COMPUTER CALCULATION OF THE PHASE DIAGRAMS OF SILICATE SYSTEMS II. REGRESSION TREATMENT FOR SYSTEMS CONTAINING INCOGRUENTLY MELTING COMPOUNDS.

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An original algorithm and a FORTRAN program developed to calculate phase diagrams and/or thermodynamic characteristics in simple eutectic multicomponent systems yet not experimentally measured, was extended to the systems that may contain incongruently melting compounds. Additionally, enthalpy of fusion as a function of temperature was taken into account. Complete statistical analysis of results was also proposed. The method was applied to the binary system $CaSiO_3$-Ca_2SiO_4 containing the compound rankinite ($Ca_3Si_2O_7$) which melts incongruently at the temperature of 1464 °C. The enthalpy of this decomposition was estimated to be 72 kJ mol^{-1}. Other unknown parameters, i. e., the enthalpy and the heat capacity of fusion of dicalciumsilicate and hypothetical temperature of fusion of rankinite were calculated by the least squares method. The obtained values are 81.6±1.2 kJ/mol, 90±3 J/mol K and 1497±11°C, respectively.

INTRODUCTION

An algorithm and a FORTRAN program for the calculation of isobaric phase diagrams of simple polymeric oxide systems were published in [1]. The method was based on a simple LeChatelier-Schreder equation provided enthalpy of fusion being constant. To express the activities of constituents involved in a liquid, a model of ionic solutions by Haase was used in which the bridging (O^0), non-bridging (O^-) and free (O^{2-}) oxygen atoms were taken into account. The amounts of various kinds of oxygen atoms were calculated from material balance. The fraction of cations ^jA built into a polyanionic network as the groups $^jAO_3$ and $^jAO_4$ is given by parameters $\alpha_{3,j}$ and $\alpha_{4,j}$. As the input data, the list of oxides $^jA_xO_y$ together with the values of $\alpha_{3,j}$ and $\alpha_{4,j}$ and the list of possible crystalline phases with corresponding values of temperature and constant heat of fusion were used.

This method can also be used to solve an inverse problem, particularly to determine some of the input parameters from the known phase diagram by the least squares method. Such procedure has been applied to investigate coordination of aluminum in container glasses [2].

This paper extends the problem to the systems containing incongruently melting compounds including statistical analysis, particularly determination of standard deviations of estimated unknown parameters in a model as well as of linear dependencies between them. In addition, the temperature dependence of enthalpy of fusion is taken into account. Moreover, we have inserted all these extensions into an original FORTRAN program. The new algorithm was applied to the system $CaSiO_3$-Ca_2SiO_4 which contains incongruently melting compound rankinite ($Ca_3Si_2O_7$).

METHOD

In our method a peritectic point is treated as a special case of more general approach in which at composition of incongruently melting compound, the temperature of primary crystallization of other crystalline phase is higher than the hypothetical melting temperature of pure, incongruently melting constituent. This means that one of the crystalline phases melts incongruently when the temperature of primary crystallisation in the point corresponding to its composition is lower than the liquidus temperature. Such compound is therefore characterized by the hypothetical values of its temperature and enthalpy of fusion. From the point of view of input data we therefore need not to distinguish between congruently and incongruently melting constituents. In this sense we also applied regression analysis to estimate unknown parameters that characterize incongruently melting compound(s).

Sum of squares of deviations between experimental and calculated liquidus temperature is minimized during the calculation. This sum is somewhat specifically constructed. First, a point k of phase diagram in which only one crystalline phase i is in equilibrium with a liquid contributes to this sum by the value of $(T_{i,k}^{\rm clc} - T_k^{\rm exp})^2$, where $T_k^{\rm exp}$ and $T_{i,k}^{\rm clc}$ are the experimental and calculated liquidus temperatures, respectively. Secondly, a point in which several (q) crystalline phases are in equilibrium with a liquid contribute by the value of

$$\sum_{i=1}^{q}(T_{i,k}^{\rm clc} - T_k^{\rm exp})^2 + \sum_{\substack{i,j=1\\ i<j}}^{q}(T_{i,k}^{\rm clc} - T_{j,k}^{\rm clc})^2.$$

If only the position of such figurative point is known, only the second term can be used. On the other hand, when the experimental temperature T^{exp} is known, the use of the second term is optional. In this manner constructed the residual sum of squares U is then minimized using the simplex method [3]. As a result the estimates of unknown parameters are obtained.

The estimates of standard deviations of unknown parameters p_i can be obtained if the function $U(\boldsymbol{p})$ in the vicinity of its minimum U_{min} is replaced with the quadratic form

$$\Delta U(\boldsymbol{p}) = U(\boldsymbol{p}) - U_{\mathrm{min}} = \boldsymbol{x}^T \mathbf{A} \boldsymbol{x} \qquad (1)$$

where $\mathbf{A}$ is the Hess information matrix, $\boldsymbol{x}$ is the column vector of deviations of p_i's from their optimal values $\widehat{\boldsymbol{p}}$; then $\boldsymbol{x}^T$ (the row vector to vector $\boldsymbol{x}$) can be expressed in the form

$$\boldsymbol{x}^T = \{x_1, \ldots, x_n\} = \{p_1 - \widehat{p}_1, \ldots, p_n - \widehat{p}_n\} \qquad (2)$$

Hereby U_{min} is a function of vector $\boldsymbol{p}$. Diagonal elements A_{ii} of matrix $\mathbf{A}$ can be numerically estimated after the choice of elements of the vector $\boldsymbol{x}$ in the form $x_i = \pm\, \delta_{ij} d_j$, where $i = 1, \ldots, n$ and $d_j > 0$ is the adopted step, which adequate parameter is changed with. The values of diagonal elements can be then computed as the average of ΔU for positive and negative shift of parameters p_i according to the relations

$$\begin{aligned} A_{ij} &= [\Delta U(\widehat{p_1}, \ldots, \widehat{p_i} + d_i, \ldots, \widehat{p_n}) \\ &\quad + \Delta U(\widehat{p_1}, \ldots, \widehat{p_i} - d_i, \ldots, \widehat{p_n})]/2d_i^2 \end{aligned} \qquad (3)$$

Non diagonal elements of matrix $\mathbf{A}$ can be calculated as arithmetic mean of ΔU for combination of shifts of parameters p_i in both positive and negative directions in the form

$$\begin{aligned} &A_{ij} = A_{ji} = \qquad (4) \\ &\frac{1}{8}[\Delta U(\widehat{p_1}, \ldots, \widehat{p_i} + d_i, \ldots, \widehat{p_j} + d_j, \ldots, \widehat{p_n}) + \\ &+\Delta U(\widehat{p_1}, \ldots, \widehat{p_i} - d_i, \ldots, \widehat{p_j} - d_j, \ldots, \widehat{p_n}) - \\ &-\Delta U(\widehat{p_1}, \ldots, \widehat{p_i} + d_i, \ldots, \widehat{p_j} - d_j, \ldots, \widehat{p_n}) - \\ &-\Delta U(\widehat{p_1}, \ldots, \widehat{p_i} - d_i, \ldots, \widehat{p_j} + d_j, \ldots, \widehat{p_n})]/(d_i d_j) \end{aligned}$$

The values of standard deviation and covariance of parameters can be evaluated from elements of the inverse matrix $(\mathbf{A}^{-1})_{ij}$ in the form

$$s(p_i) = \sqrt{\frac{(\mathbf{A}^{-1})_{ii} U_{\mathrm{min}}}{\nu - 2}} \qquad (5)$$

$$\mathrm{cov}(p_i, p_j) = \frac{(\mathbf{A}^{-1})_{ij} U_{\mathrm{min}}}{\nu - 2} \qquad (6)$$

The correlation coefficients r_{ij} can be determined from the relation

$$r_{ij} = \frac{\mathrm{cov}(p_i, p_j)}{s(p_i) s(p_j)} \qquad (7)$$

Presented procedure is acceptable from the point of view of applied approximation of U, if relations $d_i \approx s(p_i)$ are fulfilled. Therefore the calculation is repeated cyclically, so that in the next iteration the steps d_i are substitued by the values of $s(p_i)$ from the foregoing iteration. By a reasonable choice of starting estimate of d_i's the first two iterations are usually sufficient. From the values of correlation coefficients between parameters, linear dependencies between them were investigated.

Next extension was introduction of temperature dependence of the heat of fusion, which is significant especially when a constituent crystallizes within a wide range of temperatures. We have considered the most simple dependence given by

$$\Delta_{\mathrm{f}} H_i(T) = \Delta_{\mathrm{f}} H_i(T_{\mathrm{f},i}) + \Delta_{\mathrm{f}} C_{p,i}(T - T_{\mathrm{f},i}) \qquad (8)$$

where $T_{\mathrm{f},i}$ and $\Delta_{\mathrm{f}} H_i(T_{\mathrm{f},i})$ are the temperature and enthalpy of fusion of the i-th constituent, respectively and $\Delta_{\mathrm{f}} C_{p,i}$ is the heat capacity of fusion of the constituent i which we assume to be constant. Substituting last equation into LeChatelier-Schreder equation

$$\left[\frac{\partial \ln a_i}{\partial T}\right]_p = \frac{\Delta_{\mathrm{f}} H_i(T)}{RT^2} \qquad (9)$$

we obtain after integration and rearrangement a transcendental equation for the unknown liquidus temperature $T_{i,\mathrm{l}}$

$$\begin{aligned} &\mathrm{f}(T_{i,\mathrm{l}} = \qquad (10) \\ &= \frac{\Delta_{\mathrm{f}} C_{p,i} T_{i,\mathrm{l}} \ln T_{i,\mathrm{l}} - \Delta_{\mathrm{f}} H_i(0)}{R \ln a_i + \Delta_{\mathrm{f}} C_{p,i} \ln T_{\mathrm{f},i} - \Delta_{\mathrm{f}} H_i(0)/T_{\mathrm{f},i}} - T_{i,\mathrm{l}} = 0 \end{aligned}$$

where a_i is the activity of the i-th constitutent and $\Delta_{\mathrm{f}} H_i(0)$ is given by the relation

$$\Delta_{\mathrm{f}} H_i(0) = \Delta_{\mathrm{f}} H_i(T_{\mathrm{f},i}) - \Delta_{\mathrm{f}} C_{p,i} T_{\mathrm{f},i} \qquad (11)$$

It can be easily shown that Eq. (10) may have no, one or two roots within the temperature range from 0 to $T_{\mathrm{f},i}$ depending on the $\Delta_{\mathrm{f}} C_{p,i}$ and a_i values. Supposing $\Delta_{\mathrm{f}} C_{p,i}$ is fixed the number of roots depends on the a_i only. When we define a critical value a_0 by

$$\begin{aligned} &a_0 = \exp \qquad (12) \\ &\left\{ \frac{\Delta_{\mathrm{f}} H_i(0) \left[\frac{1}{T_{\mathrm{f},i}} + \frac{\Delta_{\mathrm{f}} C_{p,i}}{\Delta_{\mathrm{f}} H_i(0)}\right] + \Delta_{\mathrm{f}} C_{p,i} \ln \left[-\frac{\Delta_{\mathrm{f}} H_i(0)}{\Delta_{\mathrm{f}} C_{p,i} T_{\mathrm{f},i}}\right]}{R} \right\} \end{aligned}$$

then Eq. (10) has no root for $a_i < a_0$, just one root for $a_i = a_0$ and two roots for $a_i > a_0$ (see Fig. 1). Physically acceptable is the one confined within the limits $T_0 \leq T_{i,\mathrm{l}} \leq T_{\mathrm{f},i}$ where T_0 is given by

$$T_0 = T_{\mathrm{f},i} - \frac{\Delta_{\mathrm{f}} H_i(T_{\mathrm{f},i})}{\Delta_{\mathrm{f}} C_{p,i}} \qquad (13)$$

There are several possible methods to solve Eq. (10) which can be divided into three groups. First group are fast methods, for example Newton-Raphson

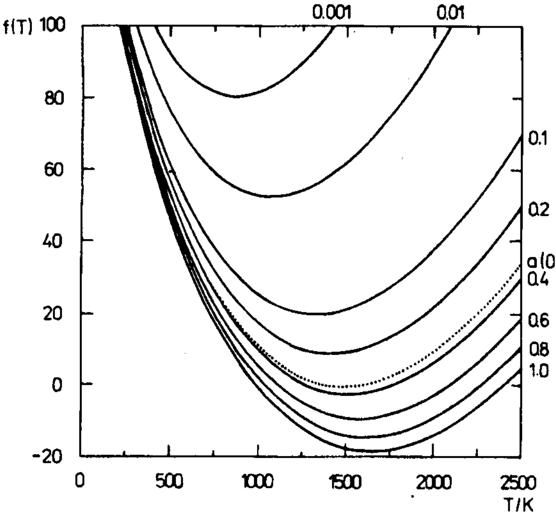

Fig. 1. Plot of the function $f(T)$ given by Eq. (10) versus T. The curves are labeled with values of activity $a(Ca_2SiO_4)$; Dotted line corresponds to the critical value a_0 given by Eq. (12).

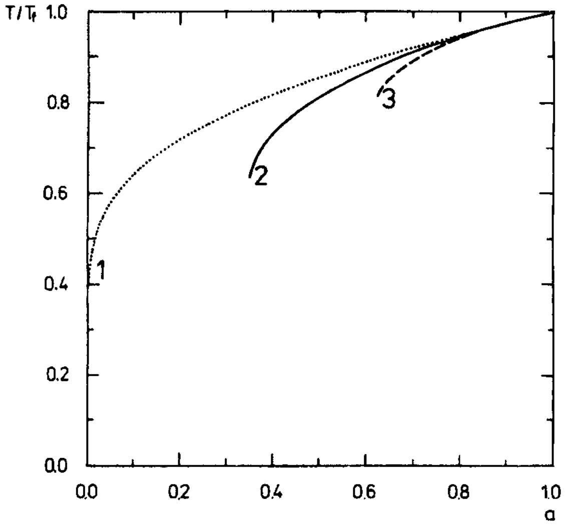

Fig. 2. Plot of normalized liquidus temperature versus activity of dicalciumsilicate. 1 – constant enthalpy of fusion, 2 – exact solution of Eq. (10), 3 – approximation by Eq. (14).

method of tangent lines, second group are slow but reliable ones, e. g., method of dividing interval, and third group are approximate ones. The last group is represented by a method in which the correct solution of Eq. (10) is replaced with the solution of Eq. (14)

$$T_{il} = \frac{\Delta_f H_i(T_{i,l})T_{f,i}}{\Delta_f H_i(T_{i,l}) - RT_{f,i}\ln a_i} \qquad (14)$$

which can be solved analytically. The equation was formally derived from the integral form of LeChatelier-Schreder equation valid for temperature independent enthalpy of fusion.

Plot of liquidus temperature divided by the melting temperature of pure i-th constituent versus activity is shown in Fig. 2. Curves 1, 2 and 3 are the solutions of simple LeChatelier-Schreder equation with $C_{p,i} = 0$, the correct solution of Eq. (10) and the solution of Eq. (14), respectively. This figure was constructed using thermodynamic data of dicalciumsilicate with the $\Delta_f C_p$ value obtained in this work. It can be seen that using temperature independent enthalpy of fusion yields liquidus temperature with the relative error less than 5% for the activity of rankinite greater than 0.5. It is obvious that the relative error dependes on particular values of $\Delta_f H(T_f)$, $\Delta_f C_p$, T_f and a. Therefore it is better to use exact solution of Eq. (10) in computer programs for calculation of phase diagrams, especially when regression analysis is performed.

The method described above was implemented into the original FORTRAN program presented in [1] and used to investigate the phase diagram of the binary system wollastonite/dicalciumsilicate.

RESULTS AND DISCUSSION

Experimental phase diagram was taken from [4]. From the diagram the compositions corresponding to the liquidus temperatures ranging from 1500°C to 1900°C with the step of 100°C as well as the composition and temperature for both eutectic and peritectic points were determined. These values were used to calculate residual sum of squares which in this case consists of six single contributions $(T_{i,k}^{\mathrm{clc}} - T_k^{\mathrm{exp}})^2$ and two extended contributions

$$\sum_{i=1}^{q}(T_{i,k}^{\mathrm{clc}} - T_k^{\mathrm{exp}})^2 + \sum_{\substack{i,j=1\\ i<j}}^{q}(T_{i,k}^{\mathrm{clc}} - T_{j,k}^{\mathrm{clc}})^2$$

with $q = 2$ corresponding to the eutectic and peritectic points. This implies the number of degrees of freedom $\nu = 12 - n$, where n is the number of unknown parameters p_i. Some parameters needed for our calculations were obtained from yet published experimental data. Melting temperatures of pure wollastonite and dicalciumsilicate were taken from [4]. The values of Kosa [5] were used for the enthalpy of fusion and $\Delta_f C_p$ of wollastonite. Because of too high melting temperature these values cannot be measured for dicalciumsilicate and they were therefore included into regression analysis.

Three hypothetical parameters (T_f, $\Delta_f H$ and $\Delta_f C_p$) characterize incongruently melting rankinite. Due to narrow temperature range of rankinite liquidus curve the effective constant value of $\Delta_f H$ may be used instead of $\Delta_f H(T)$ and $\Delta_f C_p$. On the

Table I

Least squares estimates, their standard deviations (s. d.) and standard deviations of approximation (s_a) obtained using different hypothetical enthalpy of fusion of rankinite

Method	$T_f(Ca_3Si_2O_7)$ [K]	s. d. [K]	$\Delta_f H(Ca_2Si_2O_7)$ [kJ/mol]	s. d. [kJ/mol]	$\Delta C_p(Ca_2Si_2O_7)$ [J/mol K]	s. d. [J/mol K]	s_a [K]
$\Delta_f H(Ca_3Si_2O_7) =$ 72 kJ/mol iterative scheme	1770	11	81.6	1.2	90	3	17.9
$\Delta_f H(Ca_3Si_2O_7) =$ 65 kJ/mol trial estimate	1774	11	81.6	1.1	90	3	18.0

other hand the limited temperature and compositional range of rankinite phase boundary causes the strong linear dependence between its hypothetical enthalpy and temperature of fusion. Thus it is necessary to preliminary estimate one of these quantities by an independent way. We have estimated enthalpy of fusion using the following procedure:

- using only the experimental points of dicalciumsilicate liquids curve an initial estimates of $\Delta_f H$ and $\Delta_f C_p$ were calculated by least squares method;
- rankinite enthalpy of fusion was approximated with the sum

$$\begin{aligned}\Delta_f H(Ca_3Si_2O_7) &= \Delta_f H[CaSiO_3, T_f(CaSiO_3)] + \\ &+ \Delta_f C_p(CaSiO_3)[T_p - T_f(CaSiO_3)] + \\ &+ \Delta_f H[Ca_2SiO_4, T_f(Ca_2SiO_4)] + \\ &+ \Delta_f C_p(Ca_2SiO_4)[T_p - T_f(Ca_2SiO_4)]\end{aligned} \qquad (15)$$

- least squares estimates of hypothetical temperature of fusion of rankinite, heat capacity and enthalpy of fusion of dicalciumsilicate were calculated using the full experimental data set;
- the last two items were repeated until self consistency was achieved.

Applying this procedure we found enthalpy of fusion of rankinite to be 72 kJ/mol. Another possibility is to choose arbitrary black box estimate of $\Delta_f H(Ca_3Si_2O_7)$ and then perform least square estimation of remaining parameters, i. e. $\Delta_f H(Ca_2Si_2O_7)$, $\Delta_f C_p(Ca_2Si_2O_7)$ and $T_f(Ca_3Si_2O_7)$. As such black box estimate we used the value of $\Delta_f H(Ca_3Si_2O_7) = 65$kJ/mol. The values of $T_f(Ca_3Si_2O_7)$ obtained by the either of the two possibilities are ambiguous because of their strong linear dependence with $\Delta_f H(Ca_3Si_2O_7)$. The quality of estimated parameters may be roughly deduced comparing the results that provide both procedures. All the obtained results are presented in Tab. I. We can see that thermodynamic parameters of dicalciumsilicate are reliable being insensitive to preliminary estimate of $\Delta_f H(Ca_3Si_2O_7)$. On the other hand, the value of ill-conditioned parameter $T_f(Ca_3Si_2O_7)$ is correlated with the preliminary estimate of $\Delta_f H(Ca_3Si_2O_7)$. Calculated and experimen-

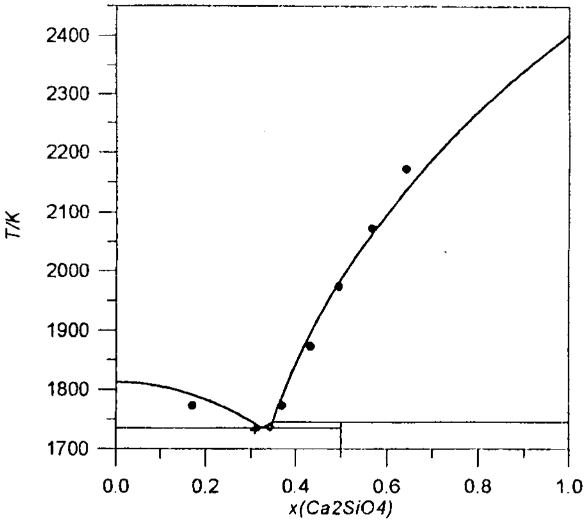

Fig. 3. Comparison of experimental (● – single points, ◇ – peritectic point, + – eutectic point) with calculated (solid line) phase diagram. Temperature dependence of heat of fusion included for wollastonite and dicalciumsilicate, $\Delta_f H(Ca_3Si_2O_7) = 65$ kJ/mol.

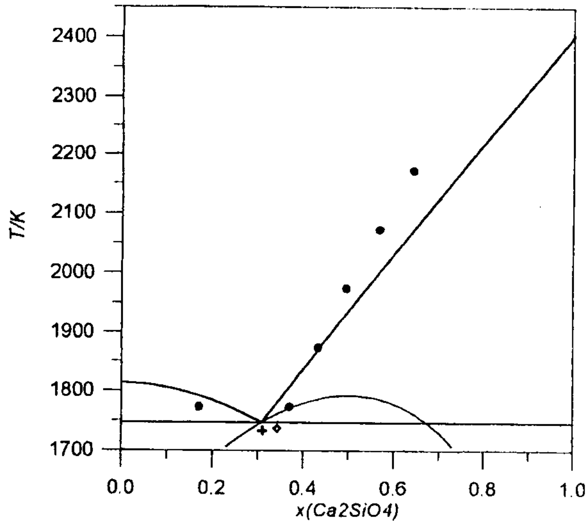

Fig. 4. Comparison of experimental (● – single points, ◇ – peritectic point, + – eutectic point) with calculated (thick solid line) phase diagram. Temperature dependence of heat of fusion neglected for all components. Thin solid line stands for the virtual liquidus curve of rankinite.

tal phase diagrams are compared in Fig. 3 where only the results for $\Delta_f H(Ca_3Si_2O_7) = 65 kJ/mol$ are visualized as far as the difference between both cases considered are practically negligible. The importance of introducing heat capacity into calculations is demonstrated in Fig. 4 where experimental and calculated phase diagrams are compared obtained when $\Delta_f C_p$ was neglected. As it can be seen from this figure, the liquidus curve of rankinite was completely hidden by those of wollastonite and dicalciumsilicate. Thus the simple eutectic two-component system has arisen.

CONCLUSIONS

From the comparison of the calculated and experimental phase diagrams it follows that the proposed method is suitable for describing phase equilibria in multicomponent silicate systems including incongruently melting compounds. A satisfactory description of the entire temperature and composition range requires to involve temperature dependent enthalpy of fusion of at least the constituent with wide temperature range of its primary crystallization.

From the statistical point of view the estimates of unknown parameters are relatively robust. Regarding them as thermodynamic quantities, their values are acceptable but estimated standard deviations seem to be underestimated.

We believe that suggested thermodynamic model supplemented with nonlinear regression analysis provides valuable results also in other silicate systems. Further improvements we see in extension of the model to more detailed description of different structural groups occurred in the melt.

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VÝPOČET FÁZOVÝCH DIAGRAMOV SILIKÁTOVÝCH SÚSTAV.
II. REGRESNÁ ANALÝZA SÚSTAV OBSAHUJÚCICH INKONGRUENTNE SA TOPIACE ZLÚČENINY.

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V práci [1] bol publikovaný algoritmus a fortranovský program na výpočet izobarických fázových diagramov jednoduchých oxidových sústav. V tejto práci sa problematika rozširuje o sústavy, ktoré obsahujú inkongruentne sa topiace zlúčeniny. Navyše sme do programu zradili štatistickú analýzu štandardných odchúlok odhadu neznámych parametrov modelu, ako aj určenie ich vzájomnej lineárnej závislosti. Ďalším rozšírením výpočtu bolo uvažovanie lineárnej závislosti entalpie topenia zložiek tvoriacich vyšetrovanú sústavu. Algoritmus sa aplikoval na sústavu $CaSiO_3$-Ca_2SiO_4, ktorá obsahuje inkongruentne sa topiacu zlúčeninu rankinit ($Ca_3Si_2O_7$).

Rankinit sa inkongruentne rozkladá pri teplote 1464°C na taveninu zloženia 34 mólových % dikalciumsilikátu, 66 mólových % wollastonitu a kryštalický dikalciumsilikát. Uvedený algoritmus sme aplikovali na výpočet troch neznámych parametrov: hypotetickú teplotu topenia rankinitu, entalpiu topenia a tepelnú kapacitu topenia dikalciumsilikátu. Posledné dva parametre neboli doteraz namerané kvôli veľmi vysokej teplote topenia dikalciumsilikátu. Vypočítané hodnoty neznámych parametrov sú 1497±11°C, 81.6±1.2 kJ/mol a 90±3 J/mol K. Entalpiu topenia rankinitu pri teplote peritektického rozkladu sme odhadli z rov. (15) na 72 kJ/mol. Entalpiu topenia wollastonitu a jej teplotnú závislosť sme prevzali z [5] a experimentálny fázový diagram zo [4].

Z porovnania vypočítaného a experimentálneho fázového diagramu vyplynulo, že navrhnutá metóda je vhodná na popis fázových rovnováh vo viaczložkových silikátových

systémoch, ktoré môžu obsahovať inkongruentne sa topiacu zlúčeninu. Uspokojivý popis celej krivky likvidus si vyžaduje zahrnúť do výpočtu teplotnú závislosť entalpie topenia spoň tej zložky, ktorá má širokú teplotnú oblasť svojej primárnej kryštalizácie. Odhady neznámych parametrov sú z termodynamického hľadiska akceptovateľné, avšak ich štandardné odchýlky sa zdajú byť podcenené.

Ďalšie zlepšenie očakávame v rozšírení modelu o podrobnejší popis štruktúrnych jednotiek, ktoré sú v tavenie prítomné.

Obr. 1. Priebeh funkcie $\mathrm{f}(T)$ *danej rovnicou (10) oproti* T. *Krivky sú označené hodnotami aktivít* $a(\mathrm{Ca_2SiO_4})$. *Bodkovaná čiara zodpovedá kritickej hodnote* a_0, *ktorá je daná rovnicou (12).*

Obr. 2. Závislosť normovanej teploty likvidus od aktivity dikalciumsilikátu.
1 – pri konštantnej entalpii topenia, 2 – presné riešenie rov. (10), 3 – aproximácia rovnicou (14).

Obr. 3. Porovnanie experimentálneho (● – jednoduché body, ◇ – peritektický bod, + – eutektický bod) a vypočítaného (plná čiara) fázového diagramu so zahrnutím teplotnej závislosti tepla topenia wollastonitu a dikalciumsilikátu. $\Delta_\mathrm{f} H(\mathrm{Ca_3Si_2O_7}) = 65 kJ/mol$.

Obr. 4. Porovnanie experimentálneho (● – jednoduché body, ◇ – peritektický bod, + – eutektický bod) a vypočítaného (hrubá plná čiara) fázového diagramu so zanedbaním teplotnej závislosti tepla topenia všetkých zložiek. Tenká plná čiara zodpovedá virtuálnej krivke likvidus rankinitu.