathtt{mix}}(T,y)\right) \\
&\quad +(1-2y)R\frac{df_1(y)}{dy}+(1-2y)R\left(\ln\left(\frac{1-y}{1-2y}\right)\right. \\
&\quad \left.+\frac{\Delta g_{12}}{2}\right)
\end{aligned}
\qquad (24)
$$

Using Eq. (13) and the well-known property that $\lim\limits_{x\to 0} x\ln x = 0$, the limit of the first derivative of $F(T,y)$ with respect to T, as $y \to 1/2-0$, can be found:

$$
\begin{aligned}
\lim_{y\to 1/2-0}\frac{\partial F(T,y)}{\partial T} &= \lim_{y\to 1/2-0}\frac{\partial}{\partial T}\left(-g^{\mathtt{sol}}_{\tilde{A}_1\tilde{A}_2}(T)+\tilde{g}_1(T)+\tilde{g}_2(T)\right. \\
&\quad \left.+2g_{\mathtt{mix}}(T,y)\right) = -\Delta s_{\mathtt{fus}}\ ,
\end{aligned}
\qquad (25)
$$

where $\Delta s_{\mathtt{fus}}$ is the molar entropy of fusion of the compound $\tilde{A}_1\tilde{A}_2$.

One can verify that

$$
\frac{\partial F(T,y)}{\partial y} = (1-2y)\frac{\partial^2 g_{\mathtt{mix}}(T,y)}{\partial y^2} \qquad (26)
$$

Using Eqs. (7), (12) and (15), the second order derivative of the molar Gibbs free energy of mixing with respect to y is expressed as follows:

$$
\begin{aligned}
\frac{\partial^2 g_{\mathtt{mix}}(T,y)}{\partial y^2} &= RT\frac{d^2 f_1(y)}{dy^2}+\frac{RT}{2}\frac{\partial^2 f_2(T,y,\xi)}{\partial y^2} \\
&= \frac{RT}{z_1 z_2}\left(\frac{z_1}{y}+\frac{z_2}{1-y}-\frac{(z_1-z_2)^2}{z_2(1-y)+z_1 y}\right) \\
&\quad +RT\left(\frac{2}{1-2y}-\frac{1}{1-y}\right)\ .
\end{aligned}
\qquad (27)
$$

Substitution of Eqs. (25), (26) and (27) to Eq.(21) gives

$$
\begin{aligned}
\frac{dT_{\mathtt{liq}}}{dy} &= \frac{(1-2y)}{\Delta s_{\mathtt{fus}}}\left[\frac{RT_{\mathtt{liq}}}{z_1 z_2}\left(\frac{z_1}{y}+\frac{z_2}{1-y}-\frac{(z_1-z_2)^2}{z_2(1-y)+z_1 y}\right)\right. \\
&\quad \left.+RT_{\mathtt{liq}}\left(\frac{2}{1-2y}-\frac{1}{1-y}\right)\right]\ ,
\end{aligned}
\qquad (28)
$$

when $y < 1/2$ and

$$
\lim_{y\to 1/2-0}\frac{dT_{\mathtt{liq}}}{dy} = \frac{2RT_{\mathtt{liq}}}{\Delta s_{\mathtt{fus}}}\ . \qquad (29)
$$

Similarly, one verifies that

$$
\lim_{y\to 1/2+0}\frac{dT_{\mathtt{liq}}}{dy} = -\frac{2RT_{\mathtt{liq}}}{\Delta s_{\mathtt{fus}}}\ . \qquad (30)
$$

Eqs. (29) and (30) are similar to the well-known van't Hoff relationship for the slopes at terminal compositions. As pointed out by Hillert [15], possible physical interpretation of the above described shape of the liquidus is that a system with high degree of ordering splits to two separate subsystems. If Δg_{12} is a large negative, almost only (A_1-A_2) and (A_1-A_1) pairs exist on the left from the composition of maximum ordering, while mostly (A_1-A_2) and (A_2-A_2) pairs are present on the right. This means that there are two different liquids: a solution of (A_1-A_2) and (A_1-A_1) pairs on the left and a solution of (A_1-A_2) and (A_2-A_2) pairs on the right. From this point of view, the described shape of the liquidus curve does not appear to be unusual.

4. Re-optimisation of the thermodynamic model for the system K_2O-SiO_2

As demonstrated above, the compound K_4SiO_4 needs to be incorporated in order to extend the thermodynamic model of the system K_2O-SiO_2 for the entire compositional range, if the MQSM is used for the liquid. Otherwise, the liquid of the orthosilicate composition, which is the composition of maximum ordering in silicate systems, is predicted to be stable at low temperatures as is seen from Fig. 1. The compound K_4SiO_4 was reported by Bernet and Hoppe [16], with its melting temperature reported to be 912^0C by Stypula et al. [17]. No data on the molar heat capacity, c_p, molar enthalpy of formation, Δh_{298} and molar entropy, s_{298}, at 298 K for this compound have been found in the literature. The c_p and s_{298} of the compound K_4SiO_4 have then been preliminarily estimated using the corresponding properties of K_2O and K_2SiO_3. In order to reproduce reasonable phase relations in the K_2O-reach part of the diagram, the preliminary estimations were decreased by approximately 5%. The value of Δh_{298} was selected to reproduce the melting temperature reported by Stypula et al.

Natola and Touzain [18] studied the system $K-K_2O$ and reported the melting temperature of K_2O to be 685 ^{0}C. The molar enthalpy and entropy of fusion are reported to be 33.472 kJ/mol and 36.4 J/(mol·K), respectively. However, for the sake of consistency with the existing FactSage oxide solution database, it was decided to take the thermodynamic properties of solid and liquid K_2O from the FactSage compound database. For the same reason, the thermodynamic properties of all solid polymorphs and liquid SiO_2 were also taken from the FactSage compound database.

Following Wu et al. [3], incremental estimations suggested by Berman and Brown [19] were used for the c_p of K_2SiO_3 and $K_2Si_2O_5$. The expression suggested by Fasshauer et al. [20], however, was taken for the c_p of $K_2Si_4O_9$. The latter expression was obtained by fitting the results of the heat capacity measurements in the temperature range $195-600$ K with the function recommended by Berman and Brown.

For the compounds K_2SiO_3, $K_2Si_2O_5$ and $K_2Si_4O_9$, the values of Δh_{298} and s_{298} were taken as reported by Zaitsev et al. [21] and Spencer [22], respectively. Heats of solid-solid inversions were taken as reported by Kracek et al. [12] for the compound $K_2Si_4O_9$ and as reported by Kubaschewski et al. [23] for the compound $K_2Si_2O_5$. In the course of the thermodynamic optimisation, the values of Δh_{298} were changed by -8871 J/mol, 7000 J/mol and -8750 J/mol for the compounds K_2SiO_3, $K_2Si_2O_5$ and $K_2Si_4O_9$, respectively. These adjustments are within the range of uncertainties reported by Zaitsev et al. The optimised values of Δh_{298} and s_{298} for the potassium silicates, as well as the heat capacities expressions, are given in Table 1.

Previously suggested values [3] of the parameters of the MQSM have been adjusted to maintain acceptable fit of the experimental liquidus data reported by Kracek et al [12] and the activities of K_2O measured by Frohberg et al. [24], Ravaine et al. [25], Steiler [26] and Zaitsev et al. [27]. Among the activity

Table 1
Thermodynamic properties of the potassium silicates relative to elements at 298.15 K

Phase	Δh_{298}	s_{298}	$c_p(T)$
	J/mol	J/(mol·K)	J/(mol·K)
K_4SiO_4(s) (298-1185) K	-2182945	240.000	$306.42 - 2182.99T^{-1/2}$
K_2SiO_3(s) (298-1249) K	-1560620	146.147	$225.99 - 1986.60T^{-1/2} + 14.896 \cdot 10^7 T^{-3}$
$K_2Si_2O_5$(α)(298-510) K	-2503491	182.004	$240.72 - 147.934 \cdot 10^5 T^{-1/2} + 228.921 \cdot 10^7 T^{-3}$
$K_2Si_2O_5$(β)(510-867) K	-2502236	184.465	$240.72 - 147.934 \cdot 10^5 T^{-1/2} + 228.921 \cdot 10^7 T^{-3}$
$K_2Si_2O_5$(γ)(867-1318) K	-2500647	186.298	$240.72 - 147.934 \cdot 10^5 T^{-1/2} + 228.921 \cdot 10^7 T^{-3}$
$K_2Si_4O_9$(α)(298-865) K	-4338350	265.684	$499.13 - 4350.14T^{-1/2}$
$K_2Si_4O_9$(β)(865-1043) K	-4335131	269.406	$499.13 - 4350.14T^{-1/2}$

data, preference was given to the latest measurements by Zaitsev et al. At the same time, the convexity of the molar Gibbs free energy of mixing of the liquid, at least for the temperature range where liquid is stable, was maintained in the K_2O-reach part of the diagram. The following quasichemical parameters were found for the liquid:

$$\begin{aligned} \omega = {} & -439590 - 22000 \cdot Y_{K_2O}^3 - 812800 \cdot Y_{SiO_2}^6 \\ & +685900 \cdot Y_{SiO_2}^7 \ \text{J/mol} \qquad (31) \\ \eta = {} & -61.0 - 60.0 \cdot Y_{SiO_2}^7 \ \text{J/(mol} \cdot \text{K)}, \end{aligned}$$

where ω, η, Y_{K_2O} and Y_{SiO_2} have the same meaning as in the work by Wu et al. [3].

The re-optimised phase diagram calculated with the help of the FactSage package and the experimental liquidus data are presented in Fig. 2. The calculated activities of K_2O and the experimental data, as reported by Yazhenskikh et al. [9], are presented in Fig. 3.

Fig. 2 and Fig. 3 show that the new set of model parameters allows fitting of the experimental liquidus data in the silica-reach part of the phase diagram with the acceptable quality. At the same time, reasonable phase relations are represented in the region of high content of K_2O. However, as pointed out by Yazhenskikh et al. [9] more experimental information is clearly required for the latter compositional range.

As is seen from Fig. 1, the previous set of model parameters predicts the compound $K_2Si_4O_9$ to be unstable below 646 K. Later, Fasshauer et al. [20] measured the heat capacity of this compound in the temperature range 195 – 600 K and no dissociation of the compound $K_2Si_4O_9$ was reported. This discrepancy is also resolved in the new set of model parameters (see Fig 2). Note that the experimental work was done by Fasshauer et al. after the previous thermodynamic optimisation had been completed by Wu et al. [3].

5. Conclusions

The specific feature of the MQSM which is typical for binary solutions with very strong short-range ordering have been analysed in the present study. The feature is originated from the described non-smoothness of the Gibbs free energy of mixing expressed by the MQSM at the composition of maximum ordering. It has been demonstrated that the compound whose composition coincides with that of maximum ordering in the liquid is required for reasonable representation of phase equilibria in the vicinity of this composition. Limiting slopes of the liquidus curve of the compound have also been calculated.

The thermodynamic model for the system K_2O-SiO_2 has been re-optimised. The new parameters of the model fits the available experimental data and represents reasonable phase relations for the entire compositional range.

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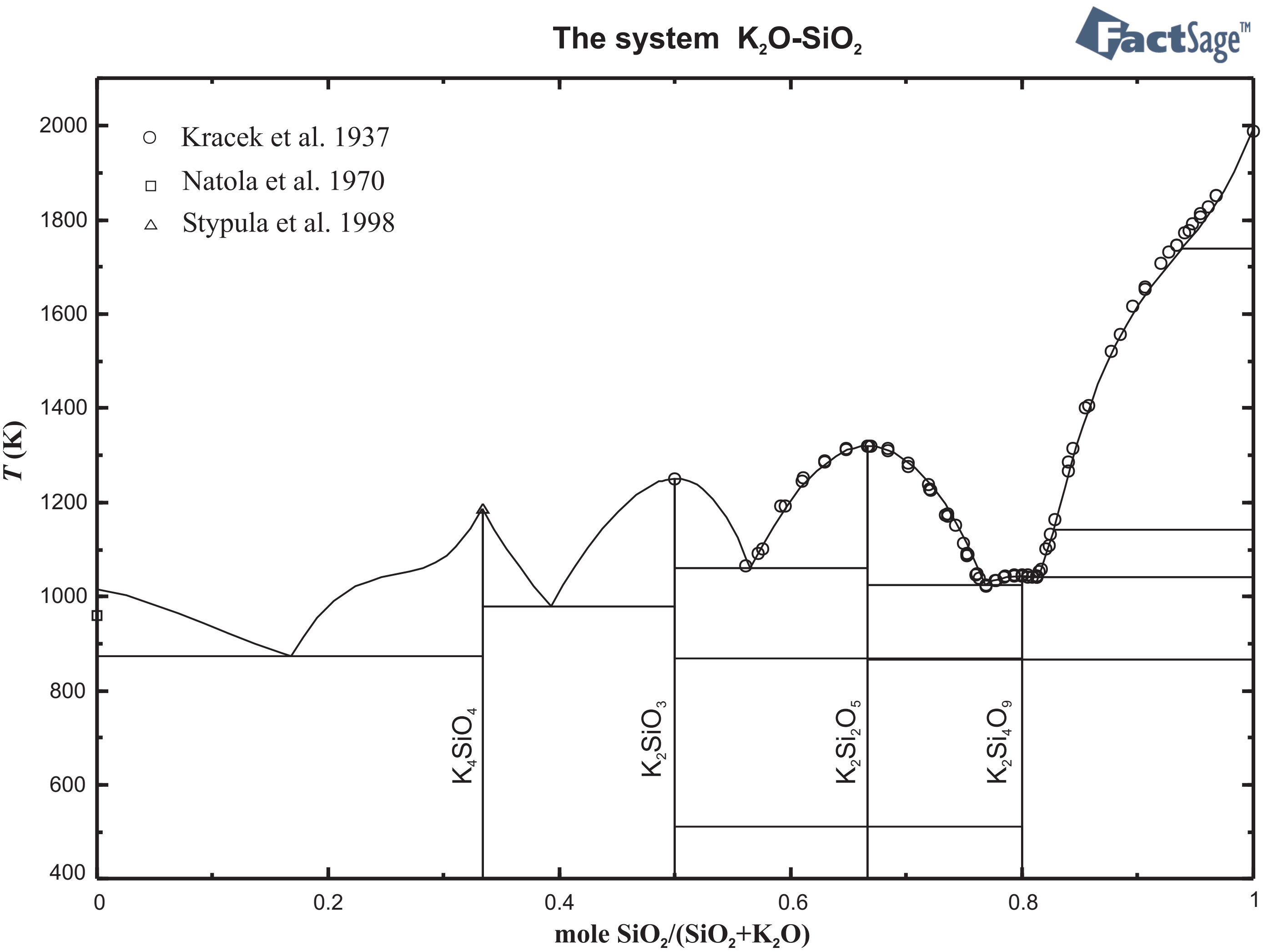

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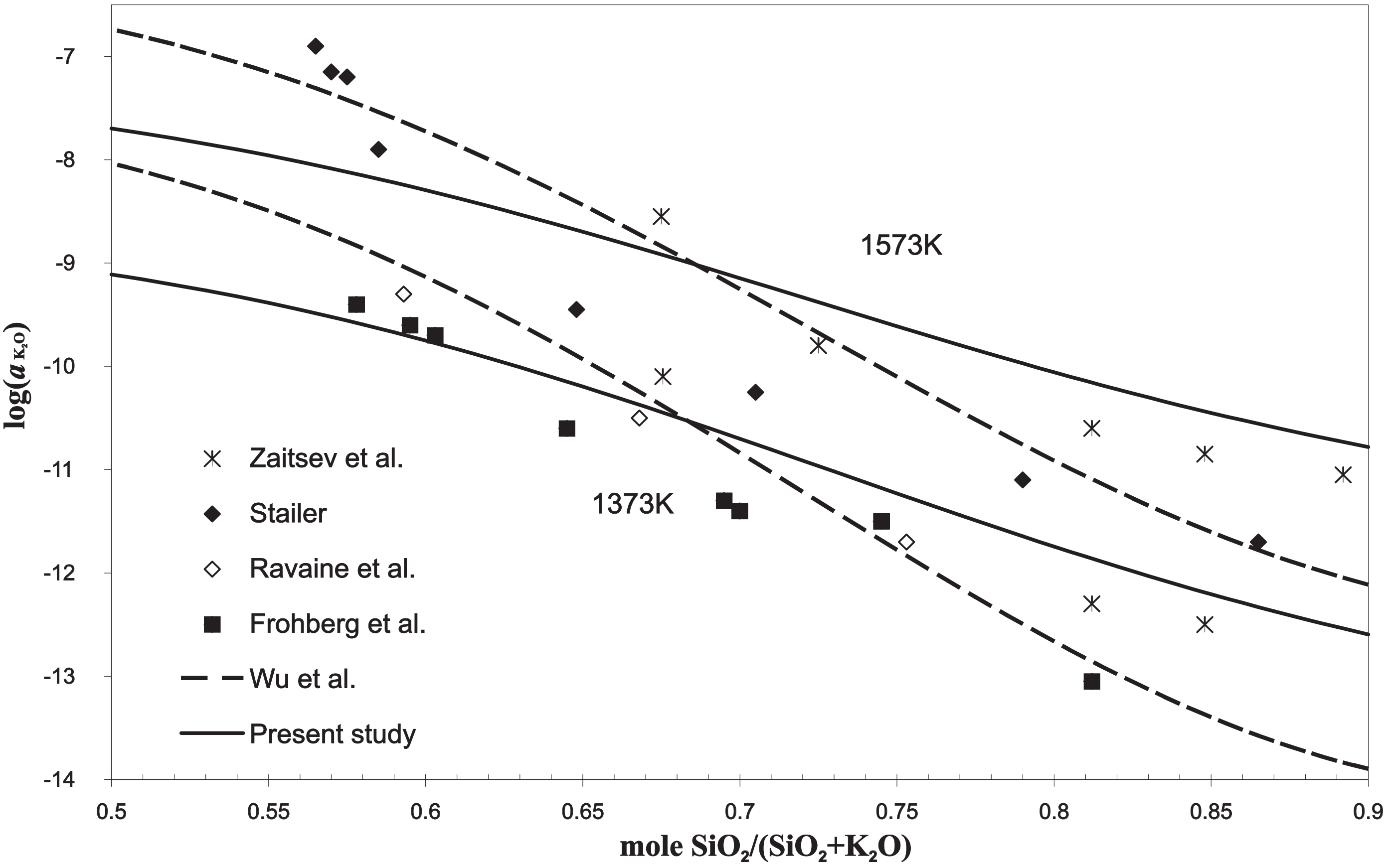

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